



รายงานวิจัยฉบับสมบูรณ์

โครงการ

การพัฒนาตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับขนาดนาโนสำหรับปฏิกิริยา

ไฮโดรจิเนชัน

โดย

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สนับสนุนโดยสำนักงานคณะกรรมการอุดมศึกษาและสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกอ.และสกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

Abstract

Nanocrystalline SiO_2 , Al_2O_3 , TiO_2 , and ZnAl_2O_4 have been synthesized by different methods, namely sol-gel, solvothermal, and flame spray pyrolysis and employed as supports for Pd catalysts. The catalyst performance in selective hydrogenation of alkyne to alkene was correlated with physicochemical properties of the catalysts such as the nature of supports, the metal particle size, and the degree of metal-support interaction. Higher metal dispersion and improved catalyst performance was obtained using these nanometer-sized supports.

Keywords nanocrystalline materials; hydrogenation; Pd catalyst

บทคัดย่อ

งานวิจัยนี้ทำการสังเคราะห์ผลึกขนาดนาโนเมตรของซิลิกาอะลูมินาไทเทเนียมไดออกไซด์ และซิงค์อะลูมินาโดยวิธีการต่างๆ ได้แก่วิธีโซล-เจลวิธีโซลโวเทอร์มอลและวิธีเฟลมสเปรย์ไพโรไลซิสและศึกษาการนำไปประยุกต์ใช้เป็นตัวรองรับตัวเร่งปฏิกิริยาแพลเลเดียมสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของสารอัลไคน์เป็นอัลคีนพบว่าประสิทธิภาพในการเร่งปฏิกิริยาในปฏิกิริยาตั้งกล่าวมีความสัมพันธ์กับสมบัติเชิงกายภาพและเคมีของตัวเร่งปฏิกิริยาได้แก่ชนิดของตัวรองรับ ขนาดอนุภาคของโลหะและอันตรกิริยาระหว่างโลหะและตัวรองรับโดยสามารถเตรียมตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสูงบนตัวรองรับที่มีขนาดผลึกระดับนาโนเมตรเหล่านี้

คำสำคัญ ผลึกขนาดนาโนเมตร ตัวเร่งปฏิกิริยาแพลเลเดียม ไฮโดรจิเนชัน

Executive Summary

ปฏิกิริยาไฮโดรจิเนชันเป็นปฏิกิริยาที่มีการใช้งานอย่างแพร่หลายในอุตสาหกรรมเคมี อุตสาหกรรมการกลั่นน้ำมันและอุตสาหกรรมปิโตรเคมีเช่นการผลิตสารไฮโดรคาร์บอนซึ่งเป็นสารตั้งต้นที่ใช้ในการผลิตในลอนโดยปฏิกิริยาไฮโดรจิเนชันของเบนซีนการจัดสารปนเปื้อนจำพวกอะโรมาติกส์ซึ่งเป็นพิษในอุตสาหกรรมการกลั่นน้ำมันดิบการจัดอะเซทิลีนออกจากสายป้อนเอทิลีนในอุตสาหกรรมการผลิตพอลิเอทิลีนนอกจากนี้ปฏิกิริยาไฮโดรจิเนชันยังเป็นปฏิกิริยาที่สำคัญในการสังเคราะห์สารอินทรีย์ต่างๆเช่นสารเคมีที่มีมูลค่าเพิ่มสูงที่มักใช้เป็นสารตั้งต้นในการผลิตยาอมอเมอร์สำหรับสังเคราะห์พอลิเมอร์ ไบโมาและน้ำมันสังเคราะห์ เป็นต้นตัวเร่งปฏิกิริยาที่ว่องไวสำหรับปฏิกิริยาไฮโดรจิเนชันได้แก่โลหะมีตระกูลต่างๆเช่นแพลเลเดียม (Pd) แพลตินัม (Pt) โรเดียม (Rh) และรูเทเนียม (Ru) โดยที่แพลเลเดียมจะให้ความว่องไวและค่าการเลือกเกิดเป็นผลิตภัณฑ์จำพวกอัลคีนสูงกว่าโลหะชนิดอื่นๆเพื่อเพิ่มความว่องไวและความเสถียรของตัวเร่งปฏิกิริยาตัวเร่งปฏิกิริยาแพลเลเดียมมักเตรียมบนตัวรองรับที่เป็นโลหะออกไซด์ที่มีพื้นที่ผิวสูงเช่นคาร์บอนซิลิกาอะลูมินาไทเทเนียมไดออกไซด์และซีโอไลท์ทั้งนี้ตัวรองรับต่างชนิดกันพบว่าส่งผลต่อทั้งความว่องไวการเลือกเกิดของผลิตภัณฑ์และการเสื่อมสภาพของตัวเร่งปฏิกิริยา

ปัจจุบันได้มีการสังเคราะห์โลหะออกไซด์ที่มีผลึกขนาดนาโนเมตรโดยวิธีต่างๆเช่นวิธีโซล-เจลวิธีโซลโวลเทอรัมอลวิธีเฟลม-สเปรย์ไพโรไลซิสพบว่าโลหะออกไซด์ที่มีขนาดนาโนเมตรมีสมบัติและคุณลักษณะที่แตกต่างไปจากโลหะออกไซด์แบบดั้งเดิมที่มีผลึกขนาดใหญ่เช่นไทเทเนียมไดออกไซด์ที่มีผลึกขนาดเล็กในระดับนาโนให้ความว่องไวในการเร่งปฏิกิริยาด้วยแสงสูงกว่าตัวเร่งปฏิกิริยาขนาดใหญ่ ในงานวิจัยนี้ศึกษาการประยุกต์ใช้โลหะออกไซด์ขนาดนาโนเมตรเป็นตัวรองรับตัวเร่งปฏิกิริยาโดยมุ่งเน้นการพัฒนาตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับโลหะออกไซด์ขนาดนาโนเมตรต่างๆอาทิซิลิกาอะลูมินาไทเทเนียมไดออกไซด์และซิงค์อะลูมิเนียมที่สังเคราะห์โดยวิธีการต่างๆได้แก่วิธีโซล-เจลวิธีโซลโวลเทอรัมอลและวิธีเฟลมสเปรย์ไพโรไลซิสสำหรับใช้ในปฏิกิริยาไฮโดรจิเนชันของสารอัลไคน์เป็นอัลคีนพบว่าประสิทธิภาพในการเร่งปฏิกิริยาในปฏิกิริยาดังกล่าวมีความสัมพันธ์กับสมบัติเชิงกายภาพและเคมีของตัวเร่งปฏิกิริยาได้แก่ชนิดของตัวรองรับขนาดอนุภาคของโลหะและอันตรกิริยาระหว่างโลหะและตัวรองรับโดยสามารถเตรียมตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสูงบนตัวรองรับที่มีขนาดผลึกระดับนาโนเมตรเหล่านี้

1. วัตถุประสงค์ของงานวิจัย

เพื่อพัฒนาตัวเร่งปฏิกิริยาแพลเลเดียมที่มีประสิทธิภาพสูงบนตัวรองรับโลหะออกไซด์ขนาดนาโนเมตรต่างๆ เช่น ซิลิกาอะลูมินาและไทเทเนียมไดออกไซด์ สำหรับใช้ในปฏิกิริยาไฮโดรจิเนชัน

2. ระเบียบวิธีวิจัย

- 2.1 รวบรวมงานวิจัยที่เกี่ยวข้อง (literature review)
- 2.2 สังเคราะห์โลหะออกไซด์ที่มีผลึกขนาดนาโนเมตร
- 2.3 สังเคราะห์ตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับขนาดนาโนที่เตรียมขึ้น
- 2.4 ทดสอบคุณลักษณะและสมบัติทางกายภาพและเคมี (physical and chemical properties) ของตัวเร่งปฏิกิริยาที่เตรียมได้
- 2.5 ทดสอบประสิทธิภาพสำหรับปฏิกิริยาไฮโดรจิเนชันของสารอินทรีย์ต่างๆ เช่น อะเซทิลีน (วัฏภาคแก๊ส) ฟีนิลอะเซทิลีน (วัฏภาคของเหลว) 1-เฮปไทด์ (วัฏภาคของเหลว)
- 2.6 ทดสอบการเสื่อมสภาพของตัวเร่งปฏิกิริยาหลังการทำปฏิกิริยา
- 2.7 วิเคราะห์ข้อมูล จัดทำรายงาน นำเสนอผลงานเพื่อตีพิมพ์ในวารสาร

3. รายชื่อและสังกัดของผู้ร่วมวิจัย ผู้ช่วยวิจัย นักศึกษา ที่ร่วมวิจัยในโครงการ ผู้ร่วมวิจัย

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4. เนื้อหานิพนธ์

ในส่วนของเนื้อหานิพนธ์นี้ได้แบ่งเป็น 5 ส่วนดังนี้ (1) การสังเคราะห์ผลึกโลหะออกไซด์ขนาดนาโนเมตร(2)การเตรียมตัวเร่งปฏิกิริยาแพลเลเดียมบนโลหะออกไซด์ขนาดนาโนเมตรที่สังเคราะห์ขึ้นโดยเทคนิคการเคลือบฝังแบบเปียก(3)การวิเคราะห์คุณลักษณะและสมบัติทางกายภาพและเคมีของตัวเร่งปฏิกิริยาโดยเครื่องมือวิเคราะห์ต่างๆ (4) การทดสอบความว่องไวในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาในปฏิกิริยาไฮโดรจิเนชันของสารประกอบจำพวกอัลไคน์และ(5)ผลการทดลองและอภิปรายผล

4.1 การสังเคราะห์ผลึกโลหะออกไซด์ขนาดนาโนเมตร

4.1.1 การสังเคราะห์ผลึกโลหะออกไซด์ขนาดนาโนเมตรโดยวิธีโซลเจล

ตัวอย่างการสังเคราะห์ SiO_2 โดยวิธีโซลเจล

Silica was prepared by the sol-gel technique using the sol composition of 40 ml of tetraethylorthosilicate (TEOS), 10.5 ml of ethanol, 12.5 ml of de-ionized water, and 1 ml of hydrochloric acid (HCl). The mixtures were stirred vigorously for 1 h. Then the gel was calcined at 500°C for 6 h in order to remove any organic.

4.1.2 การสังเคราะห์ผลึกโลหะออกไซด์ขนาดนาโนเมตรโดยวิธีโซลโวลเทอรัมอล

ตัวอย่างการสังเคราะห์ ZnAl_2O_4 โดยวิธีโซลโวลเทอรัมอล

Zinc aluminate spinel (ZnAl_2O_4) was prepared by the solvothermal technique using aluminium isopropoxide (Aldrich) and zinc (II) acetylacetonate (Merck) (Zn/Al molar ratio = 0.5) as reactants suspended in toluene (Carlo Erba Reagenti). First, the mixture of aluminium isopropoxide, 15.0 g and appropriate amount of zinc (II) acetylacetonate (Zn/Al molar ratio = 0.5) was prepared in 100 cm^3 toluene in a 1.5 dm^3 autoclave reactor. The suspension was heated to 300°C at the rate of $2.5^\circ\text{C}/\text{min}$ and held at that temperature for 2 h. The resulting products were washed with methanol and dried in air and then calcined in a furnace at various temperatures (500, 700, 900, or 1150°C) for 1 h.

4.1.3 การสังเคราะห์ผลึกโลหะออกไซด์ขนาดนาโนเมตรโดยวิธีเฟลมสเปรย์ไฟโรไลซิส

ตัวอย่างการสังเคราะห์ TiO_2 โดยวิธีเฟลมสเปรย์ไฟโรไลซิส

Synthesis of TiO_2 was carried out using a spray flame reactor [see Figure 1]. Titanium (IV) tert-butoxide (TNB; Aldrich) was chosen as raw materials for preparation of a liquid-phase precursor. The precursors were prepared by dissolving the appropriate amounts of substance in xylene (MERCK; 99.8 vol.%)/acetonitrile (Fluka; 99.5 vol.%) mixtures (70/30 vol%). During particle synthesis, 5 ml/min of liquid precursor are fed to the flame by a syringe pump and disperse with 5 l/min oxygen forming fine spray

droplets. The pressure drop at the capillary tip was maintained at 1.5 bar by adjusting the orifice gap area at the nozzle. The spray was ignited by supporting flamelets feed with oxygen (3 l/min) and methane (1.5 l/min) which were positioned in a ring around the nozzle outlet. A sintered metal plate ring (8 mm wide, starting at a radius of 8 mm) provided additional 25 l/min of oxygen as sheath for the supporting flame. The product particles were collected on a glass fiber filter (Whatman GF/D, 15 cm in diameter) with the aid of a vacuum pump.

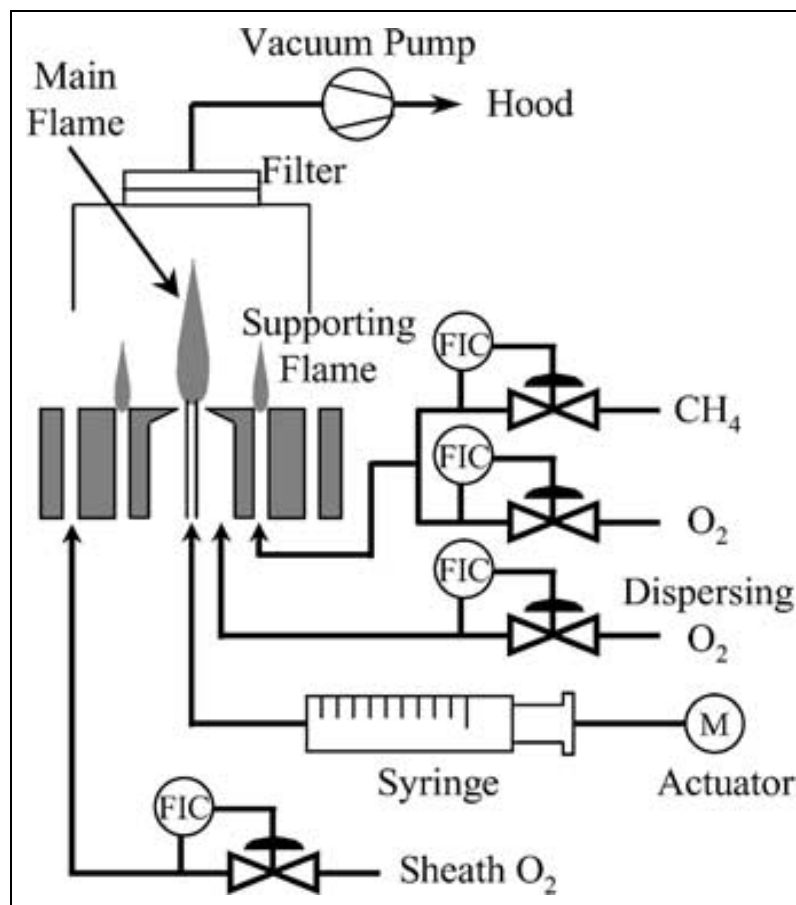


Figure 1 Schematic of the FSP process for nanomaterials synthesis

4.2 การเตรียมตัวเร่งปฏิกิริยาแพลเลเดียมบนโลหะออกไซด์ขนาดนาโนเมตรที่สังเคราะห์ขึ้นโดยเทคนิคการเคลือบฝังแบบเปียก (Incipient Wetness Impregnation method)

Supported Pd catalysts were prepared by the incipient wetness impregnation method using $\text{Pd}(\text{NO}_3)_2$ (Aldrich) as the palladium precursor. The support was

impregnated to incipient wetness with an aqueous solution containing sufficient palladium to result in 1 wt% Pd catalysts. The catalyst samples were dried in an oven at 100°C overnight and calcined in air at 400°C for 6 h prior to characterization.

4.3 การวิเคราะห์คุณลักษณะและสมบัติทางกายภาพและเคมีของตัวเร่งปฏิกิริยาโดยเครื่องมือวิเคราะห์ต่าง ๆ ได้แก่

4.3.1 N₂ physisorption

ปริมาณพื้นที่ผิวปริมาตรรูพรุนและขนาดของรูพรุนโดยเฉลี่ยทำการตรวจวัดโดยเครื่อง Micromeritics ASAP 2020 ที่ศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

4.3.2 X-ray diffraction (XRD)

รูปแบบของ XRD ของตัวเร่งปฏิกิริยาวัดโดยเครื่อง SIEMENS D5000 X-ray diffractometer ที่มี CuK α radiation และ Ni Filter ที่ศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยาภาควิชาวิศวกรรมเคมีคณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

4.3.3 Scanning electron microscopy (SEM)

ลักษณะพื้นผิวของตัวเร่งปฏิกิริยาทดสอบโดยเครื่อง JEOL JSM-35CF scanning electron microscope (SEM) ที่ดำเนินการที่ 20 kV ที่ศูนย์เครื่องมือวิเคราะห์แห่ง จุฬาลงกรณ์มหาวิทยาลัย

4.3.4 Transmission electron microscopy (TEM)

ขนาดผลึกของแพลเลเดียมออกไซด์และการกระจายตัวของแพลเลเดียมวิเคราะห์โดยเครื่อง JEOL-JEM 2010 transmission electron microscope ที่ดำเนินการที่ 80-200 kV ที่ National Metal and Materials Technology Center (MTEC)

4.3.5 CO-pulse chemisorption

ปริมาณแพลเลเดียมที่ว่องไวสามารถวัดได้โดยเทคนิค CO-chemisorption โดยประมาณ 0.2 กรัมของตัวเร่งปฏิกิริยาจะถูกบรรจุในเครื่องปฏิกิริยาที่อยู่ในเตาอบหลังจากรีดิวซ์ในบรรยากาศไฮโดรเจนที่อุณหภูมิห้องและไล่แก๊สที่เหลือด้วยฮีเลียมแล้วแก๊ส

คาร์บอนมอนนอกไซด์จะถูกฉีดเข้าไปบนตัวเร่งปฏิกิริยาเพื่อให้เกิดการดูดซับปริมาณแก๊สที่ดูดซับวัดได้โดยเครื่องthermal conductivity detector (TCD) ทำการทดสอบที่ศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยาภาควิชาวิศวกรรมเคมีคณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

4.3.6 X-ray photoelectron spectroscopy (XPS)

The XPS measurement was carried out using an AMICUS photoelectron spectrometer equipped with an Mg K_{α} X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. All the binding energies were referenced to the C 1s peak at 285 eV of the surface adventitious carbon.

4.3.7 Electron spin resonance (ESR)

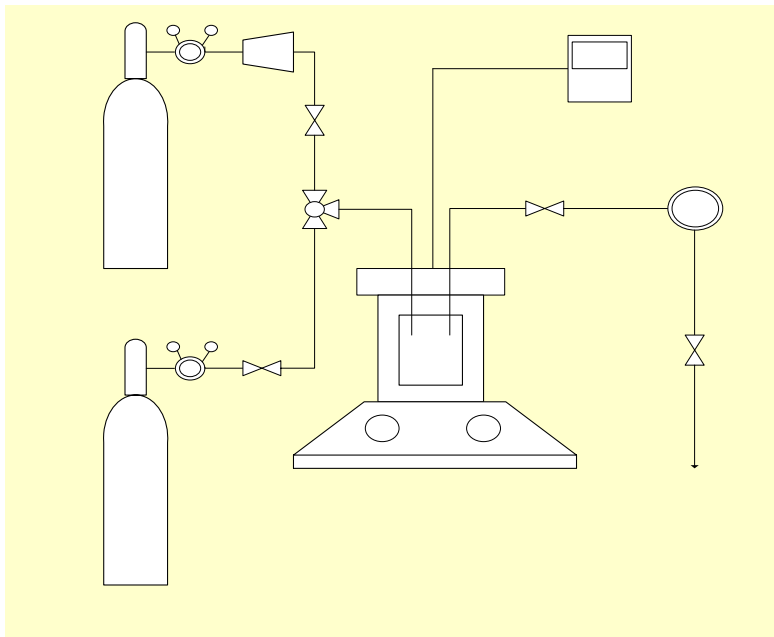
Electron spin resonance spectroscopy (ESR) was conducted using a JEOL JESRE2X electron spin resonance spectrometer. The intensity of ESR was calculated using a computer software program ES-PRIT ESR DATA SYSTEM version 1.6.

4.3.8 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

The bulk composition of catalyst quantitatively is determined by ICP-OES method using Optima 2100 DV. Often special procedures are needed to dissolve catalysts in preparation for analysis, particularly refractory materials such as certain noble metals and ceramics.

4.4 วิธีการทดสอบความว่องไวในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาในปฏิกิริยาไฮโดรจิเนชันของสารประกอบจำพวกอัลไคน์เช่นอะเซทิลีนฟิโนลอะเซทิลีนและเฮปไทน์ในเครื่องปฏิกรณ์แบบเบดนิ่งหรือแบบหม้ออัดความดัน

Liquid-phase partial hydrogenation of 1-heptyne was carried out in a 50 cm³ stainless steel autoclave. Approximately 0.02 g of supported Pd catalyst was placed in the reactor with 10 cm³ of 2 vol% of 1-heptyne in toluene. Afterward the reactor was filled with hydrogen at 1 bar pressure. Stirring was switched on to start the reaction, and reaction was carried out for 5 min. The products were analyzed by gas chromatography with a flame ionization detector.

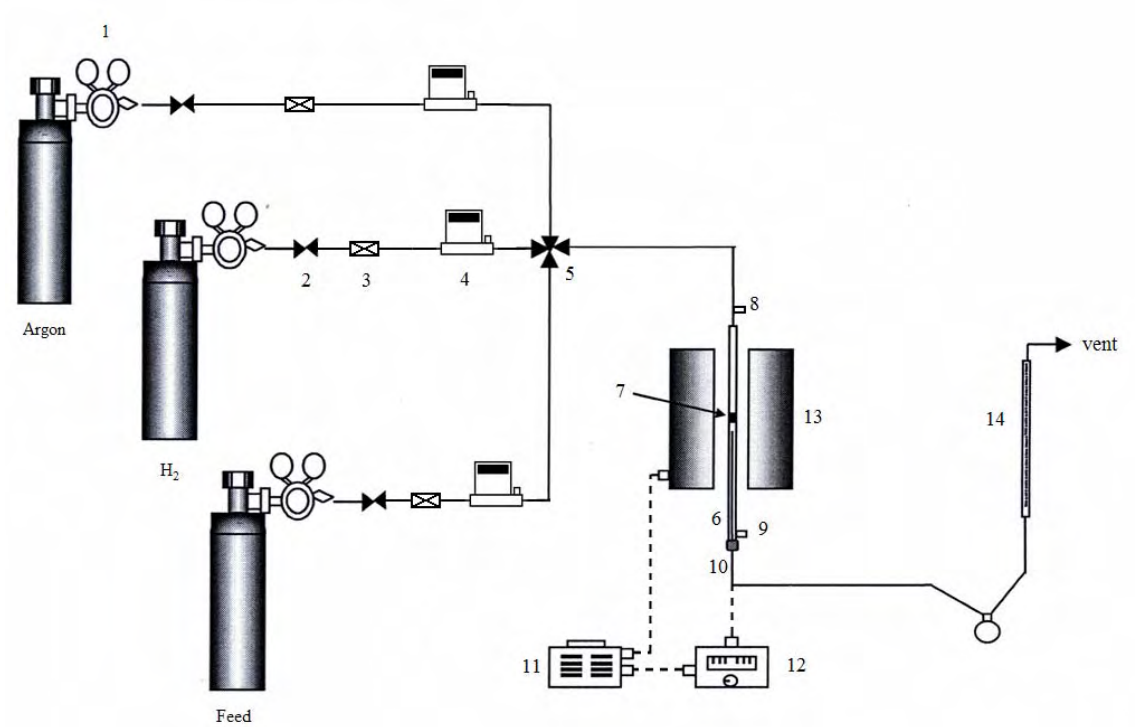


CO₂

Figure 2 A schematic diagram of the liquid-phase hydrogenation system

Selective acetylene hydrogenation was performed in a quartz tube reactor (ID 9 mm). Prior to the start of each run, the catalyst was reduced in H₂ at 500°C for 2 h. Then the reactor was purged with argon and cooled down to the reaction temperature, 40°C. Feed gas composed of 1.46% C₂H₂, 1.71% H₂, 15.47% C₂H₆ and balanced C₂H₄ (Rayong Olefin Co., Ltd) and a GHSV of 5400 h⁻¹ were used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). Acetylene conversion as used herein is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated.

H₂



- | | |
|-------------------------|----------------------------------|
| 1. pressure regulator | 8. sampling point (feed) |
| 2. on-off valve | 9. sampling point (product) |
| 3. filter | 10. thermocouple |
| 4. mass flow controller | 11. variable voltage transformer |
| 5. 4-ways fitting | 12. temperature controller |
| 6. reactor | 13. electric furnace |
| 7. catalyst bed | 14. bubble flow meter |

Figure 3 Flow diagram of the selective hydrogenation of acetylene

4.5 ผลการทดลองและอภิปรายผล

4.5.1 Selective hydrogenation of acetylene in excess ethylene on micron-sized and nanocrystalline TiO₂ supported Pd catalysts

The use of pure anatase TiO₂ (either micron- or nano-sized) as supports for Pd catalysts produced high ethylene selectivities during selective acetylene hydrogenation in excess ethylene. In contrast, the use of pure rutile TiO₂ supported ones resulted in ethylene loss due to over-hydrogenation of ethylene to ethane. The differences in ethylene selectivity of the various Pd/TiO₂ were due mainly to the presence/absence of the Ti³⁺ defective sites on the TiO₂ support, rather than the difference in the crystallite sizes of the TiO₂ support.

Table 1.1 Properties of the various TiO₂ supports

Sample	BET S.A. ^a (m ² /g)	crystallite size ^b (nm)	Atomic concentration ^c (%) Ti/O
TiO ₂ -com-A	64.4	n.d.	0.287
TiO ₂ -com-R	18.3	n.d.	0.250
TiO ₂ -sol gel	39.3	10	0.232
TiO ₂ -solvothermal	26.8	17	0.220

Table 1.2 Characteristics of the various TiO₂-supported Pd catalysts

Catalyst	BET S.A. ^a (m ² /g)	CO pulse chemisorption ^b (x10 ⁻¹⁸ molecule CO/g cat.)	Pd dispersion ^c (%)	d _p ^d Pd ⁰ (nm)	%atomic concentration ^e	
					Ti/O	Pd/Ti
Pd/TiO ₂ -com-A	44.5	2.23	3.93	28.5	0.253	0.084
Pd/TiO ₂ -com-R	17.2	1.55	2.73	41.0	0.240	0.168
Pd/TiO ₂ -sol gel	33.8	1.19	2.10	53.3	0.282	0.011
Pd/TiO ₂ -solvothermal	26.0	0.49	0.86	130.2	0.274	0.006

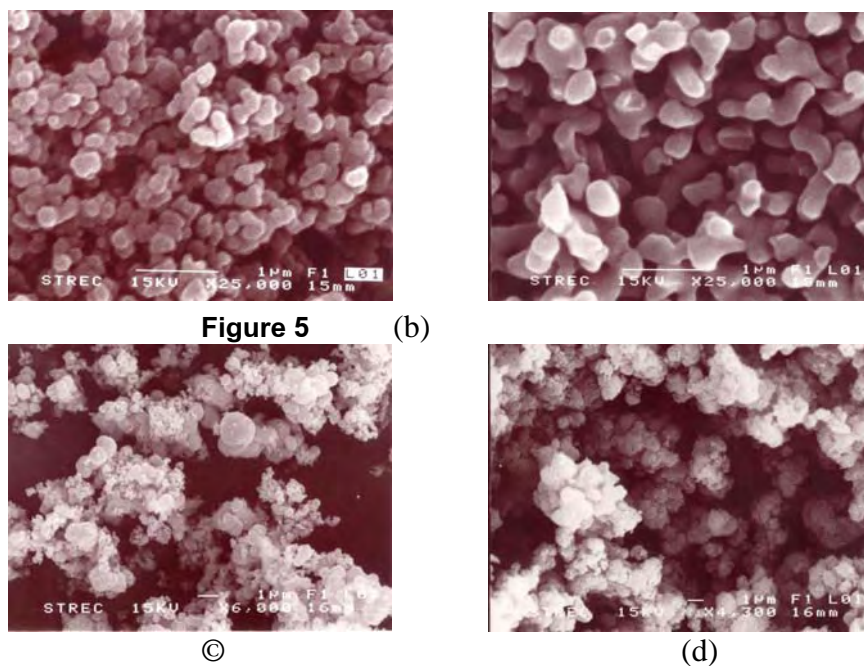


Figure 1.1 SEM micrographs of (a) TiO₂-com-A (b) TiO₂-com-R (c) TiO₂-sol-gel and (d) TiO₂-solvothermal

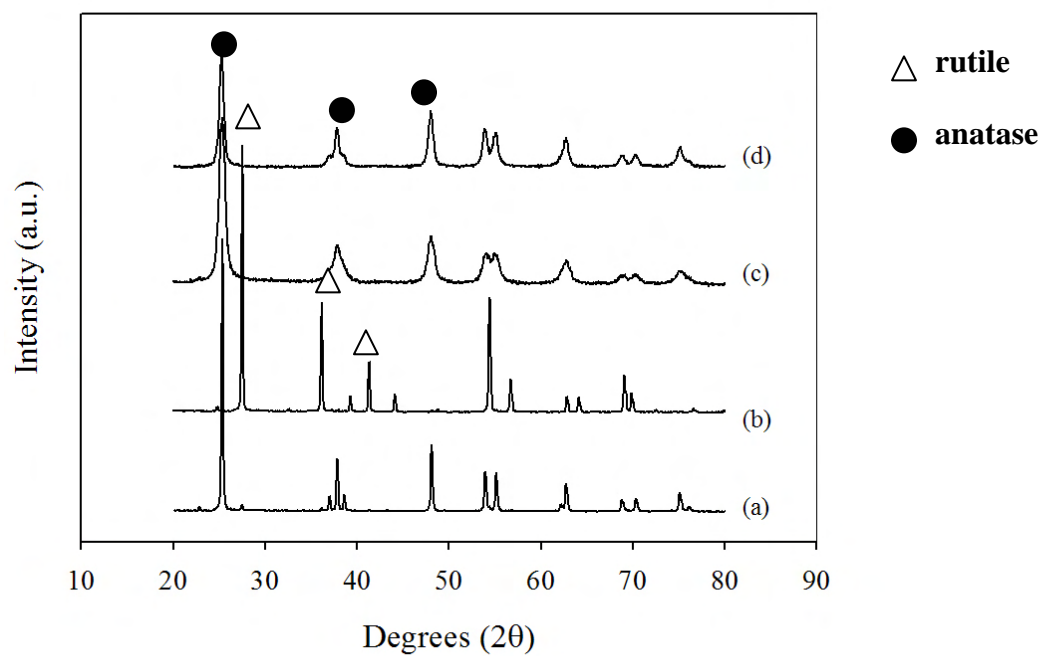


Figure 1.2 XRD results of (a) TiO₂-com-A (b) TiO₂-com-R (c) TiO₂-sol-gel and (d) TiO₂-solvothermal

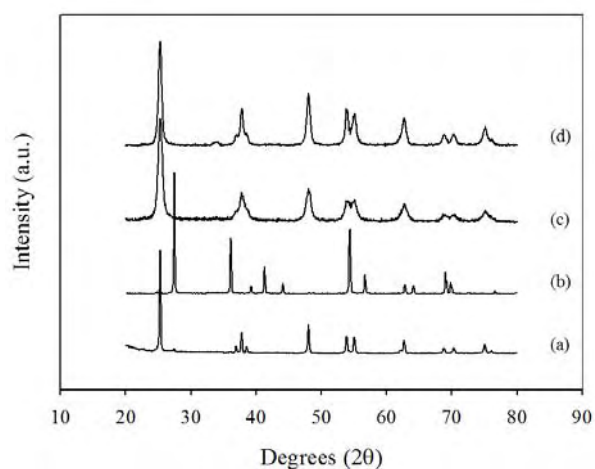


Figure 1.4 XRD results of (a) Pd/TiO₂-com-A (b) Pd/TiO₂-com-R (c) Pd/TiO₂-sol-gel and (d) Pd/TiO₂-solvothermal

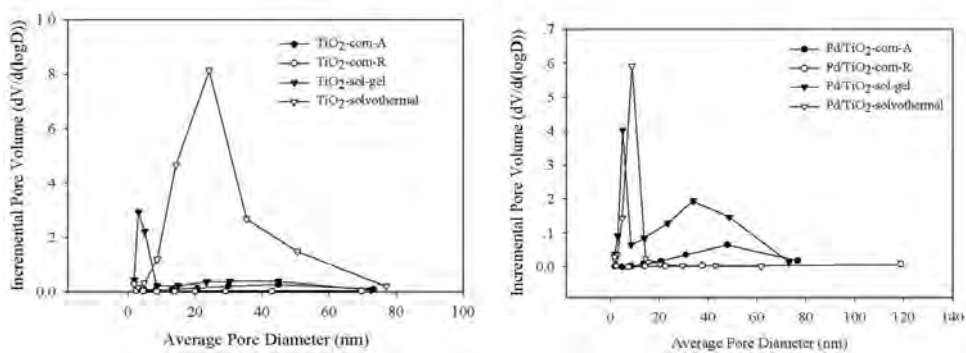


Figure 1.5 Pore size distribution results of the various Pd/TiO₂ catalysts

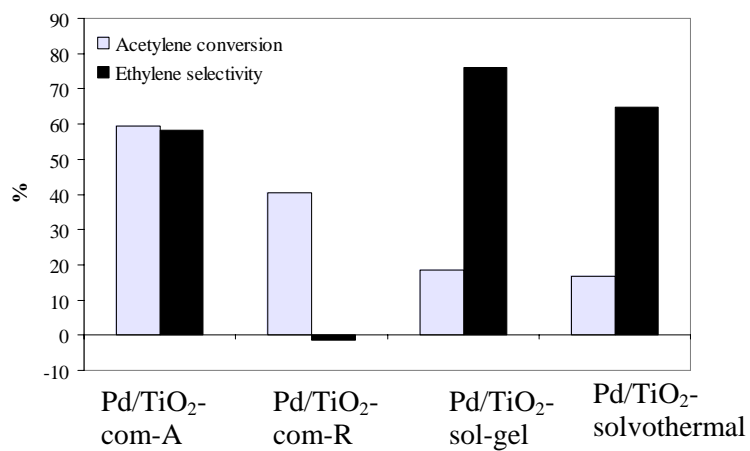


Figure 1.6 Catalyst performances in selective acetylene hydrogenation

4.5.2 Characteristics and Catalytic Properties of Pd/SiO₂ Synthesized by One-Step Flame Spray Pyrolysis in Liquid-Phase Hydrogenation of 1-Heptyne

Pd/SiO₂ catalysts with 0.5-10 wt% Pd loadings were prepared by one-step flame spray pyrolysis (FSP) and characterized by N₂ physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), CO chemisorption, and X-ray photoelectron spectroscopy (XPS). The average cluster/particles size of Pd as revealed by TEM were ca. 0.5 to 3 nm. The turnover frequencies (TOFs) of the flame-made catalysts decreased from 66.2 to 4.3 s⁻¹ as Pd loading increased from 0.5 to 10 wt%, suggesting that the catalytic activity was dependent on Pd particle/cluster size. However, there were no appreciable influences on 1-heptene selectivity. The flame-made Pd/SiO₂ showed better properties than the conventional prepared catalysts. Their advantages are not only the presence of large pores that facilitates diffusion of the reactants and products, but also the high catalytic activity of as-synthesized catalysts so that further pretreatment is not necessary.

Table 2.1 Physicochemical Properties of Flame-Made SiO₂ and Pd/SiO₂ Catalysts

Catalyst	BET Surface Areas ^a (m ² /g)	Pore Volume ^a (cm ³ /g)	CO chemisorption results ^b			XPS results Pd 3d _{5/2}		Atomic ratio ^c Pd/Si
			CO uptake (x10 ⁻¹⁸ molecule CO/g cat.)	%Pd dispersion ^c	d _{Pd} ^{0,d} (nm)	B.E. (eV)	FWHM	
SiO ₂	196	0.48	n/a ^f	n/a	n/a	n/a	n/a	n/a
0.5%Pd/SiO ₂	246	0.43	1.0	3.42	33	n/a	n/a	0.0011
0.5%Pd/SiO ₂ _R ^g	-	-	1.1	3.53	32	-	-	-
1%Pd/SiO ₂	251	0.46	1.9	3.40	33	n/a	n/a	0.0014
2%Pd/SiO ₂	260	0.49	3.3	2.88	39	n/a	n/a	0.0018
5%Pd/SiO ₂	306	0.59	13.4	4.71	24	337.4	2.389	0.0139
10%Pd/SiO ₂	299	0.69	25.8	4.55	25	337.4	3.189	0.0404
1% Pd/SiO ₂ -com	234	1.02	3.3	5.81	19	-	-	0.0033

^a Error of measurement was $\pm 10\%$.

^b Error of measurement was $\pm 5\%$ as determined directly.

^c Based on the total palladium loaded and an assumption of CO/Pd = 1.

^d Based on $d = (1.12/D)$ nm [25], where D = fractional metal dispersion.

^e Based on XPS results.

^f n/a = not available.

^g R = after reduced for 2 h in H₂ at room temperature.

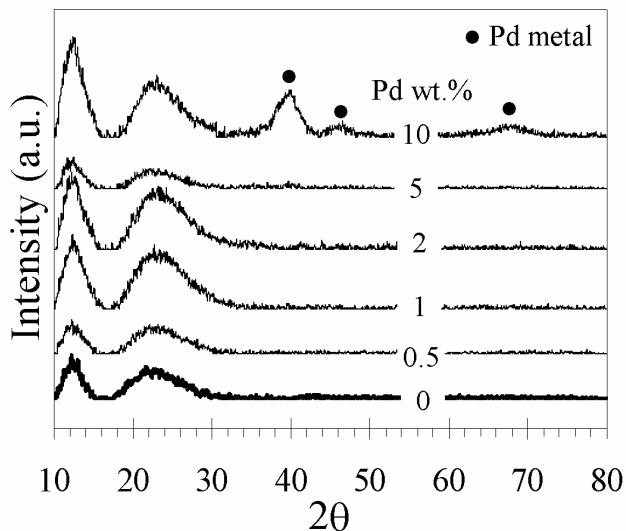
Table 2.2 Catalytic Properties for Liquid-Phase 1-Heptyne Selective Hydrogenation^a

Catalyst	Conversion (%)	1-Heptene Selec. (%)	TOF ^b (s ⁻¹)
0.5%Pd/SiO ₂	42	93	66.2
1%Pd/SiO ₂	43	92	34.1
	100 ^c	62 ^c	-
2%Pd/SiO ₂	54	94	25.3
5%Pd/SiO ₂	75	95	8.6
10%Pd/SiO ₂	73	94	4.3
1% Pd/SiO ₂ -com	20	100	7.7
	100 ^c	13 ^c	-

^a Reaction conditions were 105 kPa, 30°C, 5 min, and catalyst/substrate molar ratio = 1/1,600

^b TOF = mole product/mole Pd metal/s. Based on the amount of active Pd atoms Measured by CO chemisorption.

^c Reaction conditions were 105 kPa, 30°C, 40 min, and catalyst/substrate molar ratio = 1/500

**Figure 2.1** XRD patterns of the flame-made Pd/SiO₂ catalysts (as synthesized)

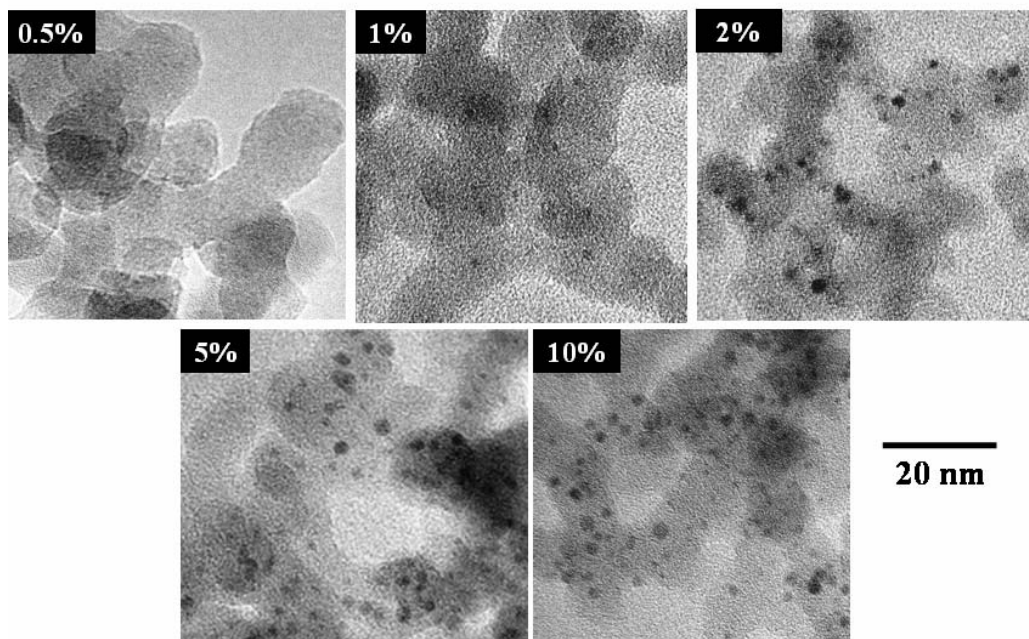


Figure 2.2 TEM micrographs of (a) the as-synthesized and (b) the spent flame-made Pd/SiO₂ catalysts (after reaction)

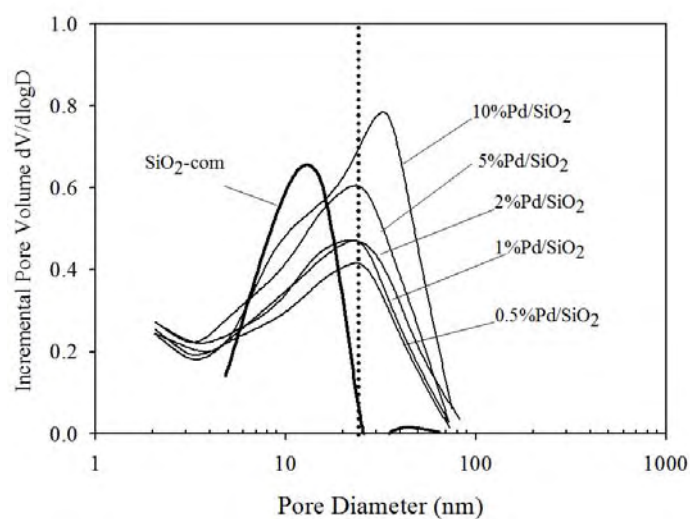


Figure 2.3 Pore size distribution of the flame-made Pd/SiO₂ catalysts with 0.5-10 wt% Pd loading

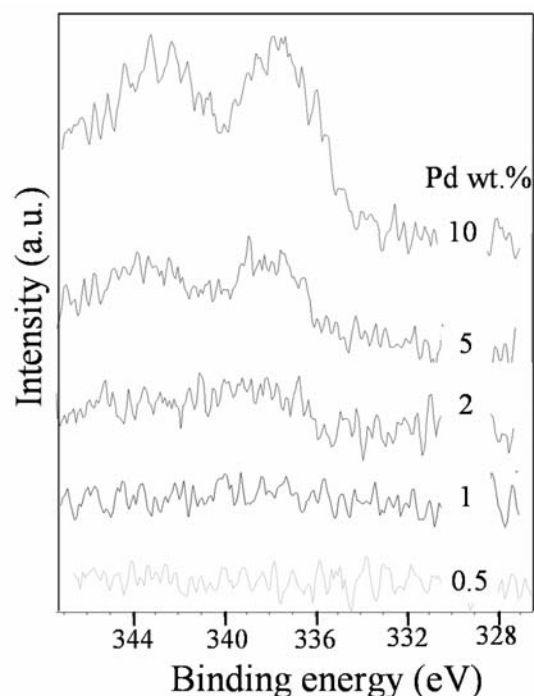


Figure 2.4 XPS results for Pd 3d_{5/2} of the flame-made Pd/SiO₂ catalysts

4.5.3 Performance of Pd Catalysts Supported on Nanocrystalline α -Al₂O₃ and Ni-Modified α -Al₂O₃ in Selective Hydrogenation of Acetylene

Nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ have been prepared by sol-gel and solvothermal methods and employed as supports for Pd catalysts. Regardless of the preparation method used, NiAl₂O₄ spinel was formed on the Ni-modified α -Al₂O₃ after calcination at 1150°C. However, an additional of NiO peaks was also observed by X-ray diffraction for the solvothermal-made Ni-modified α -Al₂O₃ powder. Catalytic performances of the Pd catalysts supported on these nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ in selective hydrogenation of acetylene were found to be superior to those of the commercial α -Al₂O₃ supported one. Ethylene selectivities were improved in the order: Pd/Ni-modified α -Al₂O₃-sol-gel > Pd/Ni-modified α -Al₂O₃-solvothermal \approx Pd/ α -Al₂O₃-sol-gel > Pd/ α -Al₂O₃-solvothermal \gg Pd/ α -Al₂O₃-commercial. As revealed by NH₃ temperature program desorption studies, incorporation of Ni atoms in α -Al₂O₃ resulted in a significant decrease of acid sites on the alumina supports. Moreover, XPS revealed a shift of Pd 3d binding energy for Pd catalyst supported on Ni-modified α -Al₂O₃-sol-gel where only NiAl₂O₄ was formed, suggesting that the electronic properties of Pd may be modified.

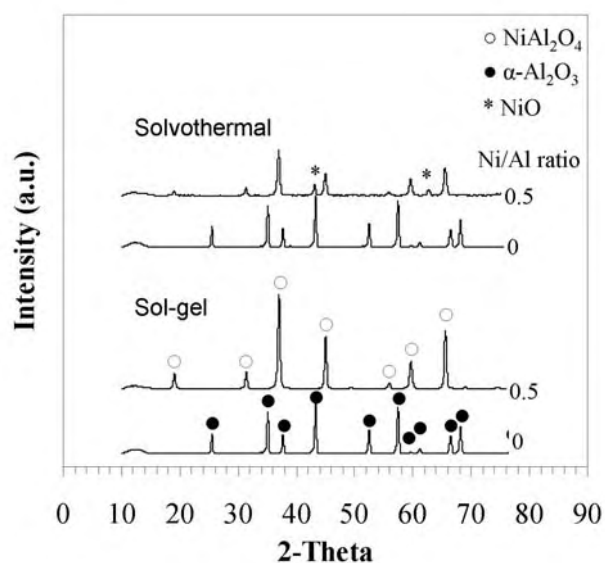


Figure 3.1 XRD patterns of the various Pd catalysts supported on nanocrystalline $\alpha\text{-Al}_2\text{O}_3$ and Ni-modified $\alpha\text{-Al}_2\text{O}_3$ prepared by sol-gel and solvothermal methods.

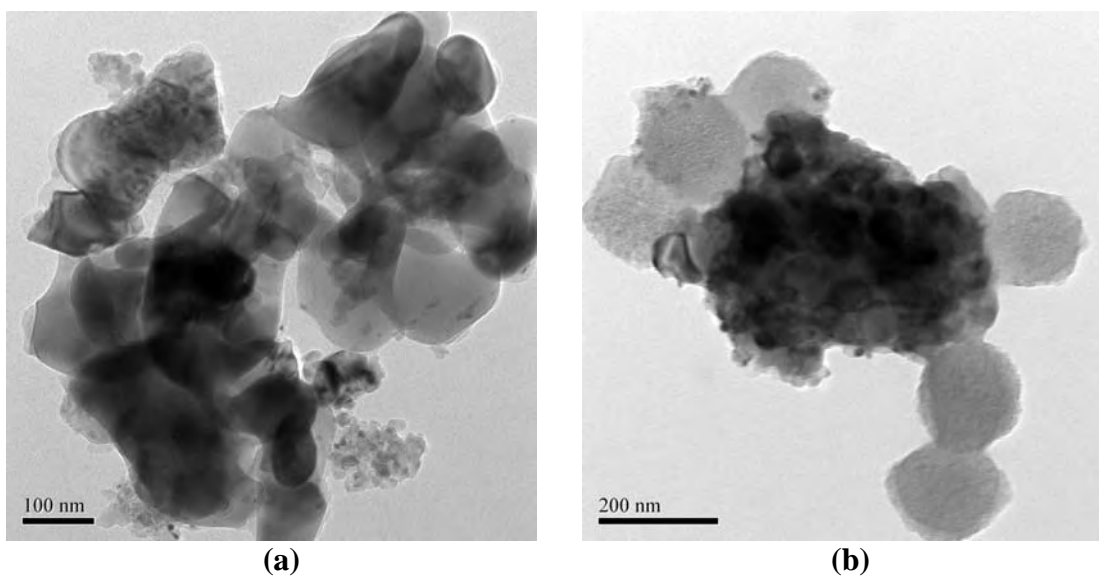


Figure 3.2 TEM micrographs of (a) Pd/ $\alpha\text{-Al}_2\text{O}_3$ -solvothermal, and (b) Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -solvothermal.

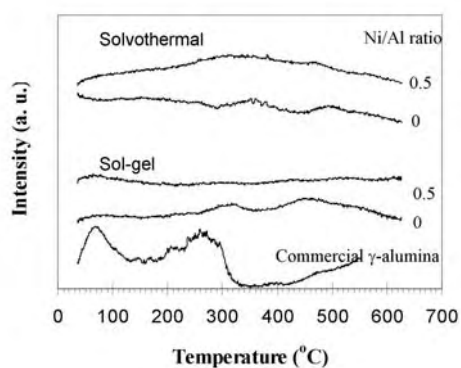


Figure 3.3 NH_3 temperature program desorption profiles for the sol-gel and solvothermal-made $\alpha\text{-Al}_2\text{O}_3$ and the Ni-modified $\alpha\text{-Al}_2\text{O}_3$ supports.

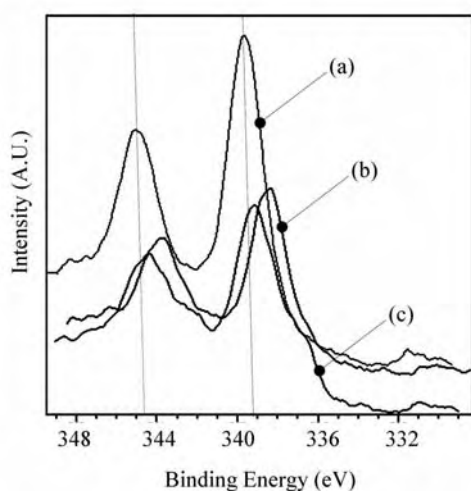


Figure 3.4 XPS results of Pd 3d for (a) Pd/ $\alpha\text{-Al}_2\text{O}_3$ -sol-gel (b) Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -sol-gel and (c) Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -solvothermal.

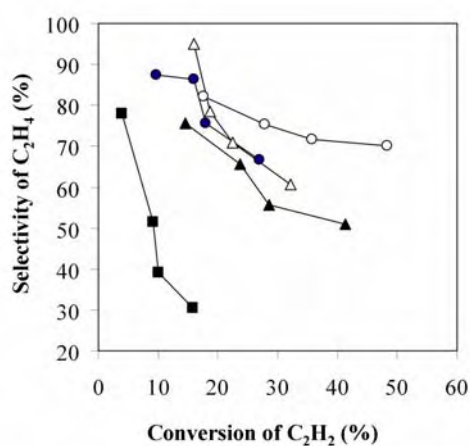


Figure 3.5 Performance of sol-gel (circle; \circ) and solvothermal (triangle; Δ) made Pd/ $\alpha\text{-Al}_2\text{O}_3$ (filled symbols), Pd/commercial $\alpha\text{-Al}_2\text{O}_3$ (filled square; \blacksquare) and Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ (open symbols) catalysts in selective acetylene hydrogenation.

4.5.4 A Comparative Study of Strong Metal-Support Interaction and Catalytic Behaviors of Pd Catalysts Supported on Micron- and Nano-sized TiO₂ in Liquid-Phase Selective Hydrogenation of Phenylacetylene

The strong metal-support interaction and catalytic behaviors of Pd catalysts supported on micron- (0.1 μm) and nano-sized (14 nm) TiO₂ were investigated in the liquid-phase selective hydrogenation of phenylacetylene to styrene. It was found that when supported on the nano-sized TiO₂, the Pd/TiO₂ catalyst that reduced by H₂ at 500°C exhibited strong metal-support interaction (SMSI) and much improved catalyst performance in liquid-phase selective hydrogenation of phenylacetylene. However, as revealed by CO pulse chemisorption, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and CO-temperature program desorption results, the SMSI effect was not detected for the micron-sized TiO₂ supported ones. It is suggested during high temperature reduction, the inner Ti³⁺ in large crystallite size TiO₂ was more difficult to diffuse to the Pd surface than the surface Ti³⁺ in the smaller crystallite size ones. Sintering of Pd⁰ metal was observed instead.

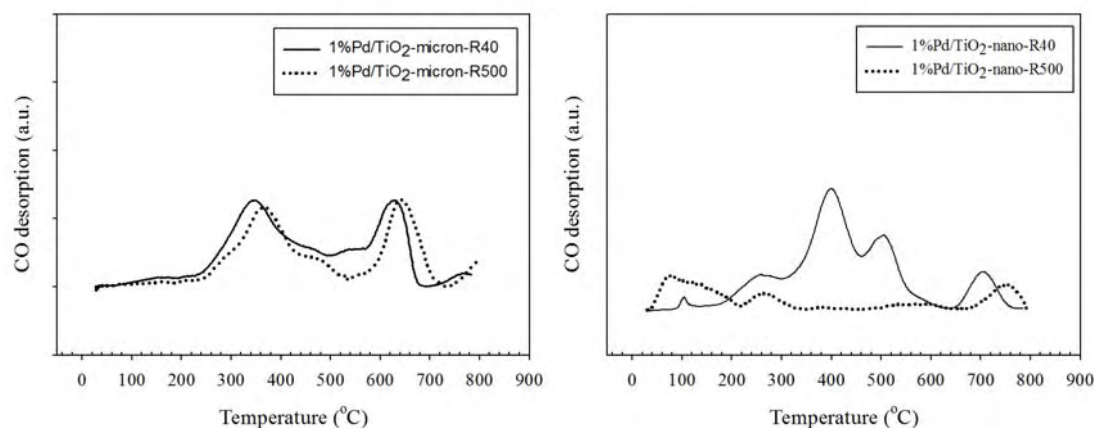


Figure 4.1 CO-temperature programmed desorption profiles of 1%Pd/TiO₂-micron and 1%Pd/TiO₂-nano reduced at 40 and 500°C

3.5.5 Effect of strong metal-support interaction on the catalytic performance of Pd/TiO₂ in the liquid-phase semihydrogenation of phenylacetylene

Liquid-phase semihydrogenation of phenylacetylene under mild conditions has been investigated on a series of solvothermal-derived nano-TiO₂ supported Pd catalysts with various TiO₂ crystallite sizes in the range of 9-23 nm. As revealed by CO chemisorption and transmission electron microscopy, all the catalysts exhibited strong metal-support interaction (SMSI) when reduced at 500°C. The catalysts with SMSI show remarkably high catalytic performance in terms of both hydrogenation activities (turnover frequencies (TOFs) 9.1-21.4 s⁻¹) and moderate-high selectivities to styrene (86-90%) at complete conversion of phenylacetylene. Without SMSI effect (the catalysts reduced at 40°C), styrene selectivity and catalytic activity depended largely on the Pd particle size in which small Pd particles (formed on small crystallite size TiO₂ supports) exhibited lower phenylacetylene conversion and poor styrene

selectivity. Moreover, the TOF values of the non-SMSI catalysts were similar to those reported in the literature for other supported Pd catalysts in liquid-phase semihydrogenation of phenylacetylene under mild conditions (TOFs 1.3-2.8 s⁻¹).

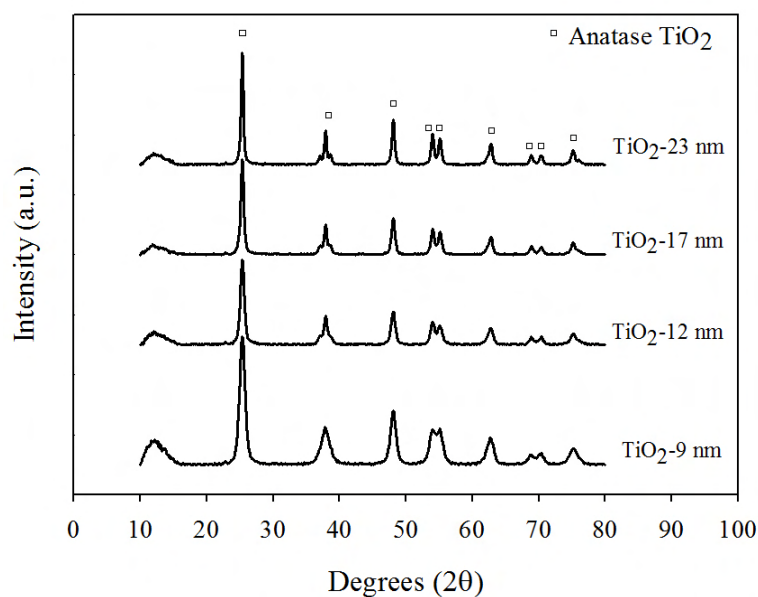


Figure 5.1 XRD patterns of the solvothermal-derived TiO₂ with different crystallite sizes

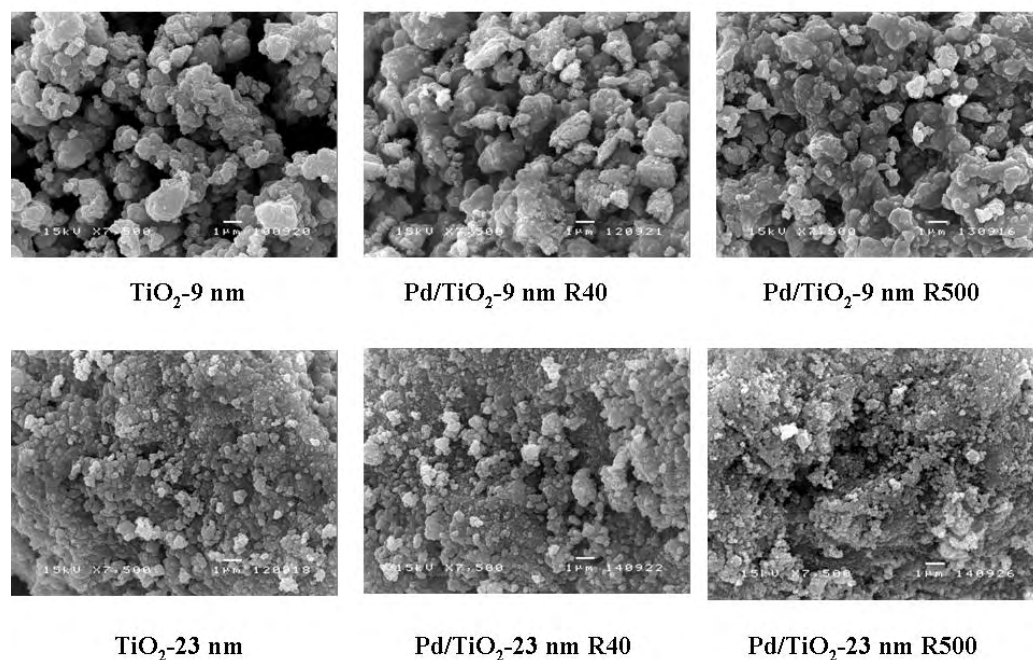


Figure 5.2 SEM micrographs of calcined and reduced Pd/TiO₂ catalysts. Reduction temperature = 40°C (R40), 500°C (R500)

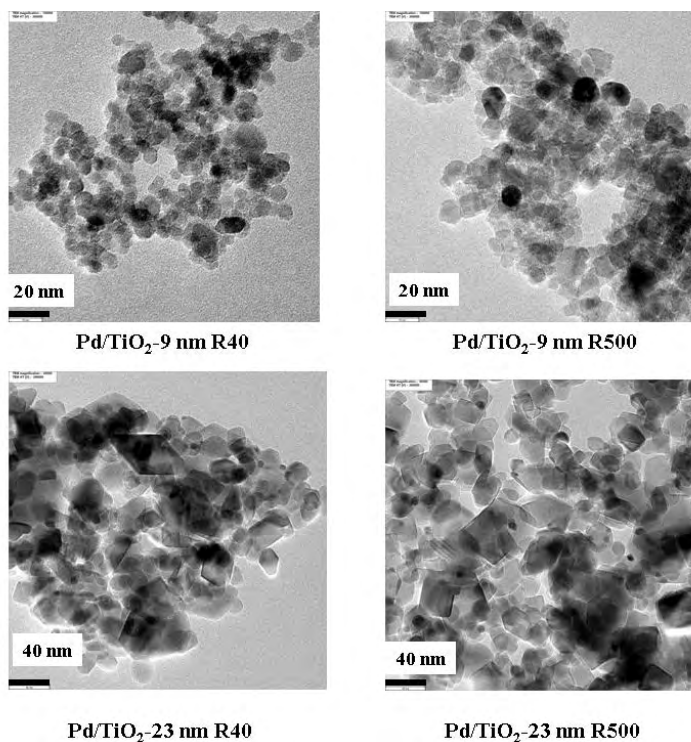


Figure 5.3 TEM micrographs of Pd/TiO₂-9 nm and Pd/TiO₂-23 nm reduced at 40°C (R40) and 500°C (R500)

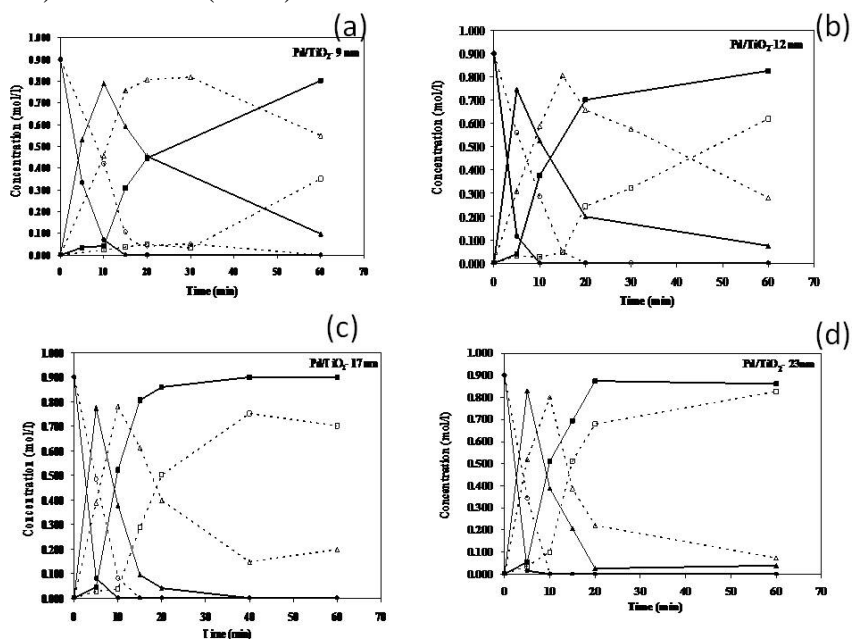


Figure 5.4 Liquid-phase semihydrogenation of phenylacetylene over the Pd/TiO₂ catalysts: \bullet = phenylacetylene \blacktriangle = styrene \blacksquare = ethylbenzene, solid symbols = Pd/TiO₂ catalysts reduced at 40°C and open symbols = Pd/TiO₂ catalysts reduced at 500°C (a) Pd/TiO₂-9 nm (b) Pd/TiO₂-12 nm (c) Pd/TiO₂-17 nm (d) Pd/TiO₂-23 nm (reaction conditions were H₂ pressure = 5 bar and 30°C).

4.5.6 Selective Hydrogenation of Acetylene over Pd Catalysts Supported on Nanocrystalline α -Al₂O₃ and Zn-Modified α -Al₂O₃

The catalytic performance of Pd catalysts supported on nanocrystalline α -Al₂O₃ and Zn-modified α -Al₂O₃ prepared by sol-gel and solvothermal methods was studied in the selective hydrogenation of acetylene. Acidity of the nanocrystalline α -Al₂O₃ was significantly decreased by incorporation of Zn atoms in the α -Al₂O₃. Both of acetylene conversions and ethylene selectivities were improved in the order: Pd/Zn-modified α -Al₂O₃-sol-gel > Pd/Zn-modified α -Al₂O₃-solvothermal > Pd/ α -Al₂O₃-sol-gel \approx Pd/ α -Al₂O₃-solvothermal >> Pd/ α -Al₂O₃-commercial. As revealed by thermal gravimetric and differential temperature analysis (TG-DTA), Pd catalysts on the nanocrystalline Zn-modified α -Al₂O₃ also showed less deactivation by coke formation.

Table 6.1 Characteristics of the various Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ catalysts.

Sample	Crystallite size		BET surface area	Pore Vol.	Avg. Pore Diameter	Pd active sites ($\times 10^{-17}$ molecule CO /g cat.)	Pd dispersion (%)	d_p Pd ⁰ (nm)
	(nm)		(m ² /g)	(cm ³ /g)	(nm)			
	α -Al ₂ O ₃	ZnAl ₂ O ₄						
Pd/Al ₂ O ₃ SG	31.0	n.d. ^a	1.6	0.011	20.4	11.3	8.8	13
Pd/Zn-Al ₂ O ₃ SG	40.4	28	1.9	0.020	11.8	4.9	3.9	29
Pd/Al ₂ O ₃ SV	69.5	n.d.	14.9	0.075	13.6	32.9	20.8	5
Pd/Zn-Al ₂ O ₃ SV	32.8	14.9	10.7	0.100	22.4	22.8	16.6	7

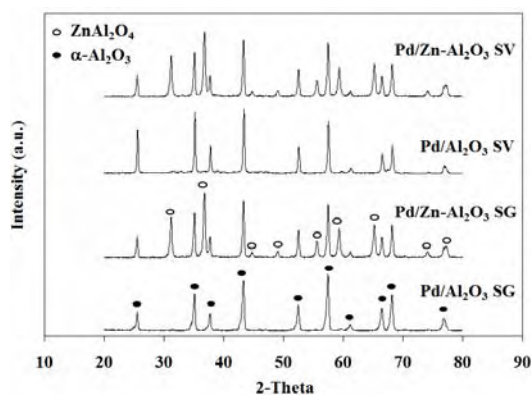


Figure 6.1 XRD patterns of the Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ supports prepared by sol-gel (SG) and solvothermal (SV) methods.

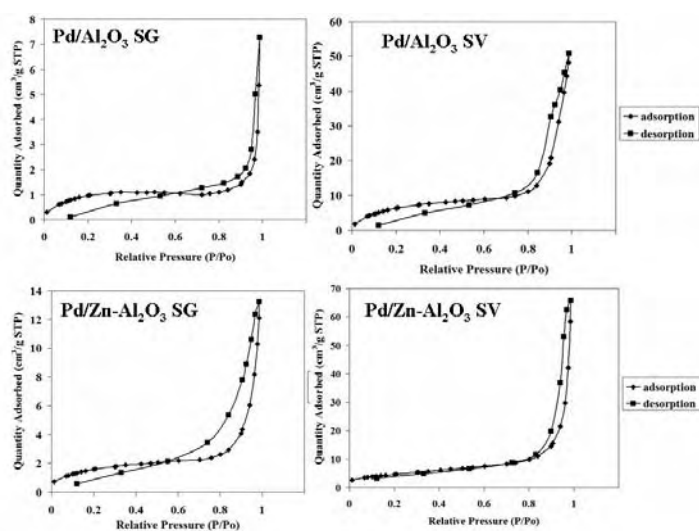


Figure 6.2 N₂ adsorption-desorption isotherms of the Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ supports prepared by sol-gel (SG) and solvothermal (SV) methods

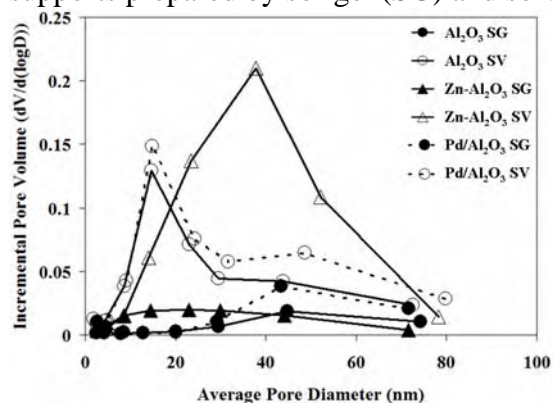


Figure 6.3 Pore size distributions of the α -Al₂O₃, Zn-modified α -Al₂O₃, and Pd/ α -Al₂O₃

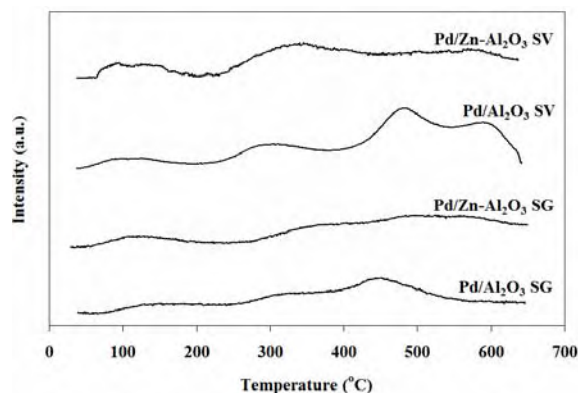


Figure 6.4 NH₃ temperature program desorption profiles for the Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ supports prepared by sol-gel (SG) and solvothermal (SV) methods.

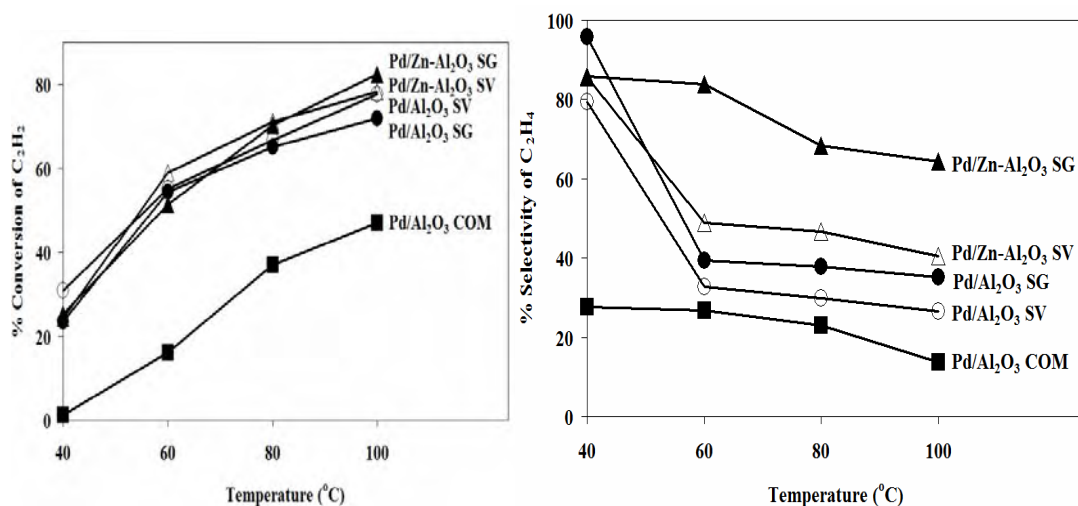


Figure 6.6 Temperature dependence of the catalytic performance of Pd/ α - Al_2O_3 and Pd/Zn-modified α - Al_2O_3 catalysts; (A) in terms of % conversion of C_2H_2 (B) in terms of % selectivity of C_2H_4 .

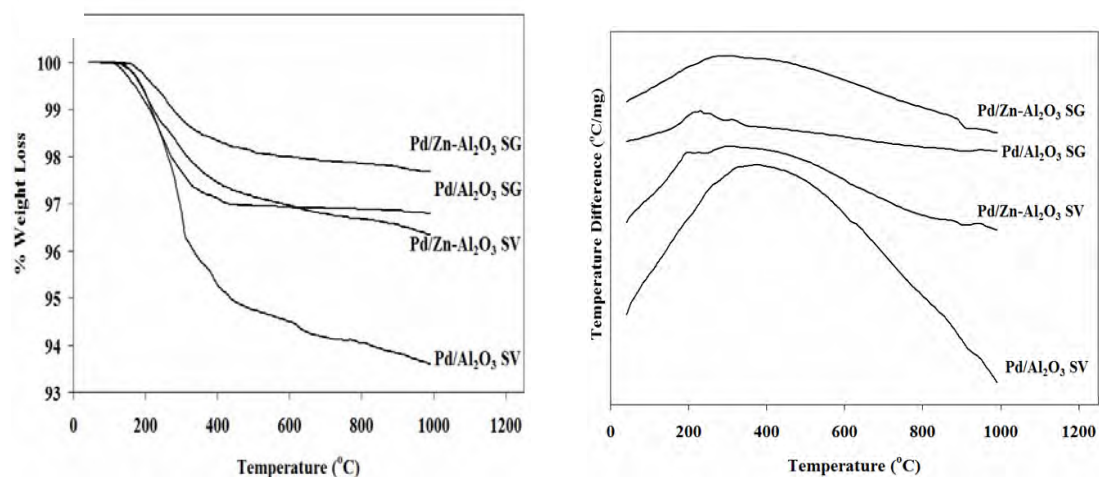


Figure 6.7 Thermal gravimetric and differential temperature analysis (TG/DTA) of Pd/ α - Al_2O_3 and Pd/Zn-modified α - Al_2O_3 catalysts after reaction; (A) in terms of temperature ($^{\circ}C$) and weight loss (%), (B) in terms of temperature ($^{\circ}C$) and temperature difference ($^{\circ}C/mg$).

4.5.7 Improvement of Pd/Al₂O₃ Catalyst Performance in Selective Acetylene Hydrogenation using Mixed-Phases Al₂O₃ Support

The catalytic performances of Pd catalysts supported on γ -Al₂O₃, α -Al₂O₃, and mixed phases Al₂O₃ were investigated in the selective hydrogenation of acetylene in ethylene feed stream. It was found that the use of mixed phases Al₂O₃ with approximately 64% of α -phase resulted in significant improvements in both acetylene conversion and ethylene selectivity. The presence of small amount of transition-phase in the alumina supports brought about higher BET surface area and Pd dispersion as well as improvement of reduction ability of the Pd/Al₂O₃ catalysts. On the other hand, significant amount of α -Al₂O₃ is necessary for high ethylene selectivity due to the lower amount of ethylene adsorbed.

Table 7.1 The physical properties of alumina with various phase compositions.

Samples	α -Phase (%)	BET Surface Area (m ² /g)	Crystallite Size (nm) ^a		Pore Volume ^b (cm ³ /g)	Average Pore Diameter ^b (Å)
			γ -phase	α -phase		
Al- α 100	100	12.3	n.d.	44.5	0.03	90.1
Al- α 64	64	36.1	28.3	45.8	0.14	129.6
Al- α 47	47	45.4	17.8	48.9	0.20	151.9
Al- α 14	14	67.3	11.8	46.0	0.30	143.8
Al- α 0	0	244.1	3.7	n.d.	0.66	78.9

Table 7.2 Physiochemical properties of Pd supported on alumina with various phase compositions.

Samples	Pd Active Sites ^a ($\times 10^{-18}$ CO molecule/g-cat)	%Pd Dispersion ^b	d_p^c (Pd ⁰) (nm)	Pd 3d _{5/2} ^d		Atomic Concentration ^d Pd/Al
				B.E. (eV)	FWHM	
Pd/Al- α 100	7.4	12.5	8.9	336.9	1.8	0.034
Pd/Al- α 64	11.0	18.5	6.1	336.9	2.0	0.027
Pd/Al- α 47	25.4	42.9	2.6	336.4	2.4	0.020
Pd/Al- α 14	31.7	53.5	2.1	336.4	2.3	0.011
Pd/Al- α 0	35.1	59.2	1.9	336.4	2.2	0.001

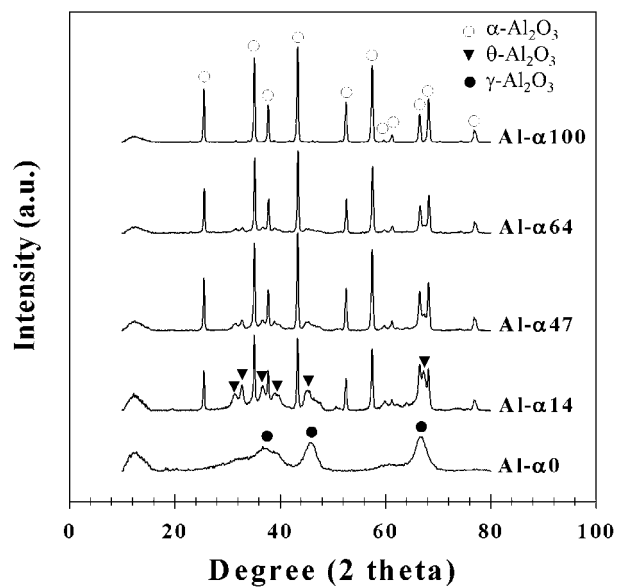


Figure 7.1 The XRD patterns of the Al₂O₃ supports containing various % of α-phase

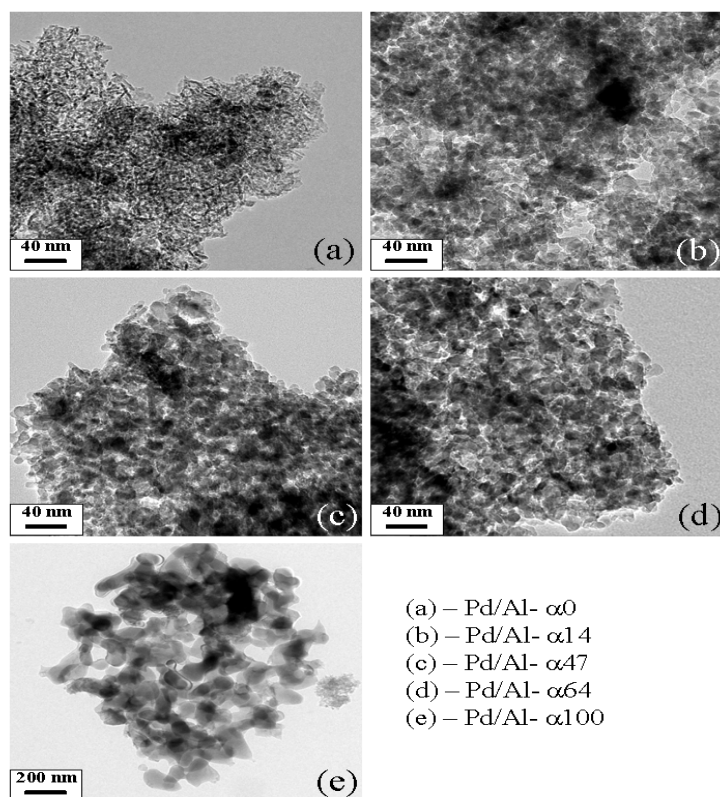


Figure 7.2 Transmission electron micrographs of the Pd/Al₂O₃ catalysts

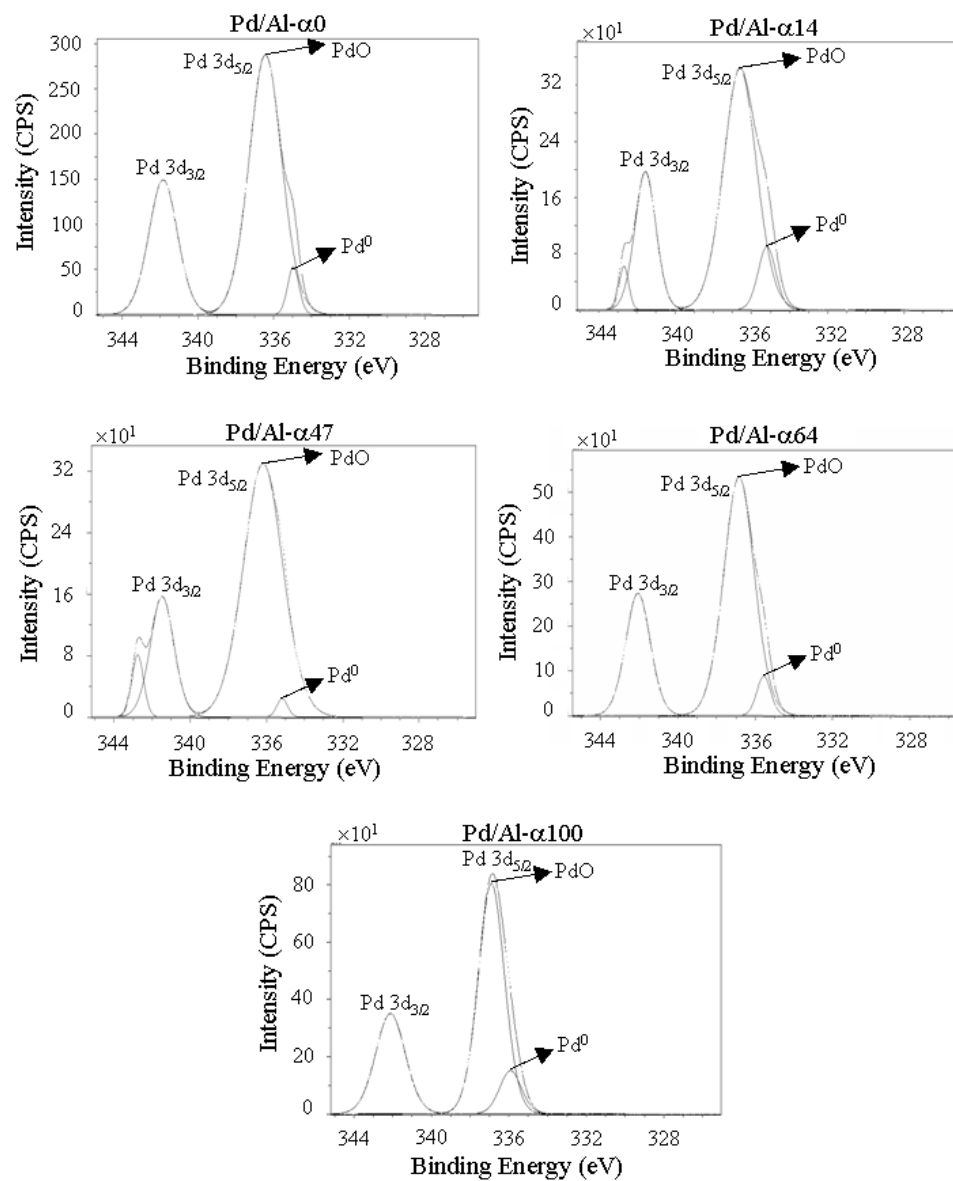


Figure 7.3 The XPS deconvoluted spectra of the Pd/Al₂O₃ catalysts

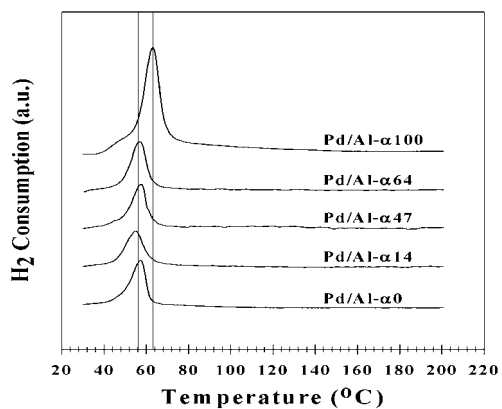


Figure 7.4 TPR profiles of the Pd/Al₂O₃ catalysts

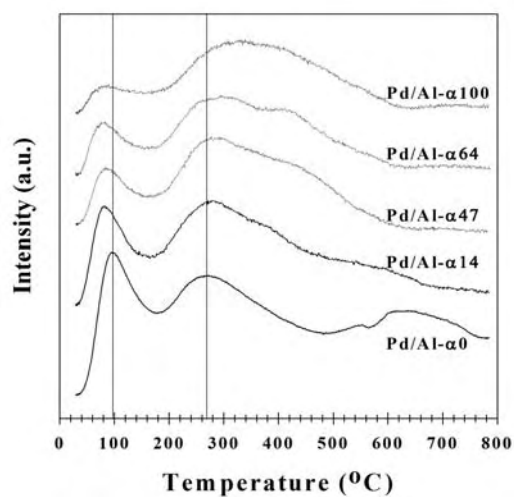


Figure 7.5 Ethylene TPD results of the Pd/Al₂O₃ catalysts

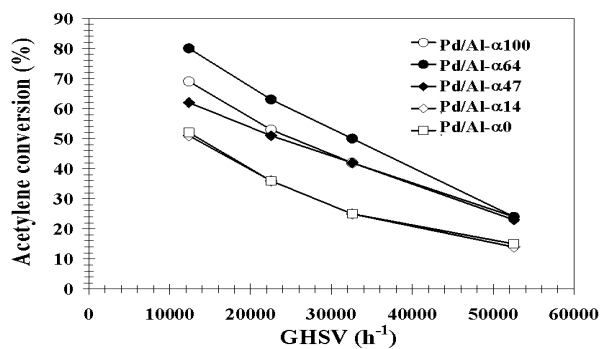


Figure 7.6 Catalyst performances in selective hydrogenation of acetylene in terms of GHSV values and acetylene conversion (%)

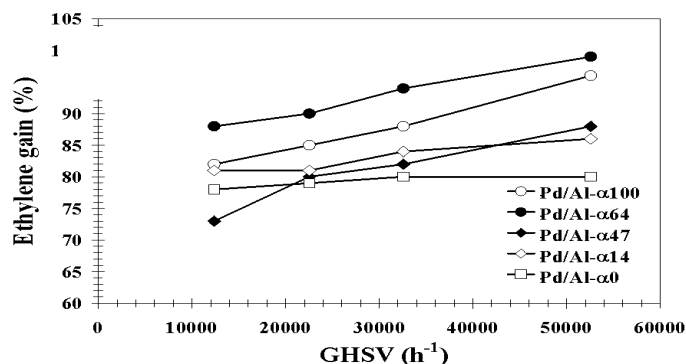


Figure 7.7 Catalyst performances in selective hydrogenation of acetylene in terms of GHSV values and ethylene gain (%)

4.5.8 Effect of Support Crystallite Size on Catalytic Activity and Deactivation of Nanocrystalline ZnAl_2O_4 Supported Pd Catalysts in Liquid-Phase Hydrogenation

The catalytic activity and deactivation of nanocrystalline ZnAl_2O_4 -supported Pd catalysts were investigated for the liquid-phase hydrogenation under mild conditions. Nanocrystalline ZnAl_2O_4 spinels with average crystallite size between 8-33 nm were synthesized by the solvothermal method in toluene. Higher turnover frequencies for 1-heptyne hydrogenation and less deactivation due to Pd leaching were obtained for the Pd/ ZnAl_2O_4 -33 nm catalyst. XPS and ESR results suggest that the presence of defects in larger crystallite size ZnAl_2O_4 resulted in higher Pd dispersion and stronger interaction between Pd and the support.

Table 8.1 N_2 physisorption results^a and XRD determined average crystallite sizes of the as-synthesized and the calcined ZnAl_2O_4 supports prepared by the solvothermal method

Sample	BET S.A. (m^2/g)	Pore Volume (m^3/g)	Avg. Pore Diameter (nm)	Avg. XRD Crystallite Size (nm)
ZnAl_2O_4 -as-syn	130	0.18	4.2	8.2
ZnAl_2O_4 -500	116	0.19	4.6	9.0
ZnAl_2O_4 -700	63	0.20	8.5	10.9
ZnAl_2O_4 -900	28	0.19	22.0	17.6
ZnAl_2O_4 -1150	15	0.08	36.6	33.3

^a Error of measurements as determined directly were $\pm 10\%$.

Table 8.2 Physicochemical properties of the various Pd catalysts

Catalyst	BET S.A. ^a (m ² /g)	Pore Vol. ^a (m ³ /g)	Avg. Pore Diameter ^a (nm)	CO chemisorption ^b (10 ¹⁸ molecules CO/g cat.)	%dispersion ^c	Pd ⁰ d _p ^d (nm)
Pd/ZnAl ₂ O ₄ -as-syn	106	0.20	4.6	7.4	13.0	7.8
Pd/ZnAl ₂ O ₄ -500	104	0.21	4.8	7.4	13.1	7.8
Pd/ZnAl ₂ O ₄ -700	66	0.21	8.9	7.2	12.8	7.4
Pd/ZnAl ₂ O ₄ -900	28	0.18	21.5	7.3	12.8	8.0
Pd/ZnAl ₂ O ₄ -1150	16	0.10	29.2	8.7	15.3	6.7

Table 8.3 Catalytic properties for liquid-phase 1-heptyne hydrogenation^a

Catalysts	Conversion of 1-heptyne (%)	1-Heptene selectivity (%)	Estimated TOF ^b (s ⁻¹) ^c	%Pd leached ^d
Pd/ZnAl ₂ O ₄ -as-syn	52	97	0.24	36
Pd/ZnAl ₂ O ₄ -500	51	100	0.23	38
Pd/ZnAl ₂ O ₄ -700	45	100	0.22	30
Pd/ZnAl ₂ O ₄ -900	49	100	0.24	35
Pd/ZnAl ₂ O ₄ -1150	66	100	0.32	6

^a Reaction conditions were 105 kPa, 30°C, 5 min, and catalyst/substrate molar ratio = 1,600

^b TOF = mole product/mole Pd metal surface atoms/s. Based on the amount of potentially active Pd atoms measured by CO chemisorption.

^c Estimated since at high conversion.

^d Based on atomic absorption spectroscopy results. Error of measurement as determined directly was ±10%.

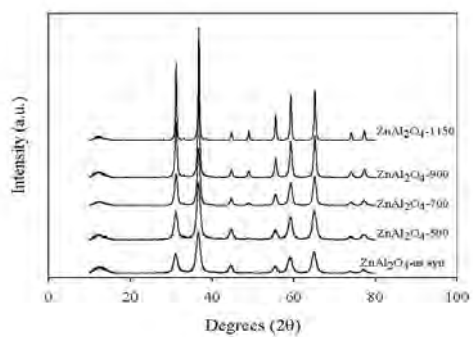


Figure 8.1 XRD patterns of the as-synthesized and the calcined ZnAl_2O_4

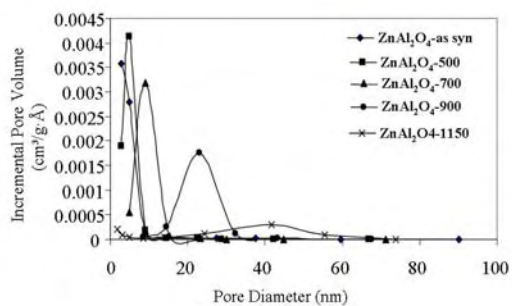


Figure 8.2 Pore size distribution of the as-synthesized and the calcined ZnAl_2O_4

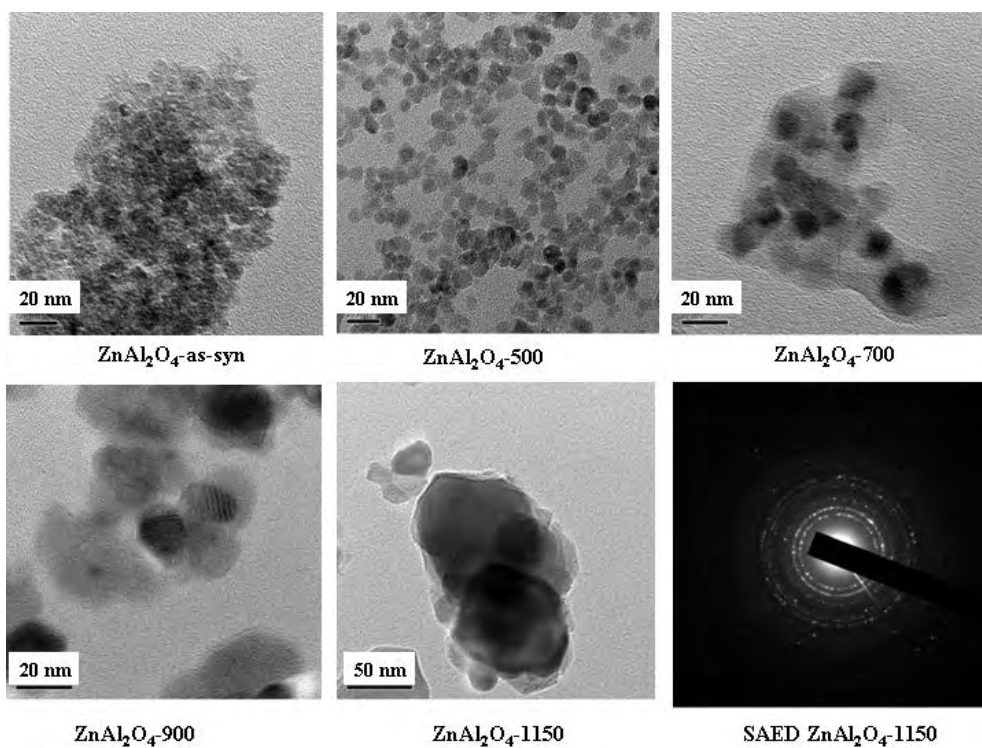


Figure 8.3 TEM micrographs and selected area electron diffraction of various ZnAl_2O_4 samples

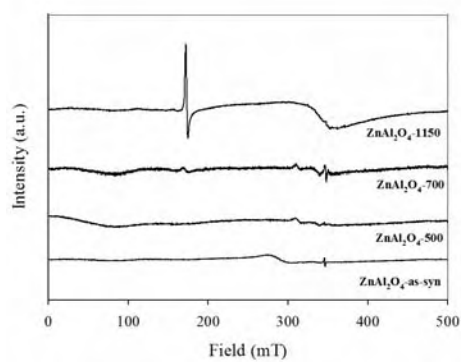


Figure 8.4 ESR results of the solvothermal-derived ZnAl_2O_4

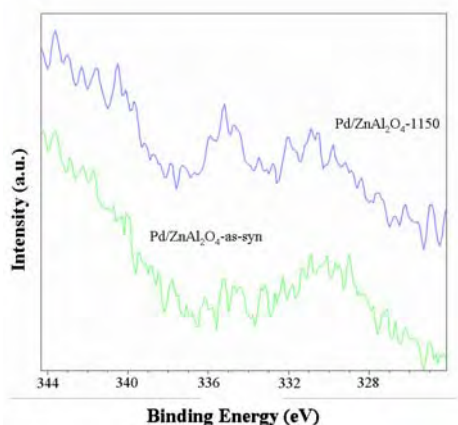


Figure 8.5 XPS spectra of Pd 3d_{5/2} for Pd/ZnAl₂O₄ catalysts

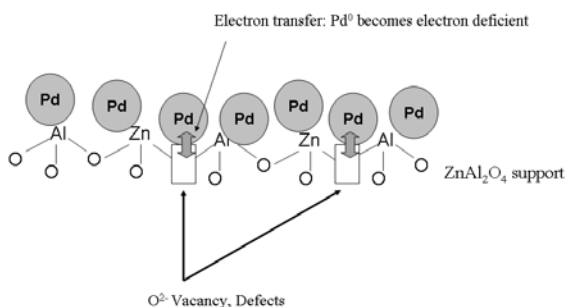


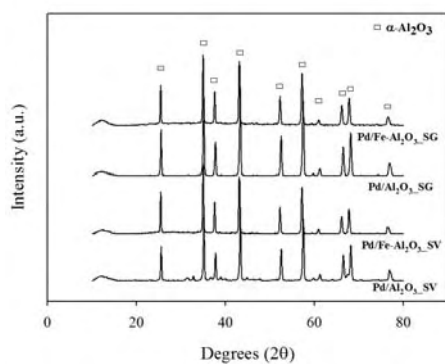
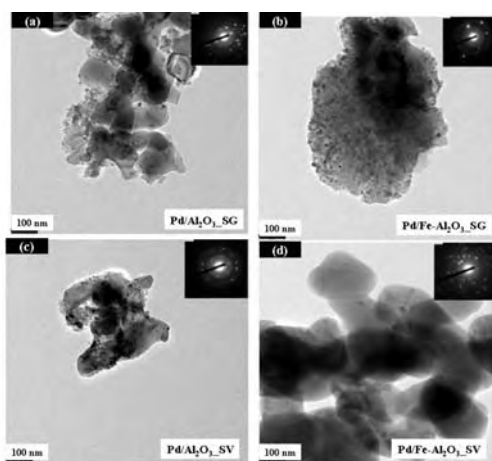
Figure 8.6 A conceptual model for stronger metal-support interaction induced by defect sites of the nanocrystalline material

4.5.9 Effect of Fe-modified α -Al₂O₃ on the properties of Pd/ α -Al₂O₃ catalysts in selective acetylene hydrogenation

The use of nanocrystalline Fe-modified α -Al₂O₃ prepared by sol-gel and solvothermal method as supports for Pd catalysts resulted in an improved catalyst performance in selective acetylene hydrogenation. Moreover, the amount of coke deposits was reduced due to lower acidity of the Fe-modified α -Al₂O₃ supports.

Table 9.1 Physicochemical properties of Pd/Al₂O₃ and Pd/Fe-Al₂O₃ catalysts

	BET surface area (m ² /g)	Avg. crystallite size ^a (nm)	CO chemisorption (×10 ¹⁷ site/g cat.)	% Pd Dispersion	d _p Pd ⁰ (nm)
Pd/Al ₂ O ₃ _SG	1.0	46	10.0	8.4	13
Pd/Fe-Al ₂ O ₃ _SG	1.4	62	4.1	2.7	42
Pd/Al ₂ O ₃ _SV	5.1	52	11.0	7.2	16
Pd/Fe-Al ₂ O ₃ _SV	3.9	63	7.8	5.1	22

**Figure 9.1** XRD patterns of the Pd/α-Al₂O₃ and Pd/Fe-modified α-Al₂O₃ prepared by sol-gel (SG) and solvothermal (SV) methods.**Figure 9.2** TEM micrographs of Pd/α-Al₂O₃ and Pd/Fe-modified α-Al₂O₃ catalysts.

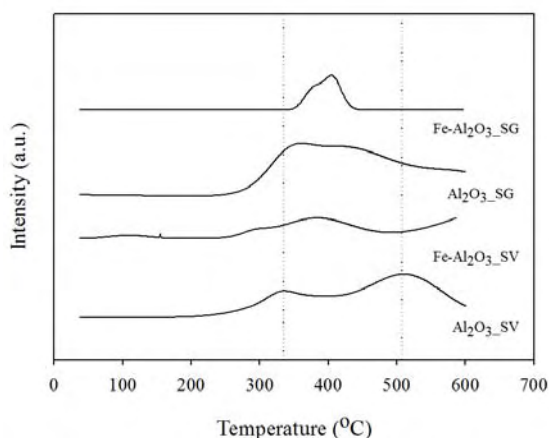


Figure 9.3 NH_3 temperature program desorption profiles for $\alpha\text{-Al}_2\text{O}_3$ and Fe-modified $\alpha\text{-Al}_2\text{O}_3$ supports.

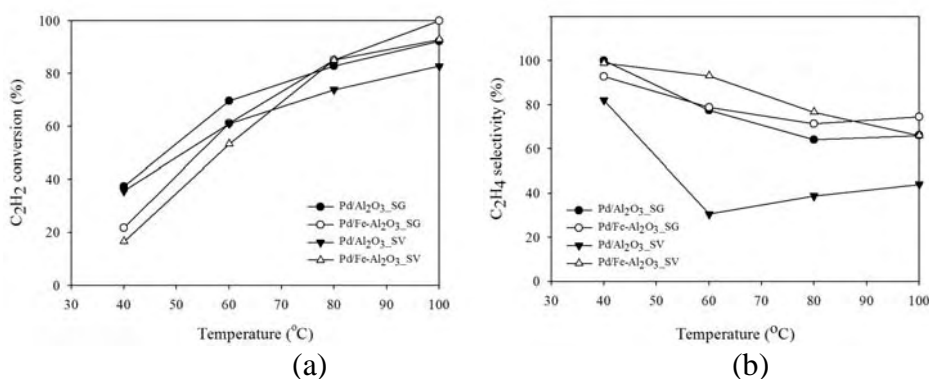


Figure 9.4 Temperature dependence of the catalytic performance of $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ and $\text{Pd}/\text{Fe-modified } \alpha\text{-Al}_2\text{O}_3$ catalysts; (A) % conversion of C_2H_2 (B) % selectivity of C_2H_4 .

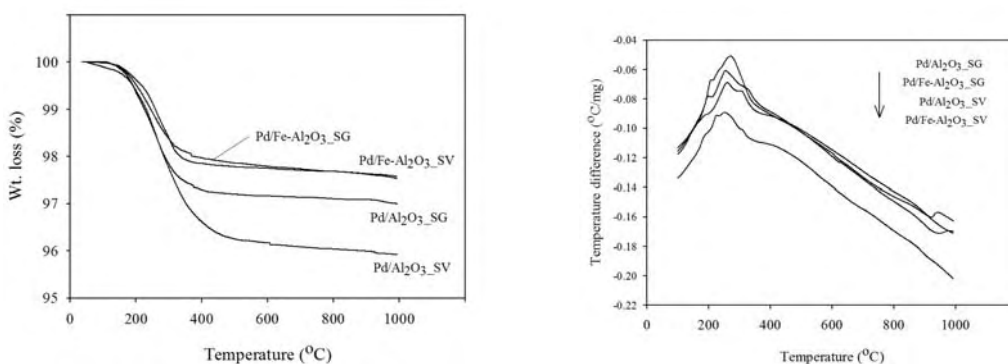


Figure 9.5 Thermal gravimetric and differential temperature analysis (TG/DTA) of $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ and $\text{Pd}/\text{Fe-modified } \alpha\text{-Al}_2\text{O}_3$ catalysts after reaction; (A) in terms of temperature ($^{\circ}\text{C}$) and weight loss (%), (B) in terms of temperature ($^{\circ}\text{C}$) and temperature difference ($^{\circ}\text{C}/\text{mg}$).

4.5.10 Influence of preparation method on the nanocrystalline porosity of α -Al₂O₃ and the catalytic properties of Pd/ α -Al₂O₃ in selective acetylene hydrogenation

Nanocrystalline α -Al₂O₃ powder with average crystallite sizes 34-68 nm have been synthesized by three different methods, namely, solvothermal, sol-gel, and precipitation. Although smallest crystallite size of α -Al₂O₃ was obtained via the sol-gel synthesis, the α -Al₂O₃ sol-gel possessed the least amount of specific surface area and pore volume. A narrow pore size distribution with average pore diameter 15 nm can be obtained via solvothermal method while precipitation method yielded α -Al₂O₃ with larger pore size and wider pore size distribution. When employed as a support for Pd catalyst, the α -Al₂O₃ solvothermal provided the highest Pd dispersion and the best catalyst performance in selective hydrogenation of acetylene. The catalytic properties of Pd/ α -Al₂O₃ solvothermal were improved in terms of both acetylene conversion and ethylene selectivity. As shown by temperature program studies, the use of solvothermal-derived α -Al₂O₃ facilitated H₂ reduction at low temperature and desorption of ethylene and CO.

Table 10.1 Physicochemical properties of α -Al₂O₃ various preparation methods and 0.3%Pd/Al₂O₃catalysts.

Catalysts	BET surface area (m ² /g) ^{a,*}	Pore volume (cm ³ /g) ^{b,*}	Average pore diameter (nm) ^{b,*}	Crystallite size (nm) ^{c,*}	Pd active sites ($\times 10^{-17}$ sites/g-catalyst) ^d	%Pd dispersion ^e	Average Pd ⁰ particle size (nm) ^f
Pd/Al ₂ O ₃ Solvothermal	19.8	0.0739	14.9	53	11.5	7.6	14.7
Pd/Al ₂ O ₃ Sol-Gel	1.7	0.0065	46	33.8	3.9	2.6	43.2
Pd/Al ₂ O ₃ Precipitation	41.2	0.2020	26.9	67.6	2.1	1.4	80.2

Table 10.2 Consumption of hydrogen in TPR, amount of ethylene and CO desorption.

Catalysts	Temperature at maximum (°C)			H ₂ consumption (μmol)*	Amount of ethylene desorption (μmol)*	Amount of CO desorption (μmol)*
	Peak 1	Peak 2	Peak 3			
Pd/Al ₂ O ₃ Solvothermal	60 ^a ,90 ^b ,90 ^c	240 ^b ,230 ^c	420 ^b	658	131	76
Pd/Al ₂ O ₃ Sol-Gel	65 ^a ,100 ^b ,90 ^c	280 ^b ,230 ^c	500 ^b	488	75	10
Pd/Al ₂ O ₃ Precipitation	70 ^a ,100 ^b ,90 ^c	260 ^b ,250 ^c	440 ^b	610	122	33

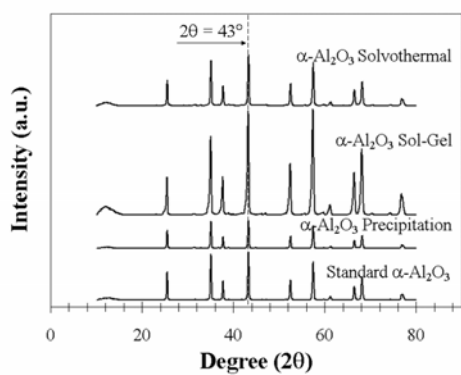


Figure 10.1 XRD patterns of the α -Al₂O₃ supports: solvothermal, sol-gel, and precipitation method.

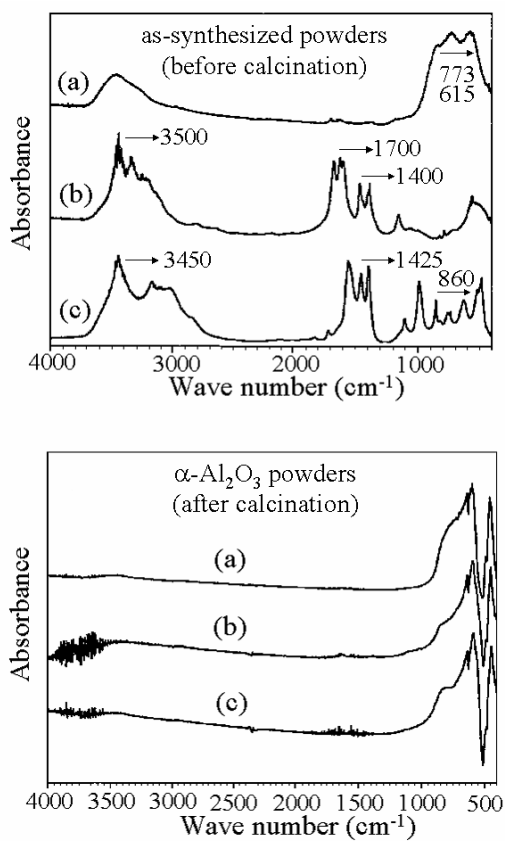


Figure 10.2 IR spectra of α -Al₂O₃ from solvothermal (a), sol-gel (b), and precipitation (c) method.

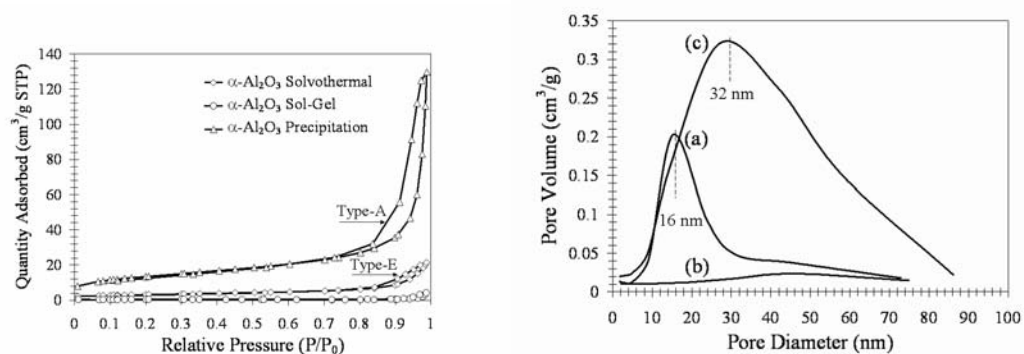


Figure 10.3 Pore size distribution results of the α -Al₂O₃ supports from solvothermal (a), sol-gel (b), and precipitation (c) method. **Figure 10.4** N₂ adsorption isotherms.

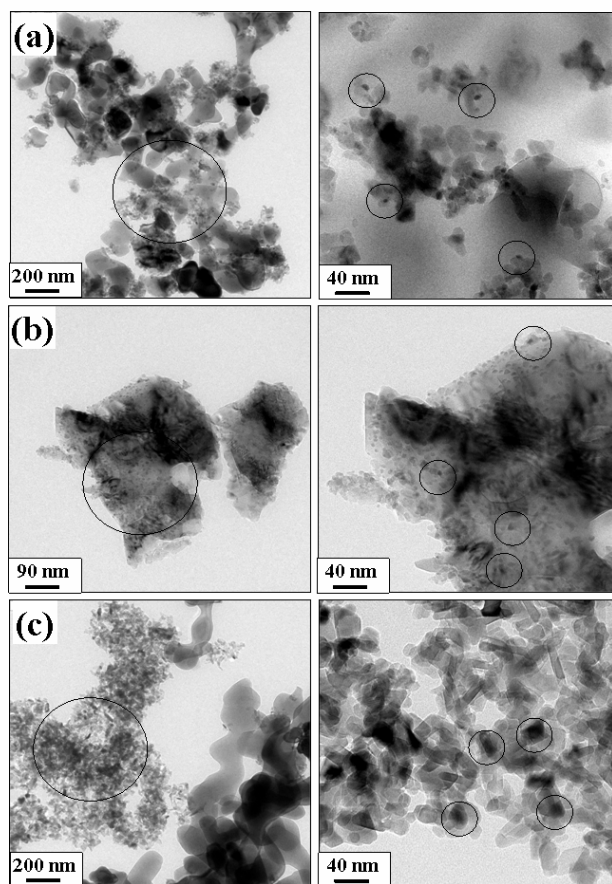


Figure 10.5 TEM image of the Pd supported by α -Al₂O₃ from solvothermal (a), sol-gel (b), and precipitation (c) method, showed Pd characteristics within the circles.

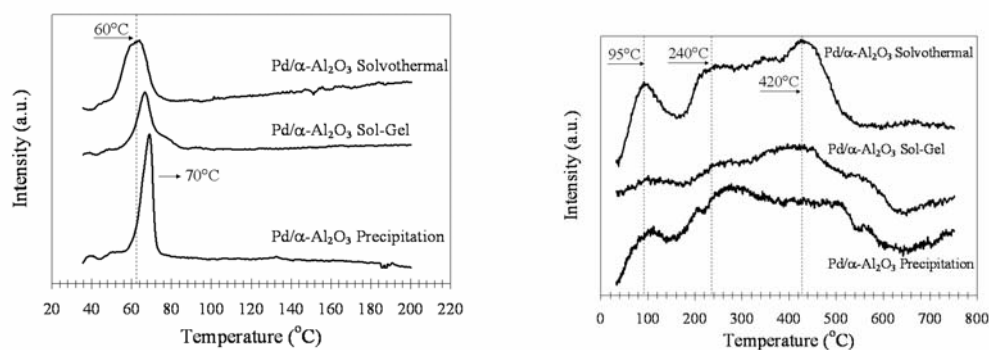


Figure 10.6 H₂-TPR profiles for the various Pd/α-Al₂O₃ catalysts. **Figure 10.7** C₂H₄-TPD profiles for the various Pd/α-Al₂O₃ catalysts.

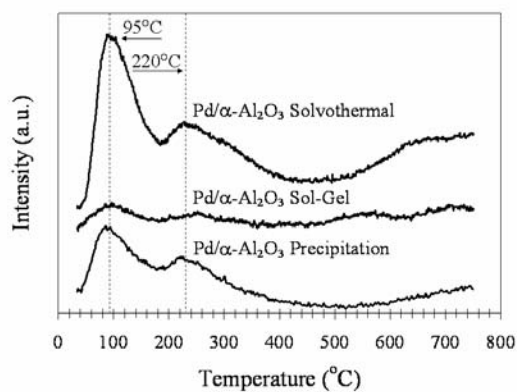


Figure 10.8 CO-TPD profiles for the various Pd/α-Al₂O₃ catalysts.

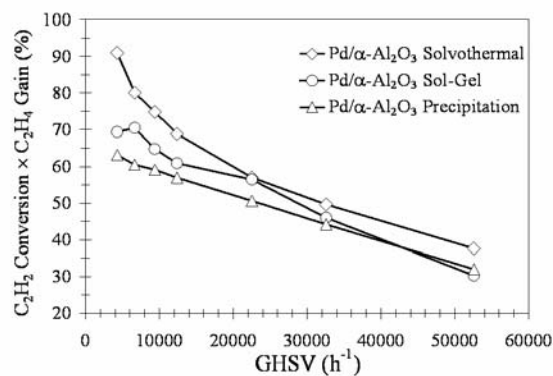


Figure 10.9 Performance of Pd/α-Al₂O₃ catalysts in the selective acetylene hydrogenation.

Output ที่ได้จากโครงการ

งานวิจัยนี้ได้เริ่มดำเนินงานตั้งแต่ 25 มิ.ย. 2550 สิ้นสุดโครงการ 24 มิ.ย. 2553 รวมระยะเวลาดำเนินงาน 3 ปี ผลที่ได้รับจากงานวิจัย ได้แก่

1. สามารถสังเคราะห์ผลึกขนาดนาโนเมตรของโลหะออกไซด์หลายชนิดได้แก่ซิลิกาอะลูมินา ไทเทเนียมไดออกไซด์ซิงค์ออกไซด์ซิงค์อะลูมิเนียมและสังเคราะห์ตัวเร่งปฏิกิริยา แพลเลเดียมบนผลึกขนาดนาโนเมตรของโลหะออกไซด์ที่ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
2. ได้องค์ความรู้ใหม่เกี่ยวกับการสังเคราะห์ตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสูงสำหรับใช้ในปฏิกิริยาไฮโดรจิเนชันของสารไฮโดรคาร์บอนไม่อิ่มตัวต่างๆ
3. ได้ผลงานวิจัยที่ได้รับการตีพิมพ์ในวารสารระดับนานาชาติที่มีค่าImpact Factor สูงทางด้านคาตาไลซิสและวิศวกรรมเคมี อาทิ **Journal of Catalysis** (IF 2009 = 5.288), **Applied Catalysis A. General** (IF2009 = 3.564), **Catalysis Today** (IF2009 = 3.526), **Journal of Molecular Catalysis A. Chemical** (IF2009 = 3.135), **Catalysis Communications** (IF2009 = 3.00) จำนวน 17 บทความ Impact factor (ปี 2009) รวม **43.858** โดยเป็น Corresponding author 13 บทความและเป็นผู้ร่วมวิจัย (co-author) 4 บทความ (ภาคผนวก ก และ ข)

ภาคผนวก ก

บทความที่เป็นผู้วิจัยหลัก (Corresponding author) Impact factor รวม 34.643

เอกสารแนบ 1-13

No.	ชื่อบทความ	ผู้แต่ง	Corresponding Author	วารสาร	Impact factor (FY2008)
1	Selective Hydrogenation of Acetylene in Excess Ethylene on Micron-Sized and Nanocrystalline TiO ₂ Supported Pd Catalysts	Joongjai Panpranot, Kunyaluck Kontapakdee, Piyasan Prasertthdam	Joongjai Panpranot	Applied Catalysis A: General 314 (2006) 128-133.	3.564
2	Characteristics and Catalytic Properties of Pd/SiO ₂ Synthesized by One-Step Flame Spray Pyrolysis in Liquid-Phase Hydrogenation of 1-Heptyne	Sirima Somboonthanakij, Okorn Mekasuwandumrong, Joongjai Panpranot*, Tarit Nimmanwudtipong, Reto Strobel, Sotiris E. Pratsinis, and Piyasan Prasertthdam	Joongjai Panpranot	Catalysis Letters, 119 (2007) 346-352	2.021
3	Performance of Pd Catalysts Supported on Nanocrystalline α -Al ₂ O ₃ and Ni-Modified α -Al ₂ O ₃ in Selective Hydrogenation of Acetylene	Nitikon Wongwaranon, Okorn Mekasuwandumrong, Piyasan Prasertthdam, and Joongjai Panpranot	Joongjai Panpranot	Catalysis Today 131 (2008) 553-558	3.526
4	A Comparative Study of Strong Metal-Support Interaction and Catalytic Behaviors of Pd Catalysts Supported on Micron- and Nano-sized TiO ₂ in Liquid-Phase Selective Hydrogenation of Phenylacetylene	Patcharaporn Weerachawanasak, Piyasan Prasertthdam, Masahiko Arai, and Joongjai Panpranot	Joongjai Panpranot	Journal of Molecular Catalysis A: Chemical, 279 (2007) 133-139	3.135
5	Effect of Ni-Modified α -Al ₂ O ₃ Prepared by Sol-Gel and Solvothermal Methods on the Characteristics and Catalytic Properties of Pd/ α -Al ₂ O ₃ Catalysts	Okorn Mekasuwandumrong, Nitikon Wongwaranon, Piyasan Prasertthdam, and Joongjai Panpranot	Joongjai Panpranot	Materials Chemistry and Physics, 111 (2008) 431-437	2.015
6	Selective Hydrogenation of Acetylene over Pd Catalysts Supported on Nanocrystalline α -Al ₂ O ₃ and Zn-Modified α -Al ₂ O ₃	Suthana Chinayon, Okorn Mekasuwandumrong, Piyasan Prasertthdam, and Joongjai Panpranot	Joongjai Panpranot	Catalysis Communications, 9 (2008) 2297-2302	3.000
7	Improvement of Pd/Al ₂ O ₃ Catalyst Performance in Selective Acetylene Hydrogenation using Mixed-Phases Al ₂ O ₃ Support	Sataporn Komhom, Piyasan Prasertthdam, Okorn Mekasuwandumrong, Joongjai Panpranot	Joongjai Panpranot	Catalysis Communications, 10 (2008) 86-91	3.000
8	Effect of Support Crystallite Size on Catalytic Activity and Deactivation of Nanocrystalline ZnAl ₂ O ₄ Supported Pd Catalysts in Liquid-Phase Hydrogenation	Terachai Sirikajorn, Okorn Mekasuwandumrong, Piyasan Prasertthdam, James G. Goodwin, Jr., and Joongjai Panpranot	Joongjai Panpranot	Catalysis Letters, 126 (2008) 313-318	2.021
9	Effect of strong metal-support interaction on the catalytic performance of Pd/TiO ₂ in the liquid-phase semihydrogenation of phenylacetylene	Patcharaporn Weerachawanasak, Okorn Mekasuwandumrong, Piyasan Prasertthdam, Masahiko Arai, Shin-Ichiro Fujita, Joongjai Panpranot	Joongjai Panpranot	Journal of Catalysis, 262 (2009) 199-205	5.288
10	Preparation of Nano-Pd/SiO ₂ by One-Step Flame Spray Pyrolysis and its Hydrogenation Activities: Comparison to Conventional Impregnation Method	Okorn Mekasuwandumrong, Sirima Somboonthanakij, Piyasan Prasertthdam, and Joongjai Panpranot	Joongjai Panpranot	Industrial Engineering and Chemistry Research, 48 (2009) 2819-2825	1.758
11	Synthesis of nanocrystalline Au-ZnO and Pt-ZnO by flame spray pyrolysis and its application for photocatalytic degradation of dyes	Pongsapak Pawinrat, Okorn Mekasuwandumrong, Joongjai Panpranot	Joongjai Panpranot	Catalysis Communications, 10 (2009) 1380-1385	3.000
12	Influence of preparation method on the nanocrystalline porosity of α -Al ₂ O ₃ and the catalytic properties of Pd/ α -Al ₂ O ₃ in selective acetylene hydrogenation	Sataporn Komhom, Okorn Mekasuwandumrong, Joongjai Panpranot, Piyasan Prasertthdam	Joongjai Panpranot	Industrial Engineering and Chemistry Research, 48 (2009) 6273-6279.	1.758
13	Effect of Fe-Modified α -Al ₂ O ₃ on the Properties of Pd/ α -Al ₂ O ₃ Catalysts in Selective Hydrogenation of Acetylene	Tatiya Sangkam, Okorn Mekasuwandumrong, Piyasan Prasertthdam, Joongjai Panpranot	Joongjai Panpranot	Reaction Kinetics and Catalysis, 97 (2009) 115-123.	0.557

ภาคผนวก ข

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No.	ชื่อบทความ	ผู้แต่ง	Corresponding Author	วารสาร	Impact factor (FY2008)
14	Synthesis of Nanocrystalline Al_2O_3 by Thermal Decomposition of Aluminum Isopropoxide and its Application as Co Catalyst Support for Carbon Monoxide Hydrogenation	Kamonchanok Pansanga, Okorn Mekasuwandumrong, Joongjai Panpranot, and Piyasan Praserttham	Piyasan Praserttham	Korean Journal of Chemical Engineering 24 (2007) 397-402	0.893
15	Copper-Modified Alumina as a Support for Iron Fischer-Tropsch Synthesis Catalysts	Kamonchanok Pansanga, Nattaporn Lohitharn, Andrew C. Y. Chien, Edgar Lotero, Joongjai Panpranot, Piyasan Praserttham, and James G. Goodwin, Jr.	James G. Goodwin, Jr.	Applied Catalysis A. General, 332 (2007) 130-137.	3.564
16	Effect of Mixed γ and χ Crystalline Phases in Nanocrystalline Al_2O_3 on the Dispersion of Cobalt on Al_2O_3	Kamonchanok Pansanga, Joongjai Panpranot, Okorn Mekasuwandumrong, Chairit Satayaprasert, James G. Goodwin, Jr., and Piyasan Praserttham	Piyasan Praserttham	Catalysis Communications 9 (2008) 207-212.	3.000
17	Dependence of Quenching Process on the Photocatalytic Activity of Solvothermal-Derived TiO_2 with Various Crystallite Sizes	Piyawat Supphasirongjaroen, Wilasinee Kongsuebchart, Joongjai Panpranot, Okorn Mekasuwandumrong, Chairit Satayaprasert, and Piyasan Praserttham	Piyasan Praserttham	Industrial Engineering and Chemistry Research 47 (2008) 693-697	1.758

Selective hydrogenation of acetylene in excess ethylene on micron-sized and nanocrystalline TiO₂ supported Pd catalysts

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Abstract

Physicochemical properties and catalytic performances of Pd catalysts supported on commercial micron-sized and nanocrystalline TiO₂ synthesized by sol–gel and solvothermal method were studied for the selective hydrogenation of acetylene in the presence of excess ethylene. While acetylene conversions were found to be merely dependent on Pd dispersion, ethylene selectivity appeared to be strongly affected by the presence of Ti³⁺ in the TiO₂ samples. The use of pure anatase TiO₂ (either micron- or nano-sized) that contained significant amount of Ti³⁺ as supports for Pd catalysts gave high ethylene selectivities, while the use of pure rutile TiO₂ (without Ti³⁺ present) resulted in ethylene loss. The results suggest that the effect of Ti³⁺ on the TiO₂ supports was more important for high ethylene selectivity than the effect of TiO₂ crystallite size for selective acetylene hydrogenation over Pd/TiO₂ catalysts.

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Keywords: Selective acetylene hydrogenation; Pd/TiO₂; Nanocrystalline TiO₂; Sol–gel; Solvothermal; Defect

1. Introduction

Removal of trace amount of acetylene in ethylene feed stream is vital for the commercial production of polyethylene since acetylene acts as a poison to the polymerization catalysts. In order to prevent ethylene loss, when acetylene is catalytically hydrogenated, it is desirable that ethylene remains intact during hydrogenation. Supported Pd-based catalyst is known to be the best catalyst so far for such reaction with good activity and selectivity. The commonly used support for palladium catalyst in selective acetylene hydrogenation is α -alumina, however, oligomer or green oil formation during reaction is inevitable over Pd/Al₂O₃ catalysts resulting in ethylene loss and shorten catalyst lifetime especially at high levels of acetylene conversion [1–6]. Several attempts to improve ethylene selectivity of the palladium catalyst have been made by many researchers, including incorporation of a second metal such as Ag [7–10], Au [11,12], Cu [13], Si [14], K [15], and Co [16], pre-treatment with oxygen-containing compounds such as CO

and N₂O [17–20], and modification of the catalyst supports [21,22].

Among the various supports studied, TiO₂ is of particular interest because of its ability to manifest a strong metal–support interaction (SMSI) with group VIII metals and its low acidity compared to alumina. Moon and co-workers [21] reported an improved selectivity for ethylene production in selective acetylene hydrogenation over TiO₂-modified Pd catalysts. The authors suggest that charge transfer from Ti species to Pd weakened the adsorption strength of ethylene on the Pd surface hence higher ethylene selectivity was obtained. Moreover, the amount of green oil formation was reduced on the TiO₂-added Pd catalysts due to suppression of the multiply coordinated Pd sites resulting in an improved catalyst lifetime [23]. Fan and co-workers [24] studied selective hydrogenation of long chain alkadienes, it was shown that the presence of SMSI for Pd/TiO₂ catalysts led to higher selectivity of alkenes.

Recently, our group has reported the synthesis of nanocrystalline TiO₂ by solvothermal method and their applications as Pd catalyst supports in selective acetylene hydrogenation [25]. The solvothermal-derived TiO₂ supported Pd catalysts exhibited relatively high acetylene conversions and ethylene selectivities in the temperature range 40–90 °C in selective acetylene hydrogenation using trace amount of C₂H₂

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in N₂ balance. Nevertheless, their catalytic activities and selectivities have not yet been compared to those of commercial TiO₂ supported ones under real commercial ethylene feed stocks. Thus, it is the aim of this study to investigate and compare the catalytic performances of commercial micron-sized and nanocrystalline TiO₂ supported Pd catalysts in selective acetylene hydrogenation in the presence of excess ethylene. The effects of crystallite size as well as other physicochemical properties such as the presence of Ti³⁺ defective sites of the TiO₂ on the catalytic properties of Pd/TiO₂ catalysts were investigated by means of X-ray diffraction (XRD), N₂ physisorption, X-ray photoelectron spectroscopy (XPS), CO chemisorption, scanning electron microscopy (SEM), and electron spin resonance (ESR).

2. Experimental

2.1. Preparation of TiO₂ and Pd/TiO₂ catalyst samples

The commercial anatase TiO₂ was obtained from Aldrich. By calcination in air at 1010 °C for 4 h using a space velocity of air flow 16,000 h⁻¹, the anatase TiO₂ was gradually transformed into rutile TiO₂. The commercial anatase and rutile TiO₂ were denoted as TiO₂-com-A and TiO₂-com-R, respectively.

Titanium ethoxide (Ti 20%) from Aldrich was used as Ti precursor for preparation of the nanocrystalline TiO₂ by sol–gel method [26]. A specific amount of the precursor was dissolved in ethanol and mixed with a water–ethanol solution at water to alkoxide molar ratio 165. The precursor solution was added drop wise to the aqueous solution and stirred by ultrasonic vibration at room temperature. White precipitates of hydrous oxides formed instantly and the mixture was stirred for at least two more hours. The amorphous precipitates were separated from the mother liquor by centrifugation and were re-dispersed in ethanol for five times to minimize particle agglomeration. The resulting materials were then dried and calcined at 450 °C in flowing oxygen for 2 h at the heating rate of 10 °C/min. The sol–gel derived TiO₂ was denoted hereafter as TiO₂-sol-gel.

The solvothermal-derived TiO₂ was prepared according to the method described in Ref. [27] using 25 g of titanium(IV) *n*-butoxide (TNB) 97% from Aldrich. The starting material was suspended in 100 ml of 1,4-butanediol in a test tube and then set up in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of solvent was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to 320 °C at 2.5 °C/min and held at that temperature for 6 h. Autogenous pressure during the reaction gradually increased as the temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting powders were collected after repeated washing with methanol by centrifugation. They were then air-dried at room temperature. The solvothermal derived TiO₂ was denoted hereafter as TiO₂-solvothermal.

One percent Pd/TiO₂ were prepared by the incipient wetness impregnation technique using an aqueous solution of the desired amount of Pd(NO₃)₂ (Wako). The catalysts were dried overnight at 110 °C and then calcined in N₂ flow 60 cm³/min

with a heating rate of 10 °C/min until the temperature reached 500 °C and then in air flow 100 cm³/min at 500 °C for 2 h.

2.2. Catalyst characterization

The BET surface areas of the samples were determined by N₂ physisorption using a Micromeritics ASAP 2000 automated system. Each sample was degassed under vacuum at <10 μm Hg in the Micromeritics ASAP 2000 at 150 °C for 4 h prior to N₂ physisorption. The XRD spectra of the catalyst samples were measured from 20–80° 2θ using a SIEMENS D5000 X-ray diffractometer and Cu Kα radiation with a Ni filter. Electron spin resonance spectra were taken at –150 °C using a JEOL JES-RE2X spectrometer. Relative percentages of palladium dispersion were determined by pulsing carbon monoxide over the reduced catalyst. Approximately 0.2 g of catalyst was placed in a quartz tube in a temperature-controlled oven. The amounts of CO chemisorbed on the catalysts were measured using a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. Prior to chemisorption, the sample was reduced in a H₂ flow at 500 °C for 2 h then cooled down to ambient temperature in a He flow. The particle morphology was obtained using a JEOL JSM-35CF scanning electron microscope operated at 20 kV. Surface compositions of the catalysts were analyzed using an AMICUS photoelectron spectrometer equipped with a Mg Kα X-ray as a primary excitation and a KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV.

2.3. Reaction study

Selective acetylene hydrogenation was performed in a quartz tube reactor (i.d. 9 mm). Prior to the start of each run, the catalyst was reduced in H₂ at 500 °C for 2 h. Then the reactor was purged with argon and cooled down to the reaction temperature, 40 °C. Feed gas composed of 1.46% C₂H₂, 1.71% H₂, 15.47% C₂H₆ and balanced C₂H₄ (Rayong Olefin Co., Ltd.) and a GHSV of 5400 h⁻¹ were used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). Acetylene conversion as used herein is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated.

3. Results and discussion

3.1. Physicochemical properties of the TiO₂ supports

The SEM micrographs of various titania samples are shown in Fig. 1. The commercial anatase TiO₂ had a uniform particle

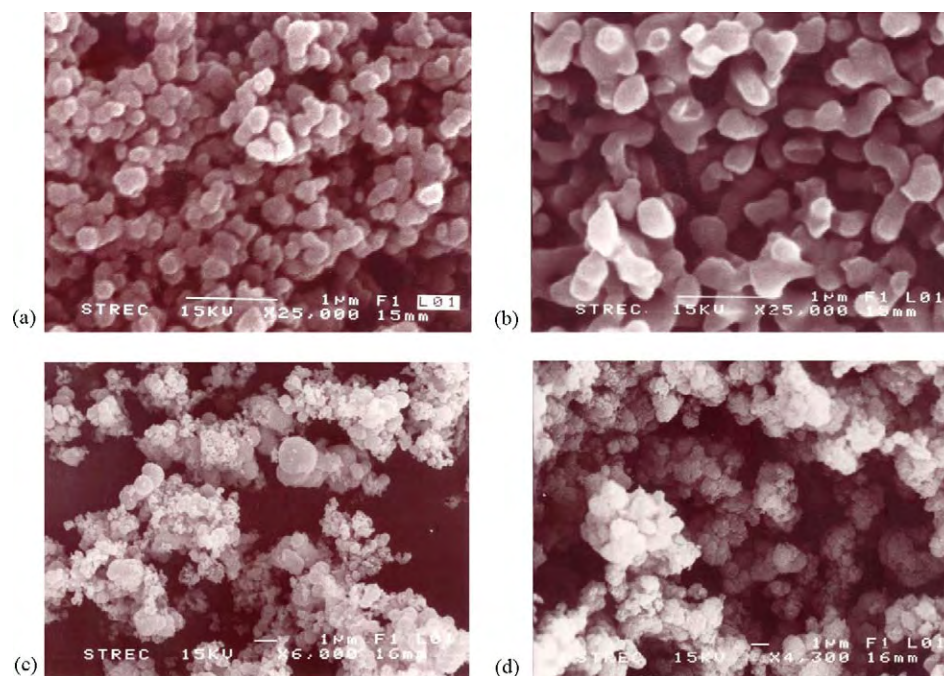


Fig. 1. SEM micrographs of: (a) TiO₂-com-A (b) TiO₂-com-R (c) TiO₂-sol-gel and (d) TiO₂-solvothermal.

size ca. 0.2 μm. After being subjected to thermal treatment (calcination) at 1010 °C for 4 h, pure anatase titania was gradually transformed into rutile titania and the particle size increased to ca. 0.4 μm. The morphology of pure anatase nanocrystalline TiO₂ prepared by sol-gel and solvothermal method was consisted of irregular shape of fine particles. However, some of the particles of those synthesized by the sol-gel method appeared to agglomerate into spherical micron-size particles. The crystallization mechanism of TiO₂ was probably different for these two methods resulting in different properties of the TiO₂ obtained. It was suggested that anatase titania synthesized by solvothermal in 1,4-butanediol was resulted from direct crystallization [27] while sol-gel method yielded a solid precipitate at relatively low temperature used and

crystallization occurred during the subsequent calcination step. XRD patterns of the calcined TiO₂ samples are shown in Fig. 2. For the anatase titania (TiO₂-com-A, TiO₂-sol-gel, and TiO₂-solvothermal), XRD peaks at $2\theta = 25$ (major), 37, 48, 55, 56, 62, 71, and 75° 2θ were evident. The TiO₂-com-R exhibited XRD peaks for rutile phase at $2\theta = 28$ (major), 36, 42, and 57°. BET surface areas, average crystallite sizes, and percentages of atomic concentration (Ti/O) of the various TiO₂ samples are given in Table 1. The average crystallite sizes of the TiO₂ prepared by sol-gel and solvothermal calculated from the full width at half maximum of the XRD peak at $2\theta = 25^\circ$ using Scherrer equation are in nanometer range (10 and 17, respectively) while those of the commercial ones could not be determined by this method due to the calculation limit of the Scherrer equation (the crystallite size may be too large). BET surface areas of the commercial anatase TiO₂ decreased essentially from 64.4 to 18.3 m²/g after calcination in order to transform the crystalline phase to rutile phase TiO₂. It is surprising that the BET surface areas of the nano-sized TiO₂ prepared by sol-gel and solvothermal method were much lower

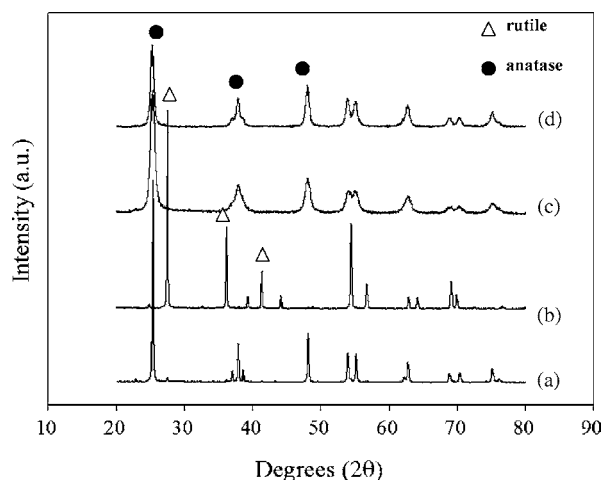


Fig. 2. XRD results of: (a) TiO₂-com-A (b) TiO₂-com-R (c) TiO₂-sol-gel and (d) TiO₂-solvothermal.

Table 1
Properties of the various TiO₂ supports

Sample	BET surface area ^a (m ² /g)	Crystallite size ^b (nm)	Atomic concentration ^c (%), Ti/O
TiO ₂ -com-A	64.4	n.d.	0.287
TiO ₂ -com-R	18.3	n.d.	0.250
TiO ₂ -sol-gel	39.3	10	0.232
TiO ₂ -solvothermal	26.8	17	0.220

^a Error of measurement = ±10%.

^b Determined from XRD line broadening.

^c Determined from XPS analysis.

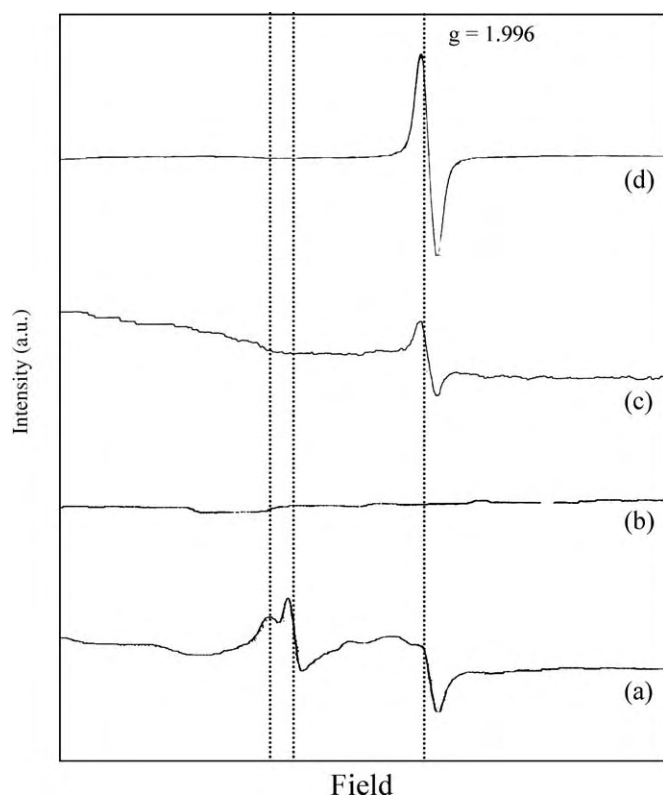


Fig. 3. ESR spectra of: (a) TiO_2 -com-A (b) TiO_2 -com-R (c) TiO_2 -sol-gel and (d) TiO_2 -solvothermal.

than that of the commercial anatase TiO_2 . Such results suggest that the nano-crystals were closely packed resulting in low pore volume in the samples. Percentages of atomic concentrations of Ti and O on the surface of the TiO_2 were determined by the X-ray photoelectron spectroscopy. The Ti/O ratios were not significantly different among the four TiO_2 samples. There was probably an oxygen-rich layer near the surface of the TiO_2 particles, which is formed by oxygen adsorption and easy oxidation of titanium surface [28]. The ESR spectra of the TiO_2 samples are shown in Fig. 3. The signals of g values less than 2 were assigned to Ti^{3+} ($3d^1$) [29,30]. Nakaoka and Nosaka [31] reported six signals of ESR measurement occurring on the surface of titania: (i) $\text{Ti}^{4+}\text{O}^-\text{Ti}^{4+}\text{OH}^-$, (ii) surface Ti^{3+} , (iii) adsorbed oxygen (O^{2-}), (iv) $\text{Ti}^{4+}\text{O}^{2-}\text{Ti}^{4+}\text{O}^{2-}$, (v) inner Ti^{3+} , and

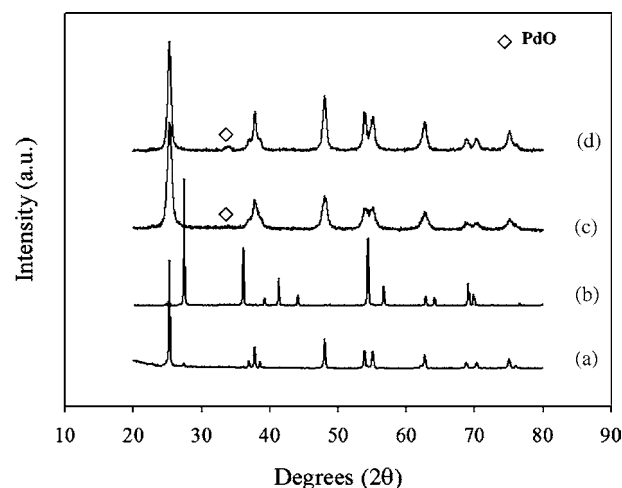


Fig. 4. XRD results of: (a) Pd/TiO_2 -com-A (b) Pd/TiO_2 -com-R (c) Pd/TiO_2 -sol-gel and (d) Pd/TiO_2 -solvothermal.

(vi) adsorbed water. In this study, it is seen that the sol-gel and solvothermal-derived TiO_2 exhibited only one signal at g value of 1.996 which can be attributed to Ti^{3+} at the surface. Many Ti^{3+} ESR signals were observed for the commercial anatase TiO_2 , it is indicated that more than one type of Ti^{3+} defects were presented in the sample, i.e. surface Ti^{3+} and inner Ti^{3+} . It should be noted that the Ti^{3+} ESR signal was observed only for the anatase TiO_2 (both micron- and nano-sized). The rutile TiO_2 did not exhibit any ESR signal. It is suggested that Ti^{4+} in the rutile TiO_2 is more difficult to be reduced to Ti^{3+} . As rutile titania is more thermodynamically and structurally stable than anatase titania so that the Ti^{3+} ions fixed in the surface lattice of anatase TiO_2 is easier to diffuse to the surface than one in the surface lattice of rutile TiO_2 [24]. The intensity of the Ti^{3+} signal was highest for the solvothermal-derived TiO_2 suggesting that this preparation method produces the highest amount of defects on the TiO_2 .

3.2. Characteristics and catalytic properties of Pd/TiO_2 catalysts

The XRD patterns of the various Pd/TiO_2 catalysts are shown in Fig. 4. There were no changes in the crystalline phase of the TiO_2 after impregnation of palladium for all the catalyst samples. The major XRD characteristic peak for PdO at $2\theta = 33.8^\circ$ were

Table 2
Characteristics of the various TiO_2 -supported Pd catalysts

Catalyst	BET surface area ^a (m^2/g)	CO pulse chemisorption ^b ($\times 10^{-18}$ molecule CO/g catalyst)	Pd dispersion ^c (%)	d_p^d Pd ⁰ (nm)	Atomic concentration ^e (%)	
					Ti/O	Pd/Ti
Pd/TiO_2 -com-A	44.5	2.23	3.93	28.5	0.253	0.084
Pd/TiO_2 -com-R	17.2	1.55	2.73	41.0	0.240	0.168
TiO_2 -sol-gel	33.8	1.19	2.10	53.3	0.282	0.011
Pd/TiO_2 -solvothermal	26.0	0.49	0.86	130.2	0.274	0.006

^a Error of measurement = $\pm 10\%$.

^b Error of measurement = $\pm 5\%$.

^c Based on the total amount of palladium loaded.

^d Based on $d = 1.12/D$ (nm), where D = fractional metal dispersion [34].

^e Determined from XPS analysis.

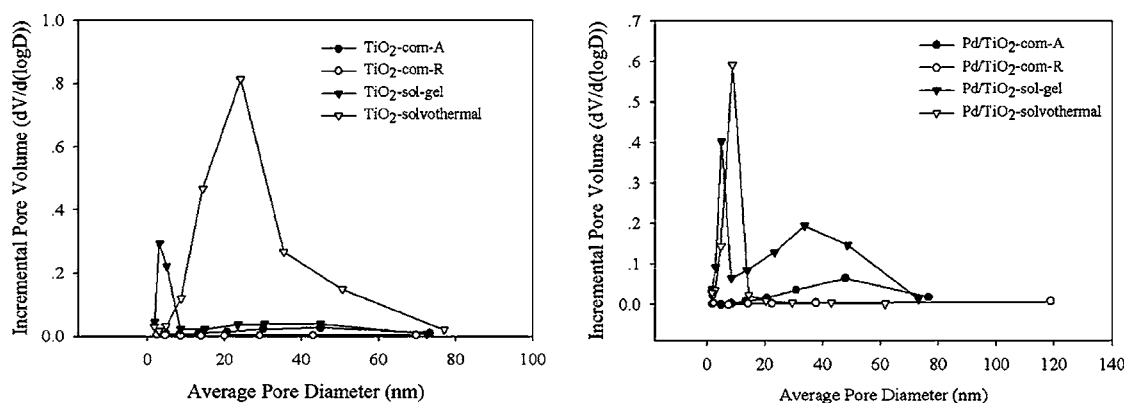


Fig. 5. Pore size distribution results of the various Pd/TiO₂ catalysts.

evident only for the catalyst prepared with the solvothermal-derived TiO₂. The BET surface areas, CO chemisorption results, and atomic concentration of surface element of the Pd/TiO₂ catalyst samples are given in Table 2. The BET surface area of the Pd catalysts were not significantly different from the original TiO₂ supports, however, changes in the pore size distribution of the catalysts due to Pd loading were observed for both sol-gel and solvothermal-derived TiO₂ supported ones suggesting that Pd was deposited in some of the pores of the TiO₂ (Fig. 5). It should also be noted that Pd/TiO₂-com-A was not heat-treated prior to the impregnation step, while the other supports were treated at 1010, 450, and 320 °C. Accordingly, it is also possible that a large decrease in the surface area of the anatase supported catalyst is caused by the calcination of the catalyst at 500 °C after the Pd loading. The percentages of Pd dispersion calculated from the CO chemisorption results were in the order Pd/TiO₂-com-A > Pd/TiO₂-com-R > Pd/TiO₂-sol-gel > Pd/TiO₂-solvothermal. The largest Pd particle size calculated from the CO chemisorption for the Pd/TiO₂-solvothermal catalyst is in a good agreement with the XRD results. It should be noted that as the anatase TiO₂ was transformed to rutile phase TiO₂, the amount of CO chemisorption decreased from 2.23×10^{18} to 1.55×10^{18} molecules CO while the calculated average particle size of Pd⁰ metal increased from 28.5 to 41.0 nm. Thus, the presence of rutile phase significantly decreased dispersion of palladium on the titania supports. XPS analysis revealed an increasing Pd/Ti surface concentration from 0.084 to 0.168 when rutile TiO₂ was employed instead of anatase TiO₂. In contrast, the Pd/Ti atomic concentration ratios for those supported on sol-gel and solvothermal derived TiO₂ were much lower than those of the commercial TiO₂ supported ones.

In order to investigate the catalytic performance of the different types of TiO₂ supported Pd catalysts, selective hydrogenation of acetylene in excess ethylene was performed in a fixed bed flow reactor. Fig. 6 shows acetylene conversions and ethylene selectivities obtained from the various Pd/TiO₂ catalysts. Acetylene conversions were in the range of 20–59% and were found to be merely dependent on the Pd dispersion. The selectivities of ethylene were varied from –1.4 to 76.2% with the commercial rutile and the sol-gel derived TiO₂ supported Pd catalysts exhibited the lowest and the highest selectivities, respectively. However, it should be noted that the

high ethylene selectivities of the nano-TiO₂ supported Pd catalysts may be because their conversions of acetylene were low. It is thus more appropriate to use the results from Fig. 6 only to compare the selectivities of Pd/TiO₂-com-A and Pd/TiO₂-com-R catalysts. The use of anatase TiO₂ as supports for Pd catalysts resulted in positive values of ethylene selectivity while the use of rutile TiO₂ produced ethylene loss due to over-hydrogenation of ethylene to ethane. Ethylene hydrogenation is usually believed to take place on the support by means of a hydrogen transfer mechanism [32]. Thus, the rutile phase of TiO₂ may be responsible for such reaction. Moreover, the presence of Ti³⁺ ions in anatase TiO₂ supports has a positive effect on high ethylene selectivity, i.e. increasing desorption of ethylene from the catalyst surface. It has been reported that the presence of Ti³⁺ on TiO₂ can lower the temperature to induce a strong metal–support interaction [24]. The SMSI between Pd and TiO₂ support can result in lower adsorption strength of ethylene on the catalyst surface and promotes ethylene desorption [21]. There were no such differences in ethylene selectivities for the micron- and the nano-anatase TiO₂ supported Pd catalysts. This indicates that the crystallite size of TiO₂ support did not have a significant impact on ethylene selectivity; the difference in selectivity of ethylene was due mainly to the presence/absence of Ti³⁺ defective sites on the TiO₂ support. However, in the other studies reported previously by our group [25,33], we have found that there was an optimum amount of Ti³⁺ sites to produce high ethylene selectivity since

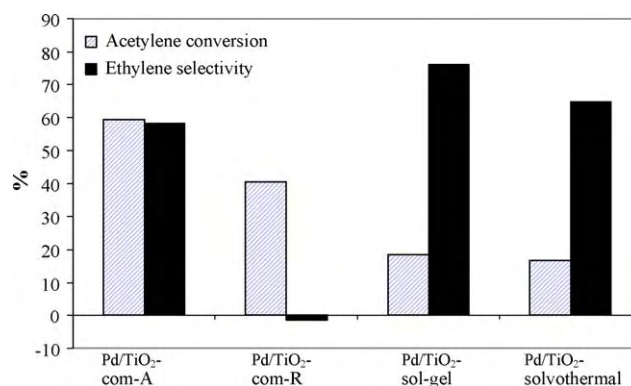


Fig. 6. Catalyst performances in selective acetylene hydrogenation.

only Ti^{3+} species that were in contact with palladium surface promoted SMSI effect and ethylene desorption [24]. Too many Ti^{3+} sites that were not in contact with Pd may result in an over-hydrogenation of ethylene to ethane. This is probably why ethylene selectivity of the Pd/ TiO_2 -solvothetmal is not the highest among four catalysts although the ESR results of Fig. 3 indicated that the intensity of the Ti^{3+} signal was the highest for TiO_2 -solvothetmal.

4. Conclusions

The use of pure anatase TiO_2 (either micron- or nano-sized) as supports for Pd catalysts produced high ethylene selectivities during selective acetylene hydrogenation in excess ethylene. In contrast, the use of pure rutile TiO_2 supported ones resulted in ethylene loss due to over-hydrogenation of ethylene to ethane. The differences in ethylene selectivity of the various Pd/ TiO_2 were due mainly to the presence/absence of the Ti^{3+} defective sites on the TiO_2 support, rather than the difference in the crystallite sizes of the TiO_2 support.

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Characteristics and Catalytic Properties of Pd/SiO₂ Synthesized by One-step Flame Spray Pyrolysis in Liquid-phase Hydrogenation of 1-Heptyne

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Abstract In this study, Pd/SiO₂ catalysts with 0.5–10 wt.% Pd loadings were prepared by one-step flame spray pyrolysis (FSP) and characterized by N₂ physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), CO chemisorption, and X-ray photoelectron spectroscopy (XPS). The average cluster/particles size of Pd as revealed by TEM were *ca.* 0.5–3 nm. The turnover frequencies (TOFs) of the flame-made catalysts decreased from 66.2 to 4.3 per s as Pd loading increased from 0.5 to 10 wt.%, suggesting that the catalytic activity was dependent on Pd particle/cluster size. However, there were no appreciable influences on 1-heptene selectivity. The flame-made Pd/SiO₂ showed better properties than the conventional prepared catalysts. Their advantages are not only the presence of large pores that facilitates diffusion of the reactants and products, but also the high-catalytic activity of as-synthesized catalysts so that further pre-treatment is not necessary.

Keywords Flame spray pyrolysis · Pd/SiO₂ · Liquid phase hydrogenation · 1-Heptyne hydrogenation · Pd nanoparticle

1 Introduction

The selective hydrogenation of alkynes to alkenes is an important reaction in the synthesis of biologically active compounds such as insect sex pheromones (pest control) and vitamins [1]. Palladium (Pd) is the most selective of the noble metal catalysts for alkyne semihydrogenation with respect to over all alkene formation [2]. The classic Lindlar catalyst, consisting of metallic Pd on calcium carbonate support modified with lead(II) acetate, is the well known commercially available catalyst for such reaction. As reported by several authors, high activity and selectivity may be obtained over other catalyst systems in which modifiers are not necessary such as supported Pd complexes [3–5], bimetallic Pd–Cu/SiO₂ [6], Pd/montmorillonite [7], Pd/pumice [8], Pd/MCM-41 [9], Pd/activated carbon, and Pd/Al₂O₃ [10]. The advantages of the reaction in heterogeneous conditions are easy separation from the reaction media and possibility of continuous operation [11]. These catalyst systems, however, may require several steps during preparation such as calcination and high-temperature reduction pretreatment in order to obtain high-catalytically active components.

Flame synthesis, especially flame spray pyrolysis (FSP), is a relatively new process for one-step synthesis of supported metal catalysts. It is generally known as a method for making nanoparticles such as fume silica, titania, and carbon black in large quantity at low cost [12]. Supported metal catalysts synthesized via one-step FSP have been employed in various catalytic reactions

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and they often showed improved catalytic performances [13–18]. Their differences in catalytic behaviors were suggested to be due to the structural differences of the flame-made and the conventionally prepared catalysts.

In this work, Pd/SiO₂ catalysts with 0.5–10 wt.% Pd loadings were prepared in one-step by FSP. The catalysts were characterized by N₂ physisorption, X-ray diffraction (XRD), CO pulse chemisorption, transmission electron spectroscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The catalytic behaviors of the flame-made Pd/SiO₂ were evaluated in the liquid-phase selective hydrogenation of 1-heptyne under mild conditions.

2 Experimental

2.1 Catalyst Preparation

Synthesis of Pd/SiO₂ was carried out using a flame spray reactor similar to that of Ref. [19]. Palladium acetylacetonate and tetraethylorthosilicate (TEOS) from Aldrich, Tanfkirchen, Germany, were used as palladium and silicon precursors, respectively. Precursors were prepared by dissolving in xylene (MERCK, Hohenbrunn, Germany; 99.8 vol.%)/acetonitrile (Fluka, Steinheim, Germany; 99.5 vol.%) mixtures (70/30 vol.%) with total metal concentration maintained at 0.5 M. The palladium concentration was ranged between 0.5 and 10 wt.%. Using a syringe pump, 5 ml/min of precursor solution was dispersed into fine droplets by a gas-assist nozzle fed by 5 l/min of oxygen (Thai Industrial Gas Limited, Bangkok, Thailand; purity >99%). The pressure drop at the capillary tip was maintained at 1.5 bar by adjusting the orifice gap area at the nozzle. The spray was ignited by supporting flamelets fed with oxygen (3 l/min) and methane (1.5 l/min) which are positioned in a ring around the nozzle outlet. A sintered metal plate ring (8 mm wide, starting at a radius of 8 mm) provided additional 10 l/min of oxygen as sheath for the supporting flame. The product particles were collected on a glass fiber filter (Whatman GF/C, Kent, UK, 15 cm in diameter) with the aid of a vacuum pump.

For comparison purposes, 1 wt.% Pd on a commercial SiO₂ (Strem Chemicals, Newburyport, MA, USA, *specific surface area* 243.8 m²/g *V*_{Pore} 1.06 m³/g *d*_{Pore} 17.4 nm) was prepared by incipient wetness impregnation using Pd(NH₃)₄Cl₂ (Aldrich) as palladium precursor. The catalyst was dried in oven at 100 °C and calcined in air at 450 °C for 3 h. Prior to reaction, the catalyst was reduced ex situ in H₂ flow at room temperature for 2 h. Properties of the reference catalyst can be found in Ref. [20].

2.2 Catalyst Characterization

X-ray diffraction patterns were recorded with a Siemens D5000 using nickel filtered CuK_α radiation. The crystallite size (*d*_{XRD}) was determined using the Scherrer equation and α-alumina as the external standard. The Brunauer Emmett Teller (BET) surface area, average pore size diameters, and pore size distribution are determined by physisorption of nitrogen (N₂) using a Micromeritics ASAP 2020 automated system. The average palladium cluster/particle size and distribution of palladium on silica was observed using a JEOL-JEM 200CX transmission electron microscope operated at 100 kV. The active sites and relative percentages dispersion of palladium catalyst were determined by CO-pulse chemisorption technique using a Micromeritics ChemiSorb 2750 system attached with ChemiSoft TPx software at room temperature. XPS analysis was performed using an AMICUS photoelectron spectrometer equipped with a Mg K_α X-ray as a primary excitation and a KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The C 1 s line was taken as an internal standard at 285.0 eV.

2.3 Catalytic Evaluation

The selective hydrogenation of 1-heptyne (Aldrich) was carried out in magnetically stirred 50-ml stainless steel autoclave reactor (JASCO, Tokyo, Japan). Approximately 20 mg of Pd/SiO₂ catalyst was dispersed in a 10 ml of 2% (v/v) solution of 1-heptyne (Fluka) in toluene. The reaction was carried out under ultra high-purity hydrogen atmosphere at 1 bar and 30 °C for 5 min. The liquid reactants and products were analyzed by gas chromatography equipped with an FID detector (Shimadzu GC-14A, Kyoto, Japan) and a GS-alumina (length = 30 m, I.D. = 0.53 mm) packed column.

3 Results and Discussion

3.1 Catalyst Properties

Figure 1 shows the XRD patterns of the flame-made SiO₂ and Pd/SiO₂ catalysts with Pd loadings 0.5–10 wt.%. All the catalyst samples exhibited only the characteristic peaks of amorphous silica except that of 10 wt.% Pd/SiO₂ where additional peaks corresponding to Pd⁰ metal were apparent (major peak at 40.1° 2θ). It is suggested that very fine palladium metal clusters/particles were finely dispersed in the silica matrix for the catalysts with low-Pd loadings. Unlike typical supported metal catalysts prepared by wet

impregnation that calcination and reduction steps are required in order to obtain catalytically active metal surface, the flame-made supported metal catalysts can be used as synthesized and calcination/reduction step is not necessary since the metal is available in its reduced form as synthesized [14–16]. Figure 2a shows typical TEM micrographs of the flame-made Pd/SiO₂ catalysts with different Pd contents. The Pd clusters were found to be in spherical shape with average diameters *ca.* 0.5–3 nm with narrow size distribution confined to the surface of SiO₂ particles. The TEM images were quite similar to those of Pd/Al₂O₃ catalysts prepared via flame process reported by Strobel et al. [16]. However, it is surprising that for Pt/SiO₂ prepared by FSP under similar conditions using platinum acetylacetonate as Pt precursor, some very large Pt particles (>100 nm) were obtained due to incomplete evaporation [15]. This was not the case for the flame-derived Pd/SiO₂ in which only small Pd particles were observed. The average clusters sizes of palladium increased from 0.5 to 3 nm as Pd loading increased from 0.5 to 2 wt.% and remained at *ca.* 3 nm even after increasing of Pd loading to 10 wt.%.

Table 1 summarizes some physicochemical properties of the SiO₂, the flame-made Pd/SiO₂ catalysts, and the 1%Pd on commercial SiO₂. The BET surface area of the flame-made SiO₂ was 196 m²/g whereas those of the flame-made Pd/SiO₂ catalysts were in the range of 246–306 m²/g. The BET surface areas of the flame-made catalysts increased as Pd contents increased from 0.5 to 5 wt.% and were slightly decreased when Pd loading was increased from 5 to 10 wt.% (from 306 to 299 m²/g). An increase in BET surface areas of the flame-made catalysts compared to the SiO₂ support was due probably to inhibition of the growth of the SiO₂ particles by Pd dopant. Such result is similar to the works reported by Hannemann et al. [21] for Au–Ag/SiO₂ nanoparticles prepared by FSP

that adding metal particles resulted in an increase in BET surface area of the SiO₂ support. Pore volumes of the flame-made catalysts also increased with increasing Pd loading and were determined to be 0.43–0.69 cm³/g. The pore size distribution patterns of the flame-made samples as calculated by BJH desorption equation suggest the presence of mostly meso- and macro-pores (Fig. 3). The average pore diameters were unaltered for the flame-made Pd/SiO₂ catalysts with Pd loading between 0.5 and 5 wt.% while that of the 10%Pd/SiO₂ increased slightly. The presence of large pores in the flame-made catalysts can help facilitating diffusion of both reactants and products. It has been reported that diffusion limitation of reactants occurred when much smaller pore sizes of the supports were used (average pore size <10 nm) for Pd catalysts in liquid phase hydrogenation [22, 23]. These pores were larger than that of the commercial SiO₂ used in this study.

Typically, BET surface areas of supported metal catalysts are less than that of the original support due to pore blockages of metal particles during impregnation and/or calcination step. Structural difference of the flame-made catalysts suggests different mechanism for the formation of metal/metal oxide particles. Formation of Pd/SiO₂ nanoparticles by FSP was considered as follows: the sprayed droplets of precursor solution were evaporated and combusted as soon as they met the flame at very high temperature and released the metal atoms, then nucleation and growth of particles by coagulation and condensation occurred along the axial direction of the flame. Comparing to silica, the vapor pressure of Pd/PdO was higher in the hot flame environment, and consequently SiO₂ particle formation started earlier. Further downstream of the flame at lower temperatures, Pd/PdO started to form small particles which were deposited directly on the SiO₂. Similar particle formation mechanism has been suggested for Pd/Al₂O₃ and Pt/TiO₂ [16–24].

On the other hand, the 1%Pd/SiO₂-com exhibited XRD characteristic peaks of PdO at 2θ degree = 33.8, and less so at 42.0, 54.8, 60.7, and 71.4 (results not shown). The average PdO crystallite sizes calculated from the full width at half maximum of the XRD peak at $2\theta = 33.8^\circ$ using Scherrer equation was 11.4 nm. The relative amounts of active surface Pd metal on the as-synthesized FSP-catalyst samples were calculated from CO chemisorption experiments at room temperature and are given in Table 1. It has been confirmed by CO chemisorption experiments that these FSP-derived Pd/SiO₂ catalysts with or without H₂ reduction adsorbed similar amounts of CO. Thus, it is likely that palladium were deposited on the as-synthesized Pd/SiO₂ catalysts as Pd⁰ metal. The Pd active sites were then calculated based on the assumption that one carbon monoxide molecule adsorbs on one palladium site [25, 26]. The Pd active sites were found to increase from

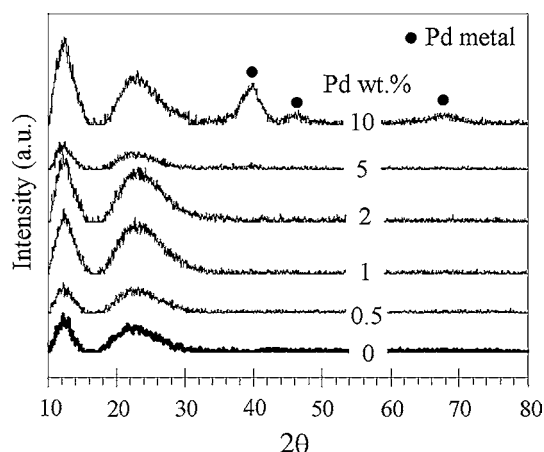
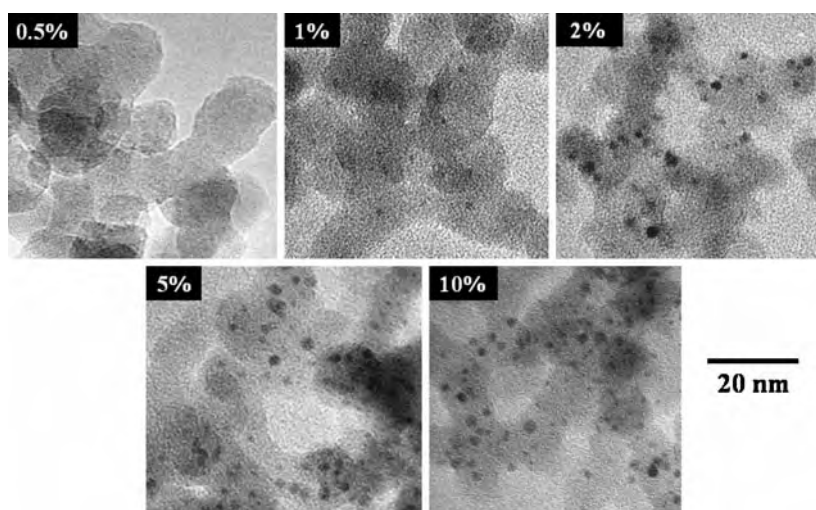


Fig. 1 XRD patterns of the flame-made Pd/SiO₂ catalysts (as synthesized)

Fig. 2 TEM micrographs of (a) the as-synthesized and (b) the spent flame-made Pd/SiO₂ catalysts (after reaction)



0.97×10^{18} to 25.84×10^{18} sites/g catalyst as the Pd contents increased from 0.5 to 10 wt.% and corresponding to increasing of %Pd metal dispersion from 3.4 to 4.6%. The average Pd⁰ metal particle sizes calculated from CO chemisorption were found to be in the range of 24–39 nm which were much larger than those based on XRD and TEM analyses. In general, low-metal dispersion and overestimation of metal particle sizes in supported metal catalysts based on CO chemisorption have possibly been due to (a) partial blockage of CO adsorption as a result of pore blockage by agglomeration of metal particles [27] and (b) localized destruction of the pore structure forming cracks and holes where larger metal particles could form and chemisorption would also be restricted [28], or (c)

chemisorption suppression due to strong support-metal interactions [29]. In this case, low-CO chemisorption uptake of the catalysts with relatively low-metal loadings may be due to the formation of Si–O groups covering the small Pd metal clusters/particles resulting in an inhibition of CO chemisorption. Otherwise, an alloy of Pd and Si may be formed resulted in a strong interaction between Pd and SiO₂. Chemisorption suppression may relate to a decrease in the kinetics of chemisorption as a result of it becoming highly activated, therefore, resulting in poor uptake at a given temperature.

X-ray photoelectron spectroscopy is a powerful tool for determination of the surface compositions of the catalysts and the interaction between Pd and silica supports. The

Table 1 Physicochemical properties of flame-made SiO₂ and Pd/SiO₂ catalysts

Catalyst	BET surface areas ^a (m ² /g)	Pore volume ^a (cm ³ /g)	CO chemisorption results ^b			XPS results Pd 3d _{5/2}		Atomic ratio ^c (Pd/Si)
			CO uptake (×10 ⁻¹⁸ molecule CO/g cat.)	%Pd dispersion ^c	d _{Pd} ^{0,d} (nm)	B.E. (eV)	FWHM	
SiO ₂	196	0.48	n/a ^f	n/a	n/a	n/a	n/a	n/a
0.5%Pd/SiO ₂	246	0.43	1.0	3.42	33	n/a	n/a	0.0011
0.5%Pd/SiO ₂ _R ^g	–	–	1.1	3.53	32	–	–	–
1%Pd/SiO ₂	251	0.46	1.9	3.40	33	n/a	n/a	0.0014
2%Pd/SiO ₂	260	0.49	3.3	2.88	39	n/a	n/a	0.0018
5%Pd/SiO ₂	306	0.59	13.4	4.71	24	337.4	2.389	0.0139
10%Pd/SiO ₂	299	0.69	25.8	4.55	25	337.4	3.189	0.0404
1%Pd/SiO ₂ -com	234	1.02	3.3	5.81	19	–	–	0.0033

^a Error of measurement was ± 10%

^b Error of measurement was ± 5% as determined directly

^c Based on the total palladium loaded and an assumption of CO/Pd = 1

^d Based on $d = (1.12/D)$ nm [25], where D = fractional metal dispersion

^e Based on XPS results

^f n/a = not available

^g R = after reduced for 2 h in H₂ at room temperature

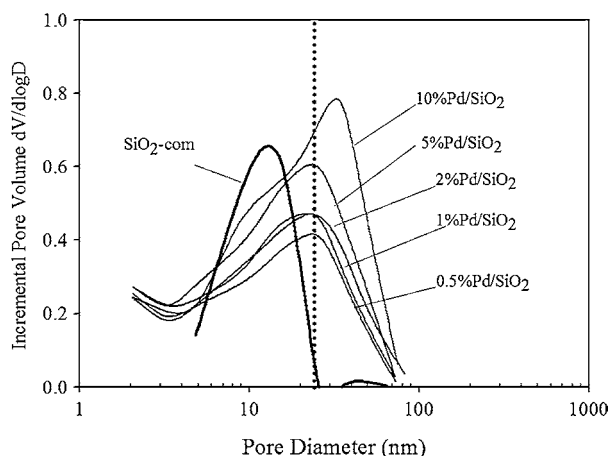


Fig. 3 Pore size distribution of the flame-made Pd/SiO₂ catalysts with 0.5–10 wt.% Pd loading

elemental scans for Pd 3d_{5/2} of the various flame-made Pd/SiO₂ catalysts are shown in Fig. 4. No distinctive peaks for Pd 3d_{5/2} were observed for the flame-made Pd/SiO₂ with Pd loading between 0.5 and 2 wt.% suggesting that very low amount of Pd present on the catalyst surface. The binding energies of Pd 3d_{5/2} for the 5 and 10 wt.% Pd/SiO₂ were 337.4 eV which was 0.2 eV higher than Pd 3d_{5/2} on the classic Lindlar catalysts according to the literature [2]. It was also 2.3 eV higher than that corresponding to Pd⁰ (335.1 eV) [30], which indicating that Pd in the flame-

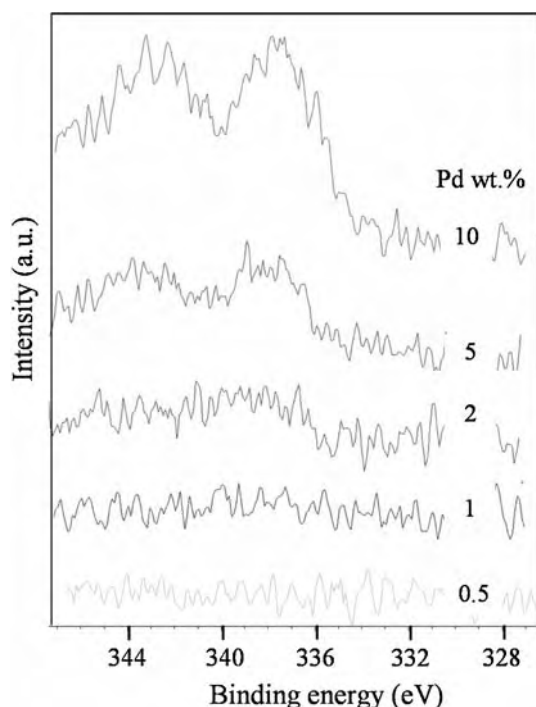


Fig. 4 XPS results for Pd 3d_{5/2} of the flame-made Pd/SiO₂ catalysts

made Pd/SiO₂ catalyst is electron-deficient. The FWHM values, higher than 2.0 eV, are also indicative that more than one Pd species may be present in the flame-made Pd/SiO₂ as have been suggested for Pd/Al₂O₃ and Pd/C catalysts prepared by conventional impregnation technique [31]. The percentages of atomic concentration for Si 2p, O 1s, and Pd 3d are also given in Table 1. For the catalysts with Pd loading 0.5–2 wt.%, much lower Pd/Si ratios were observed compared to those with higher Pd loadings (5–10 wt.%). Such results are in good agreement with the CO chemisorption results that for the catalysts with relative low-metal loadings, the metal surface may be covered by Si–O groups due to simultaneous crystallization of Pd and SiO₂ in gas-phase during FSP. It is also possible that some of the Pd metal surfaces were partially oxidized, while the kernel of the Pd particles is metallic. This would also explain the broad and not very intense XPS lines.

3.2 Selective Hydrogenation of 1-Heptyne

The catalytic behavior of the flame-made Pd/SiO₂ catalysts was investigated in the liquid-phase selective hydrogenation of 1-heptyne in a batch system. High-stirring rate (1,000 rpm) was used in order to ensure that the reaction rate does not depend on the external mass transfer of hydrogen. However, it should be noted that external mass transfer control may still exist if the relative velocity between fluid and particles is close to zero. As mentioned earlier, the average pore sizes of all the flame-made Pd/SiO₂ catalysts were much larger than those reported in the literature in which diffusion limitation of reactants occurred (usually average pore size of the supports <10 nm), therefore, the effect of pore size on the reaction rate could be negligible in this study. The catalytic performance in terms of 1-heptyne conversions and selectivities to 1-heptene and the turnover frequencies (TOFs) calculated based on CO chemisorption results of the flame-made Pd/SiO₂ catalysts are given in Table 2. The conversion of 1-heptyne increased from 42 to 75% as Pd loading increased from 0.5 to 5 wt.% and remained relatively constant when Pd loading was increased to 10 wt.%. The selectivities for 1-heptene were in the range of 92–95% for all the Pd/SiO₂ catalysts. Based on the conditions and the column used in our GC analysis, the other product found in the reaction besides 1-heptene is *n*-heptane. No other by-products were observed. For similar Pd loading, the catalytic activity of the flame-made catalyst was considerably higher than that of Pd/SiO₂ catalyst prepared by incipient wetness impregnation on a commercial SiO₂ support. The results of this study follow the trend in the literature that alkyne hydrogenation activity of Pd catalyst depends largely on Pd dispersion and there is no appreciable influence on

Table 2 Catalytic properties for liquid-phase 1-heptyne selective hydrogenation

Catalyst	Conversion (%)	1-Heptene selective (%)	TOF ^a (s ⁻¹)
0.5%Pd/SiO ₂	42	93	66.2
1%Pd/SiO ₂	43	92	34.1
	100 ^b	62 ^b	–
2%Pd/SiO ₂	54	94	25.3
5%Pd/SiO ₂	75	95	8.6
10%Pd/SiO ₂	73	94	4.3
1%Pd/SiO ₂ -com	20	100	7.7
	100 ^b	13 ^b	–

Reaction conditions were 105 kPa, 30 °C, 5 min, and catalyst/substrate molar ratio = 1/1,600

^a TOF = mole product/mole Pd metal/s. Based on the amount of active Pd atoms measured by CO chemisorption

^b Reaction conditions were 105 kPa, 30 °C, 40 min, and catalyst/substrate molar ratio = 1/500

alkene selectivity [32, 33]. In general, 1-heptene selectivity decreases with increasing 1-heptyne conversion. Under similar reaction conditions, the flame-derived catalysts exhibited higher 1-heptyne conversion than the impregnated ones and slightly lower 1-heptene selectivity. However, at 100% conversion of 1-heptyne, the selectivities for 1-heptene for the flame-made and the impregnated catalysts were 62 and 13%, respectively. The specific activities of the flame-made catalysts are also expressed in terms of TOF which is defined as mole of product/mole of metal/time. As the palladium loading increased from 0.5 to 10 wt.%, the TOFs of the flame-made catalysts decreased from 66.2 to 4.3 per s. Much higher TOFs values for the catalysts with relatively low-metal loadings (≤ 2 wt.%) are another evidence that CO chemisorption suppression occurred on these catalysts. It was probably due to the formation of very fine palladium metal clusters/particles or an alloy of Pd and Si which resulted in a strong interaction between Pd and SiO₂. Moreover, formation of Si–O groups at the metal surface due to homogeneous crystallization of Pd⁰ and SiO₂ in gas phase during flame spray synthesis or partially oxidized Pd at the surface could also result in the inhibition of CO chemisorption. For the 10 wt.% Pd/SiO₂, there was probably no CO chemisorption suppression since most of the Pd was in metallic state as indicated by XRD so the TOFs still decreased from 2 to 10 wt.% Pd loadings in spite of similar particle size of these catalysts. The remarkable high-catalytic hydrogenation activities (TOFs) of Pd nanoparticles, however, have also been reported for other Pd/SiO₂ systems [34–36]. The durability of the catalysts under repeated catalytic cycles was tested on both the flame-made 1%Pd/SiO₂ and 1%Pd/SiO₂-com catalysts. After different numbers of reaction cycles (0, 1, 2, or 3),

the used catalyst was filtered out and dried at room temperature before being re-used in the reaction. It was found that the catalytic activity decreased by *ca.* 50 and 30% after the third cycle of run, respectively. Such results suggest that catalyst deactivation is still a problem in the liquid-phase reaction.

4 Conclusions

Flame spray pyrolysis is an effective method for one-step synthesis of Pd nanoparticles with average size of 0.5–3 nm on SiO₂ supports. The as-synthesized FSP-derived catalysts showed higher catalytic activities for selective hydrogenation of 1-heptyne under mild conditions than the conventional prepared Pd/SiO₂ catalyst. The TOFs of the flame-made Pd/SiO₂ decreased with increasing Pd particle/cluster size suggesting that alkyne hydrogenation activity depends on Pd dispersion. However, there is no appreciable influence on alkene selectivity.

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Performance of Pd catalysts supported on nanocrystalline α - Al_2O_3 and Ni-modified α - Al_2O_3 in selective hydrogenation of acetylene

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Abstract

Nanocrystalline α - Al_2O_3 and Ni-modified α - Al_2O_3 have been prepared by sol–gel and solvothermal methods and employed as supports for Pd catalysts. Regardless of the preparation method used, NiAl_2O_4 spinel was formed on the Ni-modified α - Al_2O_3 after calcination at 1150 °C. However, an addition of NiO peaks was also observed by X-ray diffraction for the solvothermal-made Ni-modified α - Al_2O_3 powder. Catalytic performances of the Pd catalysts supported on these nanocrystalline α - Al_2O_3 and Ni-modified α - Al_2O_3 in selective hydrogenation of acetylene were found to be superior to those of the commercial α - Al_2O_3 supported one. Ethylene selectivities were improved in the order: Pd/Ni-modified α - Al_2O_3 -sol–gel > Pd/Ni-modified α - Al_2O_3 -solvothermal \approx Pd/ α - Al_2O_3 -sol–gel > Pd/ α - Al_2O_3 -solvothermal \gg Pd/ α - Al_2O_3 -commercial. As revealed by NH_3 temperature program desorption studies, incorporation of Ni atoms in α - Al_2O_3 resulted in a significant decrease of acid sites on the alumina supports. Moreover, XPS revealed a shift of Pd 3d binding energy for Pd catalyst supported on Ni-modified α - Al_2O_3 -sol–gel where only NiAl_2O_4 was formed, suggesting that the electronic properties of Pd may be modified.

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1. Introduction

The selective hydrogenation of acetylene in ethylene rich stream is a crucial process in polyethylene production since acetylene poisons the polymerization catalysts [1,2]. Pd-based catalyst supported on alumina with low Pd loading (0.1–0.3 wt.%) is typically employed for this reaction due to its good activity and selectivity and the easily desorption of ethylene on the catalyst surface. With respect to selectivity changes, catalysts of low Pd dispersion have been suggested to give better selectivity towards ethylene at high acetylene conversions [3–5]. The alumina used as Pd catalyst support in this reaction contains mostly the alpha phase alumina since it possesses relatively low specific surface area and low acidity compared to other ‘transition’ alumina. Recent reports have

shown development of new efficient catalysts for the selective hydrogenation of acetylene including the glow discharge plasma-prepared Pd/ α - Al_2O_3 [6], Pd on nano-sized TiO_2 [7,8], and zeolite-supported Pd-Ag catalysts [9].

In recent years, nanocrystalline materials have gained considerable interest in the field of catalysis because they show significant differences in terms of catalytic activity and selectivity compared with those synthesized in micron scale. For examples, Co catalysts supported on nanocrystalline Al_2O_3 [10] and ZrO_2 [11] have been found to exhibit higher hydrogenation activities and selectivities toward long chain hydrocarbons than those of the commercial micron-sized Al_2O_3 and ZrO_2 supported ones. Physical and chemical properties of TiO_2 are modified when they are synthesized in the nanometer range resulting in an improvement of its photocatalytic activity [12].

Several techniques have been reported for preparation of nanocrystalline ‘transition’ alumina such as sol–gel method [13], hydrothermal synthesis [14], microwave synthesis [15], emulsion evaporation [16,17], precipitation from solution [18],

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and solvothermal synthesis [19,20]. The sol–gel method is widely used due to its simplicity, however, the precipitated powders obtained are amorphous in nature and further heat treatment is required for crystallization. Solvothermal method is an alternative route for one-step synthesis of nanocrystalline material. Desired shape and size of particles can be produced by controlling process conditions such as solute concentration, reaction temperature, reaction time, and the type of solvent [21].

In the present study, nanocrystalline α - Al_2O_3 and Ni-modified α - Al_2O_3 have been synthesized via sol–gel and solvothermal methods and employed as supports for Pd catalysts for selective hydrogenation of acetylene. Modification of nanocrystalline α - Al_2O_3 with nickel is also interesting because it can form nickel aluminate spinel (NiAl_2O_4) which is a highly stable material that can have beneficial effect on the catalyst performance. Moreover, formation of NiAl_2O_4 in some Ni-based hydrogenation catalysts has shown high resistance to coke formation [22–24].

2. Experimental

2.1. Preparation of Nanocrystalline α - Al_2O_3 and Ni-modified α - Al_2O_3

Nanocrystalline α - Al_2O_3 and Ni-modified α - Al_2O_3 were prepared by sol–gel and solvothermal methods. For the sol–gel method, 24 g of aluminium nitrate nonahydrate (Aldrich) was dissolved in 50 cc of ethanol. The experiment was conducted in the reflux-condenser reactor at the temperature about 70–80 °C for 18 h. Then, urea solution, which consist of 60 g of urea and 50 ml of distilled water, was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition. The obtained product was calcined with 2 steps heating rate to avoid overflowing of gel during calcinations, i.e. 3 °C/min from room temperature to 500 °C and continue heating at 5 °C/min to 1150 °C. Then, temperature was hold for 3 h. For the preparation of Ni-modified α - Al_2O_3 , a desired amount of nickel nitrate-6-hydrate (Aldrich) was added to the precursor mixture and then followed the same procedures as that of α - Al_2O_3 .

For the solvothermal method, α - Al_2O_3 and Ni-modified α - Al_2O_3 were prepared using a mixture of aluminum isopropoxide 15.0 g and appropriate amount of nickel(II) acetylacetonate. The starting materials were suspended in 100 mL of toluene in beaker, and then set up in autoclave. In the gap between the beaker and autoclave wall, 40 mL of toluene was added. After the autoclave was completely, the suspension was heated to 300 °C at the rate of 2.5 °C/min and held at that temperature for 2 h. However, the same synthesis method is performed at various holding temperature. Autogenous pressure during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the obtained product carried out in a furnace. The product was heated at a rate of 10 °C/min to a desired temperature 1150 °C and held at that temperature for

1 h. For comparison purposes, a commercial α - Al_2O_3 (JRC-ALO2) was also employed as Pd catalyst support.

2.2. Preparation of α - Al_2O_3 supported Pd catalysts

The Pd/ α - Al_2O_3 catalysts were prepared by incipient wetness impregnation of Al_2O_3 support with a desired amount of an aqueous solution of palladium(II) nitrate hydrate (Aldrich). The catalysts were dried overnight at 110 °C and then calcined in N_2 flow 60 cm^3/min with a heating rate of 10 °C/min until the temperature reached 500 °C and then in air flow 100 cm^3/min at 500 °C for 2 h. The final Pd loading of the catalysts was determined by atomic absorption spectroscopy (Varian Spectra A800) to be ca. 0.3 wt.%.

2.3. Catalyst Characterization

Surface area measurements were carried out by nitrogen adsorption in a Micromeritic Chemisorb 2750 system. Each sample was degassed at 200 °C for 2 h. The analysis gas consisting of 30% N_2 in helium was adsorbed on the samples at low temperature by dipping cell into liquid nitrogen dewar. X-ray diffraction patterns of the catalyst samples were obtained with a SIEMENS D5000 X-ray diffractometer using Cu K α radiation with a Ni filter. The pattern were recorded between 20° and 80° (2 θ) using a scanning velocity of 0.02°/s. Metal active sites were measured using CO chemisorption technique at room temperature in a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software. Before chemisorption measurement, the sample was reduced in a H_2 flow at 150 °C for 2 h then cooled down to ambient temperature in a He flow. Ammonia temperature program desorption (NH_3 -TPD) was also performed in a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software. Approximately 100 mg of catalyst was placed in a quartz tube in a temperature-controlled oven. The samples adsorbed ammonia at 40 °C, then heated up to 650 °C at a heating rate of 10 °C/min. The distribution of palladium on catalyst supports were observed using AJEM-200CX transmission electron microscope operated at 160 kV. Surface compositions of the catalysts were analyzed using an AMICUS photoelectron spectrometer equipped with Mg K α X-ray as primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV.

2.4. Reaction study

Catalytic performance of the catalysts was studied in selective hydrogenation of acetylene. The experiment was performed in a quartz tube reactor (i.d. 10.1 mm). Before starting of the reaction, the catalyst was reduced in H_2 at 150 °C for 2 h. Then the reactor was purged with argon and cooled down to the reaction temperature, 40 °C. Feed gas composed of 1.5% C_2H_2 , 1.7% H_2 , and balanced C_2H_4 (TIG Co., Ltd.), a GHSV of 39435, 24433, 16901 and 9288 h^{-1} were used. The

composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). Acetylene conversion as used herein is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the sol–gel- and the solvothermal-made Pd/ α -Al₂O₃ and the Pd/Ni-modified α -Al₂O₃ catalysts with Ni/Al atomic ratio 0.5 after calcinations at 1150 °C are shown in Fig. 1. The patterns in the lower half of the figure correspond to the sol–gel-made powder while the patterns in the upper part of the figure are for those prepared by solvothermal synthesis. Both the sol–gel- and solvothermal-made Pd/ α -Al₂O₃ catalysts exhibited all the characteristic peaks of α -Al₂O₃ structure. While the diffraction lines for Pd/Ni-modified α -Al₂O₃ catalyst could be assigned to a spinel-type NiAl₂O₄ structure; space group Fd3m [25]. Additional peaks corresponding to NiO were also presented at 43.3 and 62.9° 2 θ for the product obtained from solvothermal synthesis. The XRD characteristic peaks associated with Pd⁰ or PdO phase were not observed in all the samples. This was probably due to the very low amount of Pd present and/or a very good dispersion of Pd phase on all the alumina supports.

TEM micrographs were taken in order to physically measure the size of the palladium oxide particles and/or palladium

clusters. It can be seen that the sol–gel made catalyst (Fig. 2a and b) was consisted of agglomerated particles with primarily irregular shape structure. For those prepared by solvothermal method, agglomeration of finger-like particles were observed for the Pd/ α -Al₂O₃ whereas spherical-shape particles were found for the Pd/Ni-modified α -Al₂O₃ catalysts (Fig. 2c and d, respectively). The finger-like α -Al₂O₃ particles are normally obtained by calcination of the solvothermal-made α -Al₂O₃ powders at high temperature [26,27]. Based on TEM analysis, palladium particles/clusters with average particle size ca. 5–10 nm were found to be deposited on the alumina supports.

The physical and chemical properties of Pd/ α -Al₂O₃ and Pd/Ni-modified α -Al₂O₃ catalysts are summarized in Table 1. The average crystallite size of each crystal phase was calculated from the Scherrer equation. The average crystallite sizes of the α -Al₂O₃ prepared by sol–gel and solvothermal method were 34 and 58 nm, respectively. While, the crystallite sizes of NiAl₂O₄ formed in the Ni-modified α -Al₂O₃ prepared by sol–gel and solvothermal method were 23 and 27 nm, respectively. In all cases, the average crystallite sizes of NiAl₂O₄ were smaller than those of α -Al₂O₃. Such results suggest that crystal growth rate for NiAl₂O₄ was slower than that of α -Al₂O₃. The surface areas of all the catalysts were not significantly different and still quite low, due probably to high agglomeration of these nanocrystalline particles during calcinations at high temperature. The amounts of CO chemisorption on the catalysts, the Pd dispersions, and the average Pd metal particle sizes determined from CO chemisorption are also given in Table 1. The pulse CO chemisorption technique was based on the assumption that one carbon monoxide molecule adsorbs on one palladium site [28–32]. The amounts of CO chemisorption decreased from 7.5 to 5.4×10^{17} and 8.1 to 7.4×10^{17} sites/g cat. corresponding to the decreasing in Pd metal dispersion from 4.4 to 3.2 and 4.8 to 4.3% by modification with Ni atoms by sol–gel and solvothermal method, respectively. The percentages of Pd dispersion calculated from the CO chemisorption results were in the order Pd/ α -Al₂O₃-solvothermal > Pd/ α -Al₂O₃-sol-gel \approx Pd/Ni-modified α -Al₂O₃-solvothermal > Pd/Ni-modified α -Al₂O₃-sol-gel. The average Pd⁰ particle sizes for all the catalysts were calculated to be 24–35 nm.

Fig. 3 shows the NH₃ temperature program desorption profiles for the sol–gel and solvothermal-made α -Al₂O₃ and the Ni-modified α -Al₂O₃ supports. Comparing the desorption peak area of the reference γ -alumina, the desorption peak areas of the nanocrystalline α -Al₂O₃ powders obtained from both sol–gel and solvothermal syntheses were relatively low due probably to the dramatically decrease of the surface area after calcination at high temperature. However, two desorption peaks corresponding to different acid sites were still observed at ca. 320 and 400–500 °C for both α -Al₂O₃ samples. For the Ni-modified α -Al₂O₃-sol-gel, no distinctive peaks were observed and the profiles became almost flat. Such results indicate that acidity of the α -Al₂O₃ samples was drastically decreased by incorporation of Ni atoms. The results are in good agreement with those reported by other researchers. For examples, Otero Areán et al. [33] measured acidity of Ni-doped alumina by IR spectroscopy of CO adsorbed at liquid nitrogen temperature. A

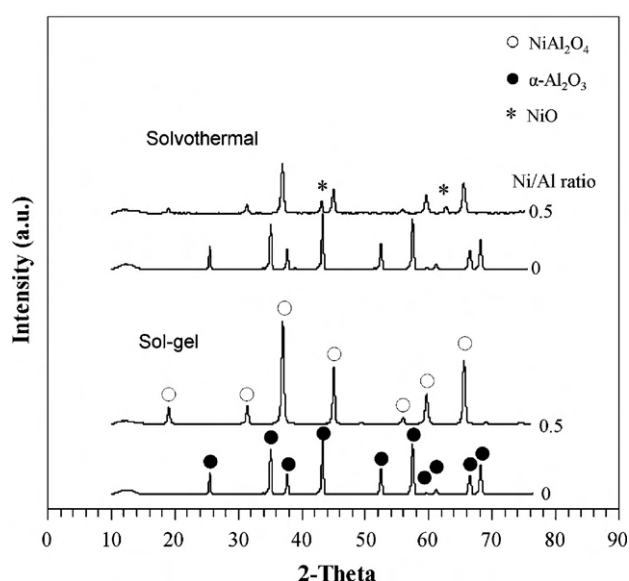


Fig. 1. XRD patterns of the various Pd catalysts supported on nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ prepared by sol–gel and solvothermal methods.

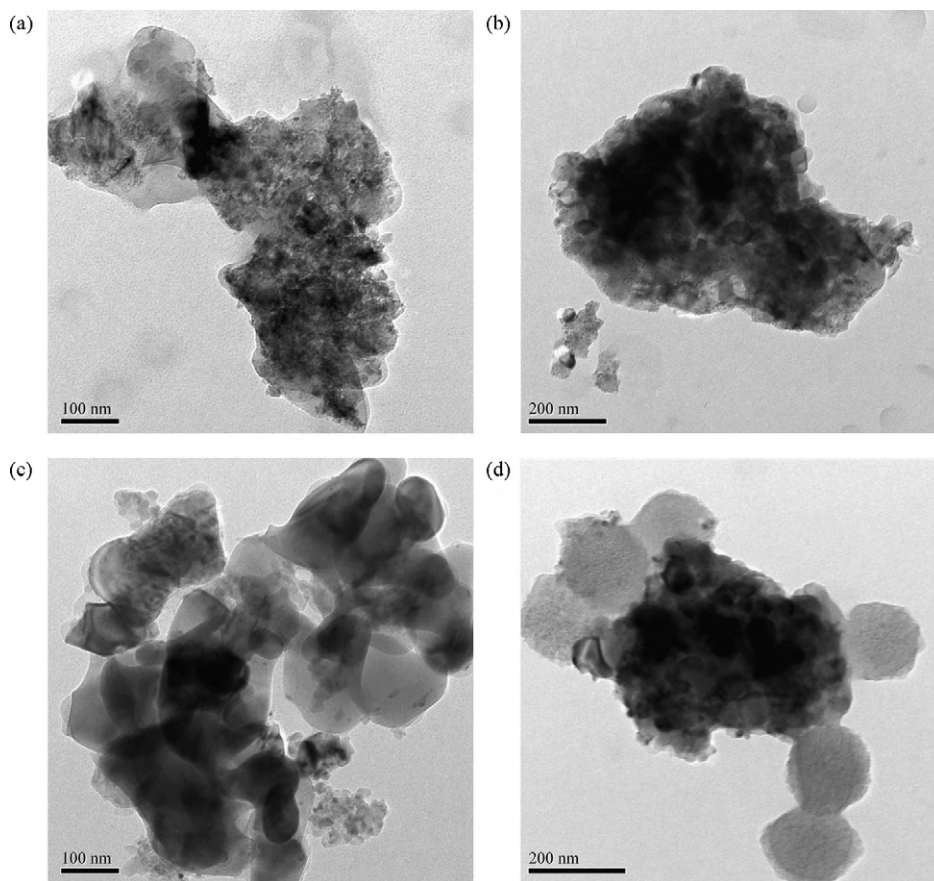


Fig. 2. TEM micrographs of (a) Pd/ α -Al₂O₃-sol-gel, (b) Pd/Ni-modified α -Al₂O₃-sol-gel, (c) Pd/ α -Al₂O₃-solvothermal, and (d) Pd/Ni-modified α -Al₂O₃-solvothermal.

decrease in both Lewis and Brønsted acidity was observed as the Ni contents increased in the Ni-alumina solid solution. The very low Brønsted acidity also appears to be typical for many oxide spinels as well as other aluminate spinels such as MgAl₂O₄ and ZnAl₂O₄ [34,35]. A small broad peak was observed for the Ni-modified α -Al₂O₃-solvothermal due probably to the formation of NiO species in which some acidity may be remained.

Because of its surface sensitivity, XPS is used to monitor the interaction between surface Pd and the alumina supports. The elemental scans for Pd 3d of the Pd/ α -Al₂O₃ and the Pd/Ni-modified α -Al₂O₃ catalysts are shown in Fig. 4. It was found that the binding energy of Pd 3d for the Pd catalyst supported Ni-modified α -Al₂O₃ prepared by sol-gel shifted to lower binding energy while for those of all the other catalysts, the binding energies for Pd 3d were at the same binding energies. It

Table 1
Characteristics of the various Pd/ α -Al₂O₃ and Pd/Ni-modified α -Al₂O₃ catalysts

Sample	$d_{\text{XRD}}^{\text{a}}$ (nm)	BET surface area (m ² /g)	CO chemisorption ($\times 10^{17}$ sites/g cat.)	% Dispersion	d_{p}^{b} Pd ⁰ (nm)
Sol-gel					
Pd/ α -Al ₂ O ₃	34 ^c	1.5	7.51	4.42	25
Pd/Ni- α -Al ₂ O ₃	27 ^d	1.9	5.37	3.16	35
Solvothermal					
Pd/ α -Al ₂ O ₃	54 ^c	4.7	8.10	4.76	24
Pd/Ni- α -Al ₂ O ₃	23 ^d , 26 ^e	1.4	7.35	4.32	26
Commercial					
Pd/ α -Al ₂ O ₃	391.6 ^c	0.5	5.91	3.48	32

^a Average crystallite size calculated by Scherrer equation.

^b Average Pd metal particle size calculated from CO chemisorption results. $d_{\text{p}} = 1.12/D$ where D = Pd dispersion [25].

^c α -Al₂O₃.

^d NiAl₂O₄.

^e NiO.

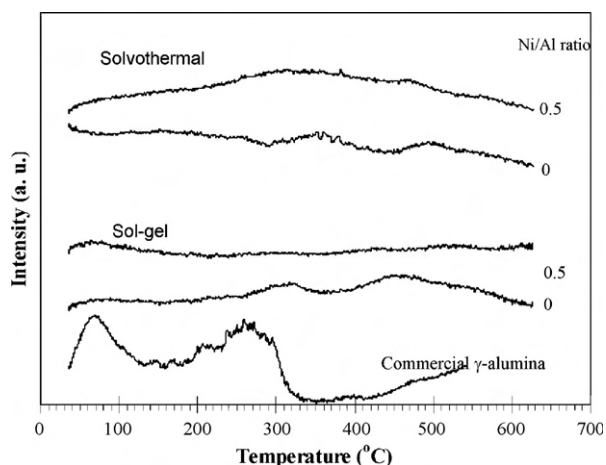


Fig. 3. NH_3 temperature program desorption profiles for the sol-gel and solvothermal-made $\alpha\text{-Al}_2\text{O}_3$ and the Ni-modified $\alpha\text{-Al}_2\text{O}_3$ supports.

is likely that Pd catalyst supported on NiAl_2O_4 spinel may result in a lower interaction between Pd and the alumina support.

3.2. Catalyst performance in selective acetylene hydrogenation

The catalyst performance in selective hydrogenation of acetylene to ethylene was studied for all the catalyst samples using a fixed bed flow reactor. Changes in ethylene selectivity with acetylene conversion for Pd/ $\alpha\text{-Al}_2\text{O}_3$ and Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ catalysts are shown in Fig. 5. In general, ethylene selectivity decreases with increasing acetylene conversion due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction. Compared to Pd catalyst supported on the commercial $\alpha\text{-Al}_2\text{O}_3$, the ones supported on

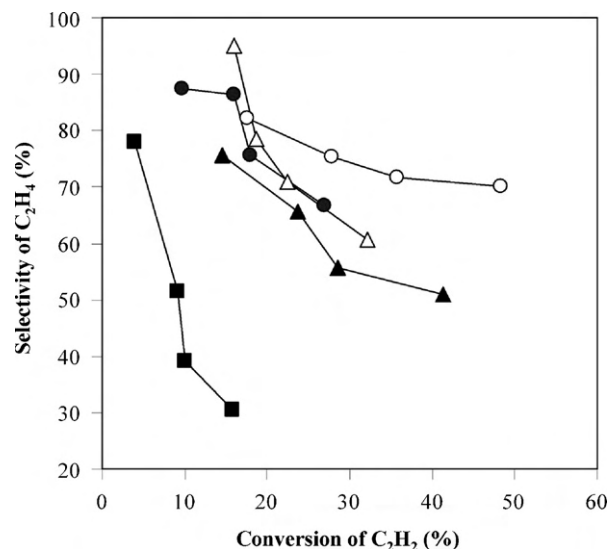


Fig. 5. Performance of sol-gel (circle; \circ) and solvothermal (triangle; \triangle) made Pd/ $\alpha\text{-Al}_2\text{O}_3$ (filled symbols), Pd/commercial $\alpha\text{-Al}_2\text{O}_3$ (filled square; \blacksquare) and Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ (open symbols) catalysts in selective acetylene hydrogenation.

nanocrystalline $\alpha\text{-Al}_2\text{O}_3$ and Ni-modified $\alpha\text{-Al}_2\text{O}_3$ showed superior catalytic performances in selective acetylene hydrogenation with Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ exhibited higher selectivity than Pd/ $\alpha\text{-Al}_2\text{O}_3$. When comparing the samples prepared by different techniques, the sol-gel-made samples showed higher ethylene selectivity than those of the solvothermal-derived ones. The ethylene selectivity was improved in the order: Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -sol-gel > Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -solvothermal \approx Pd/ $\alpha\text{-Al}_2\text{O}_3$ -sol-gel > Pd/ $\alpha\text{-Al}_2\text{O}_3$ -solvothermal \gg Pd/ $\alpha\text{-Al}_2\text{O}_3$ -commercial.

During long-time investigation by many research groups, the catalytic activity and ethylene selectivity in the selective acetylene hydrogenation in excess ethylene over Pd-based catalysts are found to be dependent on many factors such as metal dispersion (Pd metal particle size) [7], thermodynamic adsorption differences between acetylene and ethylene [36], and carbonaceous product formation [37,38], etc. Based on the reaction mechanisms for acetylene hydrogenation on Pd/ Al_2O_3 catalysts in the literatures [39], there are three active sites on the Pd metal surface and one active site on the alumina support. The three sites on the palladium surface are responsible for selective hydrogenation of acetylene to ethylene, direct ethane formation from acetylene and oligomer formation whereas ethylene hydrogenation is believed to take place on the support by means of a hydrogen transfer mechanism. It was claimed that the carbonaceous deposits present act as bridges for hydrogen spillover [40]. It is well known that acidity on alumina surface promotes formation of carbonaceous deposits on catalyst surface. When Ni was incorporated in alumina lattice (i.e., in terms of NiAl_2O_4 formation), the acidity of alumina decreased drastically and thus reduced the formation of carbonaceous deposits and hydrogen spillover. In summary, Pd catalyst supported on Ni-modified $\alpha\text{-Al}_2\text{O}_3$ can be used as an effective catalyst for producing high ethylene selectivities at relatively high acetylene conversions especially when NiAl_2O_4 are

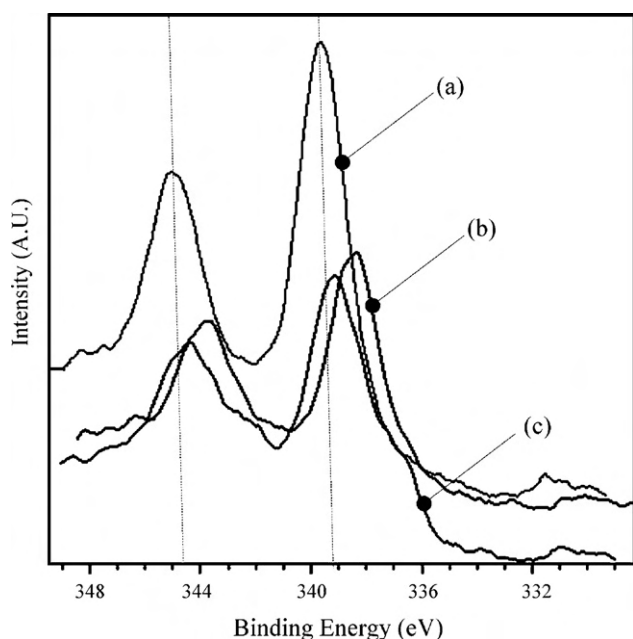


Fig. 4. XPS results of Pd 3d for (a) Pd/ $\alpha\text{-Al}_2\text{O}_3$ -sol-gel, (b) Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -sol-gel and (c) Pd/Ni-modified $\alpha\text{-Al}_2\text{O}_3$ -solvothermal.

formed. Promotion with other second metals such as Ag is then not necessary in order to improve the catalytic performance of these Pd-based catalysts.

4. Conclusions

The catalytic performance of Pd catalysts supported on nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ prepared by sol–gel and solvothermal methods was studied in the selective hydrogenation of acetylene in excess ethylene. While the use of sol–gel method resulted in only NiAl₂O₄ formation, those prepared by solvothermal gave both NiAl₂O₄ and NiO species. Acidity of the nanocrystalline α -Al₂O₃ was significantly decreased by incorporation of Ni atoms in α -Al₂O₃. Ethylene selectivities were improved in the order: Pd/Ni-modified α -Al₂O₃–sol–gel > Pd/Ni-modified α -Al₂O₃–solvothermal \approx Pd/ α -Al₂O₃–sol–gel > Pd/ α -Al₂O₃–solvothermal \gg Pd/ α -Al₂O₃–commercial. The improvement in catalyst performance is probably due to both a decrease in surface acidity of α -Al₂O₃ and modification of Pd surface activity due to NiAl₂O₄ formation.

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A comparative study of strong metal–support interaction and catalytic behavior of Pd catalysts supported on micron- and nano-sized TiO₂ in liquid-phase selective hydrogenation of phenylacetylene

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Abstract

The strong metal–support interaction and catalytic behaviors of Pd catalysts supported on micron (0.1 μm)- and nano-sized (14 nm) TiO₂ were investigated in the liquid-phase selective hydrogenation of phenylacetylene to styrene. It was found that when supported on the nano-sized TiO₂, the Pd/TiO₂ catalyst that reduced by H₂ at 500 °C exhibited strong metal–support interaction (SMSI) and much improved catalytic performance in liquid-phase selective hydrogenation of phenylacetylene. However, as revealed by CO pulse chemisorption, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and CO-temperature program desorption, the SMSI effect was not detected for the micron-sized TiO₂ supported ones. It is suggested during high-temperature reduction, the inner Ti³⁺ in large crystallite size TiO₂ was more difficult to diffuse to the Pd⁰ surface than the surface Ti³⁺ in the smaller crystallite size ones. Sintering of Pd⁰ metal was observed instead.

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Keywords: Pd/TiO₂; Liquid-phase hydrogenation; Phenylacetylene hydrogenation; Strong metal–support interaction

1. Introduction

The selective hydrogenation of alkynes to alkenes has fundamental importance in the fine chemicals production and industrial polymerization processes [1–4]. A large number of these reactions are carried out in liquid phase using batch type slurry reactors. The major advantages of supported noble metal catalysts in liquid-phase hydrogenation are their relatively high activity, mild process conditions, easy separation, and better handling properties. Pd is one of the most frequently used metals in such processes because of its unique ability to selectively hydrogenation.

Various supports have been employed for recent development of supported Pd catalysts for liquid-phase selective alkyne hydrogenation such as silica [5–8], MCM-41 [9–11], carbon [12], and titania [13–16]. Among these, titania is of particular

interest because it exhibits the strong metal–support interaction (SMSI) phenomenon after reduction at high temperatures due to the decoration of the metal surface by partially reducible metal oxides [17,18] or by an electron transfer between the support and the metals [19,20]. In selective hydrogenation of acetylene to ethylene on Pd/TiO₂ catalysts, the charge transfer from Ti species to Pd weakened the adsorption strength of ethylene on the Pd surface hence higher ethylene selectivity was obtained [21]. Fan and coworkers [13] found that Pd/TiO₂ catalysts with SMSI exhibited higher selectivity for alkenes in liquid-phase hydrogenation of long chain alkadienes. Recently, Xu et al. [16] reported that Pd/TiO₂ catalyst prepared by sol–gel produced high conversion and high yield towards butyric acid in liquid-phase hydrogenation of maleic anhydride. The excellent catalyst performances were attributed to the strong interaction between metal and support and the formation of interfacial Pd–TiO_x site, which was induced by high-temperature reduction step.

Recently, there has been a growing interest in the application of nano-sized TiO₂ in the field of catalysis. With the

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decrease in particle size to nanometer scale, photocatalytic activity of TiO₂ is enhanced because the optical band gap is widened due to surface defect [22,23] and an increase in surface area [24,25]. Various techniques have been reported for the preparation of nano-sized TiO₂ such as solvothermal method [26–28], precipitation method [29], sol–gel method [30–32], and thermal decomposition of alkoxide [33]. The sol–gel method is an easy method but the precipitated powders obtained are amorphous in nature and further heat treatment is required for crystallization. Solvothermal method is an alternative route for direct (one-step) synthesis of pure anatase TiO₂. Particle morphology, crystalline phase, and surface chemistry of the solvothermal-derived TiO₂ can be controlled by regulating precursor composition, reaction temperature, pressure, solvent property, and aging time.

In previous studies, the effect of TiO₂ polymorphs (anatase and rutile) on the strong metal–support interaction and catalytic properties of Pd/TiO₂ have been studied and compared [13,34]. It was shown that pre-reduction by H₂ at lower temperature results in SMSI for anatase titania supported palladium catalyst, but not for rutile titania supported one. A recent study from our group has shown that the use of pure anatase TiO₂ that contained significant amount of Ti³⁺ defects as supports for Pd catalysts gave high ethylene selectivities in gas-phase selective acetylene hydrogenation, while the use of pure rutile TiO₂ resulted in ethylene loss [35]. Nevertheless, the effects of Ti³⁺ and/or the TiO₂ crystallite size on the strong metal–support interaction of Pd/TiO₂ and their catalytic behavior in liquid-phase selective hydrogenation have never been reported.

Thus, it is the aim of this study to investigate the SMSI phenomena and catalytic behavior of Pd catalysts supported on micron- and nano-size TiO₂ in liquid-phase selective hydrogenation of phenylacetylene under mild reaction conditions. The nano-TiO₂ was synthesized by the solvothermal method in 1,4-butanediol using titanium *n*-butoxide as a titanium precursor. The catalysts were characterized by N₂ physisorption, X-ray diffraction (XRD), CO-temperature programmed desorption (CO-TPD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), CO pulse chemisorption, electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation of TiO₂ and Pd/TiO₂ catalysts

The solvothermal-derived nano-TiO₂ was prepared according to the method described in Ref. [36] using 25 g of titanium(IV) *n*-butoxide (TNB) 97% from Aldrich. The starting material was suspended in 100 ml of 1,4-butanediol in a test tube and then set up in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of solvent was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to desired temperature (320 °C) at the rate of 2.5 K min^{−1} and held at that temperature for 6 h. Autogeneous pressure during the reaction gradually increased as the temperature was raised. After the reaction, the autoclave was cooled to

room temperature. The resulting powders were collected after repeated washing with methanol by centrifugation. They were then air-dried at room temperature. For comparison purposes, the micron-sized anatase TiO₂ was obtained commercially from Aldrich. The micron- and nano-sized TiO₂ were denoted herein as TiO₂-micron and TiO₂-nano, respectively.

The 1%Pd/TiO₂ catalysts were prepared by the incipient wetness impregnation technique using an aqueous solution of the desired amount of Pd(NO₃)₂·6H₂O (Aldrich). The catalysts were dried overnight at 110 °C and then calcined in air at 450 °C for 3 h.

2.2. Catalyst characterization

The specific surface areas, pore volumes, and average pore diameters were determined by N₂ physisorption using a Micromeritics ASAP 2000 automated system and the Brunauer–Emmet–Teller (BET) method. Each sample was degassed under vacuum at $<1 \times 10^{-5}$ bar in the Micromeritics system at 150 °C for 4 h prior to N₂ physisorption. The XRD patterns of the catalysts were measured from 10° to 80° 2 θ using a SIEMENS D5000 X-ray diffractometer and Cu K α radiation with a Ni filter. The particle morphology was obtained using a JEOL JSM-35CF scanning electron microscope (SEM) operated at 20 kV. Catalyst crystallite sizes were obtained using the JEOL JEM 2010 transmission electron microscope that employed a LaB₆ electron gun in the voltage range of 80–200 kV with an optical point-to-point resolution of 0.23 nm. The amounts of CO chemisorbed on the catalysts were measured using a Micromeritic Chemisorb 2750 automated system with ChemiSoft TPx software. Prior to chemisorption, the sample was reduced in a H₂ flow at a desired temperature for 2 h and then cooled down to ambient temperature in a He flow. XPS analysis was performed using an AMICUS photoelectron spectrometer with Mg K α X-ray as primary excitation and equipped with KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV. Electron spin resonance spectroscopy (ESR) was conducted using a JEOL JESRE2X electron spin resonance spectrometer. The intensity of ESR was calculated using a computer software program ES-PRIT ESR DATA SYSTEM version 1.6.

2.3. Reaction study

Approximately 0.2 g of 1%Pd/TiO₂ catalyst was placed into the 50 ml autoclave. The reactant consisting of 1 ml of phenyl acetylene and 9 ml of ethanol was mixed in a volumetric flask before being introduced into the autoclave reactor. Afterward the reactor is purged with hydrogen gas. The liquid-phase hydrogenation was carried out with H₂ pressure between 1 and 3 bar at 30 °C for 10–40 min. After the reaction, the vent valve was slowly opened to prevent the loss of product. The product mixture was analyzed by gas chromatography with flame ionization detector (FID).

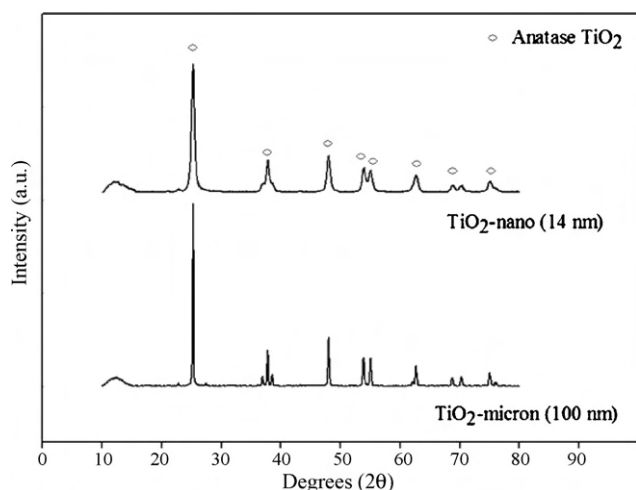


Fig. 1. XRD patterns of nano- and micron-sized TiO₂.

3. Results and discussion

Fig. 1 shows the XRD patterns of the micron- and nano-sized TiO₂. Both samples exhibited the characteristic peaks of the anatase titania at $2\theta = 25^\circ$ (major), 37° , 48° , 55° , 56° , 62° , 71° , and 75° . The average crystallite sizes of the TiO₂-micron and TiO₂-nano calculated from the full width at half maximum of the XRD peak at $2\theta = 25^\circ$ using the Scherrer equation were 100 nm ($\sim 0.1 \mu\text{m}$) and 14 nm, respectively. The average crystallite size of TiO₂-micron in this study was found to be much larger than many commercially available TiO₂ widely used in the industry such as P-25 (Degussa), PC-500 and AT-1 (Millennium Chemicals), and Hombikat UV-100 (Sachtleben Chemie) in which the TiO₂ crystallite sizes are in the range of 10–30 nm [37]. The XRD characteristic peaks corresponding to PdO and/or Pd⁰ metal were not observed after impregnation of Pd, calcination, and reduction steps due probably to the low amount of Pd present or a higher degree of Pd dispersion (results not shown).

Table 1 summarizes physicochemical properties of the TiO₂ and 1%Pd/TiO₂ catalysts. Reduction with H₂ either at 40 or 500 °C did not result in significant changes of the TiO₂ crystallite sizes. The BET surface area of the 1%Pd/TiO₂-micron was not altered from the original TiO₂-micron support suggesting that most of the palladium were deposited on the external surface of the support. In contrast, the BET surface areas of the TiO₂-nano

decreased after Pd loading followed by the high-temperature reduction at 500 °C, indicating that Pd was deposited in some of the pores of the TiO₂ support. A slight increase in the TiO₂ crystallite sizes of the TiO₂-nano from 14 to 17 nm was probably caused by high temperature calcination and reduction of the catalysts at 500 °C. The percentage of Pd dispersion estimated from CO chemisorption and Pd⁰ metal particle sizes calculated were also given in Table 1. It was found that %Pd dispersion decreased when the catalysts were reduced at 500 °C for both TiO₂-micron and TiO₂-nano-supported Pd catalysts. However, %Pd dispersion for 1%Pd/TiO₂-micron decreased by 80.5% while that of 1%Pd/TiO₂-nano decreased by only 53.5%. The corresponding Pd⁰ particle sizes calculated based on CO chemisorption were varied from 6.7 to 48.7 nm.

Fig. 2 shows the SEM micrographs of TiO₂ and 1%Pd/TiO₂ catalysts (calcined). The TiO₂-micron had a uniform particle size of 0.1–0.2 μm while the TiO₂-nano consisted of irregular shape of very fine agglomerated particles. Morphologies of the reduced 1%Pd/TiO₂ catalysts were not significantly different from the corresponding TiO₂ supports suggesting high-thermal stability of the TiO₂. TEM analysis has been carried out in order to physically measure the Pd⁰ particle sizes on the various TiO₂ supports and the results are shown in Fig. 3. The particle sizes of various TiO₂ supports were consistent to those obtained from XRD results. It is clearly seen that on the TiO₂-micron, Pd⁰ metal particle sizes increased when the catalyst was reduced at 500 °C whereas those on the TiO₂-nano were essentially the same to those reduced at 40 °C. Such results indicate that sintering of Pd⁰ metal occurred on the 1%Pd/TiO₂-micron catalyst during high-temperature reduction, in agreement with the lower amount of CO chemisorption observed (Table 1). For the 1%Pd/TiO₂-nano reduced at 500 °C, the results of TEM and low CO chemisorption (giving an over estimation of the Pd⁰ metal particle sizes) indicate that the catalyst exhibited strong metal–support interaction under high-temperature reduction since no change in the Pd⁰ particle size was observed. The SMSI effect on these catalysts was confirmed by measuring the amounts of CO chemisorption of the re-calcined (at 450 °C) and re-reduced (at 40 °C) catalysts after they were subjected to reduction at 500 °C. The results are illustrated in Fig. 4. The amount of CO chemisorption of the re-calcined and re-reduced 1%Pd/TiO₂-micron was less than that reduced at 40 °C suggesting that sintering of Pd⁰ occurred during high-

Table 1
Physicochemical properties of various TiO₂ and 1%Pd/TiO₂ catalysts

Sample ^a	Crystallite size of TiO ₂ by XRD (nm)	BET (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	%Pd dispersion ^b	d_{pPd^0} (nm) ^c
TiO ₂ -micron	100	10	0.02	7.6	–	–
TiO ₂ -nano	14	79	0.40	14.9	–	–
1%Pd/TiO ₂ -micron-R40	96	9	0.03	1.3	16.4	6.9
1%Pd/TiO ₂ -micron-R500	94	11	0.03	1.2	3.2	48.7
1%Pd/TiO ₂ -nano-R40	16	73	0.31	0.6	16.8	6.7
1%Pd/TiO ₂ -nano-R500	17	68	0.28	0.8	7.8	40.6

^a R40 and R400 indicate the samples reduced at 40 and 500 °C, respectively.

^b Determined from CO chemisorption.

^c Based on $d \text{ (nm)} = (1.12/D)$ [46], where D is the fractional metal dispersion.

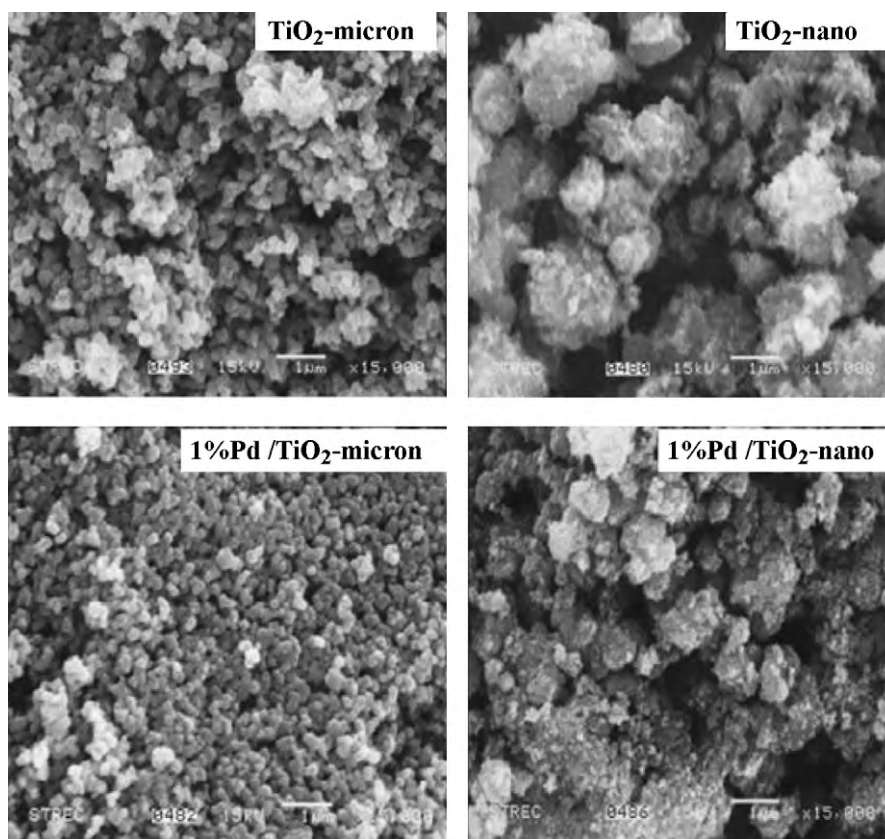


Fig. 2. SEM micrographs of TiO₂ and 1%Pd/TiO₂ (calcined).

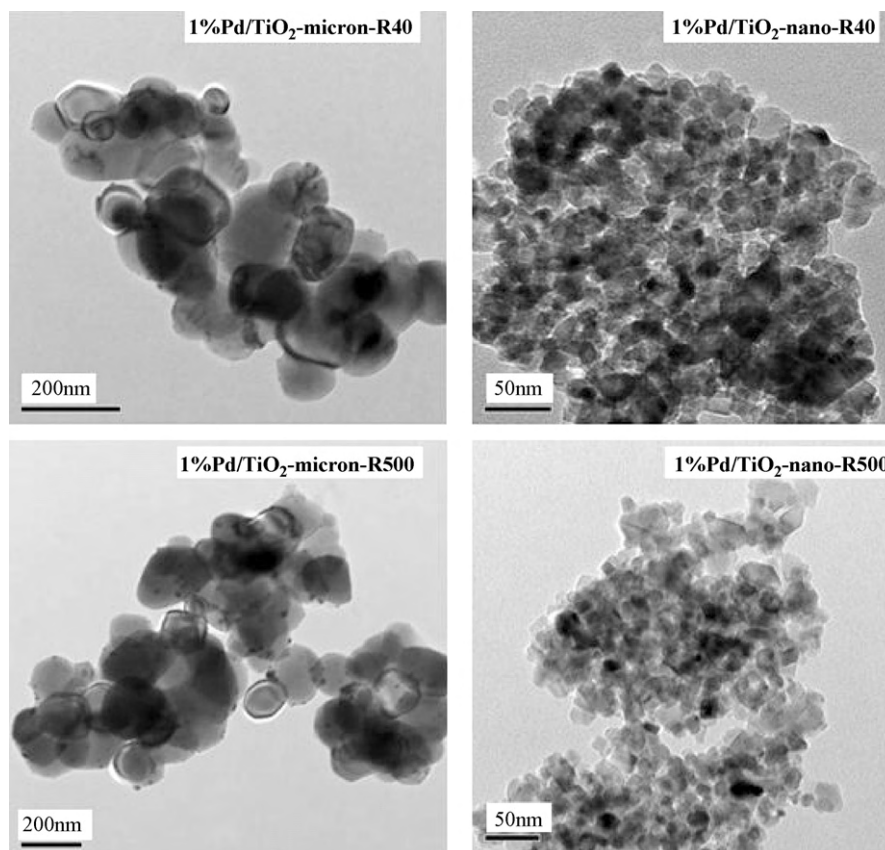


Fig. 3. TEM micrographs of the various Pd/TiO₂ catalysts.

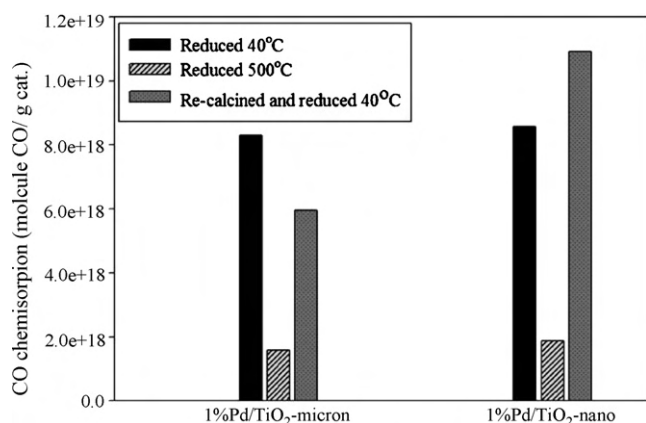
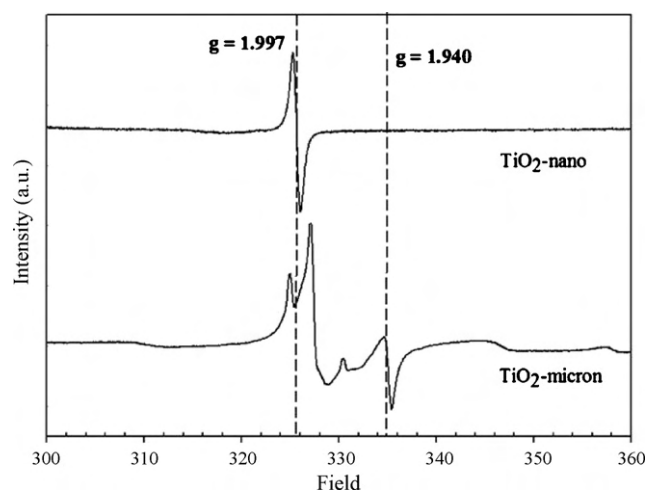


Fig. 4. CO chemisorption results.

temperature reduction while the amount of CO chemisorption of the re-calcined and re-reduced 1%Pd/TiO₂-nano can be totally recovered. It is generally known that strong metal–support interaction in TiO₂ supported Pd catalysts occurred after a high-temperature reduction $\geq 500^\circ\text{C}$. It is thus surprising that such interaction was not detected on our 1%Pd/TiO₂-micron. However, it should be noticed that the TiO₂ crystallite sizes used for preparation of Pd/TiO₂ catalysts in most studies in the literature were in nanometer range (usually less than 50 nm) [13–15,38]. Panagiotopoulou et al. [39] also reported that formation of substoichiometric TiO_x species started at lower temperature and was more facile over Pt/TiO₂ for small TiO₂ particle sizes (10–35 nm). On the other hand, a recent study by Musolino et al. [14] on the selective liquid-phase hydrogenation of *cis*-2-butene-1,4-diol to 2-hydroxy tetrahydrofuran on various supported Pd catalysts revealed the absence of SMSI effect for the Pd/TiO₂ catalyst reduced at high temperature. The interpretation of the observed behavior has not been given by those authors. However, the TiO₂ support used in their study was also anatase-phase TiO₂ from Aldrich with the specific surface area of $\sim 9\text{ m}^2/\text{g}$ similar to the micron-sized TiO₂ reported in this study.

The surface compositions of the catalysts as well as the interaction between Pd and the TiO₂ supports were confirmed by XPS analysis. The binding energies, FWHM, and atomic concentrations of Ti 2p, O 1s, and Pd 3d on various Pd/TiO₂ catalysts are given in Table 2. The Ti/O atomic ratios were found to be much higher for the TiO₂-nano than the TiO₂-micron suggesting that the solvothermal-derived TiO₂-nano possessed more oxy-

Fig. 5. ESR spectra of nano- and micron-sized TiO₂.

gen vacancies (or so-called Ti³⁺ defective sites) on the TiO₂ surface than the TiO₂-micron. However, there was also probably an oxygen-rich layer near the surface of the TiO₂ particles, which was formed by oxygen adsorption and easy oxidation of titanium surface [40]. When reduced at 500 °C, the Pd/Ti surface concentration decreased by 15 and 55% for 1%Pd/TiO₂-micron and 1%Pd/TiO₂-nano, respectively. A slight decrease of Pd/Ti surface concentration for 1%Pd/TiO₂-micron may be due to larger Pd⁰ particle size formed by sintering as shown by TEM and CO chemisorption, while a large decrease of Pd/Ti on the 1%Pd/TiO₂-nano would be due to decoration of Pd⁰ metal surface by the reducible TiO₂ support. The binding energies of Pd 3d_{5/2} (335.0–335.2 eV) and the FWHM less than 2 eV revealed that palladium was in the form of Pd⁰ metal for both cases [41].

The presence of Ti³⁺ in both TiO₂-micron and TiO₂-nano supports was revealed by electron spin resonance technique (Fig. 5). The Ti³⁺ species are produced by trapping of electrons at defective sites of TiO₂ and the amount of accumulated electrons may therefore reflect the number of defective sites [42]. The signal of g value less than two was assigned to Ti³⁺ (3d¹) [43]. Nakaoka et al. [44] reported six signals of ESR measurement occurring on the surface of titania: (i) Ti⁴⁺O[−]–Ti⁴⁺OH[−], (ii) surface Ti³⁺, (iii) adsorbed oxygen (O^{2−}), (iv) Ti⁴⁺O^{2−}–Ti⁴⁺O^{2−}, (v) inner Ti³⁺, and (vi) adsorbed water. In this study, it is clearly seen that the solvothermal-derived TiO₂ exhibited only one strong ESR signal at a g value of 1.997, which can be attributed

Table 2
XPS results

Catalysts	Ti 2p		O 1s		Pd 3d		Atomic concentration	
	B.E. (eV)	FWHM	B.E. (eV)	FWHM	B.E. (eV)	FWHM	Ti/O	Pd/Ti
TiO ₂ -micron	458.6	1.259	532.3	2.362	–	–	0.028	–
TiO ₂ -nano	458.7	1.308	530.0	1.675	–	–	0.204	–
1%Pd/TiO ₂ -micron R40	458.7	1.516	530.2	2.324	335.0	1.704	0.123	0.073
1%Pd/TiO ₂ -micron R500	458.7	1.846	530.2	1.846	335.2	1.849	0.178	0.062
1%Pd/TiO ₂ -nano-R40	458.7	1.292	530.0	1.596	335.0	1.570	0.210	0.009
1%Pd/TiO ₂ -nano-R500	458.6	1.319	529.9	1.681	n/d	n/d	0.190	0.004

to Ti^{3+} at the surface. Many Ti^{3+} ESR signals were observed for the TiO_2 -micron indicating that more than one type of Ti^{3+} defects were presented in the sample, i.e., surface Ti^{3+} and inner Ti^{3+} . Moreover, less amount of surface Ti^{3+} was present on the micron-sized TiO_2 . Literature data indicate that the presence of Ti^{3+} promotes strong metal–support interaction in Pd/TiO_2 catalysts since Ti^{3+} can easily diffuse from the lattice of TiO_2 to surface of Pd particles [13]. The results in this study, however, have shown that probably only the surface Ti^{3+} has high mobility and the other Ti^{3+} species may not be able to diffuse easily to Pd^0 surface so that Pd catalyst supported on the TiO_2 -micron with significant amount of Ti^{3+} did not exhibited the strong metal–support interaction.

Temperature programmed desorption of CO has been carried out in order to elucidate the influence of TiO_2 crystallite size, Pd dispersion, and reduction temperature on the strength and mechanism of CO adsorption on TiO_2 supported Pd catalysts. The results are shown in Fig. 6. For 1%Pd/ TiO_2 -micron reduced at 40 °C, two main desorption peaks were observed at ca. 340 and 640 °C which may be attributed to CO adsorbed on different adsorption sites probably Pd^0 with different particle sizes and/or adsorption on Ti^{3+} sites [45]. Both peaks were slightly

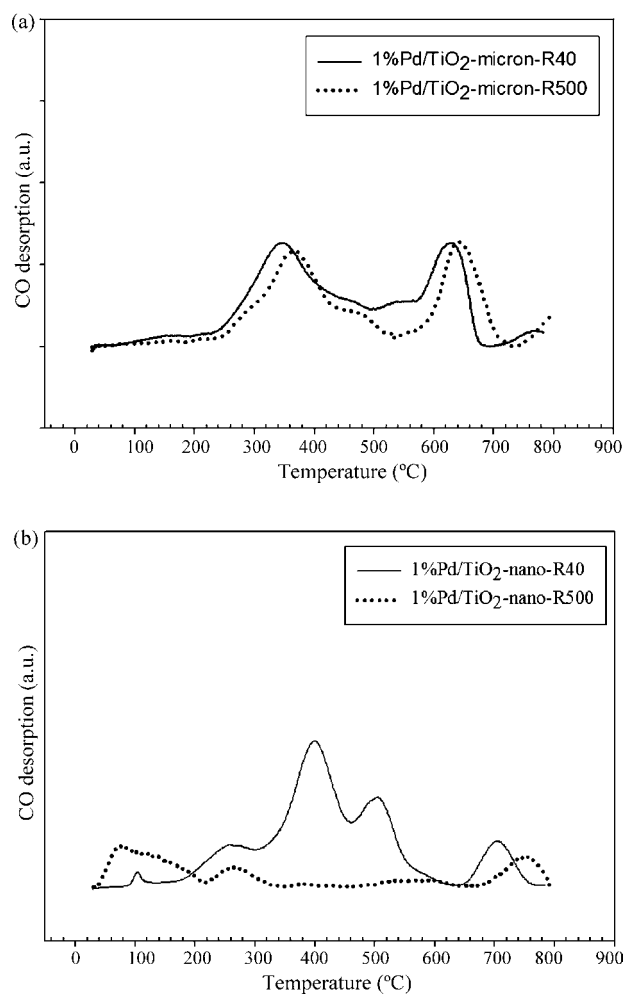


Fig. 6. CO-temperature programmed desorption profiles of (a) micron- and (b) nano-sized TiO_2 supported Pd catalysts.

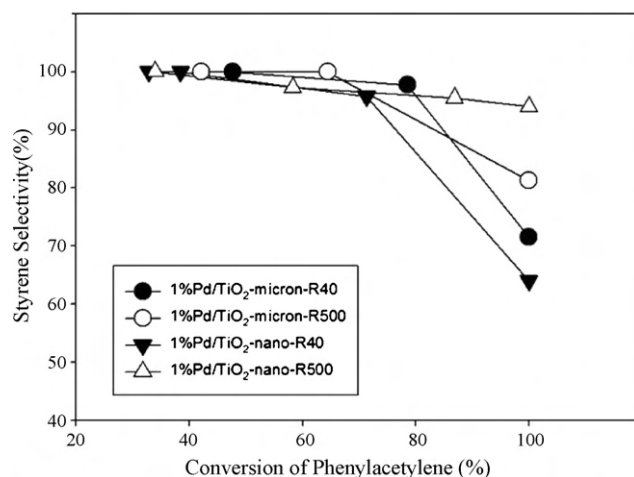


Fig. 7. Catalyst performances in liquid-phase selective hydrogenation of phenylacetylene.

shifted to higher temperature for the catalyst reduced at 500 °C. However, the amounts of CO desorption were not significant different for 1%Pd/ TiO_2 -micron reduced at 40 or 500 °C indicating that CO adsorption strength was not much different for the catalysts reduced at low and high temperatures. In contrast, 1%Pd/ TiO_2 -nano reduced at 40 °C exhibited several desorption peaks at 100–800 °C indicating various adsorption sites on the catalyst surface. However, the peaks become almost flat when the catalyst was reduced at 500 °C indicating negligible CO adsorption under such conditions. In other words, CO was weakly adsorbed under high-temperature reduction conditions due to the strong metal–support interaction effect.

Fig. 7 shows the performance of the 1%Pd/ TiO_2 -micron and 1%Pd/ TiO_2 -nano catalysts in liquid-phase selective hydrogenation of phenylacetylene under mild conditions. Both catalysts exhibited high styrene selectivities ($\geq 95\%$) for phenylacetylene conversions less than 80%. Based on the conditions and the column used in our GC analysis, the other product found in the reaction besides styrene was ethylbenzene. No other by-products were observed. The selectivity for styrene significantly dropped to 65–80% when conversion of phenylacetylene reached 100% for all the catalysts except 1%Pd/ TiO_2 -nano reduced at 500 °C that retained its high styrene selectivity $>90\%$. Such results suggest that the strong metal–support interaction on 1%Pd/ TiO_2 -nano catalyst produced great beneficial effect on the catalyst performance. The presence of SMSI effect may result in an inhibition of the adsorption of the product styrene on the 1%Pd/ TiO_2 -nano; hence high styrene selectivity was obtained.

The turnover frequencies (TOF) values were calculated from the data at a small conversion level of, for example, 30% for the catalysts except for the SMSI catalyst. It was found that the TOFs increased from 5.5 s^{-1} for 1%Pd/ TiO_2 -micron-R40 to 25.1 s^{-1} for 1%Pd/ TiO_2 -micron-R500 corresponding to the increase of Pd^0 particle size from 7 to 49 nm, respectively. The amount of exposed Pd species were estimated from CO chemisorption data with the assumption that one carbon monoxide molecule adsorbs on one palladium site [46–51]. The specific activity results were found to be in agreement with the well-established trend in the

literature that the liquid-phase hydrogenation activity decreases as Pd⁰ particle size decreases [52–58].

4. Conclusions

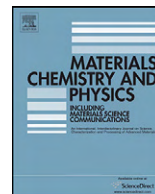
As revealed by various analytical techniques such as CO pulse chemisorption, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and CO-temperature program desorption, reduction by H₂ at 500 °C resulted in strong metal–support interaction for the nano-sized TiO₂ supported Pd catalyst, but not for the micron-sized TiO₂ supported one. The SMSI effect, however, appeared to be necessary for high catalytic performance of the Pd/TiO₂ catalysts in the liquid-phase selective hydrogenation of phenylacetylene to styrene.

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Effect of Ni-modified α -Al₂O₃ prepared by sol–gel and solvothermal methods on the characteristics and catalytic properties of Pd/ α -Al₂O₃ catalysts

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ABSTRACT

In the present study, Ni-modified α -Al₂O₃ with Ni/Al ratios of 0.3 and 0.5 were prepared by sol–gel and solvothermal method and then were impregnated with 0.3 wt.% Pd. Due to different crystallization mechanism of the two preparation methods used, addition of nickel during preparation of α -Al₂O₃ resulted in various species such as NiAl₂O₄, mixed phases between NiAl₂O₄ and α -Al₂O₃, and mixed phases between NiAl₂O₄ and NiO. As revealed by NH₃-temperature programmed desorption, formation of NiAl₂O₄ drastically reduced acidity of alumina, hence lower amounts of coke deposited during acetylene hydrogenation was found for the Ni-modified α -Al₂O₃ supported catalysts. For any given method, ethylene selectivity was improved in the order of Pd/Ni–Al₂O₃-0.5 > Pd/Ni–Al₂O₃-0.3 > Pd/Ni–Al₂O₃-0 \gg Pd/ α -Al₂O₃-commercial. When comparing the samples prepared by different techniques, the sol–gel-made samples showed better performances than the solvothermal-derived ones.

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1. Introduction

Alumina powders are very interesting crystalline materials with broad applicability as adsorbents, coatings, soft abrasives, ceramic tools, fillers, wear-resistant ceramics, catalysts, and catalyst supports [1,2]. Because of their fine particle size, high surface area, high melting point (above 2000 °C), high purity, good adsorbent, and high catalytic activity, they have been employed in a wide range of large-scale technological processes [3,4].

Various transition alumina (α , γ , χ , δ , η , and θ) has been prepared by different methods such as, sol–gel synthesis [5], hydrothermal synthesis [6], microwave synthesis [7], emulsion evaporation [8,9], precipitation from solution [10], and solvothermal synthesis [11–13]. The sol–gel method is an easy method but the precipitated powders obtained are amorphous in nature and further heat treatment is required for crystallization. Solvothermal method is an alternative route for direct (one-step) synthesis of Al₂O₃ nanoparticles. Particle morphology, crystalline phase, and surface chemistry of the products can be controlled by regulating precursor composition, reaction temperature, pressure, solvent property, and aging time [14,15]. The α -Al₂O₃ is usually used as a

thermal stabilizing material while the γ -Al₂O₃ shows a high surface area and is often used to make a dispersed metal catalyst.

Pd/ α -Al₂O₃ is typically employed in gas-phase selective acetylene hydrogenation in commercial ethylene production plant. Removal trace amount of acetylene in ethylene feedstock is very important because acetylene acts as a poison to ethylene polymerization catalysts [16,17]. The Pd/ α -Al₂O₃ catalyst is typically macroporous and has a relatively small surface area of approximately 0.1–2 m² g^{−1}. In general, α -Al₂O₃ provides low dispersion of active metal than γ -Al₂O₃ but it is desirable in selective acetylene hydrogenation reaction because α -Al₂O₃ is less acidic than γ -Al₂O₃ so that less oligomer or green oil was formed during acetylene hydrogenation reaction. Moreover, Pd/ α -Al₂O₃ has lower ability for direct ethane formation than Pd/ γ -Al₂O₃ catalyst. Recently, Pd/ α -Al₂O₃ prepared by glow discharge plasma has been studied in acetylene hydrogenation [18]. The improved catalyst performance has been suggested to be due to surface modification and changes of the interaction between metal and support as a result of plasma processing.

In this study, the properties of α -Al₂O₃ support have been modified by Ni addition during sol–gel and solvothermal syntheses. The characteristics of Pd/Ni-modified α -Al₂O₃ were investigated by means of N₂ physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), CO pulse chemisorption, thermal gravimetric and differential temperature analysis (TG–DTA), and

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NH₃ temperature program desorption. Their catalytic properties were tested in the gas-phase selective hydrogenation of acetylene.

2. Experimental

2.1. Preparation of Ni-modified α -Al₂O₃

Ni-modified α -Al₂O₃ samples were prepared by sol–gel and solvothermal methods. For the sol–gel method, mixture of 24 g aluminium nitrate nonahydrate (Aldrich) and a desired amount of nickel nitrate-6-hydrate (Aldrich) were dissolved in 50 cc of ethanol. The experiment was conducted in the reflux-condenser reactor at the temperature about 70–80 °C for 18 h. Then, urea solution, which consist of 60 g of urea and 50 mL of distilled water, was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition. The obtained product was calcined with two steps heating rate to avoid overflowing of gel during calcinations, i.e. 3 °C min^{−1} from room temperature to 500 °C and continue heating at 5 °C min^{−1} to 1150 °C. Then, temperature was hold for 3 h.

For the solvothermal method, Ni-modified Al₂O₃ were prepared using a mixture of aluminum isopropoxide 15.0 g and appropriate amount of nickel(II) acetylacetonate. The starting materials were suspended in 100 mL of toluene in beaker, and then set up in autoclave. In the gap between the beaker and autoclave wall, 40 mL of toluene was added. After the autoclave was completely, the suspension was heated to 300 °C at the rate of 2.5 °C min^{−1} and held at that temperature for 2 h. However, the same synthesis method is performed at various holding temperature. Autogenous pressure during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the obtained product carried out in a furnace. The product was heated at a rate of 10 °C min^{−1} to a desired temperature and held at that temperature for 1 h.

2.2. Preparation of Pd supported on Ni-modified α -Al₂O₃

The Pd/Ni-modified Al₂O₃ catalysts were prepared by incipient wetness impregnation of support with a desired amount of an aqueous solution of palladium(II) nitrate hydrate (Aldrich) to obtain the final Pd loading of ca. 0.3 wt%. The catalysts were dried overnight at 110 °C and then calcined in N₂ flow 60 cm³ min^{−1} with a heating rate of 10 °C min^{−1} until the temperature reached 500 °C and then in air flow 100 cm³ min^{−1} at 500 °C for 2 h.

2.3. Catalyst characterization

Surface area measurements were carried out by nitrogen adsorption in a Micromeritics Chemisorb 2750 system. Each sample was degassed at 200 °C for 2 h. The analysis gas consisting of 30% N₂ in helium was adsorbed on the samples at low temperature by dipping cell into liquid nitrogen dewar. X-ray diffraction patterns of the catalyst samples were obtained with a SIEMENS D5000 X-ray diffractometer using Cu K α radiation with a Ni filter. The pattern were recorded between 20° and 80° (2 θ) using a scanning velocity of 0.02° s^{−1}. Metal active sites were measured using CO chemisorption technique at room temperature in a Micromeritics Chemisorb 2750 automated system attached with ChemiSoft TPx software. Before chemisorption measurement, the sample was reduced in a H₂ flow at 150 °C for 2 h then cooled down to ambient temperature in a He flow. Ammonia temperature program desorption (NH₃-TPD) was also performed in a Micromeritics Chemisorb 2750 automated system attached with ChemiSoft TPx software. Approximately 0.1 g of catalyst was placed in a quartz tube in a temperature-controlled oven. The samples adsorbed ammonia at 40 °C, then heated up to 650 °C at a heating rate of 10 °C min^{−1}. The amount of acid-sites on the catalyst surface was calculated from the desorption amount of NH₃. It was determined by measuring the areas of the desorption profiles obtained from a Micromeritics Chemisorb 2750 pulse chemisorption system analyzer. For the broad desorption peak, it was separated into many sub-peaks by using the Fityk program for peak fitting. All areas of sub-peaks were summed to calculate the total amount of acid-sites [19]. The distribution of palladium on catalyst supports were observed using AJEM-200CX transmission electron microscope operated at 160 kV.

2.4. Reaction study

Catalytic performance of the catalysts was studied in selective hydrogenation of acetylene. The experiment was performed in a quartz tube reactor (i.d. 10.1 mm). Before starting of the reaction, the catalyst was reduced in H₂ at 150 °C for 2 h. Then the reactor was purged with argon and cooled down to the reaction temperature, 40 °C. Feed gas composed of 1.5% C₂H₂, 1.7% H₂, and balanced C₂H₄ (TIG Co., Ltd.), a GHSV of 39,435, 24,433, 16,901 and 9288 h^{−1} were used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). Acetylene conversion as used herein is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. The ethylene being

hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated.

3. Results and discussion

3.1. Characteristics of the Ni-modified α -Al₂O₃

3.1.1. The solvothermal-made

The XRD patterns of solvothermal-made Al₂O₃ and Ni-modified Al₂O₃ with various Ni/Al ratios (0, 0.3, and 0.5) are shown in Fig. 1. The patterns in the lower half of the figure correspond to the as-synthesized powder while the patterns in the upper part of the figure are for those which have been calcined at 1150 °C for 1 h in a post-synthesis treatment step. The as-synthesized and calcined alumina powders exhibited typical XRD characteristic peaks of χ -alumina and α -alumina, respectively. χ -Alumina powders are normally obtained by the thermal decomposition reaction of AIP in inert organic solvent which transformed directly to α -alumina at high calcination temperature [20,21]. For the as-synthesized Ni-doped samples, XRD characteristic peaks of both χ -Al₂O₃ and Ni⁰ metal were observed. After calcination, XRD characteristic peaks of NiAl₂O₄ spinel; space group Fd3m [22] (as indicated by circles in the upper frame) were apparent. For the sample with Ni/Al = 0.3, only the NiAl₂O₄ spinel was found while for Ni/Al = 0.5, both NiAl₂O₄ and NiO characteristic peaks were observed.

Thermal gravimetric and differential temperature analysis of as-synthesized solvothermal-made powders are shown in Fig. 2. The overall weight loss increased from 14 to 20% as the Ni/Al ratios increased from 0 to 0.5. Two weight-decrease steps were clearly detected. The first step observed below 250 °C was due to desorption of the physisorbed water. The second weight decrease at around 250–400 °C could be attributed to the combustion of organic moieties forming on catalyst surface. The exothermic DTA peaks were clearly observed at around 318 °C which should be assigned to the exothermic heat from the combustion process. Intensities of DTA peaks and overall weight loss increased as the

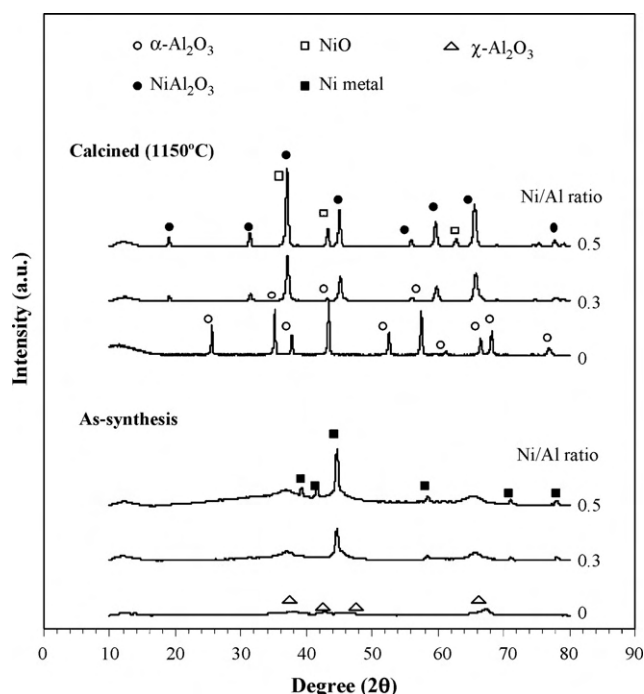


Fig. 1. XRD results of the as-synthesized and calcined α -Al₂O₃ and Ni-modified α -Al₂O₃ prepared by solvothermal method.

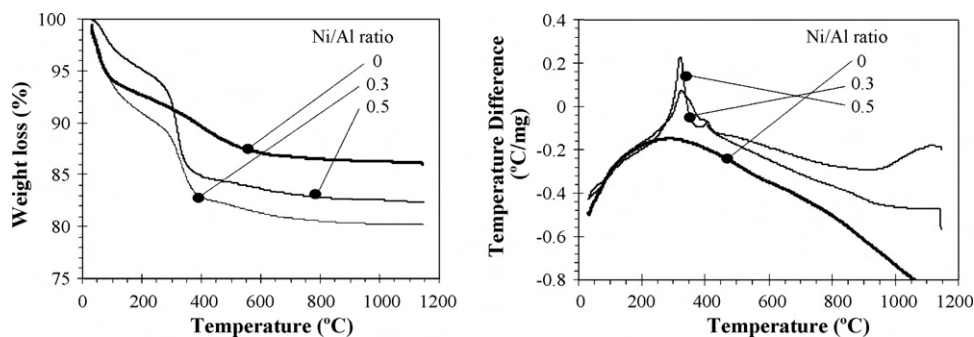


Fig. 2. TG/DTA results of the as-synthesized α - Al_2O_3 and Ni-modified α - Al_2O_3 prepared by solvothermal method.

Ni/Al ratio increased. These results suggest that the acetylacetonate groups from Ni precursor were not completely decomposed and remained on the surface of as-synthesized samples.

3.1.2. The sol-gel-made

The XRD patterns of sol-gel-made Al_2O_3 and Ni-modified Al_2O_3 with various Ni/Al ratios (0, 0.3, and 0.5) are shown in Fig. 3. The patterns in the lower half of the figure correspond to the powder calcined at 800°C while the patterns in the upper part of the figure are for those which have been calcined at 1150°C for 1 h in a post-synthesis treatment step. After calcination at 800°C , γ -alumina was formed. It was then transformed to α -alumina by calcination at 1150°C . The Ni-modified Al_2O_3 samples which have been calcined at 800°C exhibited XRD characteristic peaks of γ - Al_2O_3 and NiAl_2O_4 . On the other hand, the samples calcined at 1150°C with Ni/Al = 0.3 exhibited characteristic peaks of NiAl_2O_4 and α - Al_2O_3 while for Ni/Al = 0.5 only NiAl_2O_4 was found.

Results from thermal analysis of the obtained gel are shown in Fig. 4. Overall weight losses of all the gel samples were essentially similar at around 95%. Three weight-decrease processes were detected, which were accompanied by three endothermic peaks

in DTA. The first peak observed below 100°C was due to desorption of physisorbed water. The second and third weight decrease occurred at around 120 – 230°C and 230 – 500°C could be attributed to the elimination of chemisorption water and remaining nitrate species forming in the gel structure. The last exothermic DTA peaks without any weight loss were observed at around 520°C and were assigned to crystallization of the NiAl_2O_4 from amorphous gel. This is confirmed by the crystallization of NiAl_2O_4 by calcination of gel at 800°C .

3.1.3. Mechanism for NiAl_2O_4 formation of the sol-gel and solvothermal-made Ni-modified α - Al_2O_3

Many nanocrystalline materials with specific properties were successfully synthesized by thermal treatment of suitable precursors such as metal alkoxide, acetate and acetylacetonate in inert organic solvents. Crystallization mechanism of α - Al_2O_3 and Ni-modified α - Al_2O_3 , however, was different for the two preparation methods used (sol-gel and solvothermal). While the solvothermal reaction of aluminum isopropoxide alone in toluene gave the nanocrystalline χ -alumina particles [23], the sol-gel method yielded a solid precipitate at relatively low temperature and crystallization occurred during the subsequent calcination step at high temperature. Addition of the nickel precursor solution during the sol-gel synthesis with Ni/Al = 0.3 resulted in the mixed phases of α - Al_2O_3 and NiAl_2O_4 while increasing Ni/Al to 0.5 yielded formation of NiAl_2O_4 alone. Such results were expected based on the stoichiometric ratio of NiAl_2O_4 (Ni/Al = 0.5). However, the solvothermal synthesis of Ni-modified α - Al_2O_3 with Ni/Al = 0.3 and 0.5 resulted in the formation of NiAl_2O_4 alone and the mixed phases between NiAl_2O_4 and NiO , respectively. The crystallization mechanism of Ni-modified α - Al_2O_3 probably started with the decomposition of aluminum isopropoxide, which yielded Al-O^- and $(\text{CH}_3)_2\text{CH}^+$ and then the nucleophilic attack of Al-O^- on nickel acetylacetonate or another AIP molecule took place yielding the Al-O-Ni or the Al-O-Al bond. This crystallization mechanism was similar to that of Si-doped Al_2O_3 prepared from aluminum isopropoxide and tetraethyl orthosilicate in toluene [24]. Based on XRD results of the as-synthesized and the calcined solvothermal-made Ni-modified Al_2O_3 samples, it is indicated that Ni metal was formed at the first place together with the crystallization of Al_2O_3 . Calcination at high temperature then resulted in penetration of Ni atoms in Ni^0 metal phase to occupy the tetrahedral sites in NiAl_2O_4 matrix via a solid-state reaction. Because of the limitation of solid solution of Ni in NiAl_2O_4 phase, the excess NiO was shed from NiAl_2O_4 matrix at higher Ni/Al ratios (Ni/Al = 0.5).

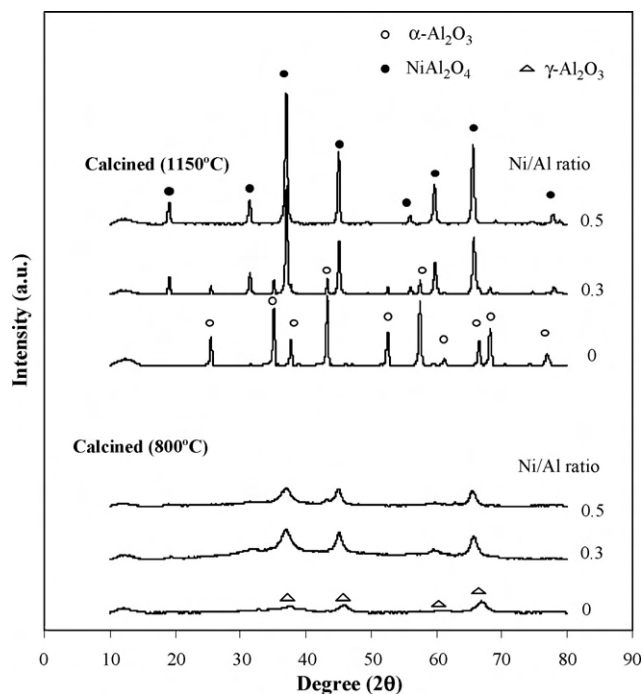


Fig. 3. XRD results of the sol-gel-derived α - Al_2O_3 and Ni-modified α - Al_2O_3 after calcination at 800 and 1150°C .

3.2. Characteristics of the Pd/Ni-modified α - Al_2O_3 catalysts

The XRD patterns of the sol-gel- and the solvothermal-made Pd/ α - Al_2O_3 and the Pd/Ni-modified α - Al_2O_3 catalysts after calci-

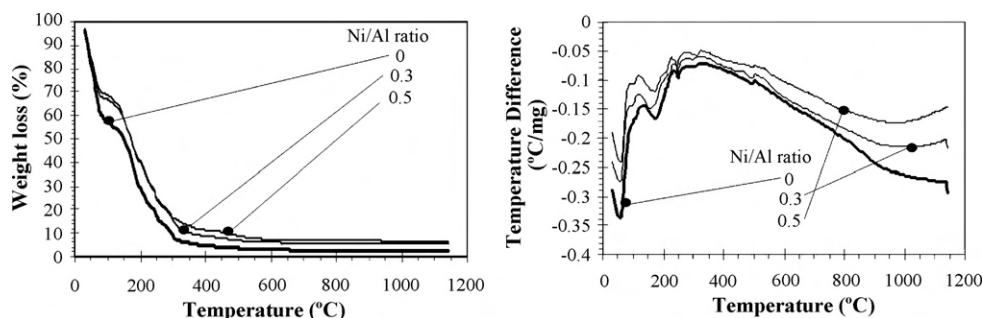


Fig. 4. TG/DTA results of the as-synthesized α - Al_2O_3 and Ni-modified α - Al_2O_3 prepared by sol-gel method.

nations at 1150°C are shown in Fig. 5. The patterns in the lower half of the figure correspond to the sol-gel-made powder while the patterns in the upper part of the figure are for those prepared by solvothermal synthesis. Both the sol-gel- and solvothermal-made Pd/ α - Al_2O_3 catalysts exhibited all the characteristic peaks of α - Al_2O_3 structure. While the diffraction lines for Pd/Ni-modified α - Al_2O_3 catalyst could be assigned to a spinel-type NiAl_2O_4 structure. Additional peaks corresponding to NiO were also presented at 43.3° and $62.9^\circ 2\theta$ for the product obtained from solvothermal synthesis with Ni/Al=0.5. The XRD characteristic peaks associated with Pd^0 or PdO phase were not observed for all the samples.

TEM micrographs were taken in order to physically measure the size of the palladium oxide particles and/or palladium clusters. For those prepared by solvothermal method, agglomeration of finger-like particles were observed for Pd/ α - Al_2O_3 whereas spherical-shape particles were found for Pd/Ni-modified α - Al_2O_3 (Fig. 6a and b), respectively. The finger-like α - Al_2O_3 particles are normally obtained by calcination of the solvothermal-made α - Al_2O_3 powders at high temperature [22,23]. It can be seen that the sol-gel-made catalyst (Fig. 6c and d) was consisted of agglomerated particles with primarily irregular shape structure. Based on TEM analysis, palladium particles/clusters with average particle size ca. 5–10 nm were deposited on the alumina supports.

The physicochemical properties of Pd/ α - Al_2O_3 and Pd/Ni-modified α - Al_2O_3 catalysts are summarized in Table 1. The average XRD crystallite size of each crystal phase was calculated from the Scherrer equation. The average crystallite sizes of the α - Al_2O_3 pre-

pared by sol-gel and solvothermal method were 34 and 58 nm, respectively. Compared to the α - Al_2O_3 , the crystallite sizes of NiAl_2O_4 formed in both cases were smaller suggesting that the presence of Ni atom in NiAl_2O_4 inhibited the growth of crystal. The surface areas of all the catalysts were not significantly different and still quite low, due probably to high agglomeration of these nanocrystalline particles during calcinations at high temperature. The amounts of CO chemisorption on the catalysts, the percentages of Pd dispersion, and the average Pd metal particle sizes determined from CO chemisorption are also given in Table 1. The pulse CO chemisorption technique was based on the assumption that one carbon monoxide molecule adsorbs on one palladium site [25–29]. It was found that the amounts of CO chemisorption slightly decreased as the Ni/Al ratio increased from 0 to 0.5 for all the Pd/Ni-modified α - Al_2O_3 catalysts. However, for Ni/Al ratio 0 and 0.3, there were no significant differences of the percentages of Pd dispersion and calculated Pd^0 metal particle sizes for the catalysts prepared by two different techniques. For Ni/Al=0.5, the solvothermal-made Pd/Ni-modified α - Al_2O_3 showed slightly higher amount of CO chemisorption than the sol-gel-made catalyst.

3.3. Catalyst performance in selective acetylene hydrogenation

The catalyst performance in selective hydrogenation of acetylene to ethylene was studied for all the catalyst samples using a fixed bed flow reactor. Changes in ethylene selectivity with acetylene conversion for Pd/ α - Al_2O_3 and Pd/Ni-modified α - Al_2O_3 catalysts are shown in Fig. 7. In general, ethylene selectivity decreases with increasing acetylene conversion due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction. In this study, it was found that Pd/Ni-modified α - Al_2O_3 exhibited better performances in selective acetylene hydrogenation Pd/ α - Al_2O_3 and Pd/commercial α - Al_2O_3 regardless of the preparation method used. For a given method, ethylene selectivity was improved in the order of Pd/Ni- Al_2O_3 -0.5 > Pd/Ni- Al_2O_3 -0.3 > Pd/Ni- Al_2O_3 -0 > Pd/ α - Al_2O_3 -commercial. When comparing the samples prepared by different techniques, the sol-gel-made samples showed higher ethylene selectivity than those of the solvothermal-derived ones.

During long-time investigation by many research groups, the catalytic activity and ethylene selectivity in the selective acetylene hydrogenation over Pd-based catalysts are found to be dependent on many factors such as metal dispersion (Pd metal particle size) [30–33], thermodynamic adsorption differences between acetylene and ethylene [34], and carbonaceous product formation [35,36], etc. Based on the reaction mechanisms for acetylene hydrogenation on Pd/ Al_2O_3 catalysts reported in the literatures [37], there are three active sites on the Pd metal surface and one active site on the alumina support. The three sites on the palladium surface are responsible for selective hydrogenation of acetylene to ethylene,

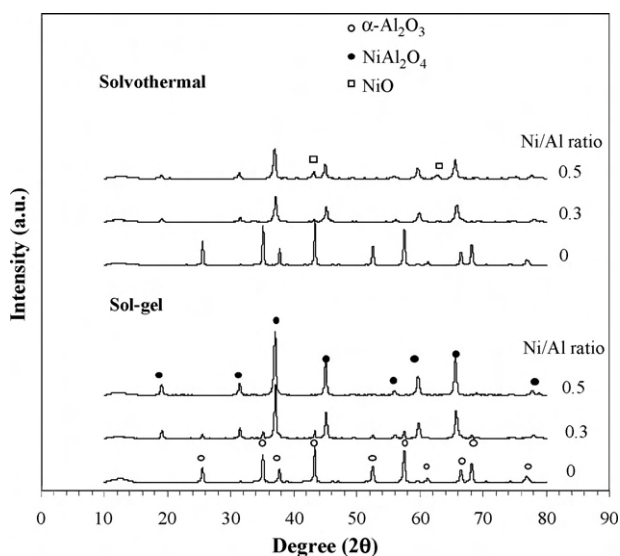


Fig. 5. XRD results of the various Pd/ α - Al_2O_3 and Pd/Ni-modified α - Al_2O_3 .

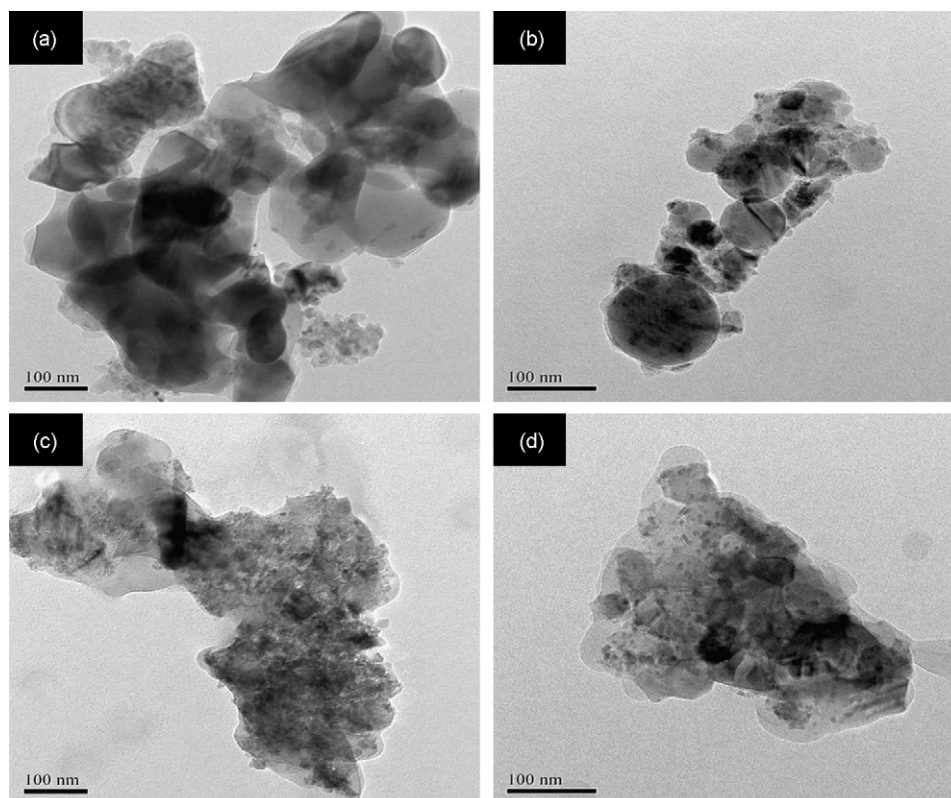
Table 1Characteristics of the various Pd/ α -Al₂O₃ and Pd/Ni-modified α -Al₂O₃ catalysts

Sample	d_{XRD}^a (nm)	BET surface area (m ² g ⁻¹)	NH ₃ uptake ($\mu\text{mol g-cat}^{-1}$)	CO chemisorption ($\times 10^{17}$ sites g-cat ⁻¹)	Pd dispersion (%)	d_p^b Pd ⁰ (nm)
Sol-gel						
Pd/Ni-Al ₂ O ₃ -0	34 ^c	1.5	339.3	7.51	4.42	25
Pd/Ni-Al ₂ O ₃ -0.3	54 ^c , 31 ^d	1.5	197.1	6.22	3.65	31
Pd/Ni-Al ₂ O ₃ -0.5	27 ^d	1.9	127.1	5.37	3.16	35
Solvothermal						
Pd/Ni-Al ₂ O ₃ -0	54 ^c	4.7	268.2	8.10	4.76	24
Pd/Ni-Al ₂ O ₃ -0.3	24 ^d	1.8	175.6	6.28	3.69	30
Pd/Ni-Al ₂ O ₃ -0.5	23 ^d , 26 ^e	1.4	380.7	7.35	4.32	26
Commercial						
Pd/ α -Al ₂ O ₃	391.6 ^c	0.5	n.d.	5.91	3.48	32

^a Crystallite size calculated by Scherrer equation.^b Average Pd metal particle sized calculated from CO chemisorption results. $d_p = 1.12 D^{-1}$, where D = Pd dispersion [25].^c α -Al₂O₃.^d NiAl₂O₄.^e NiO.

direct ethane formation from acetylene and oligomer formation whereas ethylene hydrogenation is believed to take place on the support by means of a hydrogen transfer mechanism. It was claimed that the carbonaceous deposits present act as bridges for hydrogen spillover [38]. Sarkany et al. [39] discussed a mechanism of acetylene hydrogenation and suggested that the role of coke is primarily to promote hydrogen transfer from the metal surface to the adsorbed ethene. Moreover, acidity on alumina surface is known to promote formation of carbonaceous deposits on catalyst surface. Fig. 8 shows the NH₃ temperature program desorption profiles for the sol-gel and solvothermal-made α -Al₂O₃ and the Ni-modified α -Al₂O₃ supports. Typically, acidity of α -phase Al₂O₃ was much lower than γ -phase alumina so it is used in the commercial Pd/Al₂O₃ selective acetylene hydrogenation catalysts. In

this work, desorption peak areas of the nanocrystalline powders obtained from both sol-gel and solvothermal syntheses were quite low, however, two desorption peaks corresponding to different acid sites were still observed at ca. 320 and 400–500 °C. For the sol-gel-made Ni-modified α -Al₂O₃, the desorption peaks decreased rapidly and the profiles became almost flat as the Ni/Al ratio increased from 0 to 0.5 suggesting that acidity of alumina significantly decreased with incorporation of Ni atoms and NiAl₂O₄ formation. A decrease of alumina acidity, however, was less pronounced for the solvothermal-made Ni-modified α -Al₂O₃. A broad desorption peak at ca. 250–500 °C was observed for the solvothermal-made Ni-modified α -Al₂O₃ with Ni/Al ratio = 0.5 due probably to the presence of NiO. According to the work reported by Areán et al. [40], a decrease in both Lewis and Brønsted acidity was observed for Ni-

**Fig. 6.** TEM images of (a) Pd/ α -Al₂O₃-solvothermal, (b) Pd/Ni-modified α -Al₂O₃-solvothermal, (c) Pd/ α -Al₂O₃-sol-gel, and (d) Pd/Ni-modified α -Al₂O₃-sol-gel.

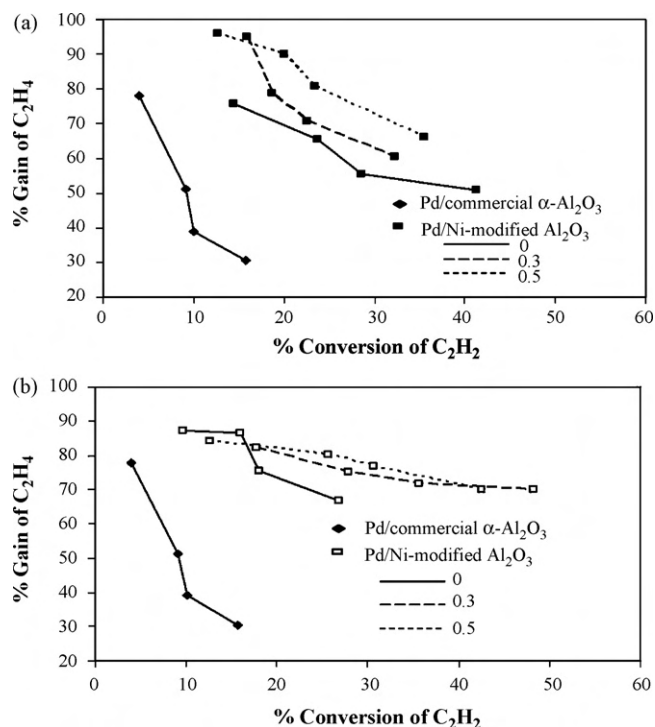


Fig. 7. Performances of the various Pd/ $\alpha-Al_2O_3$ and Pd/Ni-modified $\alpha-Al_2O_3$ in selective hydrogenation of acetylene. (a) Solvothermal method; (b) sol-gel method.

doped alumina as the Ni contents increased in the Ni-alumina solid solution as confirmed by IR spectroscopy of CO adsorbed at liquid nitrogen temperature. Moreover, the very low Brønsted acidity also appears to be typical for many oxide spinels as well as other aluminate spinels such as $MgAl_2O_4$ and $ZnAl_2O_4$ [41,42].

The amounts of coke formed on the spent catalysts were measured by TG-DTA technique and the results are shown in Fig. 9. All the catalysts were pretreated at 200 °C for 1 h in order to remove any

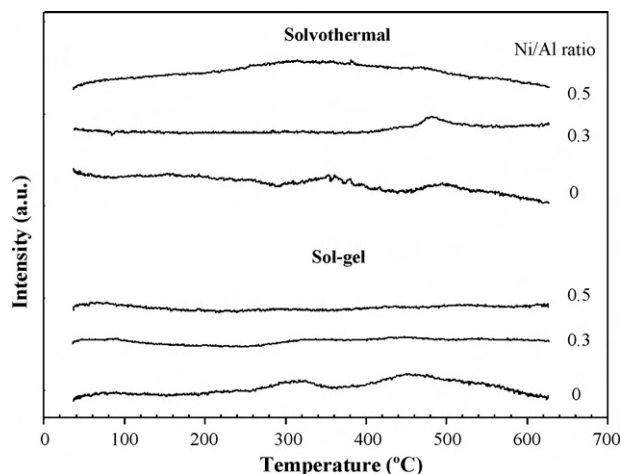


Fig. 8. NH_3 -temperature program desorption profiles of the various Al_2O_3 and Ni-modified Al_2O_3 samples.

adsorbed water remaining on the catalyst surface prior to TG/DTA experiments. Thus, one step weight loss observed with the maximum peak at ca. 250 °C can be attributed to the elimination of deposited “soft-type” coke by combustion reaction [43,44]. These also corresponded with the broad exothermic peaks observed in the plots of temperature difference versus temperature. The lower weight loss during temperature-programmed oxidation indicates a lower rate of coke deposition on the catalyst surface [45]. It was found that the use of sol-gel- and solvothermal-made Ni-modified $\alpha-Al_2O_3$ supports (Ni/Al = 0.5) reduced the amounts of coke deposited by 44 and 38%, respectively.

The results of coke formation over the various $\alpha-Al_2O_3$ and Ni-modified $\alpha-Al_2O_3$ supported Pd catalysts were in accordance with acidity measurement. Formation of $NiAl_2O_4$ spinel during the preparation of Ni-modified Al_2O_3 by sol-gel or solvothermal method resulted in a decreased acidity of $\alpha-Al_2O_3$. As a consequence, the catalysts exhibited high ethylene selectivities at high acetylene conversions and lower amounts of coke deposited. For-

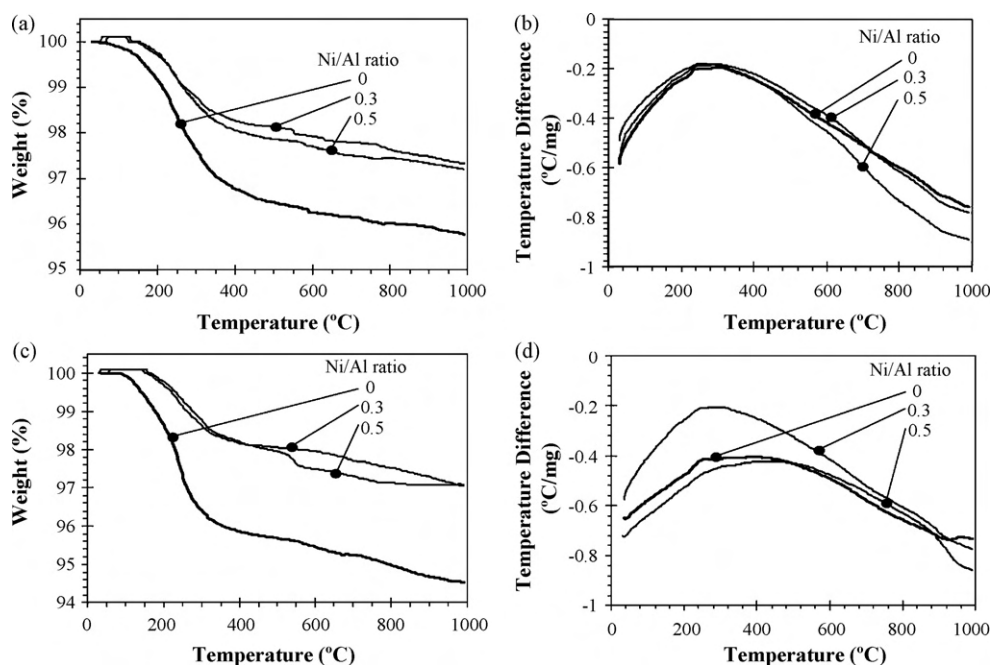


Fig. 9. TG/DTA results of the spent Pd/ $\alpha-Al_2O_3$ and Pd/Ni-modified $\alpha-Al_2O_3$ catalysts, (a and b) solvothermal-made; (c and d) sol-gel-made.

mation of NiAl_2O_4 in Ni-based hydrogenation catalysts has also shown high resistance to deactivation by coke formation [46–48]. In addition, Bhattacharyya and Chang [47] have recently proposed that the use of a nickel aluminate spinel catalyst could reduce coke formation during CH_4/CO_2 reforming. Sueiras and co-workers reported that $\text{Ni}/\text{NiAl}_2\text{O}_4$ catalysts exhibited high conversion and selectivity towards benzene in 1,2,4-trichlorobenzene hydrodechlorination [49]. Unlike the conventional $\text{Ni}/\text{Al}_2\text{O}_3$, the most selective $\text{Ni}/\text{NiAl}_2\text{O}_4$ catalysts had the highest TOF values.

4. Conclusions

This study explored the effect of Ni-modified $\alpha\text{-Al}_2\text{O}_3$ prepared by sol–gel and solvothermal methods on the properties of $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ in gas-phase selective acetylene hydrogenation. While the sol–gel-made sample with $\text{Ni}/\text{Al}=0.5$ showed formation of NiAl_2O_4 alone, the solvothermal-made resulted in the mixed phases between NiAl_2O_4 and NiO . The improved catalytic performances in terms of higher ethylene selectivity and lower amount of coke formation for the Pd/Ni -modified $\alpha\text{-Al}_2\text{O}_3$ were attributed to the lower acidity of $\alpha\text{-Al}_2\text{O}_3$ by incorporation of nickel into alumina matrix.

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Selective hydrogenation of acetylene over Pd catalysts supported on nanocrystalline α -Al₂O₃ and Zn-modified α -Al₂O₃

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ABSTRACT

The catalytic performance of Pd catalysts supported on nanocrystalline α -Al₂O₃ and Zn-modified α -Al₂O₃ prepared by sol-gel and solvothermal methods was studied in the selective hydrogenation of acetylene. Acidity of the nanocrystalline α -Al₂O₃ was significantly decreased by incorporation of Zn atoms in the α -Al₂O₃. Both of acetylene conversions and ethylene selectivities were improved in the order: Pd/Zn-modified α -Al₂O₃-sol-gel > Pd/Zn-modified α -Al₂O₃-solvothermal > Pd/ α -Al₂O₃-sol-gel \approx Pd/ α -Al₂O₃-solvothermal \gg Pd/ α -Al₂O₃-commercial. As revealed by thermal gravimetric and differential temperature analysis (TG-DTA), Pd catalysts on the nanocrystalline Zn-modified α -Al₂O₃ also showed less deactivation by coke formation.

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1. Introduction

Pd-based catalyst supported on Al₂O₃ with low Pd loading (0.1–0.3 wt.%) is typically employed for selective hydrogenation of acetylene in ethylene feedstock [1–3]. Removal of acetylene is a crucial process in polyethylene production since acetylene poisons the polymerization catalysts [4,5]. The Al₂O₃ used as Pd catalyst support in this reaction contains mostly the α -phase Al₂O₃ since it possesses relatively low specific surface area and low acidity compared to other 'transition' alumina (such as β -, γ -, η -, χ -, κ -, δ -, θ -phase Al₂O₃). With respect to selectivity changes, catalysts with low dispersion were suggested to give better selectivity toward ethylene [1,2].

In recent years, nanocrystalline materials have gained considerable interest in the field of catalysis because they show significant differences in terms of catalytic activity and selectivity compared with those synthesized in micron scale. Several techniques have been reported for preparation of nanocrystalline Al₂O₃ such as sol-gel method [6], hydrothermal synthesis [7], microwave synthesis [8], emulsion evaporation [9], precipitation from solution [10], and solvothermal synthesis [11]. The sol-gel method is widely used due to its simplicity, however, the precipitated pow-

ders obtained are amorphous in nature and further heat treatment is required for crystallization. Solvothermal method is an alternative route for one-step synthesis of nanocrystalline materials.

In the present study, nanocrystalline α -Al₂O₃ and Zn-modified α -Al₂O₃ have been synthesized via sol-gel and solvothermal methods and employed as supports for Pd catalysts for selective hydrogenation of acetylene. Modification of nanocrystalline α -Al₂O₃ with zinc is studied because it can form ZnAl₂O₄ spinel which is an interesting material with low acidity that can exhibit the strong metal-support interaction (SMSI) with noble metal [12–14]. Based on the work reported by Moon et al. [15], addition of TiO₂ to Pd/SiO₂ catalysts has shown improvement in ethylene selectivity and less catalyst deactivation during selective acetylene hydrogenation. The origin of the improvement in catalyst performance was proposed to be due to strong interaction between the added TiO₂ and Pd. Thus, the presence of ZnAl₂O₄ in the Pd/ α -Al₂O₃ catalyst may improve the catalytic performance in the selective acetylene hydrogenation as well. The molar ratio of Zn/Al = 0.1 was selected in order to avoid the formation of ZnAl₂O₄ alone so that surface area of the Zn-modified supports were not much different from that of the unmodified α -Al₂O₃. The catalysts were characterized by X-ray diffraction (XRD), N₂ physisorption, ammonia temperature program desorption (NH₃-TPD), CO chemisorption, transmission electron microscope (TEM), and thermal gravimetric and differential temperature analysis (TG/DTA).

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2. Experimental

2.1. Catalyst preparation

Nanocrystalline α -Al₂O₃ were prepared by sol–gel and solvothermal methods. In the sol–gel method, 24 g of aluminum nitrate was dissolved in 50 ml of ethanol at room temperature. The solution was then heated to 70–80 °C in the reflux-condenser reactor and held for 18 h, after which the urea solution was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition. The obtained product was calcined with two steps heating rate to avoid overflowing of gel during calcinations, i.e. 3 °C/min from room temperature to 500 °C and continue heating at 5 °C/min to 1150 °C and held at that temperature for 3 h. The solvothermal-derived α -Al₂O₃ were prepared according to the method described in Ref. [16] using aluminum isopropoxide and toluene. For the preparation of Zn-modified α -Al₂O₃ by sol–gel and solvothermal method, an appropriate amount of zinc (II) nitrate hexahydrate and zinc (II) acetylacetonate (Zn/Al molar ratio = 0.1) were added to the precursor mixture of each method, respectively.

Approximately 0.3 wt.% Pd on α -Al₂O₃ and Zn-modified α -Al₂O₃ were prepared by the incipient wetness impregnation technique using an aqueous solution of the desired amount of Pd(NO₃)₂ (Aldrich). The catalysts were dried overnight at 110 °C and then calcined in N₂ flow 60 ml/min with a heating rate of 10 °C/min until the temperature reached 500 °C and then in air flow 100 ml/min at 500 °C for 2 h. For comparison purposes, a commercial α -Al₂O₃ (JRC-ALO2) was also employed as Pd catalyst support.

2.2. Catalyst characterization

X-ray diffraction patterns of the catalyst samples were obtained with a SIEMENS D5000 X-ray diffractometer using Cu K α radiation with a Ni filter. The BET surface area measurements were carried out by nitrogen adsorption in a Micromeritic Chemisorb 2750 system. Each sample was degassed at 200 °C for 2 h. The analysis gas consisting of 30% N₂ in helium was adsorbed on the samples at low temperature by dipping cell into liquid nitrogen dewar. Ammonia temperature program desorption (NH₃-TPD) was performed in a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software. Approximately 0.1 g of catalyst was placed in a quartz tube in a temperature-controlled oven. The amounts of CO chemisorbed on the catalyst were measured using a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. Prior to chemisorption, the sample was reduced in a H₂ flow at 150 °C for 2 h then cooled down to ambient temperature in a He flow. The distribution of palladium on catalyst supports were observed using JEOL Model JEM-2010 transmission electron microscope operated at 200 keV. Thermal gravimetric and differential temperature analysis (TG/DTA) were performed using an SDT Analyzer Model Q600 from TA Instruments, USA.

2.3. Reaction study

Selective acetylene hydrogenation was performed in a pyrex tube reactor (i.d. 10.1 mm). Prior to the start of each experimental run, the catalyst was reduced in H₂ at 150 °C for 2 h. Then the reactor was purged with Ar and cooled down to the reaction temperature. Feed gas was composed of 1.5% C₂H₂, 1.7% H₂ and balanced C₂H₄ (TIG Co., Ltd.) with a GHSV of 16,901 h^{−1}. The composition of products and feeds were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carboxisieve S2 columns, respectively). The temperature dependence of

the catalytic performance was observed during the range of 40–100 °C in 20 °C increments.

Acetylene conversion is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. However, due to the difficulty in precise measurement of the ethylene change in the feed and product, the indirect calculation using the difference in the hydrogen amount (hydrogen consumed) was used. The ethylene being hydrogenated to ethane is the difference between all the hydrogen consumed and all the acetylene totally hydrogenated.

$$\text{Selectivity of C}_2\text{H}_4 (\%) = \frac{100 \times [d\text{C}_2\text{H}_2 - (d\text{H}_2 - d\text{C}_2\text{H}_2)]}{d\text{C}_2\text{H}_2} \quad (1)$$

where dC₂H₂ = mole of acetylene in feed – mole of acetylene in product, dH₂ = mole of hydrogenation in feed – mole of hydrogen in product.

3. Results and discussion

The XRD patterns of Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ are shown in Fig. 1. The diffraction patterns were not different from those of the corresponding unmodified α -Al₂O₃ and Zn-modified α -Al₂O₃ supports. The characteristic peaks of α -Al₂O₃ were evident for Pd/ α -Al₂O₃ samples while the diffraction lines of both spinel-type ZnAl₂O₄ structure and α -Al₂O₃ were apparent for the Pd/Zn-modified α -Al₂O₃ catalysts. The average crystallite sizes of each crystal phase were calculated from the Scherrer equation and are given in Table 1. The crystallite sizes α -Al₂O₃ and ZnAl₂O₄ were calculated from the full width at half maximum of the XRD peaks at 2 θ = 43° and 37°, respectively. The average crystallite sizes of the α -Al₂O₃ prepared by sol–gel and solvothermal method were 31 and 69.5 nm, respectively while the crystallite sizes of ZnAl₂O₄ formed in the Zn-modified Al₂O₃ prepared by sol–gel and solvothermal method were 28 and 14.9 nm, respectively. The surface areas of the catalysts prepared by sol–gel were ranged from 1.6 to 2.3 m²/g while those prepared by solvothermal were ranged from 10.5 to 14.9 m²/g. The surface areas were quite low probably due to high agglomeration of these nanocrystalline particles during calcination at high temperature. The nitrogen adsorption–desorption isotherms and the pore size distribution plots are shown in Figs. 2 and 3, respectively. Based on the nitrogen adsorption–desorption isotherms at 77 K, all the samples exhibited Type IV adsorption isotherms according to Brunauer Deming, Deming and Teller (BDDT) classification [17]. The sol–gel Al₂O₃, however, pos-

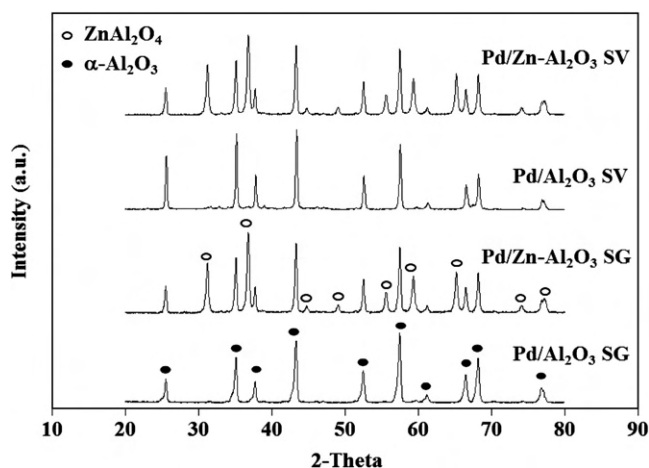
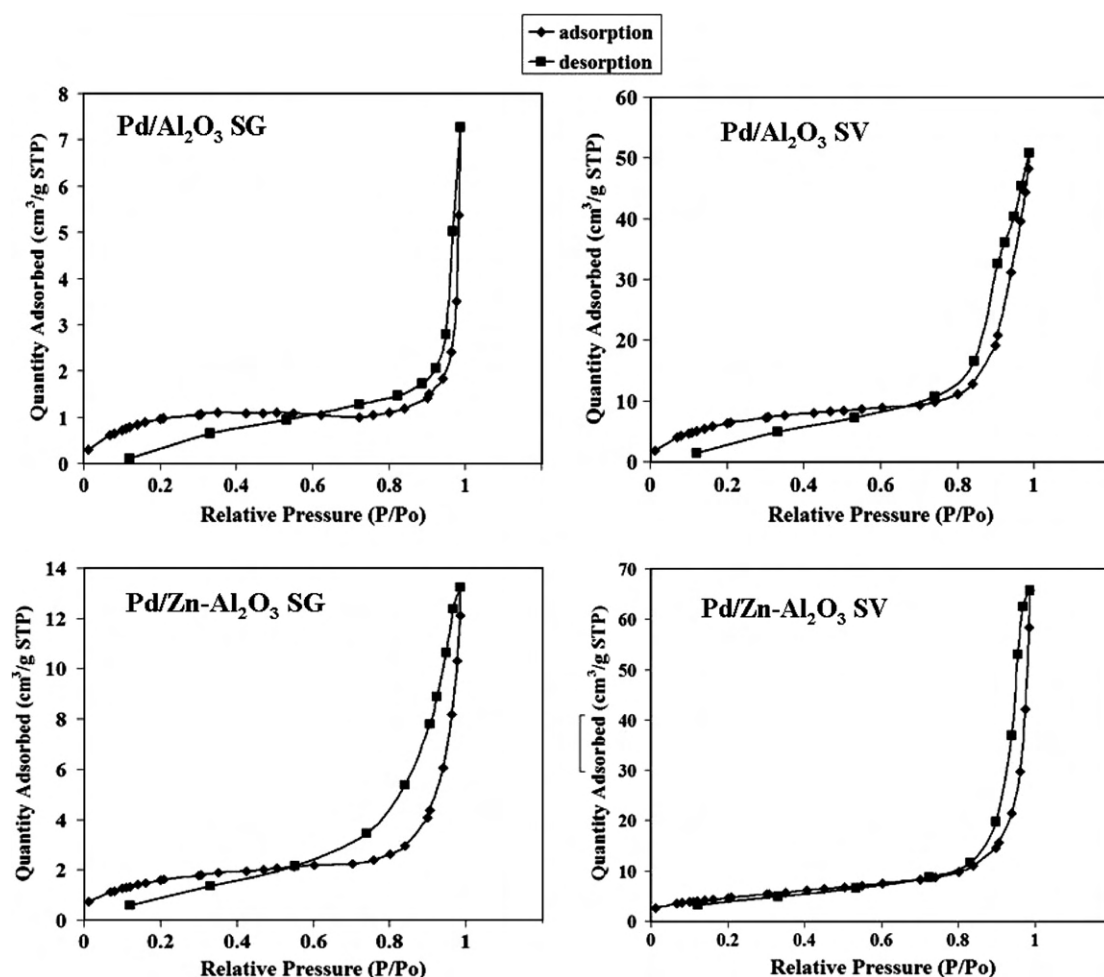


Fig. 1. XRD patterns of the Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ supports prepared by sol–gel (SG) and solvothermal (SV) methods.

Table 1Characteristics of the various Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ catalysts

Sample	Crystallite size (nm)		BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)	Pd active sites ($\times 10^{-17}$ molecule CO/g cat.)	Pd dispersion (%)	d_p Pd ⁰ (nm)
	α -Al ₂ O ₃	ZnAl ₂ O ₄						
Pd/Al ₂ O ₃ SG	31.0	n.d. ^a	1.6	0.011	20.4	11.3	8.8	13
Pd/Zn-Al ₂ O ₃ SG	40.4	28	1.9	0.020	11.8	4.9	3.9	29
Pd/Al ₂ O ₃ SV	69.5	n.d.	14.9	0.075	13.6	32.9	20.8	5
Pd/Zn-Al ₂ O ₃ SV	32.8	14.9	10.7	0.100	22.4	22.8	16.6	7

^a n.d. = not determined.**Fig. 2.** N₂ adsorption-desorption isotherms of the Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ supports prepared by sol-gel (SG) and solvothermal (SV) methods.

essed much less pore volume than the samples prepared by the solvothermal method. Incorporation of Pd particles by impregnation did not alter the textural properties of the supports as shown by similar pore size distributions in Fig. 3.

Fig. 4 shows the TEM micrographs with SAED patterns of Pd/ α -Al₂O₃ and Pd/Zn-modified α -Al₂O₃ prepared by sol-gel and solvothermal methods. It can be seen that the sol-gel made catalysts consisted of agglomerated particles with primarily irregular shape structure (average particle size around 0.5–1 μ m) whereas for those prepared by solvothermal method, agglomeration of finger-like particles were observed. The finger-like α -Al₂O₃ particles are normally obtained by calcination of the solvothermal-made α -Al₂O₃ powders at high temperature [18,19]. For Pd/Zn-modified α -Al₂O₃, the corresponding selected area diffraction patterns shows rings match d-spacing for the ZnAl₂O₄ confirmed the structure of

ZnAl₂O₄ [20]. The large particles observed maybe the secondary particles formed by agglomeration of the primary nano-particles due to heat treatment during calcinations step. Based on TEM analysis, palladium particles/clusters with average particle size ca. 5–10 nm were found to be deposited on both of the alumina supports.

The metal active sites, the Pd dispersion, and the average Pd metal particle sizes from CO chemisorption experiment are also summarized in Table 1. The technique is based on the assumption that only one CO molecule adsorbed on one metal active site [21] and it is known that CO did not chemisorb on Al₂O₃ support [22–24]. Without Zn addition on the Al₂O₃ supports, Pd/Al₂O₃ sol-gel and Pd/Al₂O₃ solvothermal possessed the amounts of Pd active sites 11.3×10^{17} and 32.8×10^{17} sites/g cat., respectively. The Pd active sites significantly decreased when the catalysts were supported on Zn-modified α -Al₂O₃. The Pd/Zn-Al₂O₃ SG and Pd/Zn-

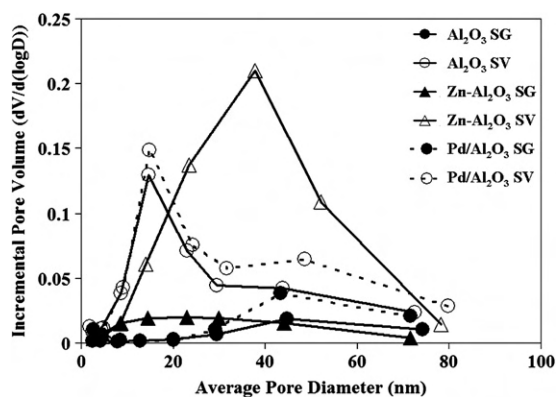


Fig. 3. Pore size distributions of the α - Al_2O_3 , Zn-modified α - Al_2O_3 , and Pd/ α - Al_2O_3 .

Al_2O_3 SV possessed the amounts of Pd active sites 4.86×10^{17} and 22.7×10^{17} sites/g cat., respectively. Thus, the catalysts on Zn-modified Al_2O_3 had lower Pd dispersion and larger Pd particle size (as determined from CO chemisorption experiments). Comparing the samples prepared by different techniques, the catalysts prepared by sol-gel method showed lower amount of Pd active sites and Pd dispersion than the catalysts prepared by solvothermal

method due probably to more agglomeration of the α - Al_2O_3 supports as noticed from TEM measurements.

NH_3 temperature program desorption was a commonly used technique for the titration of surface acid sites [25]. The strength of an acid site could be related to the corresponding desorption temperature, while the total amount of ammonia desorption after saturation coverage permits quantification of the number of acid sites at the surface. The temperature-programmed desorption profiles for the nanocrystalline α - Al_2O_3 and Zn-modified α - Al_2O_3 supports are shown in Fig. 5. It was found that the desorption peak areas of the α - Al_2O_3 samples prepared by sol-gel method were lower than that prepared by solvothermal method. Moreover, regardless of the preparation method used, the desorption peak areas of Zn-modified α - Al_2O_3 decreased. It is suggested that formation of ZnAl_2O_4 species resulted in a decrease of surface acidity of α - Al_2O_3 [26].

The catalytic properties of Pd/ α - Al_2O_3 and Pd/Zn-modified α - Al_2O_3 catalysts were evaluated in the selective hydrogenation of acetylene using a fixed bed flow reactor with a GHSV of $16,901 \text{ h}^{-1}$. Study of temperature dependence of Pd/ α - Al_2O_3 and Pd/Zn-modified α - Al_2O_3 catalysts on acetylene conversion and selectivity toward ethylene in the temperature range between 40 and 100°C are shown in Fig. 6. For comparison purposes, selective acetylene hydrogenation using Pd catalysts supported commercial

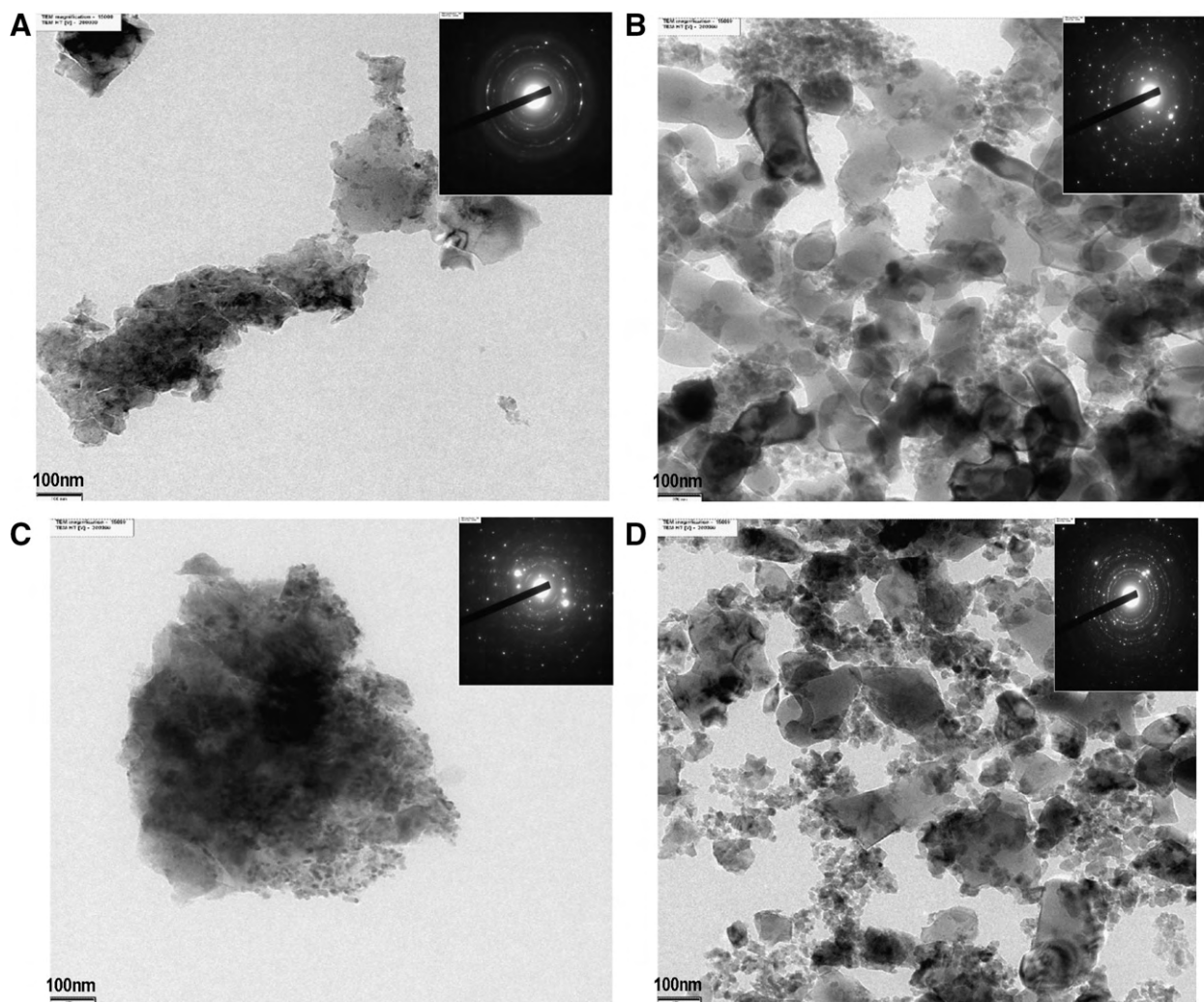


Fig. 4. TEM micrographs of Pd/ α - Al_2O_3 and Pd/Zn-modified α - Al_2O_3 catalysts prepared by sol-gel (SG) and solvothermal (SV) methods with SAED pattern: (A) Pd/ α - Al_2O_3 SG (B) Pd/ α - Al_2O_3 SV (C) Pd/Zn- Al_2O_3 SG (D) Pd/Zn- Al_2O_3 SV.

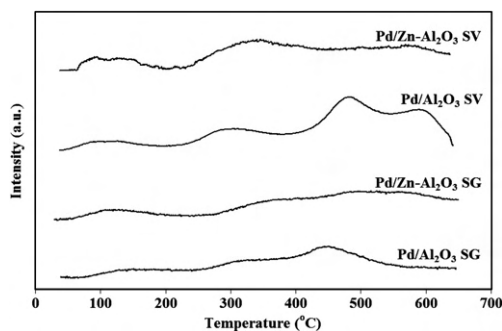


Fig. 5. NH_3 temperature program desorption profiles for the $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ and Pd/Zn -modified $\alpha\text{-Al}_2\text{O}_3$ supports prepared by sol-gel (SG) and solvothermal (SV) methods.

$\alpha\text{-Al}_2\text{O}_3$ was also carried out. In all cases, acetylene conversion increased with increasing temperature while ethylene selectivity decreases due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction. Acetylene conversion as well as ethylene selectivity was found to be in the order: Pd/Zn -modified $\alpha\text{-Al}_2\text{O}_3$ -sol-gel > Pd/Zn -modified $\alpha\text{-Al}_2\text{O}_3$ -solvothermal > $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ -sol-gel \approx $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ -solvothermal \gg $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ -commercial. It was clearly seen that the use of nanocrystalline $\alpha\text{-Al}_2\text{O}_3$ prepared by sol-gel or solvothermal method resulted in much better catalyst performance compared to the commercial one. It can be noticed that $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ -SV had the largest Pd active

sites; however, it exhibited the lowest activity. This can probably be explained by the dependent of acetylene hydrogenation activity on Pd particle size. Many researchers have shown that the specific activity of Pd decreased by an order of magnitude when the size of palladium particles were very small (1–5 nm) [27–29]. Modification of $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ catalysts with Zn, however, resulted in significantly improvement of both acetylene conversion and ethylene selectivity. Comparing the samples prepared by the different techniques, the catalysts prepared by sol-gel method showed better catalytic properties than the catalysts prepared by solvothermal method.

After reaction, the amounts of carbonaceous deposits on the catalyst samples were measured by thermal gravimetric analysis and the results are shown in Fig. 7. A small weight loss (<1%) observed in the TGA profiles (Fig. 5A) below 200 °C was probably due to the removal of physisorbed water and/or chemisorbed hydroxyl groups. The weight loss at higher temperature was due to oxidation of the carbonaceous deposited on the surface of used catalysts [30]. As shown by the exothermic peaks in Fig. 5B, the type of coke species occurred during reaction was probably “soft coke” since it could be removed from the used catalysts by oxidation at a relative lower temperature (~ 350 °C) as suggested by Xiangjing et al. [31]. Based on TGA results, the amount of coke deposits on the catalysts prepared by sol-gel method were lower than those prepared by solvothermal method while Pd/Zn -modified $\alpha\text{-Al}_2\text{O}_3$ prepared by sol-gel method showed the lowest value (2.33 wt.%) and $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ prepared by solvothermal method showed the highest value (6.39 wt.%). For $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ -commercial, the amount

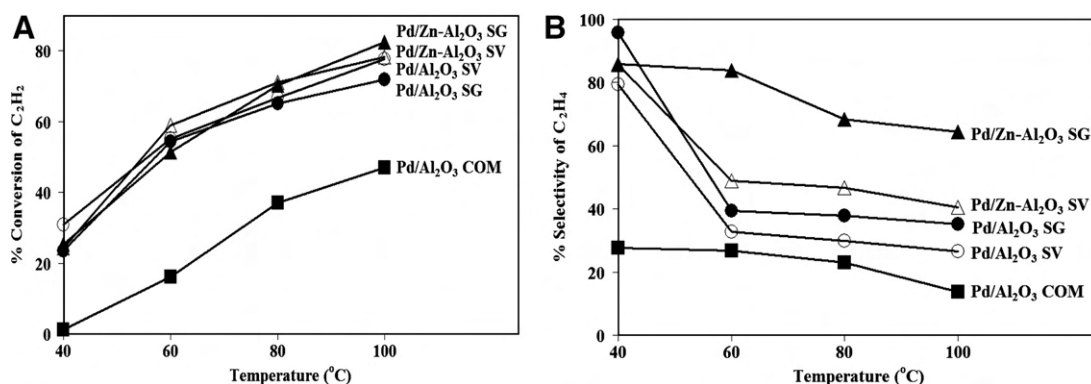


Fig. 6. Temperature dependence of the catalytic performance of $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ and Pd/Zn -modified $\alpha\text{-Al}_2\text{O}_3$ catalysts; (A) in terms of % conversion of C_2H_2 (B) in terms of % selectivity of C_2H_4 .

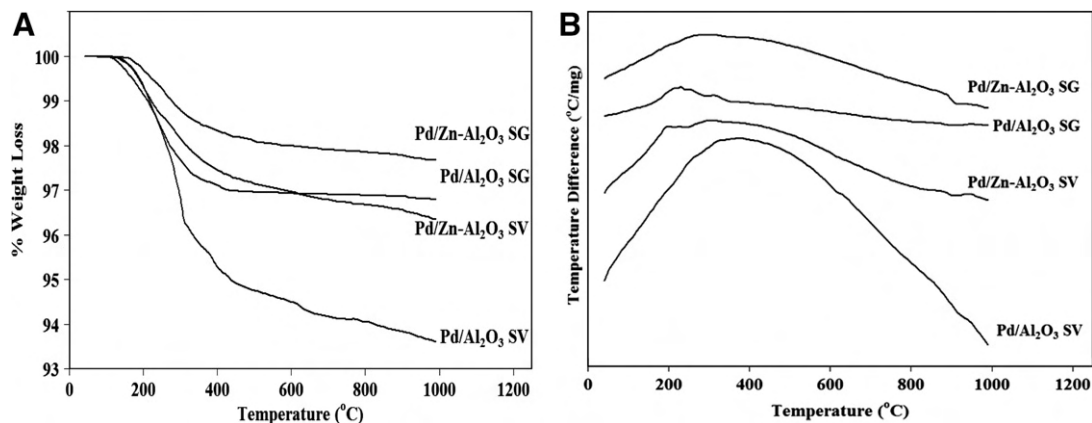


Fig. 7. Thermal gravimetric and differential temperature analysis (TG/DTA) of $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ and Pd/Zn -modified $\alpha\text{-Al}_2\text{O}_3$ catalysts after reaction; (A) in terms of temperature (°C) and weight loss (%), (B) in terms of temperature (°C) and temperature difference (°C/mg).

of coke deposits on the catalysts was 3.53 wt.%. The results were in good agreement with acidity of the Al_2O_3 supports measured from NH_3 TPD technique. Based on the mechanisms in the literature [32,33], acetylene hydrogenation was suggested to take place on the active sites on Pd surface while most of the carbonaceous deposits were found to be accumulated on the support. The carbon deposits acted as a hydrogen bridge for the hydrogen spillover from Pd to the support facilitating ethylene hydrogenation to ethane. The low concentration of acid sites on the Al_2O_3 surface considerably reduced coke deposition thus ethylene selectivity was improved.

4. Conclusions

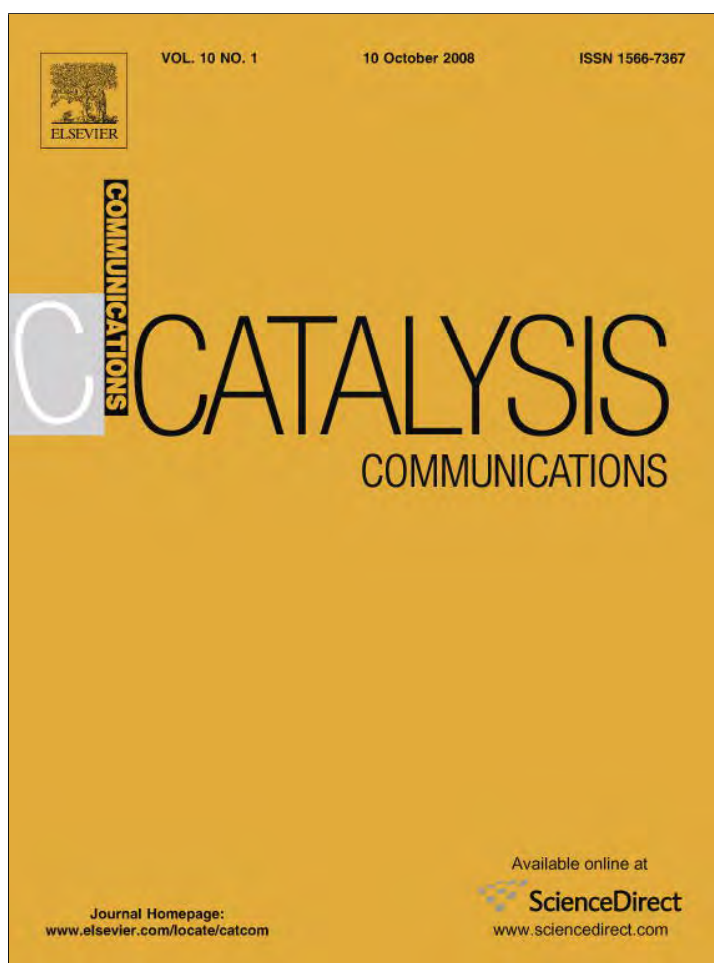
Modification of $\alpha\text{-Al}_2\text{O}_3$ supports by Zn drastically decreased surface acidity of Al_2O_3 due to formation of ZnAl_2O_4 species. When used as the supports for Pd catalysts in selective acetylene hydrogenation, the catalysts exhibited lower Pd dispersion and larger Pd particle size (as determined from CO chemisorption experiments) compared to those on the unmodified ones. The Pd/Zn-modified $\alpha\text{-Al}_2\text{O}_3$ catalysts showed higher acetylene conversion and ethylene selectivity and less amount of carbonaceous deposits than Pd on the unmodified and commercial $\alpha\text{-Al}_2\text{O}_3$. Comparing the samples prepared by the different techniques, the catalysts prepared by sol–gel method showed better catalytic properties than those prepared by solvothermal method due to larger Pd particle size and lower amount of acid sites obtained.

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Improvement of Pd/Al₂O₃ catalyst performance in selective acetylene hydrogenation using mixed phases Al₂O₃ support

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ABSTRACT

The catalytic performances of Pd catalysts supported on γ -Al₂O₃, α -Al₂O₃, and mixed phases Al₂O₃ were investigated in the selective hydrogenation of acetylene in ethylene feed stream. It was found that the use of mixed phases Al₂O₃ with approximately 64% of α -phase resulted in significant improvements in both acetylene conversion and ethylene selectivity. The presence of small amount of transition phase in the alumina supports brought about higher BET surface area and Pd dispersion as well as improvement of reduction ability of the Pd/Al₂O₃ catalysts. On the other hand, significant amount of α -Al₂O₃ is necessary for high ethylene selectivity due to the lower amount of ethylene adsorbed.

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1. Introduction

The effective removal of trace amount of acetylene in ethylene feedstock via selective hydrogenation using supported Pd-based catalysts is of particular challenge in the production of polyethylene since acetylene acts as a poison to the polymerization catalysts. The Pd/ α -Al₂O₃ catalyst commonly used for selective acetylene hydrogenation is typically macroporous with a relatively small surface area of approximately 0.1–2 m²/g. In general, α -Al₂O₃ provides low dispersion of active metal than γ -Al₂O₃ due to its lower surface area; however, it is desirable in this reaction because Pd/ α -Al₂O₃ catalyst possesses less active sites for direct ethane formation than Pd/ γ -Al₂O₃ catalyst [1]. Moreover, α -Al₂O₃ is less acidic than γ -Al₂O₃ thus less oligomer/green oil was formed during acetylene hydrogenation reaction. However, the catalysts are suffered from runaway ethylene hydrogenation especially at high levels of acetylene conversion [2]. Several attempts have been made to improve the selectivity of Pd/Al₂O₃ catalysts and also reduce green oil formation in selective hydrogenation of acetylene such as promotion with a second component such as Ag [3], SiO₂ [4], TiO₂ [5] and pre-treatment of catalysts using oxygen-containing compounds [6–8]. However, development of new efficient catalysts for selective hydrogenation of acetylene has still received

much attention and has been reported continually including Pd on nano-sized TiO₂ [9,10], Pd on Ni modified Al₂O₃ [11], and zeolite-supported Pd–Ag catalysts [12,13].

In general, the more acidic, high surface area alumina hydrates are produced at relatively low temperatures by precipitation from either acidic or basic solutions and are transformed to ‘transition’ β -, γ -, η -, χ -, κ -, δ -, θ -, and α -Al₂O₃ by dehydration and treatment at high temperatures [14]. Differences in crystalline phases may result in changes in physical and chemical properties of Al₂O₃ supports and could play an important role on the catalytic performance of Al₂O₃ supported catalysts. For example, Chary et al. [15] reported that dispersion of vanadium oxide on Al₂O₃ supports as well as their catalytic activities in partial oxidation decreased with increasing calcination temperature due to the transformation of γ -Al₂O₃ into θ -, δ -, and α -Al₂O₃. Moya et al. [16] studied silver nanoparticles supported on α -, η -, and δ -Al₂O₃ prepared by colloidal processing route. It was found that silver particle sizes varied between 1 and 100 nm depending on the Al₂O₃ phases.

In this study, the effect of mixed phases Al₂O₃ (i.e. γ -, θ -, and α -Al₂O₃) on the properties of Pd/Al₂O₃ catalysts was investigated in the gas-phase selective hydrogenation of acetylene in ethylene feed stream. The weights (%) of α -phase were 0, 14, 47, 64, and 100 depending on the calcination conditions of the starting γ -Al₂O₃. The catalysts were characterized by means of X-ray diffraction (XRD), N₂ physisorption, CO pulse chemisorption, H₂-temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and temperature programmed desorption of ethylene (C₂H₄-TPD).

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2. Experimental

2.1. Catalysts preparation

γ - Al_2O_3 used in this study was the commercial available alumina JRC-ALO-2 (JRC Co., Ltd. Japan). The mixed phases with various phase compositions were prepared by calcination of the γ - Al_2O_3 at 1100 °C for 120, 200, or 240 min. The α - Al_2O_3 was obtained by calcination of the γ - Al_2O_3 at 1175 °C for 120 min. In this paper, the alumina samples consisting of 0, 14, 47, 64, and 100% α -phase are referred to as Al- α 0, Al- α 14, Al- α 47, Al- α 64, and Al- α 100, respectively. The percentage of alpha phase was calculated using a calibration curve from XRD results of the physically mixed γ -, and α - Al_2O_3 (not shown here).

The Pd/ Al_2O_3 catalysts with weight (%) of Pd approximately 1% were prepared by the incipient wetness impregnation technique using an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (Wako, Japan) as the palladium precursor. The catalysts were subsequently dried at 110 °C for 12 h and calcined in air at 550 °C for 2 h.

2.2. Catalyst characterization

The X-ray diffraction (XRD) pattern of the Al_2O_3 supports and Pd/ Al_2O_3 catalysts were carried out using an X-ray diffractometer, SIEMENS XRD D5000, with Cu K α radiation with a Ni filter. The BET surface areas of the Al_2O_3 supports were measured by N_2 physisorption using a Micromeritics ASAP 2000 automated system. The samples were degassed at 200 °C for 1 h prior to N_2 physisorption. The amounts of CO chemisorbed on the Pd/ Al_2O_3 catalysts were measured at room temperature by using a Micromeritics Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. Prior the measurement, 30 ml/min of He gas was introduced into the sample cell in order to remove the remaining air. The system was switched to 50 ml/min of hydrogen and heated to 150 °C with a heating rate of 10 °C/min. The temperature was kept constant for 2 h and then cooled down to the room temperature. Temperature program experiments were carried out in a Micromeritics Chemisorb 2750 automated system. The temperature ramping was controlled by temperature controller, Furnace Power 48 VAC 8A MAX. The XPS analysis was performed using an AMICUS photoelectron spectrom-

eter equipped with an Mg K α X-ray as primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV. The distribution of palladium on catalyst supports were observed using JEOL Model JEM-2010 transmission electron microscope operated at 200 keV. A mixture of 10% H_2 in Ar with a flow rate of 15 cm^3/min was used in TPR experiment. Prior the experiment, the sample was treated in N_2 flow at 200 °C for 1 h in order to remove any adsorbed gas. The TPR was performed with a constant heating rate of 10 °C/min from 35 to 200 °C. For ethylene-TPD experiments, the samples were pre-reduced at 150 °C in H_2 for 2 h (flow rate 50 cm^3/min) and cooled down to room temperature. Then adsorption of ethylene was performed at room temperature for 3 h. The temperature programmed desorption was performed with a constant heating rate of 10 °C/min from 35 to 800 °C. The amount of desorbed ethylene was measured by analyzing the effluent gas with a thermal conductivity detector.

2.3. Reaction study

The catalyst performances in selective hydrogenation of acetylene were evaluated using a 10 mm (id) pyrex reactor. Prior to the start of each experimental run, the catalyst was reduced *in situ* with hydrogen by heating from room temperature to 150 °C at a heating rate of 10 °C/min. Then the reactor was purged with argon and cooled down to the reaction temperature 40 °C. The reaction was carried out using a feed composition of 1.5% C_2H_2 , 1.7% H_2 , and balanced C_2H_4 with a vary GHSV of 52,580, 32,577, 22,534 and 12,385 h^{-1} . The products and feeds were analyzed by

Table 1
The physical properties of alumina with various phase compositions

Samples	α -Phase (%)	BET surface area (m^2/g)	Crystallite size (nm) ^a		Pore volume ^b (cm^3/g)	Average pore diameter ^b (Å)
			γ -Phase	α -Phase		
Al- α 100	100	12.3	n.d.	44.5	0.03	90.1
Al- α 64	64	36.1	28.3	45.8	0.14	129.6
Al- α 47	47	45.4	17.8	48.9	0.20	151.9
Al- α 14	14	67.3	11.8	46.0	0.30	143.8
Al- α 0	0	244.1	3.7	n.d.	0.66	78.9

n.d. = Not determined.

^a Calculated from XRD results.

^b Based on BJH method.

Table 2
Physicochemical properties of Pd supported on alumina with various phase compositions

Samples	Pd active sites ^a ($\times 10^{-18}$ CO molecule/g-cat)	% Pd dispersion ^b	d_p^c (Pd ⁰) (nm)	Pd 3d _{5/2} ^d		Atomic concentration ^d Pd/Al
				BE (eV)	FWHM	
Pd/Al- α 100	7.4	12.5	8.9	336.9	1.8	0.034
Pd/Al- α 64	11.0	18.5	6.1	336.9	2.0	0.027
Pd/Al- α 47	25.4	42.9	2.6	336.4	2.4	0.020
Pd/Al- α 14	31.7	53.5	2.1	336.4	2.3	0.011
Pd/Al- α 0	35.1	59.2	1.9	336.4	2.2	0.001

V_{ads} , volume adsorbed; V_g , molar volume of gas at STP; S_f , stoichiometry factor, CO on Pd; MW, molecular weight of the metal; %M, %metal loading.

^a Pd active sites = $(V_{\text{ads}}/V_g) \times (6.02 \times 10^{23})$. Error of measurement = $\pm 5\%$.

^b % Pd dispersion = $[\text{Pd active sites} \times S_f \times (\text{M.W.}/\% \text{ M}) \times 100\% \times 100\%]/(6.02 \times 10^{23})$.

^c Based on $d_p = 1.12/D$ (nm), where D = % Pd dispersion [25].

^d Based on XPS results.

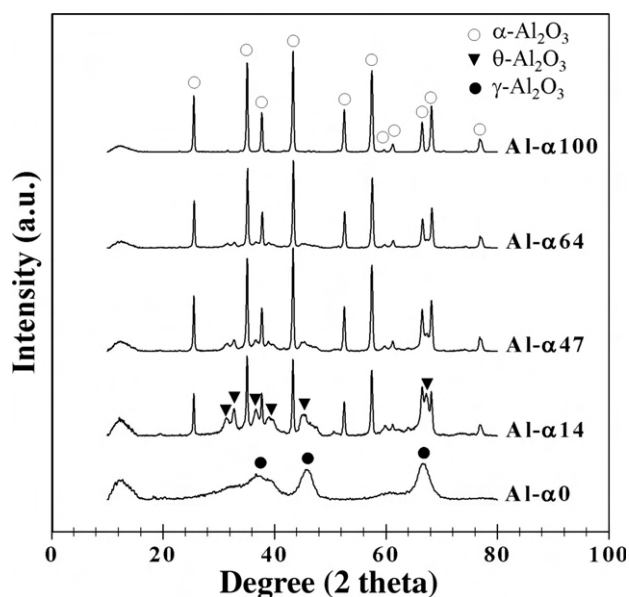


Fig. 1. The XRD patterns of the Al_2O_3 supports containing various % of α -phase.

a two gas chromatographs equipped with a FID detector (SHIMADZU FID GC 9A, carbosieve column S-2) and TCD detector (SHIMADZU TCD GC 8A, molecular sieve-5A).

3. Results and discussion

The mixed phases Al_2O_3 supports used for preparation of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts in this study were obtained by varying the calcination conditions of the $\gamma\text{-Al}_2\text{O}_3$ (calcination temperature 1100–1175 °C and holding time 2–4 h). The XRD patterns of Al_2O_3 are shown in Fig. 1. The weight (%) of α -phase in these samples were calculated to be 0%, 14%, 47%, 64% and 100% using a calibration from XRD results of the physically mixed γ - and $\alpha\text{-Al}_2\text{O}_3$ (not shown here) and were designated herein as Al- α 0, Al- α 14, Al- α 47, Al- α 64, and Al- α 100, respectively.

Table 1 summarizes physical properties of the various Al_2O_3 supports. The crystallite size of transition phase was increased from 3.7 to 28.3 nm as the weight (%) of α -phase content increased

from 0% to 64%, while the crystal size of α -phase remained constant at around 45 nm. The specific surface area and total pore volume calculated from BJH method decreased from 244 to 12 m^2/g and 0.66 to 0.03 cm^3/g with increasing amount of α -phase alumina. A drastically decrease in BET surface area and total pore volume of alumina during phase transformation can be explained by the rapidly increase of alumina crystal size. It is generally known that calcination of $\gamma\text{-Al}_2\text{O}_3$ at high temperature results in phase transformation from γ - to θ - and then $\alpha\text{-Al}_2\text{O}_3$.

The XRD characteristic peaks of all the $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts were not different from the Al_2O_3 supports after Pd loading. No XRD peaks for PdO or Pd^0 metal were observed due probably to the low loading of palladium (results not shown). The CO chemisorption results such as the number of active Pd atoms, Pd dispersion (%), and average Pd metal particle size are summarized in Table 2. Palladium dispersion was estimated from the amount of CO chemisorbed assuming a stoichiometry of $\text{CO}/\text{Pd} = 1$ [17]. The number of Pd active sites decreased from 35.1 to 7.4×10^{18} sites/

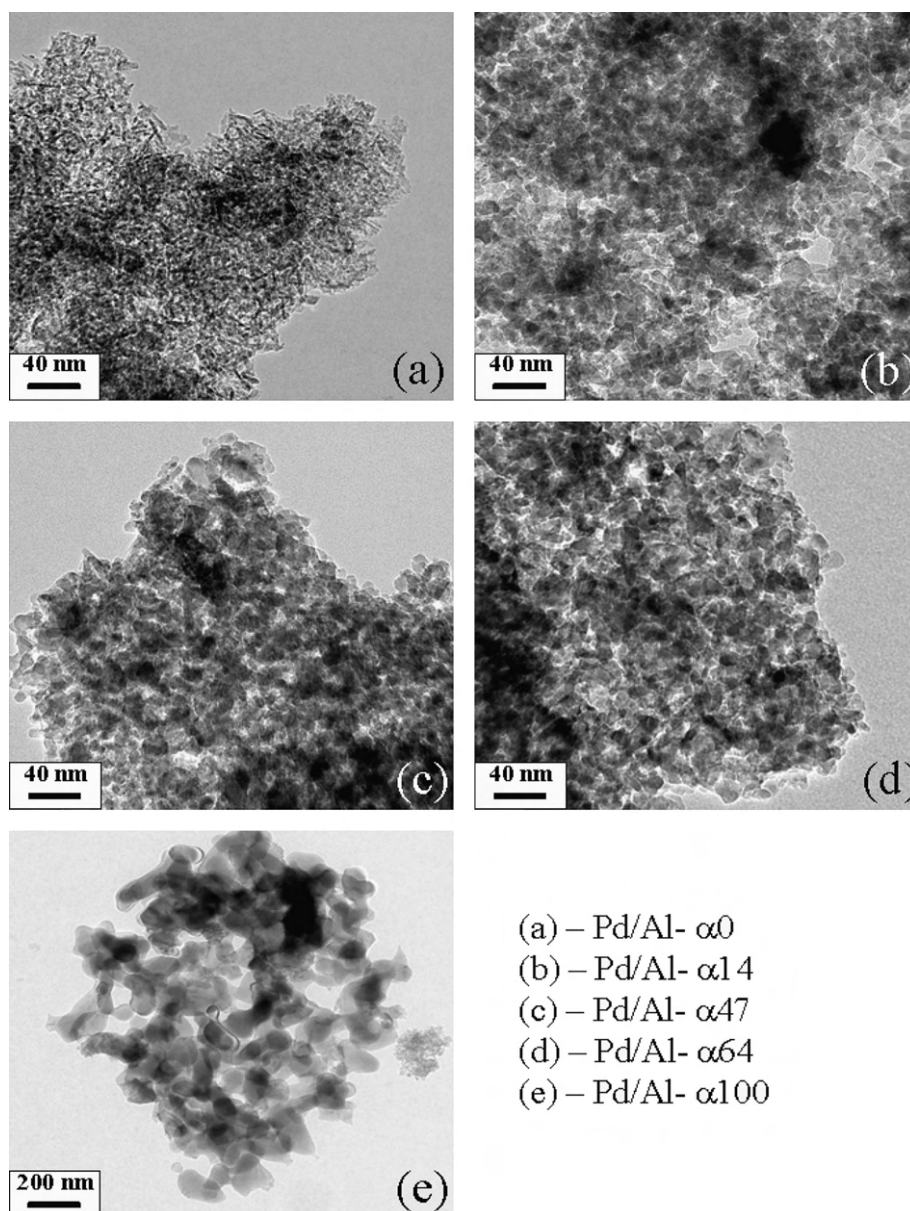


Fig. 2. Transmission electron micrographs of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts.

g-catalyst corresponding to a decrease in Pd dispersion (%) from 59.5 to 12.5 and an increase in Pd metal particle size from 1.9 to 8.9 nm as the weight (%) of α -phase contents increased from 0% to 100%.

In order to verify the Pd particle size, TEM micrographs have been acquired and are shown in Fig. 2. The Pd supported on pure γ - Al_2O_3 consisted of particles with primarily spherical shape with some needlelike structure. The particle shape appeared more uniformly spheroidal for those supported on mixed phases Al_2O_3 . Large fingerlike shape particles were observed for the catalysts containing 100% α -phase Al_2O_3 . Increasing α -phase content of the alumina supports from 0 to 100% resulted in an increase of Pd cluster/particle size from about 2 to 10 nm.

XPS is used to determine the surface compositions of the catalysts and the interaction between Pd and the Al_2O_3 supports. The deconvoluted XPS photoelectron spectra for the Pd 3d core level region of all the catalysts are shown in Fig. 3. From the figure, the Pd doublet was clearly evident. A small shoulder at the binding energy around 335.1–335.8 eV was present in every sample and was

attributed to metallic Pd^0 [18]. Such results indicated that partial reduction occurred during analysis. PdO species was observed at the binding energies in the range of 336.9–336.4 eV which was consistent to the values reported in the literature [19,20]. The percentages of atomic concentration, the binding energy, and FWHM of Pd 3d are also given in Table 2. The atomic concentration ratios for Pd/Al decreased with the decrease in α -phase Al_2O_3 contents. The results were consistent with the CO chemisorption results that larger Pd particle sizes were obtained on α - Al_2O_3 . The FWHM values larger than two for Pd $3d_{5/2}$ may be due to some differential charging that contributed to the widening of the palladium peaks [21,22].

Reduction behavior and reducibility of the catalysts were investigated by means of H_2 -temperature programmed reduction and the results are shown in Fig. 4. All the Pd/ Al_2O_3 catalysts exhibited TPR profiles with one main reduction peak which can be assigned to the reduction of PdO to Pd^0 metal. This peak remained constant at around 55 °C for those with the weight (%) of α -phase contents between 0% and 64%. The reduction peak was slightly shifted to

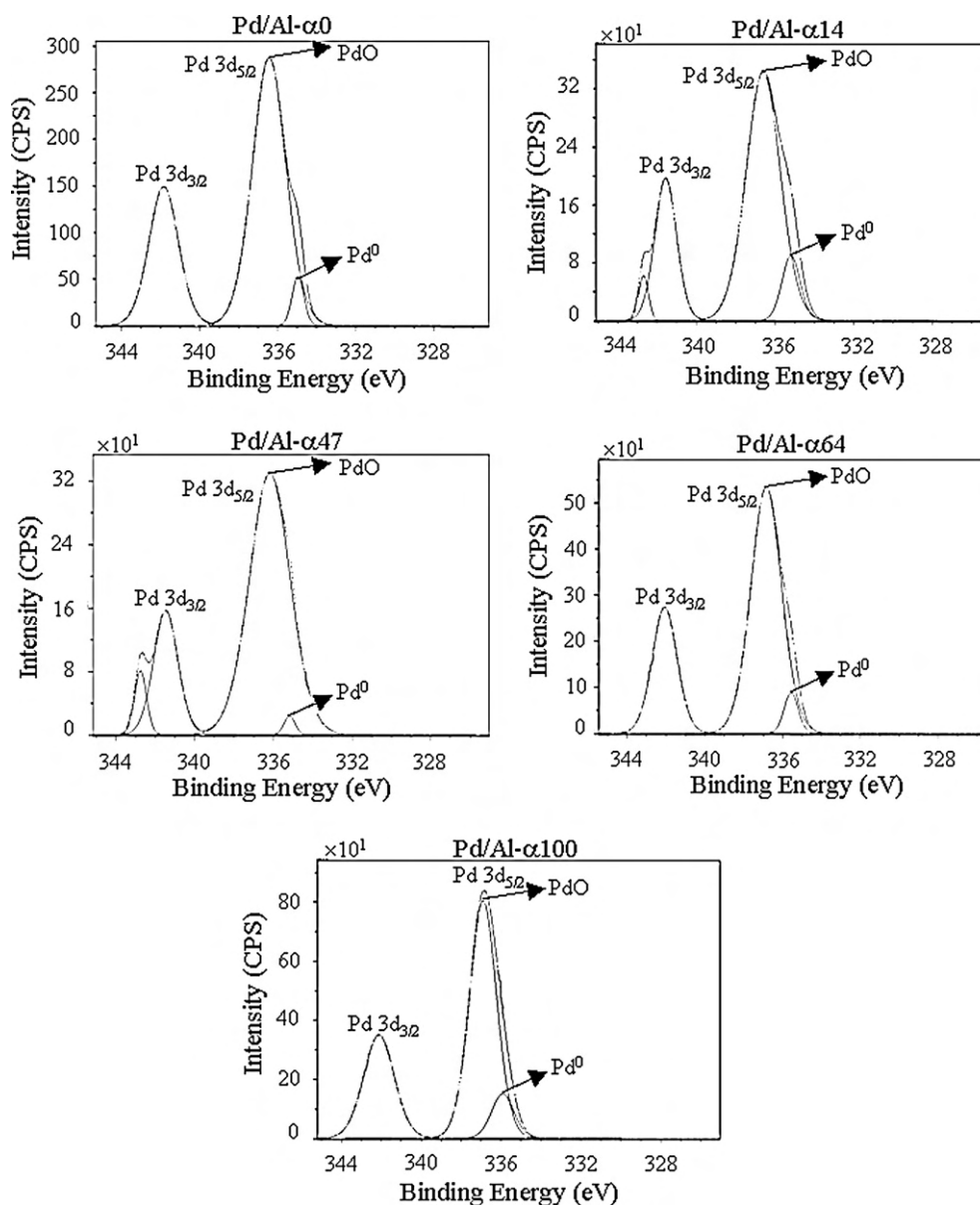


Fig. 3. The XPS deconvoluted spectra of the Pd/ Al_2O_3 catalysts.

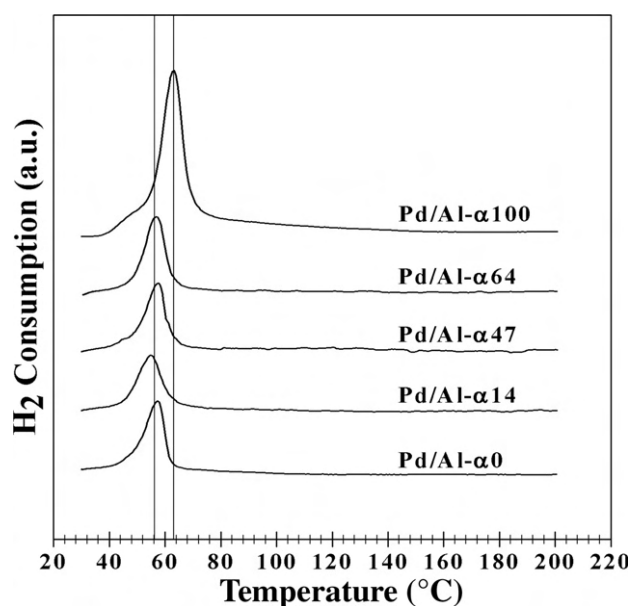


Fig. 4. TPR profiles of the Pd/Al₂O₃ catalysts.

65 °C for the Pd/Al-α100 catalyst (100% α-phase). It is suggested that the existence of transition phase Al₂O₃ (either γ- or θ-Al₂O₃) in the Al₂O₃ supports facilitated reduction at low temperature. However, the hydrogen consumptions during the transformation of PdO to metallic Pd as determined from the areas of the reduction peak for all the catalysts were essentially the same.

Ethylene-temperature programmed desorption (C₂H₄-TPD) was performed in order to obtain an information about ethylene adsorption behavior on the catalyst surfaces. The C₂H₄-TPD experiments were carried out at 35–800 °C after the samples were reduced in H₂ at 150 °C and purged with He at the same adsorption temperature. The temperature programmed study profiles of the catalysts are shown in Fig. 5. Two main desorption peaks at ca. 80–105 °C and 275–300 °C were observed for all the catalyst samples. As suggested by Moon et al. [23], the lower temperature desorption peak was assigned to π-bonded ethylene spe-

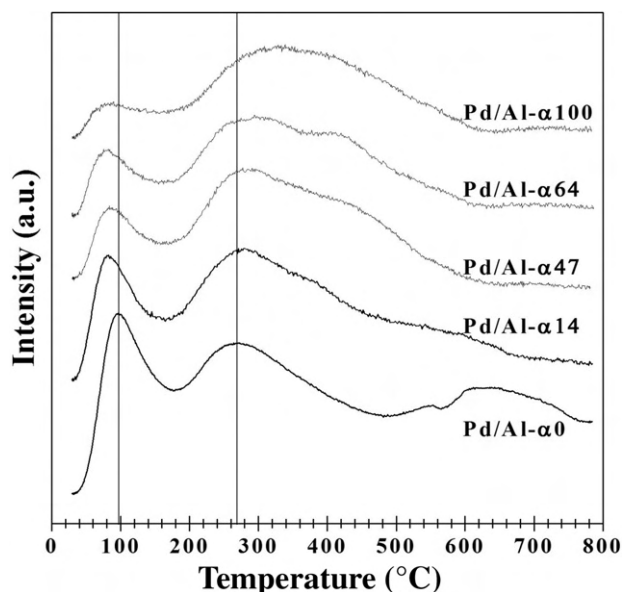


Fig. 5. Ethylene TPD results of the Pd/Al₂O₃ catalysts.

cies while the higher temperature was assigned to di-σ-bonded ethylene. The latter species were suggested to be the species that recombined with surface hydrocarbon and produced ethane. In some cases, the third peak at temperature range around 450–650 °C was observed. It was suggested to be due to decomposition of C₂ hydrocarbons adsorbed on Pd surface [24]. In the present study, the intensities of the TCD signals during ethylene temperature programmed desorption was significantly decreased when the content of α-phase in the Al₂O₃ supports increased from 0 to 100%. In other words, the amount of ethylene adsorbed was much lower when the Al₂O₃ supports contained significant amounts of α-Al₂O₃.

The catalytic performances of Pd/Al₂O₃ catalysts containing α-Al₂O₃, γ-Al₂O₃, or mixed phases alumina were evaluated in the selective hydrogenation of acetylene at 40 °C under various feed flow rates (GHSV 52,580, 32,577, 22,534, and 12,385 h⁻¹). Acetylene conversion is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene gain is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated. The plots of acetylene conversion and ethylene selectivity versus GHSV are shown in Figs. 6 and 7, respectively. In general, acetylene conversion decreased with increasing GHSV while ethylene gain increased. Since ethylene is produced as an intermediate in

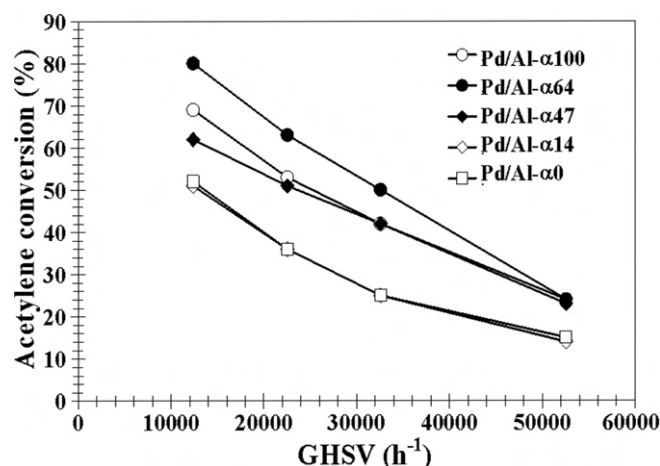


Fig. 6. Catalyst performances in selective hydrogenation of acetylene in terms of GHSV values and acetylene conversion (%).

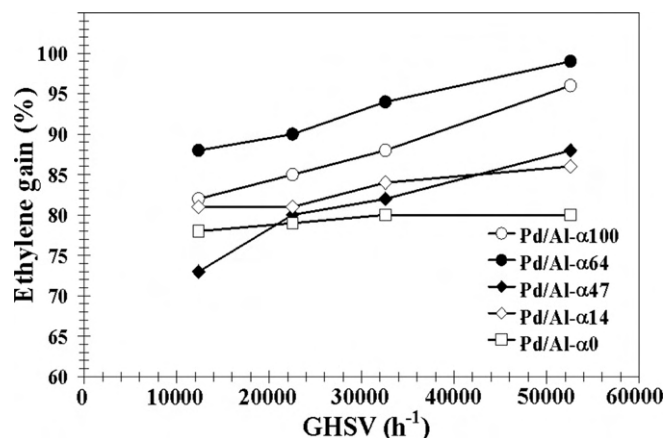


Fig. 7. Catalyst performances in selective hydrogenation of acetylene in terms of GHSV values and ethylene gain (%).

acetylene hydrogenation, which is a typical consecutive reaction, the ethylene selectivity decreases with acetylene conversion [5]. The performance of Pd/Al₂O₃ catalysts was improved in the order of Pd/Al- α 64 > Pd/Al- α 100 > Pd/Al- α 47 > Pd/Al- α 14 > Pd/Al- α 0. It is clearly shown that the Pd catalyst supported on mixed phase Al₂O₃ that contained 64% of α -phase (Pd/Al- α 64) exhibited the best catalytic performance among the five catalysts studied.

Based on the characterization results, the presence of the transition phase in α -Al₂O₃ supports increased the specific surface area, total pore volume, Pd active sites and the dispersion of Pd on Al₂O₃ supports and facilitated the reduction of PdO at lower temperature, which promoted acetylene conversion. However, the TPD profiles suggest that the amount of ethylene adsorbed on the catalyst surface decreased with increasing α -phase content. The feature is important for the improvement of ethylene gain especially at high acetylene conversion. The results in this study revealed that the beneficial properties of both α -Al₂O₃ and transition alumina can be combined to give the best catalytic performance of Pd/Al₂O₃ catalyst in selective acetylene hydrogenation. Among the five catalysts studied, the optimum amount of α -phase content was found to be at 64 wt%.

4. Conclusions

The catalytic performances of Pd/Al₂O₃ catalysts in selective hydrogenation of acetylene were significantly improved when the Al₂O₃ support consisted of mixed transition- Al₂O₃ and α -Al₂O₃ with ca. 64% of α -Al₂O₃. The presence of transition phase Al₂O₃ in α -Al₂O₃ resulted in combined properties of the transition Al₂O₃ such as higher BET surface area, higher Pd dispersion, improved reduction ability and the beneficial properties of α -Al₂O₃ for selective acetylene hydrogenation such as lower amount of ethylene adsorbed. Among the five crystalline phase compositions of alumina used in this study, the one containing 64% α -Al₂O₃ was found to be the best (optimum) composition to prepare Pd/Al₂O₃ catalysts with high acetylene conversion and high ethylene selectivity.

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Effect of Support Crystallite Size on Catalytic Activity and Deactivation of Nanocrystalline ZnAl_2O_4 -Supported Pd Catalysts in Liquid-Phase Hydrogenation

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Abstract The catalytic activity and deactivation of nanocrystalline ZnAl_2O_4 -supported Pd catalysts were investigated for the liquid-phase hydrogenation under mild conditions. Nanocrystalline ZnAl_2O_4 spinels with average crystallite size between 8 and 33 nm were synthesized by the solvothermal method in toluene. Higher turnover frequencies for 1-heptyne hydrogenation and less deactivation due to Pd leaching were obtained for the Pd/ ZnAl_2O_4 -33 nm catalyst. XPS and ESR results suggest that the presence of defects in larger crystallite size ZnAl_2O_4 resulted in higher Pd dispersion and stronger interaction between Pd and the support.

Keywords ZnAl_2O_4 spinel · Solvothermal · Nanocrystals · Pd catalyst · Liquid-phase hydrogenation · 1-heptyne hydrogenation

1 Introduction

Supported Pd catalysts are widely used in liquid-phase selective alkyne hydrogenation especially for the synthesis of fine chemicals and bio-active compounds [1–4]. The notable advantages of supported noble metal catalysts under heterogeneous conditions are relatively high activity, mild process conditions, easy separation, and better handling properties. The commonly used supports for Pd catalysts include activated carbon [5, 6], silica [7], alumina [8], and to a lesser extent, polymer [9] and zeolite [10]. It is known that the choice of an efficient support can significantly improve the activity, selectivity, recycling, and reproducibility of Pd catalyst systems [11–13]. Recently, spinel type oxides like ZnAl_2O_4 have been used as supports for Pt and Pd catalysts and a distinct metal-support interaction was found [14, 15]. It has also been reported that Rh complexes were effectively and stably bound to hydrothermally synthesized ZnAl_2O_4 better than to Al_2O_3 [16].

The solvothermal method is one of the most interesting methods for preparation of nanocrystalline materials. It has been used to successfully synthesize various types of nano-sized metal oxides with large surface areas, high crystallinities, and high thermal stabilities [17, 18]. The products obtained by solvothermal synthesis usually show uniform morphology, well-controlled chemical composition, and narrow particle size distribution. As catalyst supports, solvothermal-derived nanocrystalline oxides have been shown to provide better catalytic properties of the corresponding supported metal catalysts compared to commercially available supports [19–21]. In this study, nanocrystalline ZnAl_2O_4 spinels were prepared by the solvothermal method using toluene as the solvent and were employed as Pd catalyst supports. The effect of support crystallite size in the range of 8–33 nm on the catalytic

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activities, selectivities, and catalyst deactivation due to metal leaching of the nanocrystalline ZnAl_2O_4 -supported Pd catalysts were investigated by X-ray diffraction (XRD), N_2 physisorption, transmission electron microscopy with selected area electron diffraction (TEM with SAED), CO pulse chemisorption, electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS), and atomic absorption spectroscopy (AAS). Liquid-phase hydrogenation of 1-heptyne under mild reaction conditions was used as a test reaction.

2 Experimental

2.1 Preparation of ZnAl_2O_4 and Pd/ ZnAl_2O_4

Zinc aluminate spinel (ZnAl_2O_4) was prepared by the solvothermal technique using aluminium isopropoxide (Aldrich) and zinc (II) acetylacetonate (Merck) (Zn/Al molar ratio = 0.5) as reactants suspended in toluene (Carlo Erba Reagenti). First, the mixture of aluminium isopropoxide, 15.0 g and appropriate amount of zinc (II) acetylacetonate (Zn/Al molar ratio = 0.5) was prepared in 100 cm^3 toluene in a 1.5- dm^3 autoclave reactor. The suspension was heated to 300 °C at the rate of 2.5 °C/min and held at that temperature for 2 h. The resulting products were washed with methanol and dried in air and then calcined in a furnace at various temperatures (500, 700, 900, or 1,150 °C) for 1 h. The as-synthesized ZnAl_2O_4 was referred to as ZnAl_2O_4 -as-syn and the calcined ZnAl_2O_4 supports were denoted as ZnAl_2O_4 -500, ZnAl_2O_4 -700, ZnAl_2O_4 -900, ZnAl_2O_4 -1150 according to the calcination temperature used.

Pd/ ZnAl_2O_4 catalysts were prepared by the incipient wetness impregnation method using $\text{Pd}(\text{NO}_3)_2$ (Aldrich) as the palladium precursor. The support was impregnated to incipient wetness with an aqueous solution containing sufficient palladium to result in 1 wt% Pd catalysts. The catalyst samples were dried in an oven at 100 °C overnight and calcined in air at 400 °C for 6 h prior to characterization.

2.2 Catalyst Characterization

The specific surface areas, pore volumes, and average pore diameters were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum at <10 μm Hg in the Micromeritics system at 150 °C for 4 h prior to N_2 physisorption. The XRD patterns of the catalysts were measured from 10° to 80° 2θ using a SIEMENS D5000 X-ray diffractometer and Cu K_α radiation with a Ni filter. Catalyst crystallite sizes

and diffraction patterns of supports were obtained using the JEOL JEM 2010 transmission electron microscope that employed a LaB_6 electron gun in the voltage range of 80–200 kV with an optical point-to-point resolution of 0.23 nm. The amounts of CO chemisorbed on the catalysts were measured at room temperature using a Micromeritic Chemisorb 2750 automated system with ChemiSoft TPx software. Prior to chemisorption, the sample was reduced in a H_2 flow at 500 °C for 2 h and then cooled down to ambient temperature in a He flow. The bulk compositions of palladium in the catalysts before and after reaction were determined using a Varian Spectra A800 atomic absorption spectrometer. Electron spin resonance spectroscopy (ESR) was conducted using a JEOL JESRE2X-electron spin resonance spectrometer. The intensity of ESR was calculated using a computer software program ES-PRIT ESR DATA SYSTEM (version 1.6).

2.3 Reaction Study

Liquid-phase partial hydrogenation of 1-heptyne was carried out in a 50- cm^3 stainless steel autoclave. Approximately 0.02 g of supported Pd catalyst was placed in the reactor with 10 cm^3 of 2 vol% of 1-heptyne in toluene. Afterward the reactor was filled with hydrogen at 1 bar pressure. Stirring was switched on to start the reaction, and reaction was carried out for 5 min. The products were analyzed by gas chromatography with a flame ionization detector.

3 Results and Discussion

3.1 Catalyst Characteristics

Figure 1 shows the XRD patterns of the as-synthesized and calcined ZnAl_2O_4 powders. Reaction of the mixture of aluminum isopropoxide (AIP) and zinc acetylacetonate (ZnAcAc) in toluene yielded the nanocrystalline spinel ZnAl_2O_4 powders with no other impurities. Increasing calcination temperature resulted in a subsequent increase in the degree of crystallinity and in the crystallite size. The average crystallite size of ZnAl_2O_4 powders calculated from the Scherrer equation was found to increase linearly from 8 to 33 nm with increasing calcination temperature to 1,150 °C. The average crystallite sizes, BET surface areas, pore volumes, and average pore diameters of the solvothermal-derived ZnAl_2O_4 are given in Table 1. The BET surface areas gradually decreased with increasing calcination temperature suggesting that sintering occurred during the calcination process corresponding to the increase of crystallite size. The pore size distributions of the ZnAl_2O_4 supports are shown in Fig. 2. It was found that the calcined

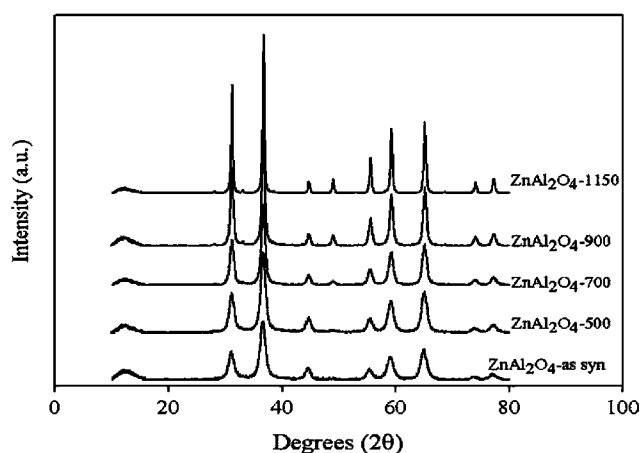


Fig. 1 XRD patterns of the as-synthesized and the calcined ZnAl₂O₄

ZnAl₂O₄ samples retained their large pore volume and narrow pore size distribution during high temperature calcination up to 700 °C. Significant loss of pore volume was found for the sample calcined at 1,150 °C (ZnAl₂O₄-33 nm).

Figure 3 shows the transmission electron micrographs with selective area electron diffraction (SAED) pattern of various ZnAl₂O₄ spinels. The crystallites of ZnAl₂O₄ consisted of particles which were agglomerates of smaller crystallites with primarily spherical shapes. The average crystal sizes of the as-prepared and the calcined samples determined from TEM were similar to those measured from the XRD line broadening. The corresponding selected area diffraction patterns confirmed the structure of ZnAl₂O₄ and there was no significantly difference in SAED patterns of the as-synthesized and the calcined samples (not shown), indicating that all the samples contained only crystalline ZnAl₂O₄.

The presence of defect sites on the nanocrystalline supports was detected using electron spin resonance spectrometry. ESR is known as an effective method for investigating of the electron spin state and the structure of the surface of nano-sized crystallites. The ESR signals from the various solvothermal-derived nanocrystalline ZnAl₂O₄ are shown in Fig. 4. It is shown that only the ZnAl₂O₄-33 nm sample exhibited very strong and stable ESR signals. These ESR signals may arise from O²⁻

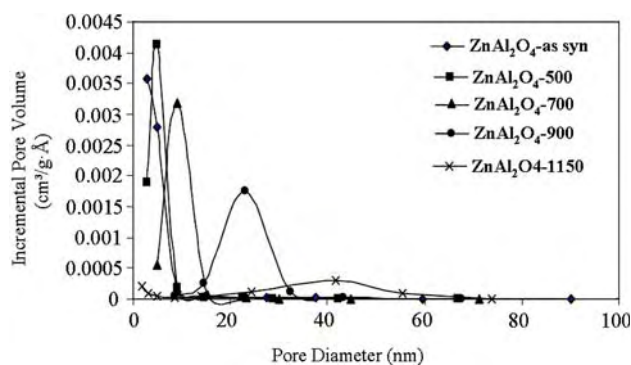


Fig. 2 Pore size distribution of the as-synthesized and the calcined ZnAl₂O₄

vacancies on the surface and/or incorporation of trace impurities in their crystal structure during high temperature calcination resulting in crystal distortion. Moreover, it has been reported that nano-sized ZnAl₂O₄ possesses inverse structure when calcined at temperatures <900 °C [22]. The highly crystalline nature (regular spinel structure) of ZnAl₂O₄ was obtained at calcination temperatures ≥1,000 °C. The result in this study, however, was in agreement with literature that larger crystallites of nanocrystalline materials synthesized by the solvothermal method contain more defects than smaller ones [23].

3.2 Characteristics and Catalytic Properties of Nanocrystalline ZnAl₂O₄-Supported Pd Catalysts

The physicochemical properties of Pd supported on as-synthesize and calcined nanocrystalline ZnAl₂O₄ are shown in Table 2. For the as-synthesized ones, the BET surface areas were slightly decreased after impregnation with Pd suggesting pore blockage by Pd/PdO clusters. However, for the calcined ZnAl₂O₄ supportd ones, there were less differences in BET surface areas of the supports and of the supported Pd catalysts suggesting that much of the Pd/PdO may have been located on the external surfaces. The relative amounts of active surface Pd metal atoms on the catalyst samples were calculated from CO chemisorption experiments at room temperature. The calculation of Pd active sites was based on the assumption that

Table 1 N₂ physisorption results^a and XRD determined average crystallite sizes of the as-synthesized and the calcined ZnAl₂O₄ supports prepared by the solvothermal method

Sample	BET S.A. (m ² /g)	Pore volume (m ³ /g)	Avg. pore diameter (nm)	Avg. XRD crystallite size (nm)
ZnAl ₂ O ₄ -as-syn	130	0.18	4.2	8.2
ZnAl ₂ O ₄ -500	116	0.19	4.6	9.0
ZnAl ₂ O ₄ -700	63	0.20	8.5	10.9
ZnAl ₂ O ₄ -900	28	0.19	22.0	17.6
ZnAl ₂ O ₄ -1150	15	0.08	36.6	33.3

^a Error of measurements as determined directly were ±10%

Fig. 3 TEM micrographs and selected area electron diffraction of various ZnAl_2O_4 samples

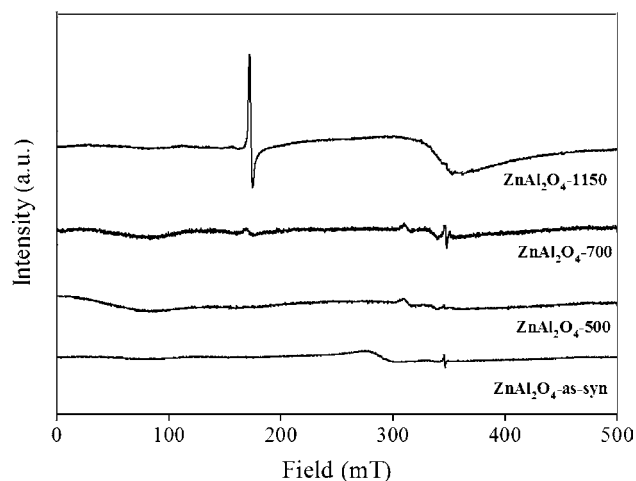
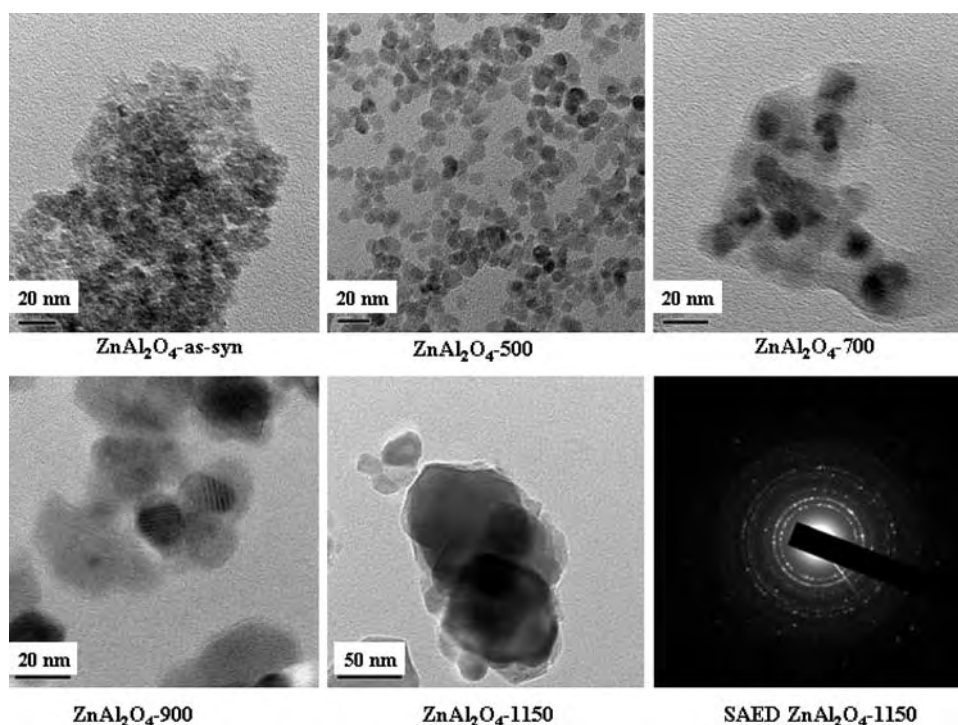


Fig. 4 ESR results of the solvothermal-derived ZnAl_2O_4

one carbon monoxide molecule adsorbs on one palladium surface atom or site [24]. It is surprising that the amounts of CO chemisorption were essentially similar for the Pd catalysts supported on ZnAl_2O_4 with the average crystallite sizes in the range of 8–18 nm. The amount of CO chemisorption was increased for the one supported on ZnAl_2O_4 -33 nm. The percentages of Pd dispersion and corresponding Pd^0 particle sizes were calculated based on the CO chemisorption results and are also given in Table 2.

The catalytic properties of all the catalyst samples were investigated for the liquid-phase hydrogenation of 1-heptyne under mild conditions using a stirred batch reactor.

The results are summarized in Table 3. The conversions of 1-heptyne for various Pd/ ZnAl_2O_4 catalysts were in the range of 45–66% with Pd/ ZnAl_2O_4 -33 nm exhibiting the highest conversion. There were no appreciable influences on 1-heptene selectivity since all the catalysts exhibited high selectivities for 1-heptene (97–100%). The specific activities of the Pd/ ZnAl_2O_4 catalysts are also expressed in terms of turnover frequency (TOF) which is defined as mole of product/mole of surface metal atoms/time. This is not a perfect measure of TOF since it is for reaction with a high conversion and therefore affected by changing reactant concentration. However, it is given here as a rough comparison of specific rate.

The actual amounts of palladium loading before and after reaction were determined by atomic adsorption spectroscopy and the %Pd leached for each catalyst is given in Table 3. Before reaction, palladium loading on all the catalyst samples was approximately 1.2 wt%. After one batch reaction period, the amount of palladium loading decreased to 0.6–1.1 wt% indicating that leaching of palladium occurred during reaction for most of the catalysts. Leaching of the active metal is one of the main causes of catalyst deactivation in liquid phase reactions. It depends upon the reaction medium (pH, oxidation potential, chelating properties of molecules) and upon bulk and surface properties of the metal [25]. The percentages of palladium leaching were found to be much lower when Pd catalysts were supported on ZnAl_2O_4 -33 nm compared to those on smaller crystallite size ones.

Table 2 Physicochemical properties of the various Pd catalysts

Catalysts	BET S.A. ^a (m ² /g)	Pore volume ^a (m ³ /g)	Avg. pore diameter ^a (nm)	CO chemisorption ^b (10 ¹⁸ molecules CO/g cat.)	Dispersion(%) ^c	Pd ⁰ dp ^d (nm)
Pd/ZnAl ₂ O ₄ -as-syn	106	0.20	4.6	7.4	13.0	7.8
Pd/ZnAl ₂ O ₄ -500	104	0.21	4.8	7.4	13.1	7.8
Pd/ZnAl ₂ O ₄ -700	66	0.21	8.9	7.2	12.8	7.4
Pd/ZnAl ₂ O ₄ -900	28	0.18	21.5	7.3	12.8	8.0
Pd/ZnAl ₂ O ₄ -1150	16	0.10	29.2	8.7	15.3	6.7

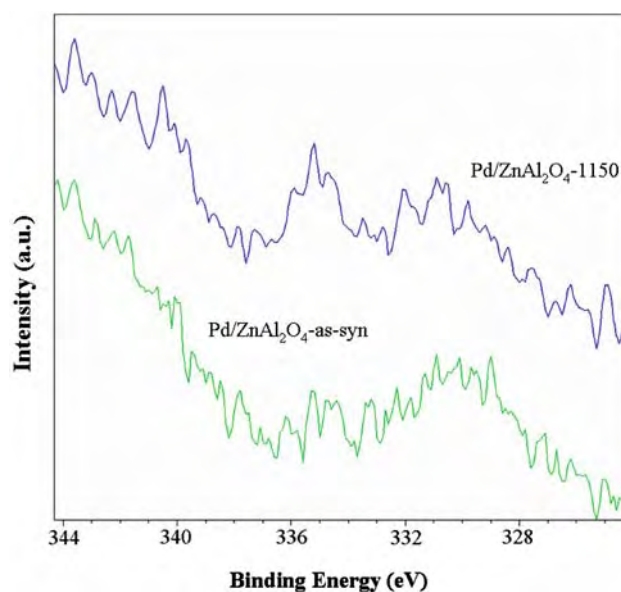
^a Determined from N₂ physisorption. Error of measurements as determined directly were $\pm 10\%$ ^b Error of measurements for CO chemisorption as determined directly were $\pm 5\%$ ^c Based on total palladium loading and an assumption of CO/Pd = 1^d Based on $d = (1.12/D)$ nm [24], where D = fractional metal dispersion**Table 3** Catalytic properties for liquid-phase 1-heptyne hydrogenation^a

Catalysts	Conversion of 1-heptyne (%)	1-Heptene selectivity (%)	Estimated TOF ^b (s ⁻¹) ^c	%Pd leached ^d
Pd/ZnAl ₂ O ₄ -as-syn	52	97	0.24	36
Pd/ZnAl ₂ O ₄ -500	51	100	0.23	38
Pd/ZnAl ₂ O ₄ -700	45	100	0.22	30
Pd/ZnAl ₂ O ₄ -900	49	100	0.24	35
Pd/ZnAl ₂ O ₄ -1150	66	100	0.32	6

^a Reaction conditions were 105 kPa, 30 °C, 5 min, and catalyst/substrate molar ratio = 1,600^b TOF = mole product/mole Pd metal surface atoms/s. Based on the amount of potentially active Pd atoms measured by CO chemisorption^c Estimated since at high conversion^d Based on atomic absorption spectroscopy results. Error of measurement as determined directly was $\pm 10\%$

The mechanism of metal leaching usually involves metal compounds that are formed and are soluble in the reaction mixture. However, it is unlikely that 1-heptyne forms a compound with Pd at room temperature, unless it is some hydrido-organic complex. It is likely that Pd was leached in the form of Pd hydride phase. Under certain conditions, Pd- β -hydride can appear as a soft material with higher mechanical abrasion [26]. Moreover, leaching of Pd may depend on Pd particle size, larger particles are more likely to be leached since larger particles formed Pd- β -hydride more easily [27, 28]. Similar results have been reported previously by our group for the deactivation of Pd/SiO₂ catalysts during liquid-phase hydrogenation [29, 30]. The leached Pd species, however, appeared to be inactive for the present hydrogenation since the catalyst recycling test showed minimal loss of activity after it was reused for several cycles. Moreover, Pd- β -hydride is expected to have a different catalytic activity from that of metallic palladium [31].

The interaction between Pd and the nanocrystalline supports was also studied by XPS analysis, the Pd 3d_{5/2} core level binding energy of the various catalyst samples are shown in Fig. 5. It can be seen that the Pd 3d_{5/2} binding energy for Pd catalyst supported on the ZnAl₂O₄-33 nm

**Fig. 5** XPS spectra of Pd 3d_{5/2} for Pd/ZnAl₂O₄ catalysts

shifted towards higher binding energy suggesting a stronger interaction between Pd and the highly crystalline supports. Among the various ZnAl₂O₄ samples in this

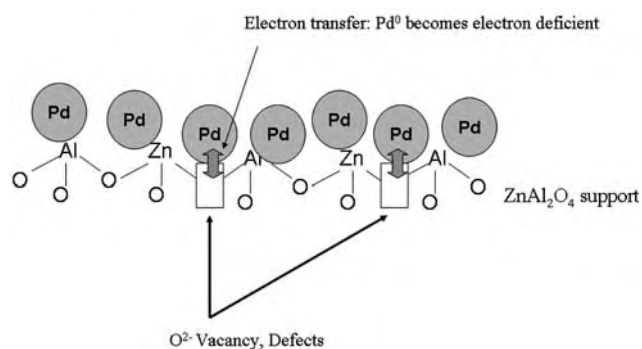


Fig. 6 A conceptual model for stronger metal-support interaction induced by defect sites of the nanocrystalline material

study, only the ZnAl_2O_4 -33 nm possessed significant amount of defects. Thus, it is hypothesized that electron transfer occurred at the defective points of the nanocrystalline materials from Pd^0 to the support, and, as a consequence, Pd^0 surface atoms became electron deficient and their catalytic properties were modified. A conceptual model for stronger metal-support interaction induced by defective sites of ZnAl_2O_4 -33 nm is illustrated in Fig. 6.

4 Conclusions

The catalytic activities and deactivation of Pd catalysts supported on the solvothermal-derived nanocrystalline ZnAl_2O_4 in liquid-phase hydrogenation of 1-heptyne were investigated. Higher turnover frequencies and less Pd leaching were obtained on the Pd catalyst supported on larger crystallite size ZnAl_2O_4 that contained significant amounts of defects (as shown by strong and stable ESR signals). It is suggested that the presence of defects on these nanocrystalline materials induced stronger metal-support interaction between Pd and the supports thus their catalytic properties were modified.

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Effect of strong metal–support interaction on the catalytic performance of Pd/TiO₂ in the liquid-phase semihydrogenation of phenylacetylene

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ABSTRACT

Liquid-phase semihydrogenation of phenylacetylene under mild conditions has been investigated on a series of solvothermal-derived nano-TiO₂ supported Pd catalysts with various TiO₂ crystallite sizes in the range of 9–23 nm. As revealed by CO chemisorption and transmission electron microscopy, all the catalysts exhibited strong metal–support interaction (SMSI) when reduced at 500 °C. The catalysts with SMSI show remarkably high catalytic performance in terms of both hydrogenation activities (turnover frequencies (TOFs) 9.1–21.4 s^{−1}) and moderate-high selectivities to styrene (86–90%) at complete conversion of phenylacetylene. Without SMSI effect (the catalysts reduced at 40 °C), styrene selectivity and catalytic activity depended largely on the Pd particle size in which small Pd particles (formed on small crystallite size TiO₂ supports) exhibited lower phenylacetylene conversion and poor styrene selectivity. Moreover, the TOF values of the non-SMSI catalysts were similar to those reported in the literature for other supported Pd catalysts in liquid-phase semihydrogenation of phenylacetylene under mild conditions (TOFs 1.3–2.8 s^{−1}).

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1. Introduction

Phenylacetylene removal by selective hydrogenation is a process of great industrial importance because phenylacetylene is a poisoning impurity in styrene feedstocks that causes deactivation of the styrene polymerization catalyst and degrades polystyrene properties [1]. From academic points of view, semihydrogenation of phenylacetylene has often been employed as a model reaction for evaluation of selective hydrogenation catalysts under very mild conditions. New heterogeneous catalysts for the liquid-phase semihydrogenation of phenylacetylene with high styrene selectivity have been continuously developed and reported. Most recent studies focus on preparation of Pd nanoparticles in the forms of dispersed colloids [2] and supported systems [3,4]. The latter, however, may be more commercially attractive for industrial applications due to their better handling properties and low separation problems. In the past, different inorganic and organic materials have been studied as Pd catalyst supports in liquid-phase semihydrogenation of phenylacetylene including carbon [2,5–7], SiO₂ [8,9], γ -Al₂O₃ [10], pumice [11,12], zeolites [4], polymers [1,13],

organic matrices [14], pillared clays [15,16], mesostructured silica such as MCM-41, HMS, MSU-X [4,17,18], and TiO₂ [19].

Despite a number of studies on support effects on the reactivity of Pd in such a reaction, controversy regarding structure sensitivity of the reaction still exists. Typically, the turnover frequencies (TOFs) were determined based on the number of palladium sites measured by irreversible CO or H₂ chemisorption. Comparing the results obtained under mild reaction conditions (ambient temperature and low H₂ pressure), the TOF values of Pd catalysts in most of the aforementioned references fall into the same range (about 1–3 s^{−1}) suggesting structure insensitive characteristic of the reaction. Nevertheless, significant increase of the TOFs of Pd nanoparticles by at least fourfold to an order of magnitude has recently been reported on some specially prepared supported Pd catalysts [4,17]. In those studies, the hydrogenation of phenylacetylene was suggested to be structure-sensitive because the TOFs were found to increase with increasing Pd nanoparticle diameter. However, it is noticed that the remarkable high activities of supported Pd catalysts coincidentally reported by the two different groups were obtained when Pd nanoparticles were supported on MCM-41 via simultaneous synthesis (simultaneous self-assembling of the MCM-41 and Pd incorporation). Conventional impregnation of palladium on MCM-41 gave similar activities compared to the others [4,18]. We speculate that by simultaneous synthesis, the Pd nanoparticles

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may be surrounded by support matrices resulting in the inhibition of CO chemisorption and as a consequence high TOF values being calculated. Such phenomenon was probably similar to the decoration of metal surface by partially reducible metal oxides after high temperature reduction or so-called “the strong metal–support interaction” (SMSI) effect [20].

Thus, it was of interest in this study to verify the effect of SMSI on the catalytic activities and selectivities of Pd catalysts in the liquid phase semihydrogenation of phenylacetylene to styrene. Nanocrystalline TiO_2 powders with various crystallite sizes in the range of 9 to 23 nm were synthesized via solvothermal method and employed as supports for Pd catalysts. It is well-known that TiO_2 manifests SMSI with group VIII transition metals (e.g. Pd, Pt, Ni, and Ir) after high temperature reduction. Significant improvement of catalyst performance due to the SMSI effect has been reported in many catalytic reactions such as CO oxidation [21], methanol synthesis [22], selective acetylene hydrogenation [23–25], and liquid-phase hydrogenation [19,26–33]. Moreover, the degree of SMSI effect on Pd/ TiO_2 has been shown to depend largely on both the TiO_2 crystal structure (anatase and rutile) [25–27] and TiO_2 crystallite size [19]. The reduction by H_2 at 200 °C resulted in SMSI for anatase titania supported palladium catalyst, but not for the rutile sample [27]. A very recent study from our group shows the absence of SMSI effect on Pd/ TiO_2 when the crystallite size of TiO_2 was fairly large ($\geq 0.1 \mu\text{m}$) [19]. Therefore, in order to ensure the occurrence of SMSI, the TiO_2 supports used in this study were pure anatase TiO_2 with average crystallite sizes in the nanometer range. The Pd/ TiO_2 catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and pulse CO chemisorption. Furthermore, the catalytic properties of the Pd/ TiO_2 catalysts were evaluated in the liquid-phase semihydrogenation of phenylacetylene to styrene under mild conditions.

2. Experimental

2.1. Preparation of TiO_2 and Pd/ TiO_2 catalysts

The solvothermal-derived nano- TiO_2 was prepared according to the method described in [34] using 15–25 g of titanium(IV) *n*-butoxide (TNB) 97% from Aldrich. The starting material was suspended in 100 ml of 1,4-butanediol in a test tube and then set up in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of solvent was added. After the autoclave was completely purged with nitrogen, it was heated to the desired temperature (300–340 °C) at a rate of 2.5 °C min^{−1} and held at that temperature for 0.5–12 h. Autogenous pressure during the reaction gradually increased as the temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting powders were collected by centrifugation after repeated washing with methanol. They were then air-dried at room temperature.

The 1%Pd/ TiO_2 catalysts were prepared by the incipient wetness impregnation technique using an aqueous solution of the desired amount of $\text{Pd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich). The catalysts were dried overnight at 110 °C and then calcined in air at 450 °C for 3 h.

2.2. Catalyst characterization

The specific surface areas, pore volumes, and average pore diameters were determined by N_2 physisorption using a Micromeritics ASAP 2020 automated system and the Brunauer–Emmett–Teller (BET) method. Each sample was degassed under vacuum at $<10 \mu\text{m Hg}$ in the Micromeritics system at 150 °C for 4 h prior to N_2 physisorption. The average pore size was calculated using the BJH desorption method. The XRD patterns of the catalysts

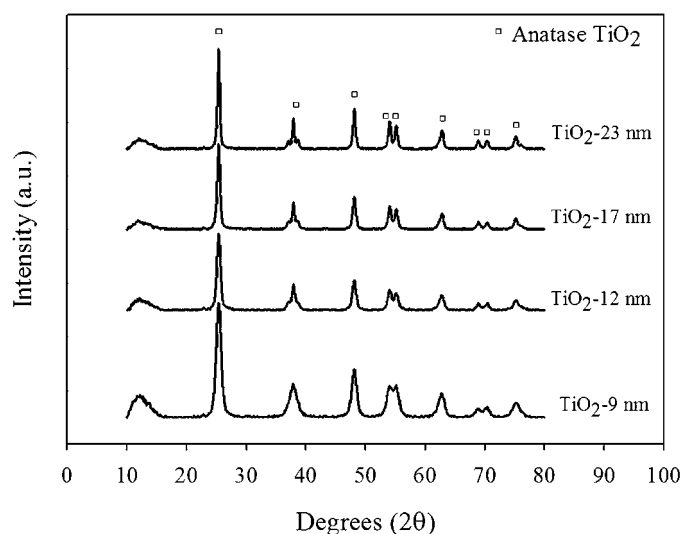


Fig. 1. XRD patterns of the solvothermal-derived TiO_2 with different crystallite sizes.

were measured from 10° to 80° 2θ using a SIEMENS D5000 X-ray diffractometer and $\text{CuK}\alpha$ radiation with a Ni filter. The catalyst morphology was obtained using a JEOL JSM-35CF scanning electron microscope (SEM) operated at 20 kV. Metal crystallite sizes were obtained using the JEOL JEM 2010 transmission electron microscope that employed a LaB_6 electron gun in the voltage range of 80–200 kV with an optical point to point resolution of 0.23 nm. The amounts of CO chemisorbed on the catalysts were measured using a Micromeritics Chemisorb 2750 automated system with ChemiSoft TPx software. Prior to chemisorption, the sample was reduced in a H_2 flow at the desired temperature for 2 h and then cooled down to ambient temperature in a He flow.

2.3. Reaction study

Approximately 0.05 g of 1%Pd/ TiO_2 catalyst was placed into a 50 ml autoclave. 0.5 ml of phenyl acetylene and 4.5 ml of ethanol (solvent) were mixed in a volumetric flask before being introduced into the autoclave reactor. Afterward the reactor is purged with hydrogen gas. The liquid phase hydrogenation was carried out with H_2 pressure of 1–5 bar and at room temperature for 5–60 min. After the reaction, the vent valve was slowly opened to prevent the loss of product. The product mixture was analyzed by gas chromatography with flame ionization detector (FID) and a GS-alumina capillary column. GC analysis of the reactant after being purged with hydrogen prior to a start of run confirmed that no catalytic reaction occurred before the actual experiment took place.

3. Results and discussion

3.1. Catalyst characterization

In this study, the crystallite size of solvothermal-derived nano- TiO_2 was varied in the range of 9–23 nm by changing the synthesis conditions such as the amount of TNB, reaction temperature, and holding time. Increasing the amount of TNB, reaction temperature, or holding time resulted in an increase of TiO_2 crystallite size. Fig. 1 shows the XRD patterns of the various nano- TiO_2 samples prepared. The characteristic peaks of pure anatase phase titania were observed at $2\theta = 25$, 38, and 48° [35] without contamination of other phases such as rutile and brookite. The average crystallite sizes of TiO_2 were calculated from the full width at half maximum of the XRD peak at $2\theta = 25^\circ$ using the Scherrer equation. The synthesis conditions and the average crystallite size, BET surface

Table 1
Synthesis conditions and physical properties of the nanocrystalline TiO₂.

Sample	TNB (g)	Temp. (°C)	Holding time ^a (h)	XRD crystallite size (nm)			BET surface area ^c (S ₁) (m ² /g)	Pore volume ^c (cm ³ /g)	Avg. pore diameter ^c (nm)
				As-syn	Reduced ^b at 40 °C	Reduced ^b at 500 °C			
TiO ₂ -9 nm	15	300	0.5	9	9	11	145	0.42	8.1
TiO ₂ -12 nm	25	300	2	12	12	13	88	0.37	12.5
TiO ₂ -17 nm	25	320	6	17	17	18	65	0.38	17.9
TiO ₂ -23 nm	25	340	12	23	23	23	51	0.32	20.2

^a Holding time during the solvothermal synthesis of TiO₂ (after the autoclave was heated to 320 °C at a rate of 2.5 °C min⁻¹).

^b After Pd was impregnated and calcined.

^c As-syn TiO₂ samples.

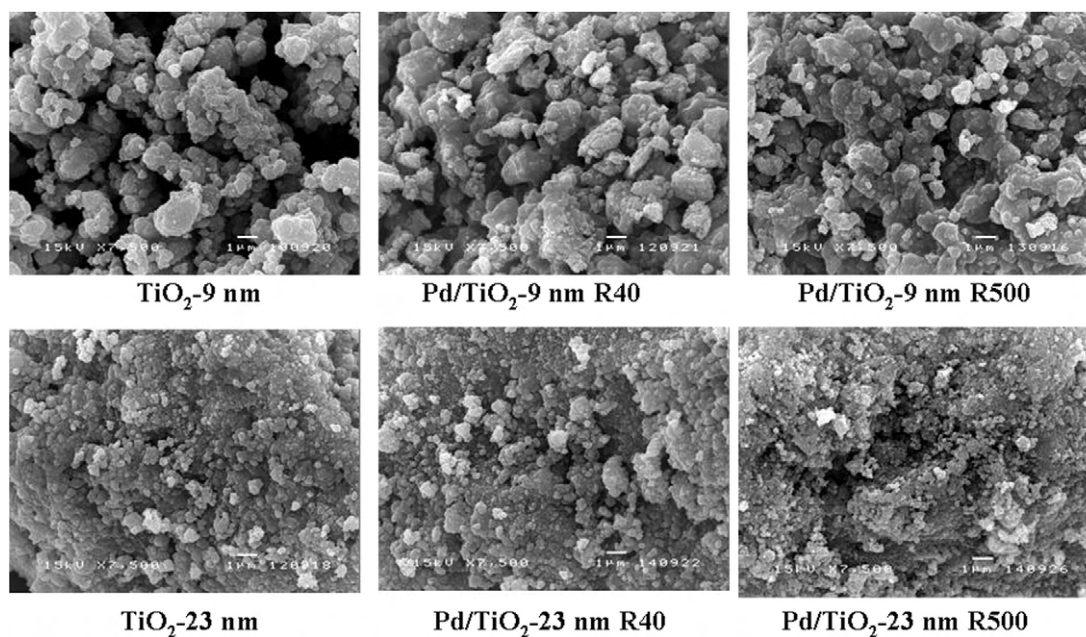


Fig. 2. SEM micrographs of calcined and reduced Pd/TiO₂ catalysts. Reduction temperature = 40 °C (R40), 500 °C (R500).

area, pore volume, and average pore diameter of the obtained TiO₂ samples are given in Table 1. As the average TiO₂ crystallite size increased from 9 to 23 nm, the BET surface area decreased monotonically from 145 to 51 m²/g. The pore size distribution of various crystallite sizes of TiO₂ supports indicated that the pores of all TiO₂ samples were mesopores (results not shown). After impregnated with approximately 1 wt% Pd, calcined, and reduced at 40 or 500 °C, the crystallite sizes of all the TiO₂ samples as determined by XRD were essentially unaltered except that of the smallest crystallite size TiO₂ (TiO₂-9 nm) in which a slight increase of the TiO₂ crystallite size from 9 to 11 nm was observed. It is generally found that the crystals of small crystallite size show less thermal stability than the crystals of large crystallite size [36].

Fig. 2 shows the SEM micrographs of TiO₂-9 nm and TiO₂-23 nm supports and the corresponding 1 wt% Pd/TiO₂ catalysts after reduced at 40 and 500 °C. The nano-TiO₂ was consisted of irregular shape of very fine particles agglomerated. Morphologies of the reduced 1%Pd/TiO₂ catalysts were not significantly different from the corresponding TiO₂ supports. The particle size and shape of the catalyst particles were also not affected by impregnation of palladium (no changes in the particle size/shape). TEM analysis has been carried out in order to physically measure the TiO₂ crystallite size as well as Pd particle/cluster sizes on the various Pd/TiO₂ catalysts. The TEM results are shown in Fig. 3. The crystallite sizes of the TiO₂ supports were consistent to those obtained from XRD results. The presence of small palladium particles/clusters with an

average particle size around 5–6 nm were apparent only on the Pd/TiO₂-23 nm.

The BET surface area, pore volume, average pore diameter, and CO chemisorption results of the various Pd/TiO₂ catalysts are shown in Table 2. The decreases in BET surface areas and pore volumes of the Pd/TiO₂ catalysts compared to the TiO₂ supports suggested that palladium was deposited in some of the pores of the TiO₂. From the CO chemisorption results, it can be seen that for the Pd/TiO₂ catalysts reduced at 40 °C, the amount of CO chemisorption decreased from 18.1×10^{18} to 9.73×10^{18} molecule CO/g cat. as the TiO₂ crystallite size increased from 9 to 23 nm. This was probably due to the lower specific surface area of the larger crystallite size TiO₂ supports that resulted in lower Pd dispersion. For the same catalyst, the amount of CO chemisorption was much lower when reduced at 500 °C. The amounts of CO chemisorption were in the range of 0.9 to 1.31×10^{18} molecule CO/g cat. However, the CO chemisorbed on all the R500 catalysts can be totally restored indicating that the palladium particles did not sinter during high temperature reduction at 500 °C and all the catalysts exhibited the SMSI effect. The Pd⁰ metal particles calculated from CO chemisorption results for the catalysts reduced at 40 °C were found to be 3.2–5.9 nm depending on the TiO₂ crystallite size. The results were consistent with TEM analyses. For the catalysts reduced at 500 °C, the Pd⁰ metal particle sizes were not determined since it would result in an over-estimation of the particle size. Low amounts of CO or H₂ chemisorption and an over-estimation of Pd particle size have occasionally been reported in other supported

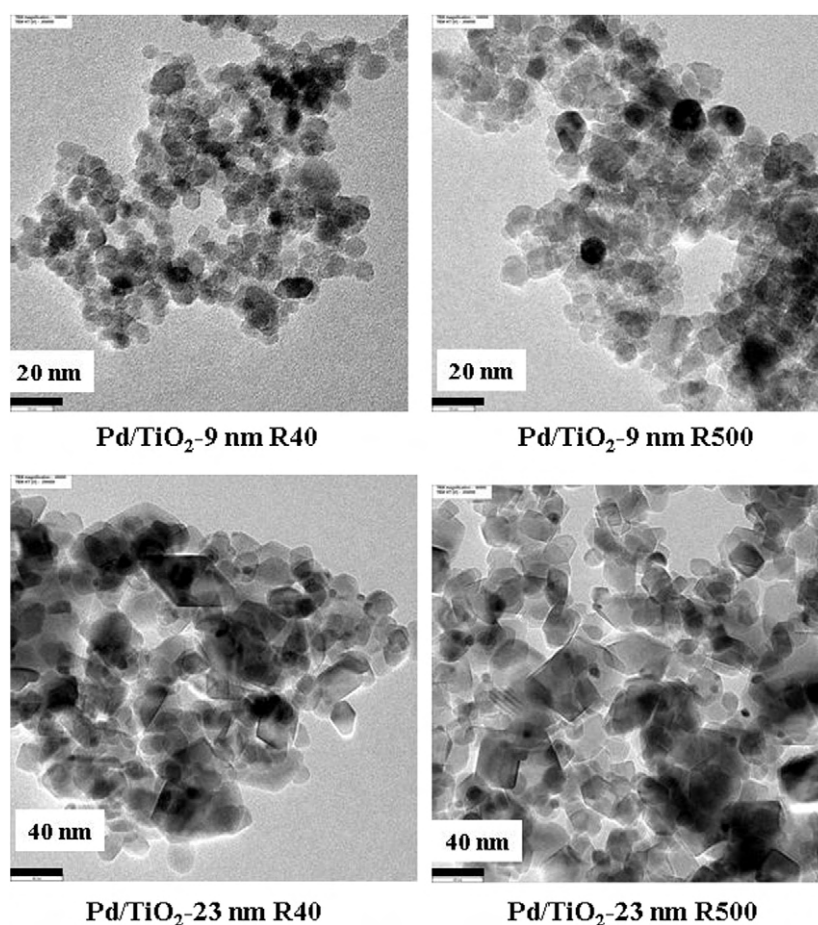


Fig. 3. TEM micrographs of Pd/TiO₂-9 nm and Pd/TiO₂-23 nm reduced at 40 °C (R40) and 500 °C (R500).

Table 2

N₂ physisorption and CO chemisorption results of the Pd/TiO₂ catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Avg. pore diameter (nm)	CO chemisorption ^a ($\times 10^{-18}$ molecule CO/g cat.)	%Pd dispersion	d_p^d Pd ⁰ (nm)
Pd/TiO ₂ -9 nm R40	135	0.30	6.3	18.1	35.5	3.2
Pd/TiO ₂ -9 nm R500	89	0.20	6.2	1.31 (18.4) ^b	n.d. ^c	n.d.
Pd/TiO ₂ -12 nm R40	84	0.31	11.1	15.6	30.5	3.7
Pd/TiO ₂ -12 nm R500	75	0.30	10.7	1.02 (16.1)	n.d.	n.d.
Pd/TiO ₂ -17 nm R40	62	0.30	14.3	12.1	23.8	4.7
Pd/TiO ₂ -17 nm R500	60	0.30	14.2	0.9 (12.0)	n.d.	n.d.
Pd/TiO ₂ -23 nm R40	47	0.28	19.8	9.73	19.1	5.9
Pd/TiO ₂ -23 nm R500	42	0.29	19.7	1.11 (11.8)	n.d.	n.d.

^a Experimental error as determined directly from the measurements = $\pm 5\%$.

^b The number in parenthesis indicated the amount of CO chemisorption after the R500 catalyst was re-calcined and re-reduced at 40 °C.

^c n.d. = not determined.

^d Based on $d = (1.12/D)$ nm [47], where D = fractional metal dispersion.

Pd catalyst systems such as Pd/MCM-41 prepared via simultaneous synthesis [4,17] and Pd/SiO₂ prepared by one-step flame spray pyrolysis [37]. In those studies, the synthesis of support phase occurred simultaneously with the formation of Pd nanoparticles so the Pd particles may be surrounded by support matrix (i.e., in the form of Si–O group). This could result in the inhibition of CO chemisorption. Such phenomena were somewhat similar to the SMSI effect on Pd/TiO₂. It is generally known that SMSI occurs after reduction at high temperature due to the decoration of the metal surface by partially reducible metal oxides [38,39] and/or by an electron transfer between the support and the metals [40,41] resulting in CO and H₂ chemisorption suppression.

3.2. Catalytic tests

The performance of Pd/TiO₂ catalysts was evaluated in the liquid-phase semihydrogenation of phenylacetylene to styrene in a batch-type stainless steel reactor under mild reaction conditions (H₂ pressure 5 bar and 30 °C). Fig. 4 shows the change in product distribution with reaction time from 5–60 min. In all cases, phenylacetylene was hydrogenated up to nearly 100% conversion within 20 min under the reaction conditions used. The hydrogenation of styrene to ethylbenzene occurred when the concentration of phenylacetylene was sufficiently low indicating a slower parallel reaction pathway for the direct hydrogenation of phenyl-

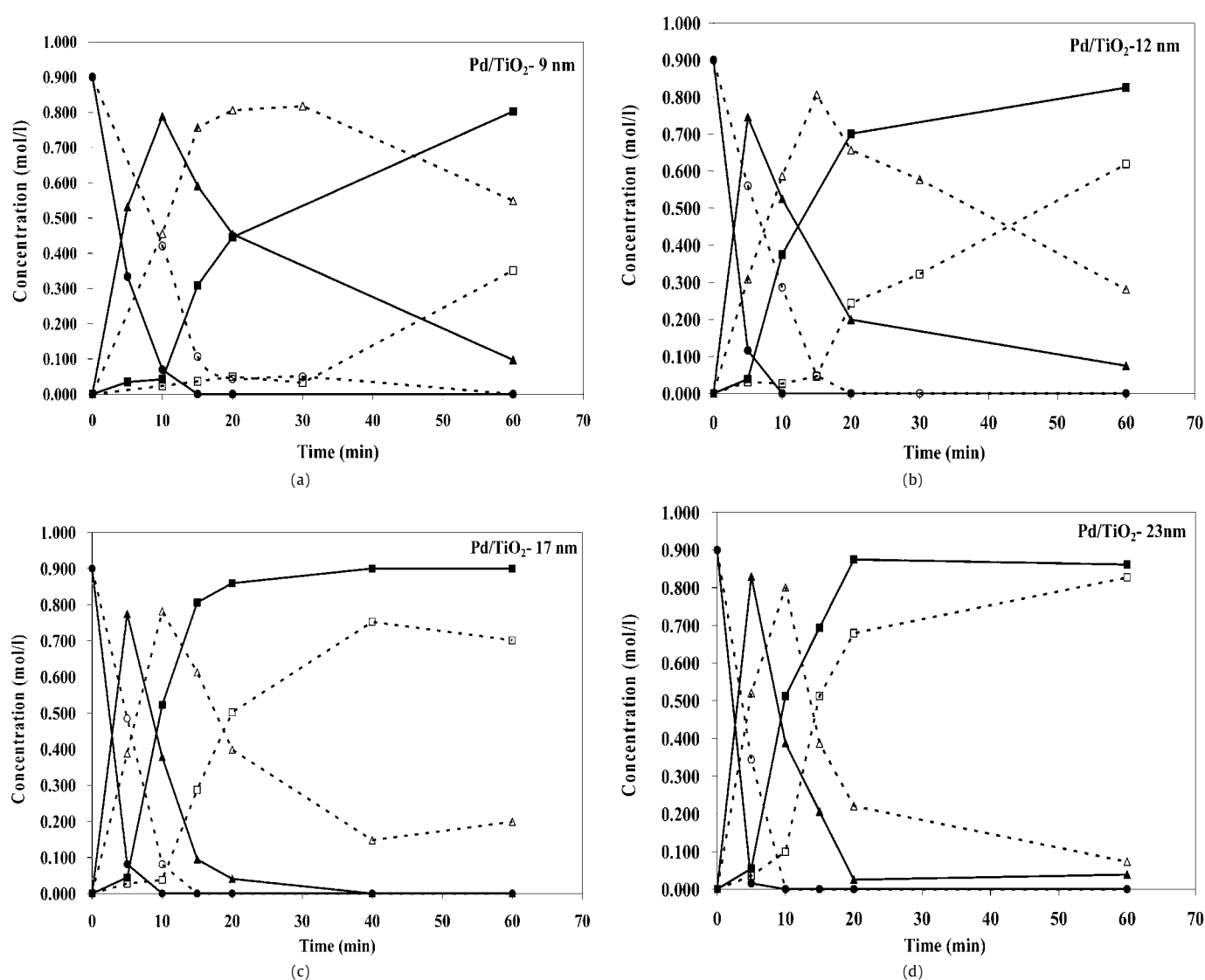


Fig. 4. Liquid-phase semihydrogenation of phenylacetylene over the Pd/TiO₂ catalysts: ○ = phenylacetylene △ = styrene □ = ethylbenzene, solid symbols = Pd/TiO₂ catalysts reduced at 40 °C and open symbols = Pd/TiO₂ catalysts reduced at 500 °C (a) Pd/TiO₂-9 nm, (b) Pd/TiO₂-12 nm, (c) Pd/TiO₂-17 nm, (d) Pd/TiO₂-23 nm (reaction conditions were H₂ pressure = 5 bar and 30 °C).

lacetylene to ethylbenzene. Similar profiles were found for other Pd catalyst systems reported in the literature such as Pd/SiO₂, Pd/C, and commercial Lindlar catalyst in semihydrogenation reaction of alkynes to alkenes [6,42]. The catalyst performance plots (styrene selectivity versus conversion of phenylacetylene) for the various Pd/TiO₂ catalysts are shown in Fig. 5. As can be observed, the catalyst performance was significantly improved when reduced at 500 °C. High styrene selectivity (around 86–90%) was achieved at complete conversion of phenylacetylene for all the catalysts reduced at 500 °C while for the non-SMSI catalysts, the selectivity for styrene significantly dropped to 20–60% when conversion of phenylacetylene reached 100%. Such results confirm the beneficial effect of SMSI in Pd/TiO₂ catalysts on the catalyst performance [8,19]. Charge transfer from the TiO₂ support to Pd during high temperature reduction caused electron enrichment of Pd particles which favored rapid desorption of styrene molecules. Similar results have also been observed for the Pd catalysts supported on organic matrices such as *oligo-p-phenylenterephthalamide* (OPTA) which induces electron transfer from support to metal surface [14]. In gas-phase selective hydrogenation of acetylene to ethylene on Pd/TiO₂ catalysts, the charge transfer from Ti species to Pd weakened the adsorption strength of ethylene on the Pd surface and,

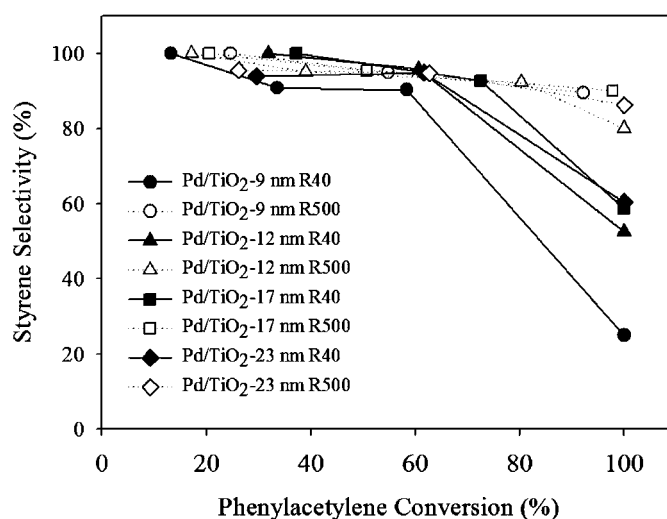


Fig. 5. Performance curves of the various Pd/TiO₂ for selective hydrogenation of phenylacetylene.

Table 3
Catalytic activity of the Pd/TiO₂ catalysts in liquid-phase semihydrogenation of phenylacetylene.

Catalyst	Initial rate ^a (mole products/g cat. s)	TOF ^b (s ⁻¹)	TOF _{R40} /TOF _{R500}
Pd/TiO ₂ -9 nm R40	0.14	1.3	
Pd/TiO ₂ -9 nm R500	0.07	9.1	7.2
Pd/TiO ₂ -12 nm R40	0.18	1.9	
Pd/TiO ₂ -12 nm R500	0.09	15.2	8.1
Pd/TiO ₂ -17 nm R40	0.20	2.8	
Pd/TiO ₂ -17 nm R500	0.11	20.3	7.3
Pd/TiO ₂ -23 nm R40	0.16	2.8	
Pd/TiO ₂ -23 nm R500	0.14	21.4	7.6

^a Reaction conditions were H₂ pressure = 1 bar, *T* = 30 °C, and reaction time = 10 min.

^b Based on CO chemisorption results.

hence, higher ethylene selectivity was obtained [23–25]. However, among the R40 series catalysts, the Pd/TiO₂-9 nm R40 exhibited the lowest styrene selectivity at complete conversion of phenylacetylene despite its highest Pd dispersion. This could probably be attributed to longer residence time of styrene on small metal particles [10]. Low dispersed palladium catalysts also showed to be more selective to partial hydrogenation than highly dispersed ones [43].

The initial rates of phenylacetylene hydrogenation and the corresponding TOF values for the eight catalyst samples are given in Table 3. The measured TOF values were based on the experimental results obtained under the reaction conditions that yielded phenylacetylene conversion less than 50% for all the catalysts (H₂ pressure 1 bar 30 °C and reaction time 10 min). For the R40 series (non-SMSI catalysts), the TOFs were not significantly different ranging from 1.3 to 2.8 s⁻¹. The values were very close to those reported in the literature for supported Pd catalysts in liquid-phase hydrogenation of phenylacetylene under mild conditions as summarized in Table 4. The relatively low activity of Pd/TiO₂-9 nm R40 can be attributed to the very small Pd particles being formed on the small crystallite size TiO₂ support. There has been an establishing trend in the literature that specific activity (turnover frequencies) of Pd in selective hydrogenation decreases as Pd particle size decreases especially when the average Pd particle size is very small (<3–5 nm) [4,8,44]. Diminishing activity of small metal particles was probably due to the different band structure characteristics of nano-sized metal compared to bulk metals and that they appear to be electron deficient [45].

Table 4
Comparison of the catalytic activities of supported Pd catalysts in liquid-phase semihydrogenation of phenylacetylene under mild conditions.

Catalyst	BET surface area (m ² /g)	Reactant: Pd molar ratio	Reaction conditions ^a	Pd ⁰ particle size (nm)	TOFs (s ⁻¹)	Source
Pd/TiO ₂ reduced 40 °C	42–135	1000	<i>T</i> = 298 K, <i>P</i> = 1 bar	3.2–5.9	1.3–2.8	This work
Pd/TiO ₂ reduced 500 °C					9.1–21.4	
Pd/C	136–1343	n/a ^b	<i>T</i> = 323 K, <i>P</i> = 1 bar	2.5–5.6	0.81–0.96	[3]
Pd/MCM-41	875–970	7300	<i>T</i> = 323 K, <i>P</i> = 1 bar	2.5–6.8	1.0–4.0	[4]
Pd/Al-MCM-41	928–1066			2.4–7.6	1.0–6.5	
Pd/Al ₂ O ₃	54			2.1	1.0	
Pd/beta zeolite	390			2.4	1.0	
Pd/SiO ₂	234–248	1000	<i>T</i> = 303 K, <i>P</i> = 1 bar	10–12	1.2–1.6	[8]
Pd/pumice	5	1000	<i>T</i> = 298 K, <i>P</i> = 1 bar	6.3–11.0	6.0–7.7	[11,12]
Pd/organic matrices	n/a	n/a	<i>T</i> = 283 K	2.0–12.8	1.3–2.7	[14]
Pd/Al ₂ O ₃ , Pd/C	n/a	2500	<i>T</i> = 298 K, <i>P</i> = 1 bar	1.9, 5.2	0.9, 2.2	[15]
Pd/MCM-41	806–1099	2000	<i>T</i> = 298 K, <i>P</i> = 1 bar	10–23	5.1–12.9	[17]
Pd/mesoporous silica	910–1469	2500	<i>T</i> = 298 K, <i>P</i> = 1 bar	0.7–3.2	2.0–4.0	[18]

^a *T* = reaction temperature, *P* = H₂ pressure.

^b n/a = not available.

For the R500 series, (SMSI catalysts), all the catalysts exhibited very high TOFs (9.1–21.4 s⁻¹). The catalyst performance was proved in terms of both hydrogenation activity and selectivity to styrene. It may be assumed that the presence of SMSI effect favors the formation of active Pd species participating in the reaction. The strong interaction between metal and support and the formation of interfacial Pd–TiO_x sites have also been found in the Pd/TiO₂ catalysts prepared by sol–gel method [28]. They were suggested to be the reasons for the catalysts exhibiting high conversion and high yield towards butyric acid in liquid-phase hydrogenation of maleic anhydride. Remarkable high activities in the hydrogenation of alkynes were also reported for the Pd/MCM-41 catalysts prepared via simultaneous synthesis [4,17] and Pd/SiO₂ prepared by one-step flame spray pyrolysis [37]. It was suggested that simultaneous formation of Pd nanoparticles in the support matrices resulted in the formation of active ensembles for the reaction. In the present study, largest improvement on the catalytic performance for Pd/TiO₂ catalysts reduced at 500 °C was observed on the smallest crystallite size TiO₂ (Pd/TiO₂-9 nm) probably because the formation of substoichiometric TiO_x species was more facile over small crystallite size TiO₂ [46]. The ratios of TOF values of the SMSI and non-SMSI catalysts for the Pd/TiO₂ with different TiO₂ crystallite sizes (see Table 3), however, were quite similar, implying that the degree of SMSI effect on the hydrogenation rate did not depend on the Pd particle size.

4. Conclusions

The presence of SMSI on Pd/TiO₂ catalysts when reduced at 500 °C has proven to produce great beneficial effect on both catalytic hydrogenation activities and selectivities to styrene in liquid-phase semihydrogenation of phenylacetylene under mild conditions (ambient temperature and low H₂ pressure). Without SMSI effect, the turnover frequencies of Pd/TiO₂ were similar to those of the other supported Pd catalysts reported in the literature and the catalyst performance depended largely on Pd particle size. In the range of Pd particle size studied (3.2–5.9 nm), the TOF values and styrene selectivity at complete conversion of phenylacetylene increased with increasing Pd particle size.

Acknowledgments

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Article

**Preparation of Nano-Pd/SiO by One-Step Flame
Spray Pyrolysis and Its Hydrogenation Activities:
Comparison to the Conventional Impregnation Method**

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Preparation of Nano-Pd/SiO₂ by One-Step Flame Spray Pyrolysis and Its Hydrogenation Activities: Comparison to the Conventional Impregnation Method

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Characteristics and catalytic properties of the nano-Pd/SiO₂ catalysts synthesized in one-step flame spray pyrolysis (FSP) were compared to those prepared on the flame-made SiO₂ supports by conventional impregnation method. Pd⁰ metal particles/clusters <3 nm in size were obtained directly from a single-step flame process, whereas the conventional impregnation method resulted in PdO with larger crystallite sizes (in the range of 5–12 nm). Although there was little difference in the turnover frequency (TOF) values for 1-heptyne hydrogenation on the different Pd/SiO₂ catalysts prepared by impregnation, the TOF values of the flame-made catalysts decreased from 66.2 s⁻¹ to 4.3 s⁻¹ as the palladium loading increased from 0.5 wt % to 10 wt %, which suggested changes in the catalytic properties when palladium nanoparticles were formed simultaneously in the support matrices by FSP method. For both preparation methods, the palladium particle sizes remained unaltered after liquid-phase hydrogenation reaction.

1. Introduction

Catalytic hydrogenation is one of the most useful, versatile, and environmentally acceptable reaction routes available for organic synthesis, because the scope of the reaction type is very broad and many functional groups can be hydrogenated with high selectivity and high conversation.¹

Palladium catalysts are preferred for the selective partial hydrogenation of alkynes, they are usually used with a variety of modifiers to improve reaction selectivity. Metal salts, amines, amine oxides, sulfur compounds, hydroxides, and carbon monoxide are among the modifiers used. For heterogeneous systems, the catalyst performance is strongly influenced by (i) the ability to get reactants to the active sites, (ii) to establish the optimum hydrogen to alkyl surface coverage, and (iii) the rapid removal of the hydrogenated products. These constitute the mass-transfer limitations and can have an overriding impact on the ability to achieve selective hydrogenation.^{2–4} Many papers in the literature involve the selective hydrogenation of double bonds. However, more challenging, from an academic and industrial point of view, is the selective hydrogenation of alkynes. Many products obtained through this type of reaction are useful in the synthesis of natural products, such as biologically active compounds. The catalysts used must be selective to avoid the total hydrogenation of the alkynes to alkanes.

Flame synthesis is an established commercial process to make nanoparticles in large quantity and low cost.⁵ Flame spray pyrolysis (FSP) is a technique that is capable of producing a wide variety of product compositions.⁶ In particular, FSP has been demonstrated for the one-step dry synthesis of high-surface-area and highly efficient noble-metal-laden catalysts.⁷ Recently, we reported the one-step flame spray synthesis of palladium nanoparticles with an average size of 0.5–3 nm on

SiO₂ supports.⁸ The as-synthesized FSP-derived catalysts showed higher catalytic activities for the selective hydrogenation of 1-heptyne under mild conditions than the commercial SiO₂ supported Pd catalyst, with no appreciable influence on alkene selectivity.

The objective of this study is to compare the characteristics and catalytic properties of the flame spray-derived Pd/SiO₂ that has been prepared in one step to those prepared on the flame-made SiO₂ via the conventional impregnation technique. The catalysts were characterized by N₂ physisorption, X-ray diffraction (XRD), CO pulse chemisorption, transmission electron spectroscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Their catalytic activities were evaluated in the liquid-phase selective hydrogenation of 1-heptyne under mild conditions.

2. Experimental Section

2.1. Catalyst Synthesis. 2.1.1. Flame Synthesis of Pd/SiO₂. The synthesis of Pd/SiO₂ was conducted using a spray flame reactor.⁹ Palladium acetylacetonate (Aldrich) and tetraethylorthosilicate (TEOS; Aldrich) were used as palladium and silicon precursors, respectively. The precursors were prepared by dissolving in xylene (Merck; 99.8 vol %)/acetonitrile (Fluka; 99.5 vol %) mixtures (70/30 vol %) with a total metal concentration that was maintained at 0.5 M. The palladium concentration was in the range of 0–10 wt %. Using a syringe pump, 5 mL/min of precursor solution was dispersed into fine droplets by a gas-assisted nozzle fed by 5 L/min of oxygen (Thai Industrial Gas Limited; purity >99%). The pressure drop at the capillary tip was maintained at 1.5 bar by adjusting the orifice gap area at the nozzle. The spray was ignited by supporting flamelets fed with oxygen (3 L/min) and methane (1.5 L/min), which are positioned in a ring around the nozzle outlet. A sintered metal plate ring (8 mm wide, starting at a radius of 8 mm) provided an additional 10 L/min of oxygen as a sheath for the supporting flame. The product particles were collected

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on a glass fiber filter (Whatman GF/C, 15 cm in diameter) with the aid of a vacuum pump.

2.1.2. Impregnation of Palladium on Flame-Made SiO_2 . Silica supports were prepared using a spray flame reactor. A mixture of TEOS and xylene (Merck; 99.8 vol %)/acetonitrile (Fluka; 99.5 vol %) mixtures (70/30 vol %) with a total silicon concentration of 0.5 M was used as the starting precursors. The flame conditions were identical to flame-made Pd/ SiO_2 catalyst (explained in Section 2.1.1). The Pd/ SiO_2 catalysts were prepared by incipient wetness impregnation of flame-made SiO_2 with a desired amount of an aqueous solution of palladium nitrate [$\text{Pd}(\text{NO}_3)_2$] (Aldrich). The palladium metal loading of the catalysts was in the range of 0–10 wt %. The catalysts were dried at 110 °C for 24 h and calcined in air at 300 °C for 2 h, using a ramp rate of 1 °C/min.

2.2. Characterization. XRD patterns were recorded with a Siemens Model D5000 system, using nickel-filtered Cu K α radiation. The crystallite size (d_{XRD}) was determined using the Scherrer equation. The specific surface areas, average pore diameters, and pore size distribution were determined via the physisorption of nitrogen (N_2) using a Micromeritics Model ASAP 2020 apparatus. The palladium oxide particle size and distribution of palladium on silica supported was observed using a JEOL-JEM Model 200CX transmission electron microscopy (TEM) microscope operated at 100 kV. The active sites and the relative percentages dispersion of palladium catalyst were determined by the CO-pulse chemisorption technique, using Micromeritics Model ChemiSorb 2750 equipment.

2.3. Selective Hydrogenation of 1-Heptyne. The catalytic hydrogenation of 1-heptyne (Aldrich) was performed in a magnetically stirred 50-mL stainless steel autoclave reactor. Twenty milligrams of Pd/ SiO_2 catalyst was dispersed in 10 mL of 2 vol % 1-heptyne (Fluka) in toluene. The reaction was performed under flowing hydrogen at 1 bar and 30 °C for 5–40 min. The liquid reactants and products were analyzed by a gas chromatography (GC) system that was equipped with a flame ionization detection (FID) detector (Shimadzu, Model GC-14A). Prior the reaction testing, the Pd/ SiO_2 catalyst was reduced by hydrogen gas at a flow rate of 50 mL/min at room temperature for 2 h.

3. Results and Discussion

3.1. Catalyst Properties. Figure 1 shows the XRD patterns of all the Pd/ SiO_2 catalysts that have palladium loadings of 0.5–10 wt %. The patterns in Figure 1a correspond to the flame-made powder, which has been prepared in one step, while the patterns in Figure 1b are for impregnation-made powder (two-step synthesis). Both flame- and impregnation-made powders for all palladium loadings exhibited the characteristic peaks of the amorphous silica. For the flame-made Pd/ SiO_2 powders, an additional peak corresponding to the Pd^0 metal was observed at $2\theta = 41^\circ$ for 10 wt % Pd/ SiO_2 catalyst. While the additional peaks corresponding to the PdO phase were observed at $2\theta = 33.8^\circ$ instead for all the impregnation-made catalysts. The broadness of the flame-made Pd phases peaks (a) compared to the impregnation-made material (b) is consistent with smaller primary particles in the flame- than in the wet-made powder. Such result suggests the better dispersion of Pd metal cluster on the silica support was obtained by one-step flame process.

Figure 2 shows the TEM micrographs of flame- and impregnation-made Pd/ SiO_2 catalysts with different palladium contents. TEM images of the flame made-powder (see Figures 2a, b, and c) show the aggregation of SiO_2 primary particles. However, the particle areas of SiO_2 cannot be observed clearly. Palladium

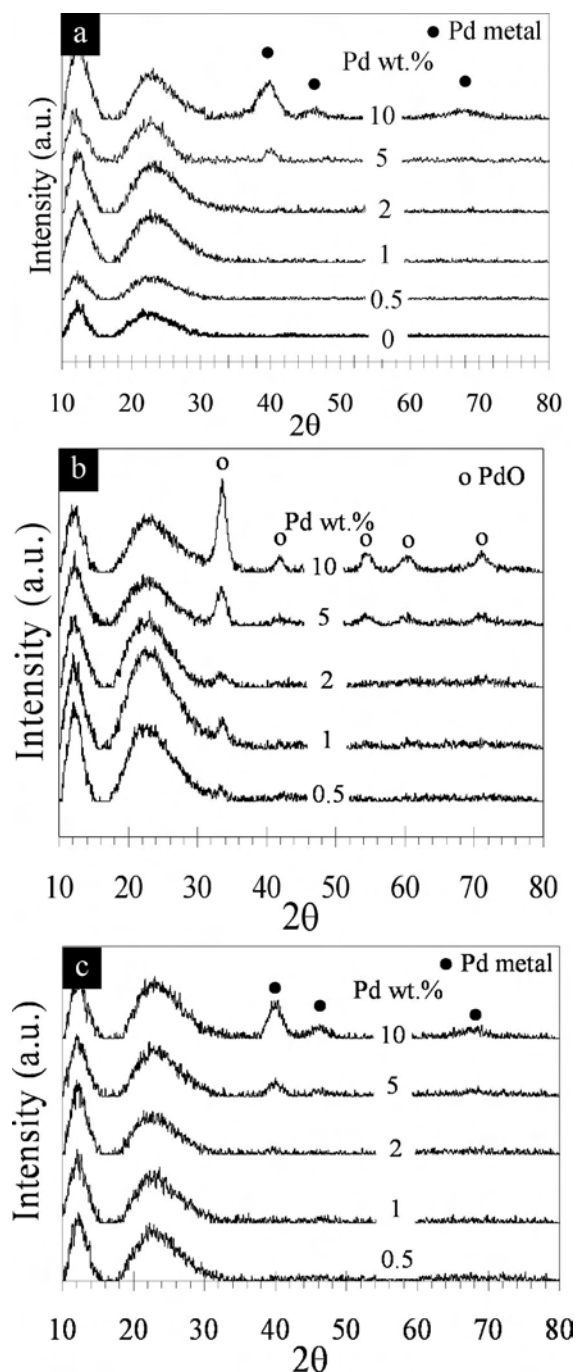


Figure 1. XRD patterns of all Pd/ SiO_2 catalyst with palladium loadings in the range of 0–10 wt %: (a) the flame-made catalyst, (b) the impregnation-made catalyst, and (c) the impregnation-made catalyst after reduction.

clusters confined to the surface of SiO_2 particles were determined to have a spherical shape, with an average diameter of 0.5–3 nm with a narrow size distribution. The results were similar to the Pd/ Al_2O_3 and Pt/ Al_2O_3 catalysts prepared via flame processing.^{6,10} It was found that the size of the palladium clusters increased from 0.5 nm to 3 nm as the palladium contents increased from 0.5 wt % to 2 wt % and remained essentially the same size even after increasing the palladium loading to 10 wt %. For the impregnation-made catalysts, the SiO_2 particles were identical to those synthesized in one step. However, the crystallite sizes of PdO were larger and were in the range of 2–10 nm for palladium loadings of 0–10 wt %. The results were in good agreement with the observation by X-ray diffraction (XRD).

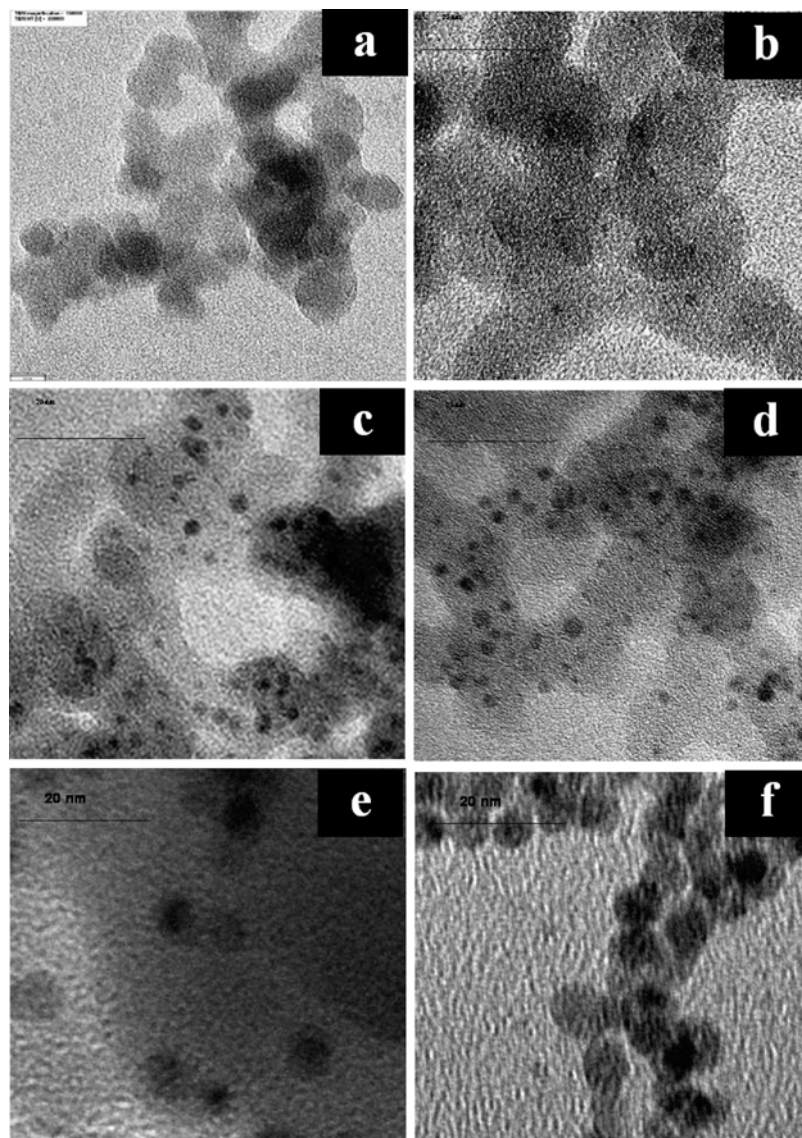


Figure 2. Transmission electron microscopy (TEM) micrographs of flame- and impregnation-made Pd/SiO₂ catalyst with different palladium contents: (a) SiO₂, (b) flame-made with 0.5 wt % palladium, (c) flame-made with 5 wt % palladium, (d) flame-made with 10 wt % palladium, (e) impregnation-made with 5 wt % palladium, and (f) impregnation-made with 10 wt % palladium.

Table 1. Physicochemical Properties of Flame- and Impregnation-Made Pd/SiO₂ Catalysts

catalyst	BET surface area (m ² /g)	Particle Size (nm)		pore volume (cm ³ /g)	average pore size (Å)	CO Chemisorption Results		
		SiO ₂	Pd phase			CO uptake (molecule CO/g-cat)	%Pd dispersion	Pd ⁰ particle size, <i>d_p</i> (nm)
Flame-Made Catalysts								
SiO ₂	196	14.0	n/a ^a	0.48	90.0	n/a	n/a	n/a
0.5% Pd/SiO ₂	246	11.1	n.d. ^b	0.43	67.3	0.97	3.42	33
1% Pd/SiO ₂	251	10.9	n.d. ^b	0.46	73.7	1.93	3.40	33
2% Pd/SiO ₂	260	10.9	n.d. ^b	0.49	77.6	3.27	2.88	39
5% Pd/SiO ₂	306	8.9	n.d. ^b	0.59	76.1	13.38	4.71	24
10% Pd/SiO ₂	299	9.1	2.8	0.69	90.9	25.84	4.55	25
Impregnation-Made Catalysts								
0.5% Pd/SiO ₂	174	15.7	n.d. ^b	0.91	204.4	3.79	14.6	7.7
1% Pd/SiO ₂	171	15.9	n.d. ^b	0.91	193.5	5.02	9.7	11.6
2% Pd/SiO ₂	133	20.5	n.d. ^b	0.60	249.1	7.70	7.4	15.2
5% Pd/SiO ₂	109	25.0	12.4	0.47	143.5	17.99	7.0	16.1
10% Pd/SiO ₂	128	21.3	5.2	0.50	168.2	27.80	5.4	20.8

^a Not available. ^b Not determined.

Table 1 summarizes the physical and chemical properties of flame- and impregnation-made Pd/SiO₂ catalysts. The Brunauer–Emmett–Teller (BET) surface areas of flame-made catalysts

increased from 195 m²/g to 305 m²/g as the palladium contents increased from 0 wt % to 5 wt % and became steady when the palladium content as increased to 10 wt %. The pore volumes

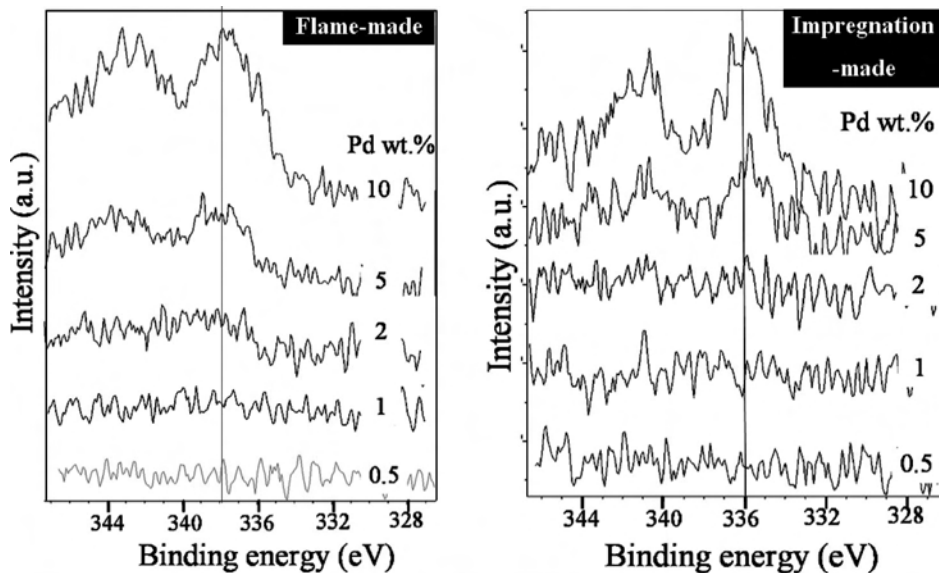


Figure 3. XPS spectra of Pd 3d_{5/2} for flame-made and impregnation-made Pd/SiO₂ catalysts.

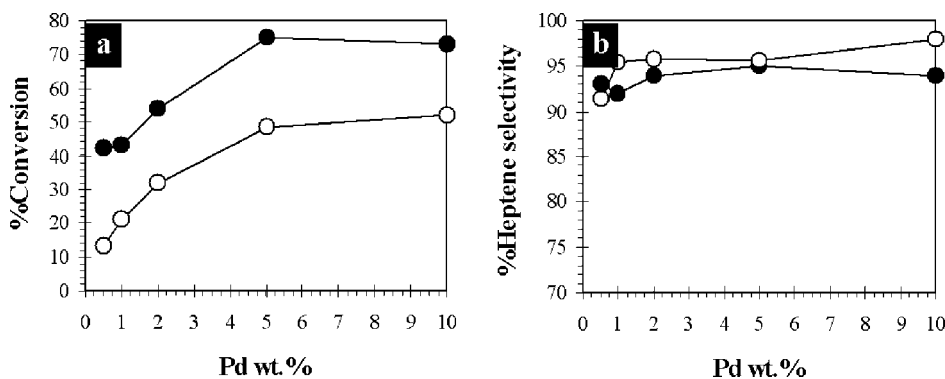


Figure 4. Plots of (a) 1-heptyne conversion and (b) heptene selectivity, relative to the palladium loading (0.5–10 wt %) of flame-made Pd/SiO₂ catalyst (solid circles, ●) and an impregnation-made Pd/SiO₂ catalysts (open circles, ○).

of flame-made catalysts were ca. 0.5 cm³/g and were not significantly changed as the palladium loading increased. The pore-size distribution patterns of flame-made samples calculated

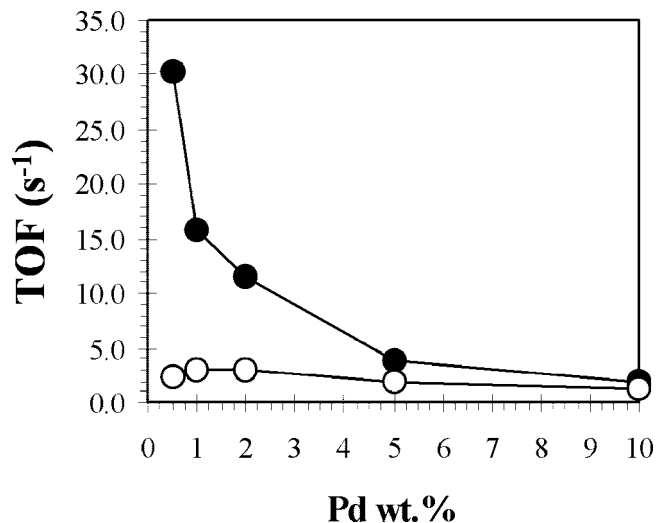


Figure 5. Plots of the turnover frequency (TOF) number, relative to the palladium loading (0.5–10 wt %) of a flame-made Pd/SiO₂ catalyst (solid circle, ●) and an impregnation-made Pd/SiO₂ catalyst (open circle, ○).

by the Barrett–Joyner–Halenda (BJH) equation exhibited the typical pattern for mesopore structure (not shown). For the impregnation-made catalysts, the BET surface areas gradually decreased from 196 m²/g to 128 m²/g as the palladium loading increased from 0 wt % to 10 wt %. A decrease in the BET surface areas with increasing metal loading is typical for supported metal catalysts prepared using a conventional impregnation method. It was probably due to sintering during the calcination process and pore blockage of Pd/PdO clusters. However, increases in the BET surface area with palladium loading is possible for the flame-made Pd/SiO₂ catalysts. Formation of the Pd/SiO₂ nanoparticles by FSP was considered as follows: the sprayed droplets of precursor solution were evaporated and combusted as soon as they met the flame at very high temperature and released the metal atoms, then nucleation and growth of particles by coagulation and condensation occurred along the axial direction of the flame. Comparing to silica, the vapor pressure of Pd/PdO was much higher in the hot flame environment, and consequently SiO₂ particle formation started earlier. Further downstream the flame, at lower temperatures, Pd/PdO started to form small particles and/or deposited directly on the SiO₂ support. This particle formation mechanism was also suggested for Pd/Al₂O₃ and Pt/TiO₂.^{10,11} With the addition of palladium, the surface area

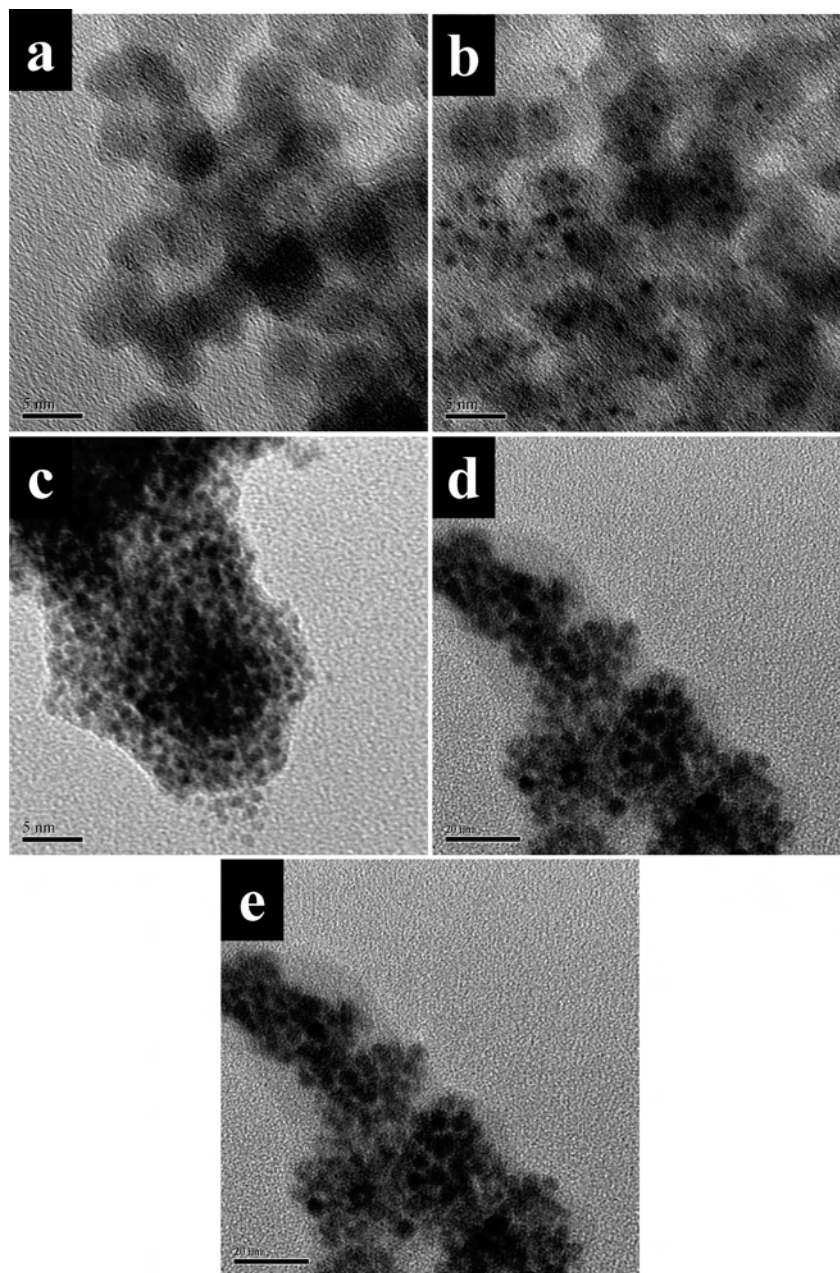


Figure 6. TEM micrographs of flame- and impregnation-made Pd/SiO₂ spent catalyst with different palladium contents; (a) flame-made with 0.5 wt % palladium, (b) flame-made with 5 wt % palladium, (c) flame-made with 10 wt % palladium, (d) impregnation-made with 5 wt % palladium, and (e) impregnation-made with 10 wt % palladium.

of the SiO₂ support increased as the particle size decreased. This suggests that the palladium dopants inhibited the growth of the SiO₂ particles. This result is in good agreement with the flame-synthesized Au–Ag/SiO₂ nanoparticles that were reported by Hannemann et al.¹²

The relative amounts of surface-active palladium metal on the catalyst samples were calculated from CO chemisorption experiments at room temperature, based on the assumption that one carbon monoxide molecule (CO) adsorbs on one palladium (Pd) site.^{13,14} The results are also given in Table 1. For the flame-made catalysts, the Pd active sites increased from 0.97×10^{18} sites/g-catalyst to 25.84×10^{18} sites/g-catalyst, corresponding to the increase in palladium metal dispersion from 6.3 to 8.4 as the palladium content increased from 0.5 wt % to 10 wt %. For the impregnated catalysts, the active sites increased from 3.79×10^{18} sites/g-catalyst to 27.8×10^{18} sites/g-catalyst, corresponding to the increase in palladium metal dispersion from

14.5 to 5.4 as the palladium contents increased from 0.5 wt % to 10 wt %. Based on CO chemisorption results, the particle size (d_p) of the impregnated-made Pd⁰ was determined to be smaller than that of the FSP-made Pd⁰. It is likely that there was an overestimation of the palladium particle size, which would have been attributed to low CO chemisorption measurement for the flame-made catalysts. The palladium particles on the FSP-made catalysts may be surrounded by a support matrix (i.e., in the form of Si–O group), resulting in the inhibition of CO chemisorption, and/or palladium on the flame-made catalysts that was in a partially oxidized state.

XPS spectra of Pd 3d for the flame- and impregnation-made catalysts are shown in Figure 3. While the binding energies of Pd 3d_{5/2} for the flame-made catalysts were observed at 337.4 eV, those of the impregnation-flame-made variety were observed at 335.7 eV. Compared to the binding energy for Pd⁰ metal, which is typically ~335.0 eV,¹⁵ it is likely that the FSP may

result in partially oxidized PdO. The results are in good agreement with extended X-ray analysis fine structure (EXAFS) results for other FSP-synthesized supported palladium catalysts reported by Baiker et al.,¹⁶ Pratsinis et al.,¹⁷ and Grunwaldt et al.¹⁸ Such phenomena strongly affected the CO chemisorption results and the dispersion of low-loaded catalysts. Moreover, it is possible that there was stronger interaction between the palladium and the SiO₂ support for the flame-synthesized catalysts, compared to those prepared by conventional impregnation.

3.2. Catalytic Behavior in Liquid-Phase Selective Hydrogenation of 1-Heptyne. Selective hydrogenation reaction of 1-heptyne to 1-heptene was used as the model reaction to investigate the catalytic properties of flame-made and impregnation-made Pd/SiO₂ catalysts. Figure 4 compares the relationship of 1-heptyne conversion and 1-heptene selectivity with palladium loading (expressed as a weight percentage) for the flame-made and impregnation-made Pd/SiO₂ catalysts. For flame-made catalysts, the conversions of 1-heptyne increased from 42% to 75% as the palladium contents increased from 0.5 wt % to 5 wt % and remained constant when the palladium content was increased to 10 wt %. The selectivity for 1-heptene also increased from 92% to 95% as the palladium content increased from 0.5 wt % to 10 wt %. Similar behavior was observed for the impregnation-made catalysts: the conversions of 1-heptyne increased from 13% to 52% as the palladium content increased from 0.5 wt % to 5 wt % and remained constant when the palladium content was increased to 10 wt %. The selectivity for 1-heptene increased from 91% to 98% as the palladium content increased from 0.5 wt % to 10 wt %. The results indicated that the activity and selectivity for the reaction increased as the active size increased, corresponding to the increasing palladium content. However, all the flame-made Pd/SiO₂ powders exhibited higher hydrogenation activity than the impregnation-made Pd/SiO₂ powders. In all cases, the other product besides heptene was heptane.

The activity for 1-heptyne hydrogenation of the catalysts was also expressed in terms of turnover frequency (TOF), which is defined as the number of 1-heptyne molecules converted per atom of exposed palladium on the surface per unit time. The Pd atomic concentrations on the catalyst surface were based on the CO chemisorption results. Figure 5 shows the correlation between TOF and the palladium loading (expressed as a weight percentage) of the flame-made and the impregnation-made Pd/SiO₂ catalysts. The flame-made powders exhibited higher TOF values than the impregnation-made powders. However, the TOF values for flame-made catalysts decreased from 66.2 s⁻¹ to 4.3 s⁻¹ as the palladium loading (expressed as a weight percentage) increased from 0.5 wt % to 10 wt %, whereas the TOF values of impregnation-made catalysts remained constant at ~1–3 s⁻¹. In liquid-phase selective hydrogenation, the palladium dispersion (palladium metal size), metal–support interaction, and electronic state of palladium usually have an important role.^{19,20} In this paper, the flame-made catalyst with low palladium contents exhibited remarkably high TOF values, compared to the literature and the impregnation-made catalysts. The results reported here were different from the study by Baiker et al.¹⁰ on the enantioselective hydrogenation over noble-metal catalysts, in which larger particles exhibited higher activities. However, it is suggested that the simultaneous formation of palladium nanoparticles in the support matrices during flame spray synthesis could result in the formation of active ensembles for the reaction. Such phenomena was somewhat similar to those of Pd/MCM-41 catalysts prepared via simultaneous synthesis (simultaneous self-assembling of the MCM-41 and Pd incor-

poration), where remarkably high activities in the alkyne hydrogenation were observed.^{21,22}

TEM micrographs of the spent catalysts for both flame- and impregnation-made catalysts are shown in Figure 6. The spherical shape of Pd⁰ metal particles was still observed, and there was no significant change in the particle/cluster size of Pd⁰ metal after reaction, regardless of the preparation method that was used.

4. Conclusions

Nanocrystalline Pd/SiO₂ catalysts were prepared via one-step flame spray pyrolysis (FSP) and compared to the conventional impregnation of palladium on flame-made SiO₂ (two-step synthesis). The flame-made catalyst powders consisted of polyhedral silica primary particles 10–20 nm in size and nanocrystals of Pd⁰ metal with average particle/cluster sizes between 0.5–3 nm for a palladium loading of 0.5–10 wt %. The PdO with average crystallite sizes of 5–12 nm was observed instead for the impregnation-made catalysts. The flame-made catalysts exhibited better catalytic performances for selective hydrogenation of 1-heptyne compared to the impregnation-made catalysts. The remarkably high turnover frequency (TOF) values of the flame-made catalyst were probably due to the formation of active ensembles of palladium nanoparticles in the support matrices during FSP synthesis.

Acknowledgment

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Synthesis of Au–ZnO and Pt–ZnO nanocomposites by one-step flame spray pyrolysis and its application for photocatalytic degradation of dyes

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ABSTRACT

Au–ZnO and Pt–ZnO nanocomposites have been synthesized by one-step flame spray pyrolysis (FSP) and characterized by X-ray diffraction (XRD), nitrogen adsorption, UV–vis spectroscopy, photoluminescence (PL), and transmission electron microscopy (TEM). The XRD and TEM results revealed that Au and Pt metallic phase were formed late during flame synthesis after ZnO was formed. Their average particle/cluster sizes were ranged between 3 and 7 nm depending on the amount loading (1 and 3 wt%). Although both of the FSP-derived Au–ZnO and Pt–ZnO possessed similar physical properties (i.e., crystallite size and specific surface area), an improvement in photocatalytic degradation of methylene blue in comparison to pure ZnO and commercial titania photocatalysts (JRC-TiO₂ and P-25) was observed only for the Au–ZnO and not for the Pt–ZnO due probably to the different type of Fermi-level equilibration between Au and Pt.

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1. Introduction

Wastewater contaminated with residual dyes from textile, paper, and other industries is a source of environmental problems. The photo-assisted catalytic decomposition of organic pollutants employing semiconductors as photocatalysts has been a promising method for the degradation of pollutants in wastewater. Among the semiconductors, TiO₂ is widely employed as a photocatalyst. However, ZnO is a low cost alternative to TiO₂ because it has similar band gap energy (3.2 eV) with relatively large quantum efficiency [1]. Higher photocatalytic efficiencies of ZnO have also been reported especially for degradation of organics in aqueous solutions [2–7].

The combination of semiconductor substrate (i.e. TiO₂ and ZnO) and metal cluster such as Ag, Au, Pd and Pt has been reported to enhance photocatalytic activity by trapping the photo-induced charge carriers, thereby improving the charge transfer processes [8–14]. The noble metals of gold and platinum were used for the metal–ZnO formation because of high electron affinity behavior [15] and the highest Schottky barrier produced among the various metals [14]. For ZnO *n*-type semiconductor (with a work function (ϕ_s) of ~ 4.3 eV) in contact with noble metals with a work function ϕ_m (Au: 5.1 eV and Pt: 5.65 eV) [9] $> \phi_s$, a Schottky barrier will form at the junction, facilitating the electron capture.

Flame aerosol synthesis is used to make commercially available nanoscale materials in bulk quantities at low cost [16], for example, the widely used photocatalyst Degussa P25-TiO₂ is produced by this technique. In particular, flame spray pyrolysis (FSP) has been demonstrated to be an effective and versatile process for one-step, dry synthesis of high surface area noble metal laden catalysts [17]. This method provides good control of particle size, particle crystal structure and also can produce highly pure particles continuously without further subsequent processes such as drying, calcination, and milling. In the present work, Au–ZnO and Pt–ZnO nanocomposites were prepared via one-step flame spray pyrolysis and characterized by X-ray diffraction (XRD), surface area analysis, transmission electron microscopy (TEM), photoluminescence, and UV–vis spectrophotometer. Their photocatalytic activities were evaluated in the degradation of methylene blue (MB) and compared to those of the commercially available TiO₂-P25 and JRC-TiO₂ photocatalysts.

2. Experimental

2.1. Flame-synthesis of Au–ZnO and Pt–ZnO

Synthesis of Au–ZnO powders were carried out using a spray flame reactor [18]. Zinc naphthanate (Aldrich, <50% in mineral spirits) and gold (III) chloride trihydrate (Aldrich, 99.9+%) were used as zinc and gold precursors. The precursors were dissolved in ethanol (J.T. Baker, 99.9%) with total metal concentration maintained at

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0.8 M and the gold concentration ranged between 0 and 5 wt%. Using a syringe pump, 8 mL/min of precursor solution was dispersed into fine droplets by a gas-assist nozzle fed by 3 L/min of oxygen designated as a 8/3 flame. The pressure drop at the capillary tip was maintained at 1.5 bar by adjusting the orifice gap between the nozzle. The reactor was water-cooled to avoid evaporation or decomposition of the precursor within the feed lines. The flame was surrounded and ignited by a concentric premixed methane/oxygen pilot flame (CH_4 1.5 L/min, O_2 3.0 L/min) that was sheathed further by flowing oxygen (25 L/min) through a sintered metal plate ring (8 mm wide, starting at a radius of 8 mm). The powder particles were collected on a glass-fiber filter (GF/D Whatman, 257 mm diameter) with the aid of a vacuum pump.

Pt-ZnO was prepared by the same condition but changed raw materials for preparation of a liquid-phase precursor from gold (III) chloride trihydrate to platinum acetylacetonate (Fluka) and solvent for dissolved platinum acetylacetonate from ethanol to xylene (MERCK, 99.8 vol.%) / acetonitrile (Fluka, 99.5 vol.%) mixtures 70/30 vol.%.

2.2. Characterization

Powder X-ray diffraction was performed by a SIEMENS XRD D5000 using CuK α radiation. The crystallite size (d_{XRD}) was estimated by using the Scherrer equation. The specific surface area was measured by N_2 physisorption using a Micromeritics ASAP 2000 automated system and the Brunauer–Emmet–Teller (BET) method. Each sample was degassed under vacuum at $<1 \times 10^{-5}$ bar in the Micromeritics system at 300 °C for 3 h prior to N_2 physisorption. The particle morphology was observed using JEOL Model JEM-2010 transmission electron microscope operated at 200 keV. PL measurement was carried out on a Fluorescence spectrophotometer (Perkin–Elmer LS-50) using a Xenon lamp as the excitation source at room temperature. The sample was dispersed in ethanol using ultrasonic bath and the excitation wavelength used in PL measurement was 325 nm. The UV–vis absorption spectra of the photocatalysts were obtained in the range of 200–900 nm using a UV–vis scanning spectrophotometer (Perkin–Elmer lampda 650).

2.3. Photocatalytic testing

A basic aniline dye, methylene blue (Unilab, Asia Pacific Specialty Chemicals Limited) was used as a probe molecule to evaluate the photocatalytic activities. The photocatalytic reaction was conducted at room temperature under UV light 2×15 W UV tube predominantly emit at 365 nm (Philips) with the average light intensity on the reaction beaker (pyrex) at a distance of 6 cm from the lamp was found to be 4.7×10^{-4} W cm^{-2} . The reaction was carried out with 20 mg of catalyst was dispersed in 200 mL of 10 ppm methylene blue aqueous solution. Prior to irradiation, the suspensions were magnetically stirred in the dark for 15 min to establish the adsorption/desorption equilibrium of methylene blue. Approximately 3.5 mL samples were withdrawn every 10 min. Before analysis, the aqueous samples were centrifuged to remove any suspended solid catalyst particles. The residual concentration of methylene blue was measured at 665 nm using the UV–vis spectrophotometer (Perkin–Elmer lampda 650) in liquid cuvette configuration with de-ionized water as reference. The percentage of degradation was calculated by using the equation given below:

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

In which C_0 is the initial dye concentration and C is the dye concentration after the treatments. The UV–vis spectra were also collected using an absorbance method.

3. Results and discussion

3.1. Particle characterization

X-ray diffraction was used to investigate the changes of phase structure and crystallite size of the FSP-made Au–ZnO and Pt–ZnO powders. The XRD patterns are shown in Fig. 1. The characteristic peaks of the ZnO wurtzite structure (JCPDS Card File No. 36-1451) were apparent for every sample. For the FSP-made Au–ZnO powders with 3 wt% Au loading, additional peaks corresponding to Au⁰ metal ((111), (200), and (220)) were clearly observed at $2\theta = 38, 44.3$ and 64.5° . Similarly, for the FSP-made Pt–ZnO powders with 3 wt% Pt loading, additional peaks corresponding to Pt⁰ metal ((111) and (200)) were observed at 39.7 and $46.2^\circ 2\theta$, respectively. Such results suggest that most of the Au and Pt atoms were not incorporated in the ZnO lattice or only to a very small extent. It is likely that Au and Pt metallic phases were formed on the ZnO surface late during flame synthesis after the ZnO particles were already formed, similar to those of Ag–ZnO synthesized by FSP method previously reported by our group [10].

The TEM images of FSP-made Au–ZnO and Pt–ZnO with 1 and 3 wt% metal loadings are shown in Fig. 2. Spherical metal nanoparticles/clusters dispersed on the surface of ZnO were clearly observed as the darker spots. Average diameters of Au particles/clusters deposited on ZnO were determined to be approximately 4.0 and 6.7 nm for 1% Au–ZnO and 3% Au–ZnO, respectively. For similar metal loading, the average particle/cluster size of Pt particles deposited on ZnO was slightly smaller than those of Au–ZnO, e.g., 3.3 nm for 1% Pt–ZnO and 5.0 nm for 3% Pt–ZnO. The corresponding selected-area electron diffraction (SAED) patterns for all the samples (results not shown) illustrated spotty rings patterns, indicating its highly crystalline ZnO wurtzite structure, which was in good agreement with the XRD results.

Table 1 summarizes the physical properties of the FSP-made pure ZnO, Pt–ZnO, and Au–ZnO catalysts. The average crystallite size (d_{XRD}) of ZnO, Au and Pt were calculated from (101), (111) and (111) diffraction peaks of ZnO, Au, and Pt, respectively using Scherrer equation. The d_{XRD} of ZnO for both Au–ZnO and Pt–ZnO catalysts were calculated to be in the range of 34.6–39.8 nm and were not significantly changed as the wt% metal (Au and Pt) content increased. The d_{TEM} data were consistent with the d_{XRD} values indicating that these particles are single crystalline. Addition of Au and Pt during flame synthesis of ZnO did not significantly alter the specific surface area of ZnO.

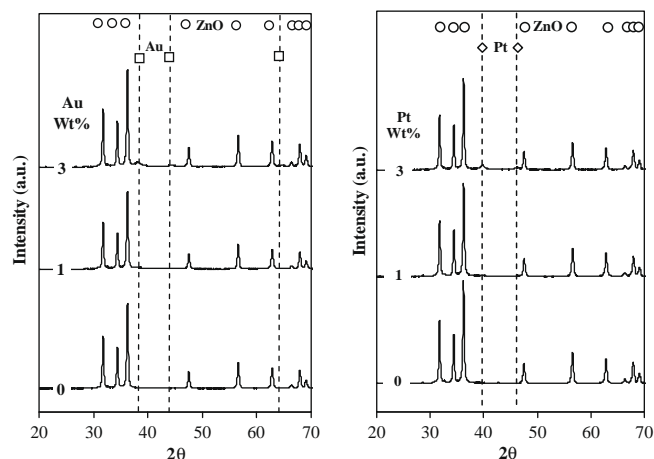


Fig. 1. XRD patterns of flame-made (a) Au–ZnO and (b) Pt–ZnO powders. All powders exhibit the typical pattern for hexagonal zincite (○). (□) and (◇) represent the characteristic pattern of Au and Pt metal, respectively.

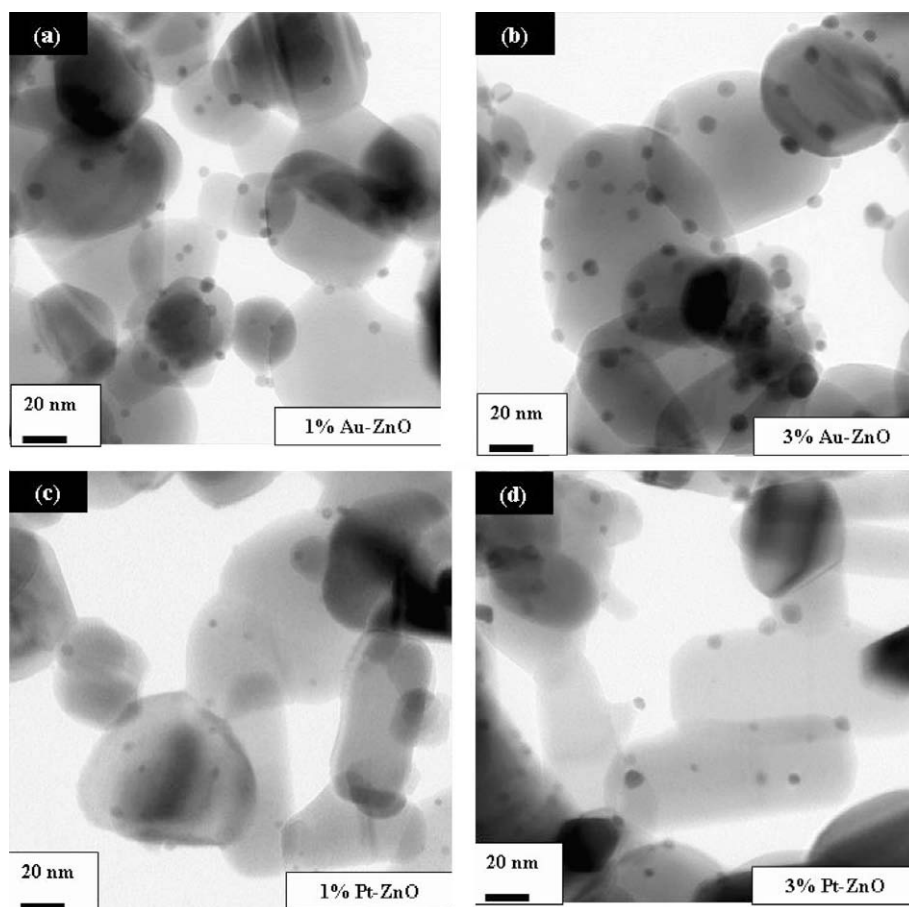


Fig. 2. TEM images of (a) 1% Au-ZnO, (b) 3% Au-ZnO, (c) 1% Pt-ZnO, and (d) 3% Pt-ZnO. The darker spots on the TEM images (a and b) are Au deposits and (c and d) are Pt deposits.

Table 1
Characteristics of the FSP-made pure ZnO, Pt-ZnO, and Au-ZnO catalysts.

Sample	<i>d</i> XRD (nm) ^a		<i>d</i> TEM (nm) ^b		BET (m ² /g)
	ZnO	Metal	ZnO	Metal	
ZnO	38.3	n.d. ^c	37.7	n.d.	18.6
1% Au-ZnO	37.3	n.d.	37.1	4.0	19.2
3% Au-ZnO	38.9	5.8	38.9	6.7	16.1
1% Pt-ZnO	34.6	n.d.	35.0	3.3	23.9
3% Pt-ZnO	38.9	5.8	36.5	5.0	19.1

^a Average crystallite size calculated by Scherrer equation.

^b Calculated from the average size of 40 particles.

^c n.d. = not determined.

The UV-vis absorbance spectra of FSP-made Au-ZnO and Pt-ZnO powders are shown in Fig. 3. The absorption at visible wavelengths (400–900 nm) of Au-ZnO increased with increasing Au contents due to the surface plasmon resonance of the Au nanoparticles, indicating the presence of Au metal clusters which is in agreement with the XRD and TEM results. The absorption results were also consistent with the visible powder color shift from white, to light purple, and dark purple, with increasing Au loadings from 0 to 3 wt%. Similarly, the UV-vis spectra of flame-made Pt-ZnO powders also show that absorption at visible wavelengths increased with increasing platinum content, consistent with the visible powder color shift from white, to light gray, and gray. It should be noticed that while the absorption at visible wavelengths of the FSP-made Pt-ZnO showed constant absorption, variation absorption was evident for the FSP-made Au-ZnO. It has been reported

that if equal sized metal clusters are formed, constant absorption in the visible region corresponding to the excitation from the valence band of ZnO to the unoccupied level of metal cluster will be observed [15].

PL emission spectra are useful to disclose the efficiency of charge carrier trapping, immigration, and transfer, and to understand the fate of electron-hole pairs in semiconductor particles since PL emission results from the recombination of free carriers. In this study, the PL emission spectra of the FSP-made Au-ZnO and Pt-ZnO with different amounts of metal loading were examined and compared to the pure ZnO with excitation wavelength of 325 nm. The results are shown in Fig. 4. The spectrum of pure ZnO powder mainly consists of two emission bands: one is the UV near-band-edge emission (NBE) at ~385 nm and the other is the visible emission that usually associates with the deep level emission (DLE) in ZnO [19]. The blue emission at ~425 nm and weak blue emission at ~445 nm most likely occurs from the donor level of Zn interstitial to acceptor energy level of Zn vacancy [20]. The blue-green band around 470 nm is induced by radiative transition of electron from shallow donor levels, created by the oxygen vacancy to valence band [21]. The green emission at ~530 nm is commonly observed for ZnO, and is attributed to the singly ionized oxygen vacancy in ZnO [22]. The UV near-band-edge emission (NBE) spectra of the Pt-ZnO, Au-ZnO and pure ZnO showed similar peak positions, but with different PL intensities. It can be concluded that deposition of Pt and Au on ZnO during flame spray synthesis did not change much the band edge, but resulted in the reduction of PL emission significantly. The decrease of PL intensity for the Au-ZnO and Pt-ZnO nanoparticles may be attributed to the

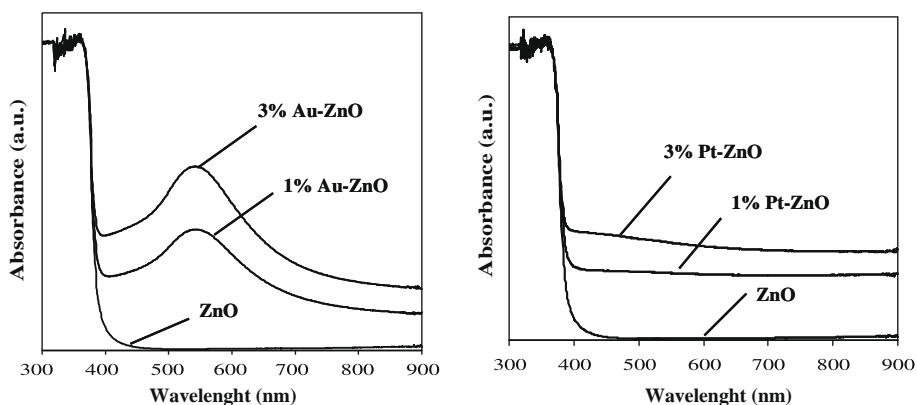


Fig. 3. UV-vis spectra of the flame-made (a) Au-ZnO and (b) Pt-ZnO.

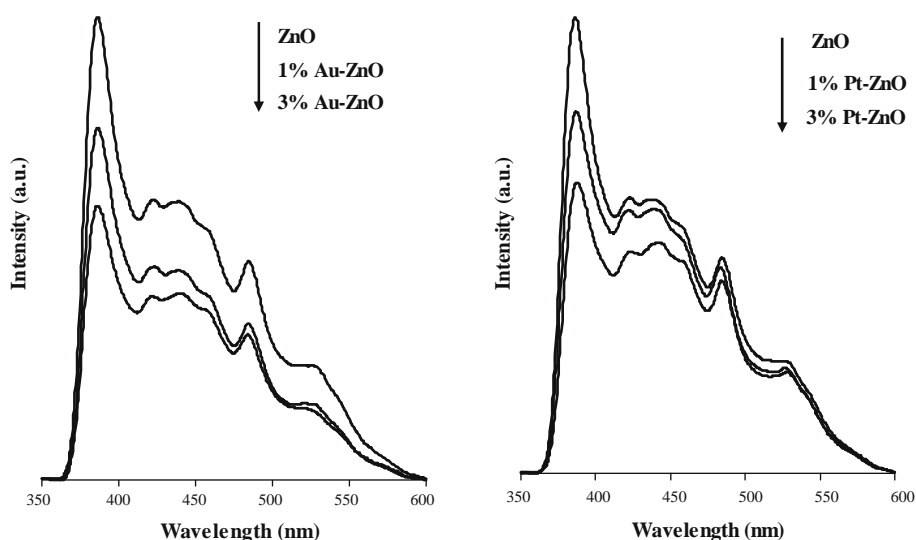


Fig. 4. PL spectra for (a) Au-ZnO and (b) Pt-ZnO with the excitation wavelength of 325 nm.

capture of noble metal ions. The PL emission mainly resulted from the recombination of excited electrons and holes, thus the lower PL intensity indicated the lower recombination rate of electron–holes under irradiation of visible light. In other words, the weaker the excitonic PL spectrum, the higher the separation rate of photo-induced charges carriers [23]. From the figures, the PL emission spectrum of Au-ZnO was lower than that of Pt-ZnO especially at deep level emission. It is likely that the FSP-made Au-ZnO had higher separation rate of photo-induced charges than the FSP-made Pt-ZnO.

3.2. Photocatalytic testing

Fig. 5 shows the catalytic performances for MB photodegradation of the flame-made ZnO, Au-ZnO and Pt-ZnO nanopowders. Irradiation in the absence of photocatalyst for 60 min revealed no change in the MB concentration, confirming that the MB cannot be degraded by 365 nm irradiation alone. For the Au-ZnO powders, the observed photocatalytic activity was enhanced especially with 3% Au-ZnO. The enhancement of photocatalytic activity of pure ZnO by doping with small amount of Au suggests that Au clusters (small size of Au nanoparticles) acted as a separation center. According to Subramanian et al. [8], the photogenerated electrons are stored in the Au nanoparticles and induce a shift of the Fermi-level toward more negative potentials. The transfer of electrons to

Au nanoparticles continues until the Fermi level reaches close to the conduction band edge of ZnO. The recombination of the photo-generated electron–hole pairs in the ZnO crystal are thus reduced, and thereby, promoting photocatalytic activity. The photocatalytic activity of the flame-made Au-ZnO showed good agreement with the PL spectra measurement. For the Pt-doped flame-made ZnO, poor photocatalytic activity for MB degradation was observed. The reason for this would be related with nature of the metal nanoparticles brought in contact with the irradiated semiconductor. Pt is ohmic type which differs from the case of FSP-made Au-ZnO. Pt deposited on ZnO neither induced the Fermi-level shift toward more negative potentials nor stored photogenerated electrons in the Pt nanoparticles. On the other hand, it merely facilitated discharge of the photogenerated electrons into the electrolyte. Thus, Pt deposited on ZnO did not produce a longer electron–hole pair separation lifetime and enhance photocatalytic activity. The results were in good agreement with the PL spectra measurement. The Schottky barrier formation in the presence of Au and the ohmic contact in the presence of Pt were found to be in good agreement with the well-established trends in the literature. Subramanian et al. [8] monitored the emission intensity of ZnO nanoparticles during Pt and Au metal ion reduction on a ZnO surface. The results show no significant changes in the emission for Pt-ZnO system suggesting that the contact between ZnO and Pt particles remained ohmic in nature and facilitated discharge of photogenerated elec-

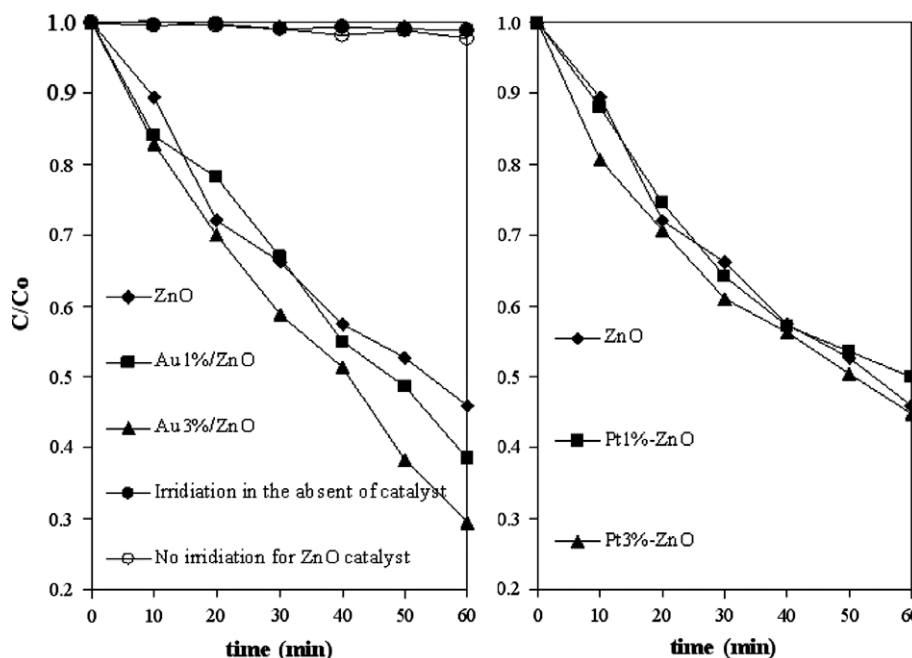


Fig. 5. Photodegradation of MB in the presence of pure ZnO, Au-ZnO, and Pt-ZnO (error of measurement was $\pm 2\%$).

Table 2

Photocatalytic performance in photodegradation of methylene blue for pure ZnO, Au-ZnO, and Pt-ZnO prepared via FSP method in comparison to P-25 and JRC-TiO₂ photocatalysts.

Sample	MB conversion after 1 h (%)	Rate constant (h^{-1})
ZnO	54	0.80
Au 1 wt%-ZnO	62	0.89
Au 3 wt%-ZnO	71	1.14
Pt 1 wt%-ZnO	50	0.73
Pt 3 wt%-ZnO	55	0.85
TiO ₂ (JRC)	18	0.19
TiO ₂ (P25)	57	0.80

trons into the solution. The difference between electron storage behavior for both catalysts has also been suggested by Wood et al. [24].

Based on the MB conversions at 1 h time-on-stream and apparent first-order reaction rate constants of the various photocatalysts (Table 2), the FSP-made Au-ZnO with 3 wt% Au loading showed the highest photocatalytic activity. Compared to the pure ZnO and the commercial Degussa P-25 and JRC-TiO₂ photocatalysts, the percent degradation of MB on 3% Au-ZnO increased by 17%, 14%, and 53%, respectively. In the present study, photocatalytic activity of the Au-ZnO catalysts increased from 0.89 to 1.14 h^{-1} when Au particle size increased from 4.1 to 6.3 nm. The effect of metal size on the photocatalytic activity of metal deposited on photocatalyst has been previously investigated by some researchers. For examples, Wu and Tseng [9] studied the effect of Au metal size on the photocatalytic properties of Au/ZnO catalyst and found that the photocatalytic degradation of methyl orange increased as the Au metal size decreased from 30 to 5 nm. They suggested that charge separation ability of the Au nanoparticles strongly depended on the Au particle size. Subramanian et al. [8] reported the size-dependent shift in the apparent Fermi level of the TiO₂-Au composite 20 mV for 8-nm diameter, 40 mV for 5-nm, and 60 mV for 3-nm Au nanoparticles, respectively. The different trend observed in this study could probably be explained by that in our case the amount of Au loading was increased from 1 to 3 wt% resulting in higher

concentration of Au nanoclusters on the ZnO surface (with little changes in Au particle size) whereas in the other studies, the amount of Au loading was kept constant (i.e., at 1 wt%) while varying Au particle size in the colloidal form.

4. Conclusions

FSP is an effective method for one-step synthesis of Au-ZnO and Pt-ZnO nanocomposites. Metallic phase of Au and Pt with average crystallite size between 3 and 7 nm were deposited directly on the ZnO during flame synthesis, no further treatment step is required. When employed as photocatalysts for methylene blue degradation, it was found that 3% Au-ZnO exhibited superior performance than the pure ZnO and the commercially available TiO₂ photocatalysts (Degussa P-25 and JRC-TiO₂). The Au-ZnO showed a stronger absorption of visible light and a lower intensity of PL emission than the undoped ZnO. The presence of discrete Au clusters may retard recombination of the photo-induced electron-hole pairs by shift in the Fermi level and store photogenerated electrons in them. On the other hand, Pt-ZnO did not enhance photocatalytic activity of the ZnO since the ohmic type of Pt may facilitate discharge of the photogenerated electrons into the electrolyte instead.

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Influence of Preparation Method on the Nanocrystalline Porosity of α -Al₂O₃ and the Catalytic Properties of Pd/ α -Al₂O₃ in Selective Acetylene Hydrogenation

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Nanocrystalline α -Al₂O₃ powder with average crystallite sizes of 34–68 nm have been synthesized by three different methods, namely, solvothermal, sol–gel, and precipitation. Although the smallest crystallite size of α -Al₂O₃ was obtained via the sol–gel synthesis, the α -Al₂O₃ sol–gel possessed the least amount of specific surface area and pore volume. A narrow pore size distribution with an average pore diameter of 15 nm can be obtained via solvothermal method, whereas the precipitation method yielded α -Al₂O₃ with larger pore size and a wider pore size distribution. When used as a support for palladium catalysts, the α -Al₂O₃ solvothermal provided the highest palladium dispersion and the best catalyst performance in selective hydrogenation of acetylene. The catalytic properties of Pd/ α -Al₂O₃ solvothermal were improved, in terms of both acetylene conversion and ethylene selectivity. As shown by temperature program studies, the use of solvothermal-derived α -Al₂O₃ facilitated H₂ reduction at low temperature and the desorption of ethylene and CO.

1. Introduction

Because of their fine particle size, high surface area, high melting point, high purity, good adsorbence, and high catalytic activity, alumina (Al₂O₃) powders find use in a myriad of applications.^{1,2} They are well-known to be used as adsorbents, coatings, soft abrasives, ceramic tools, fillers, wear-resistant ceramics, catalysts, and catalyst supports.^{3,4} Among the various transition phases of alumina (such as α -, γ -, χ -, δ -, η -, and θ -Al₂O₃), α -Al₂O₃ is the typical support used for the preparation of Pd/Al₂O₃ catalysts for the selective removal of acetylene in ethylene feed streams.

Polymer-grade ethylene has a strict specification of acetylene impurity (~1 ppm maximum), because acetylene is poison to catalysts for ethylene polymerization.^{5,6} Typically, α -Al₂O₃ provides a lower dispersion of active metal than the other transition phases of Al₂O₃, because of its lower surface area, but it is desirable in this reaction, because Pd/ α -Al₂O₃ catalysts possess less active sites for direct ethane formation than Pd/ γ -Al₂O₃ catalysts.⁷ In addition, less oligomer/green oil was formed on Pd/ α -Al₂O₃, because α -Al₂O₃ is less acidic than γ -Al₂O₃. The performance of Pd/ α -Al₂O₃ in such reactions also is dependent largely on metal dispersion and reducibility of the palladium metal.^{8,9} These properties are functions of the nature of the support, which typically is influenced by the preparation method that is used.

Many studies have shown supporting effects for palladium catalysts in selective acetylene hydrogenation.^{10–12} However, in those studies, the addition of a second component such as SiO₂, MgO, TiO₂, or Nb₂O₅ was necessary for modification of the catalyst properties. In our previous studies, we have reported the improved catalytic performance of supported palladium

catalysts in selective acetylene hydrogenation, using mixed-phase γ -/ α -Al₂O₃,¹³ nanocrystalline TiO₂,^{14,15} and nanocrystalline α -Al₂O₃¹⁶ as palladium catalyst supports. Modification of α -Al₂O₃ with a second metal such as nickel¹⁷ or zinc¹⁸ also resulted in significant improvement of Pd/ α -Al₂O₃ catalyst properties in selective acetylene hydrogenation, in terms of both acetylene conversion and selectivity to ethylene. The formation of NiAl₂O₄ or ZnAl₂O₄ spinels dramatically decreased the acidity of the alumina supports; hence, the catalysts showed less deactivation by coke formation.

Different preparation methods have been proposed for the synthesis of nanocrystalline Al₂O₃, such as solvothermal,^{19,20} sol–gel,^{21,22} and precipitation.²³ The physical properties such as crystallite size, particle shape, particle size distribution, degree of agglomeration, and porosity can be controlled by adjusting the preparation parameters and conditions. Despite much effort that has been exerted, it is, however, still unclear about the most convenient method, in terms of precursor decomposition and crystal growth.

In this work, nanocrystalline α -Al₂O₃ was prepared via solvothermal, sol–gel, and precipitation methods and then used as supports for palladium catalysts for the selective hydrogenation of acetylene. The catalyst behaviors were determined to be strongly dependent on the porosity of α -Al₂O₃ supports, which itself a function of the preparation method used. Various analytical techniques, such as N₂ physisorption, X-ray diffraction (XRD), CO pulse chemisorption, H₂ temperature-programmed reduction (H₂-TPR), temperature-programmed desorption (C₂H₄-TPD and CO-TPD), infrared spectroscopy (IR), and transmission electron microscopy (TEM) were used to investigate the physicochemical properties of α -Al₂O₃ supports and the corresponding Pd/ α -Al₂O₃ catalysts.

2. Experimental Section

2.1. Preparation of α -Al₂O₃. The Al₂O₃ support was prepared via the solvothermal, sol–gel, and precipitation methods. For the solvothermal method, aluminum isopropoxide (AIP,

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25 g) was suspended in 100 mL of toluene within a test tube, which was placed in an autoclave and then added with 30 mL of toluene in the gap between the test tube and the autoclave wall. The autoclave was completely purged by nitrogen before heating to 300 °C at a rate of 2.5 °C/min, and the autoclave was kept at that temperature for 2 h. After cooling to room temperature, the resulting product was collected after repeated washing with methanol by centrifugation and air-dried overnight. The obtainable powder was placed into a box furnace and heated to 1150 °C with a rate of 10 °C/min and kept at 1150 °C for 3 h. Finally, a white α - Al_2O_3 powder was obtained.

For the sol-gel method, 24 g of aluminum nitrate was dissolved in 50 mL of ethanol. The experiment was conducted in the reflux-condenser reactor at a temperature of ~70–80 °C for 18 h. Urea solution, which consists of urea (60 g) and distilled water (50 mL), then was added, to adjust the pH of solution. The mixture was permitted to rest at the same temperature for 24 h, to be gelled under neutral conditions. Then, it was calcined with two steps of heating rate to avoid the overflowing of gel during calcination (i.e., 3 °C/min from room temperature to 500 °C and continue heating at 5 °C/min to 1150 °C). The temperature was held for 3 h.

For the precipitation method, ammonium aluminum sulfate solution was gradually added to an ammonium hydrogen carbonate aqueous solution with a concentration ratio of 0.2: 2.0 mol/L. The experiment was controlled at temperatures in the range of 40–45 °C, a mixing speed of 450 rpm, an addition rate of 3 mL/min, and a constant pH value of 9. The mixture was aged for 15 min to permit crystal growth. The white precipitate that formed was separated from the final solution by centrifugation, repeatedly washed with methanol, and dried in an oven at 110 °C overnight. The obtainable powder was calcined in a depleted-oxygen atmosphere in a box furnace at 1150 °C for 3 h at a rate of 10 °C/min for the obtained α - Al_2O_3 .²⁴

2.2. Preparation of Pd/ α - Al_2O_3 Catalysts. The Al_2O_3 obtained from various methods were used as supports for the preparation of 0.3% Pd/ Al_2O_3 catalysts. Palladium was deposited on the alumina by incipient wetness impregnation, using $\text{Pd}(\text{NO}_3)_2 \cdot x(\text{H}_2\text{O})$ as the palladium precursor and deionized water as a solvent. After being allowed to stand at room temperature for 6 h and drying at 110 °C in air overnight, the catalyst was further calcined in a N_2 flow (60 cm^3/min) at a rate of 10 °C/min until the temperature reached 500 °C; then, the environment was switched to an air flow (100 cm^3/min) at 500 °C for 2 h.

2.3. Characterization. The XRD pattern obtained within the range of 20°–80° (2 θ), with a resolution of 0.04°, in a Siemens Model XRD D5000 system, with Cu K α radiation and a nickel filter. The specific surface area of the support with various preparations was measured by adsorption of N_2 at 77 K, using a Micromeritics ASAP 2000 automated system. The functional group in the samples was determined using infrared (IR) spectroscopy (Nicolet Impact 400). Before measurement, the sample was mixed with KBr and then was formed into a thin pellet. The amount of CO chemisorbed on the Pd/ Al_2O_3 catalyst was measured using a Micromeritics Model Chemisorb 2750 automated system, in conjunction with ChemiSoft TPx software, at room temperature. Temperature program experiments were conducted in a Micromeritics Model Chemisorb 2750 automated system. The temperature ramping was controlled by a temperature controller (Furnace Power 48 VAC 8A MAX). A mixture of 10% H_2 in argon, with a flow rate of 25 cm^3/min , was used in the TPR experiment. TPR was applied with a constant rate

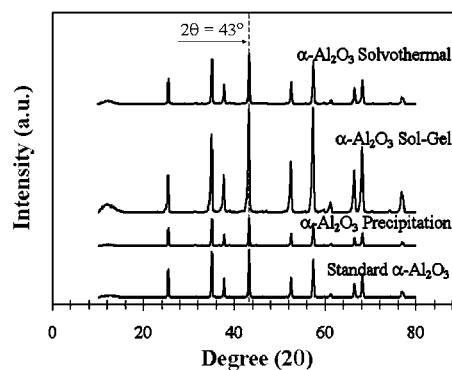


Figure 1. XRD patterns of the α - Al_2O_3 supports: solvothermal, sol-gel, and precipitation method.

of 10 °C/min from 35 °C to 300 °C. For the C_2H_4 -TPD experiment, the sample was prereduced at 150 °C in H_2 for 2 h, followed by cooling to room temperature. Ethylene adsorption then was performed at room temperature for 3 h. TPD was applied with a constant rate of 10 °C/min from 30 °C to 780 °C. For the CO-TPD experiment, the sample was prereduced at 150 °C in H_2 for 2 h (at a flow rate of 50 cm^3/min), followed by cooling to room temperature. CO adsorption then was performed at room temperature by continuous injection until the disappearance of CO adsorption. TPD was applied with a constant rate of 10 °C/min from 35 °C to 800 °C. The amount of desorbed CO was measured by analyzing the effluent gas with a thermal conductivity detector. The distribution of palladium on the catalyst support was observed using a transmission electron microscopy system (JEOL, Model JEM-2010) that was operated at 200 keV.

2.4. Reaction Study. The catalyst performance in the selective hydrogenation of acetylene was evaluated using a 10-mm (inner diameter (id)) Pyrex reactor. First, the catalyst was reduced in situ with hydrogen by heating from room temperature to 150 °C at a rate of 10 °C/min. The reactor then was purged with argon and cooled to the reaction temperature (80 °C). The reaction was performed using a feed composition of 1.5% C_2H_2 and 1.7% H_2 , with the balance being C_2H_4 , with various gas hourly space velocities (GHSV = 52580, 32577, 22534, 12385, 9366, 6660, and 4282 h^{-1}). The products and feeds were analyzed by two gas chromatographs: one that was equipped with a flame ionization detection (FID) device (Shimadzu, Model FID GC 9A, carboxieve column S-2) and another that was equipped for thermal conductivity detection (TCD) (Shimadzu, Model TCD GC 8A, molecular sieve-5A).

Acetylene conversion, as used herein, is defined as the number of moles of acetylene converted, with respect to the number of moles of acetylene in the feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over the total amount of hydrogenated acetylene. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene that has been totally hydrogenated.

3. Results and Discussion

3.1. Characteristics of α - Al_2O_3 . Figure 1 shows the XRD patterns of Al_2O_3 supports prepared by different preparation methods. The typical characteristic peaks for α - Al_2O_3 were detected for all samples, without any contamination of other transition alumina phases. The IR spectra of as-synthesized and calcined products are shown in Figure 2. In all cases, the strong H_2O peak at a wavenumber of ~3450 cm^{-1} disappeared after

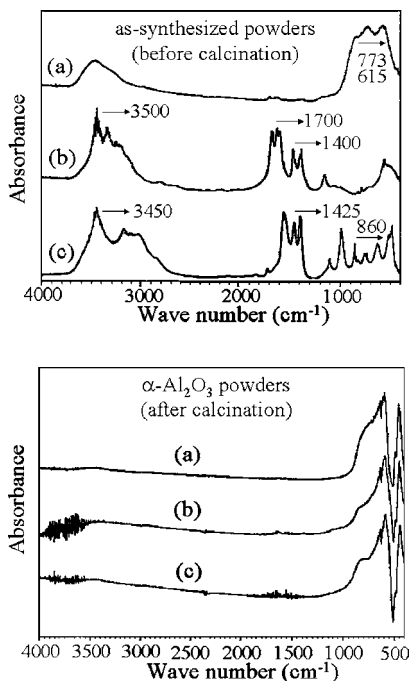


Figure 2. IR spectra of α - Al_2O_3 from (a) solvothermal, (b) sol-gel, and (c) precipitation methods.

calcination, suggesting that moisture that was trapped between crystals was removed by heat treatment. For the α - Al_2O_3 prepared by the precipitation method, absorption bands at 860 and 1425 cm^{-1} , corresponding to organic groups (CO_3^{2-} and NH_4^+), were eliminated during calcination. For the sol-gel α - Al_2O_3 , the disappearance of the absorption peaks at 1400, 1700, and 3500 cm^{-1} after calcination indicated that organic groups and the NO_3^- ion have been removed. The characteristic absorption bands of boehmite observed at 773 and 615 cm^{-1} from the as-synthesized solvothermal powder also disappeared after calcination. Boehmite resulted from the presence of a small amount of water, which was byproduct from AIP decomposition.²⁵ From IR analyses, it is confirmed that the α - Al_2O_3 powders obtained after calcination in all cases were pure Al_2O_3 , without residual organic moiety. The calcination conditions were also satisfactory for complete phase transformation or decomposition to α - Al_2O_3 .

The BET surface area, pore volume, average pore diameter, and average crystallite size of Al_2O_3 supports are given in Table 1. The average crystallite sizes of α - Al_2O_3 were calculated from XRD results using the Scherrer equation and the characteristic peak of α - Al_2O_3 at $2\theta = 43^\circ$. The crystallite size of sol-gel-derived α - Al_2O_3 support was smallest at 33.8 nm, whereas the solvothermal- and precipitation-derived α - Al_2O_3 supports gave larger crystallite sizes (53 and 67.6 nm, respectively). The specific surface area usually shows a reversed tendency with crystallite size. However, in this study, the α - Al_2O_3 obtained from the sol-gel method not only possessed the smallest crystallite size but also had the minimum value of specific surface area (1.7 m^2/g), compared to those obtained by the solvothermal (19.8 m^2/g) and precipitation (41.2 m^2/g) methods. This could possibly be due to the difference in the degree of agglomeration. From Table 1, the total pore volume of sol-gel-derived α - Al_2O_3 (0.0065 cm^3/g) was much less than those obtained from other preparation methods (0.0202 cm^3/g for the precipitation method and 0.0739 cm^3/g for the solvothermal method). These results indicated that the sol-gel-derived support had the smallest space between particles, compared to the other

supports, which prohibited the adsorption of N_2 molecules on the catalyst surface and led to the smallest surface area.

The pore size distribution curves of α - Al_2O_3 supports are shown in Figure 3. While the solvothermal- and precipitation-derived α - Al_2O_3 exhibited the typical characteristic of a mesopore system (having an average pore size of 16–32 nm), the sol-gel-derived α - Al_2O_3 did not show any distinguishing curves. Peak areas under the pore size distribution curves that were directly correlated with the pore volume increased in the following order: precipitation > solvothermal \gg sol-gel. The nitrogen adsorption isotherms for the α - Al_2O_3 prepared by different methods are shown in Figure 4. It can be seen that the precipitation-derived support represented adsorption isotherms with hysteresis loops with type-A adsorption characteristics, which corresponds to the presence of a two-ended tabular pore structure. However, the solvothermal- and sol-gel-derived alumina exhibited a Type-E hysteresis loop, which is an indication of the presence of a tabular pore structure, through short pores with winded parts of various widths.^{26,27} These pores were formed among the primary particles of alumina.

3.2. Physicochemical Properties of Pd/α - Al_2O_3 . The CO chemisorption results, such as the number of active Pd atoms, palladium dispersion (%), and average palladium-metal particle size, for the Pd/α - Al_2O_3 catalysts are given in Table 1. The mean stoichiometry of palladium metal to CO molecule ($X_{\text{Pd-CO}}$) was determined by the iterative method, according to those of Lambert et al.²⁸ A polynomial function was fitted based on the table established by Joyal and Butt,²⁹ who determined $X_{\text{Pd-CO}}$ as a function of palladium dispersion. The values of $X_{\text{Pd-CO}}$ were determined to be 0.51, 0.34, and 0.29 for palladium catalysts supported on solvothermal-, sol-gel-, and precipitation-derived α - Al_2O_3 , respectively. The numbers of active sites of palladium supported on solvothermal-, sol-gel and precipitation-derived α - Al_2O_3 catalysts were 11.5×10^{17} , 3.9×10^{17} , and 2.1×10^{17} sites/g-catalyst, corresponding to palladium dispersions of 7.6%, 2.6%, and 1.4%, respectively. The lower percentage of palladium dispersion that was obtained for the $\text{Pd}/\text{sol-gel-derived } \alpha$ - Al_2O_3 would be due to the lower specific surface area and pore volume. On the other hand, the larger pore size of precipitation-derived α - Al_2O_3 could also result in a low percentage of palladium dispersion, because of the agglomeration of palladium particles within the pores. Among the various Pd/α - Al_2O_3 catalysts, the maximum CO chemisorption was obtained on the solvothermal-derived α - Al_2O_3 with medium pore size. In a previous study from our group about palladium dispersed on silica and MCM-41 with various pore sizes, a lower percentage of palladium dispersion was found on the small pore SiO_2 , because of the significant amount of palladium being located outside the pores of the supports.³⁰ A similar result was obtained when palladium was supported on the sol-gel α - Al_2O_3 with a very low amount of porosity.

The TEM micrographs of Pd/α - Al_2O_3 catalysts were also taken to physically measure the size of the palladium oxide particles and/or palladium clusters on the various α - Al_2O_3 ; these micrographs are shown in Figure 5. The palladium catalyst supported on the sol-gel-derived support consisted of agglomerated particles primarily with irregularly shaped structure, whereas, for those prepared by the solvothermal and precipitation methods, the agglomeration of fingerlike and rodlike particles was observed. The palladium metal cluster size on the various alumina supports increased in the following order:

$$\alpha\text{-Al}_2\text{O}_3 (\text{precipitation}) \approx \alpha\text{-Al}_2\text{O}_3 (\text{sol-gel}) > \alpha\text{-Al}_2\text{O}_3 (\text{solvothermal})$$

Table 1. Physicochemical Properties of α -Al₂O₃ Various Preparation Methods and 0.3% Pd/Al₂O₃ Catalysts

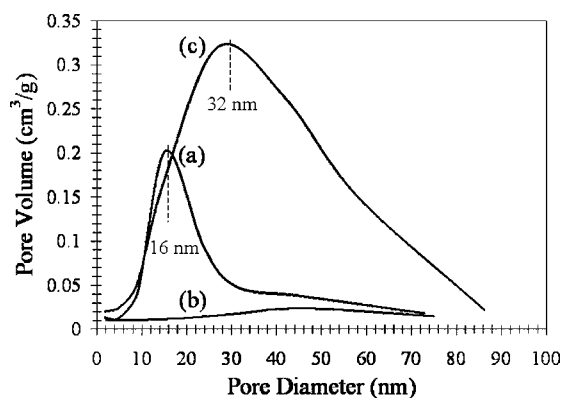
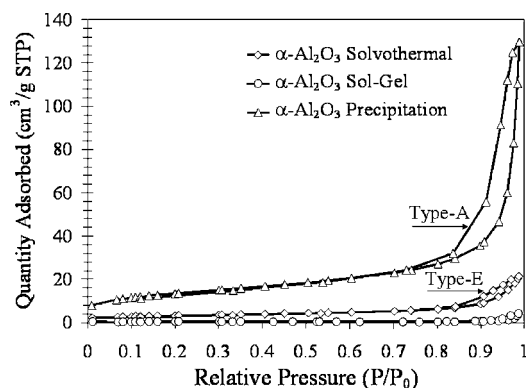
Pd/Al ₂ O ₃ catalyst	BET surface area ^{a,b} (m ² /g)	pore volume ^{b,c} (cm ³ /g)	average pore diameter ^{b,c} (nm)	crystallite size ^{b,d} (nm)	Pd active sites ^e ($\times 10^{-17}$ sites/ g-catalyst)	Pd dispersion ^f (%)	average Pd ⁰ particle size ^g (nm)
solvothermal-derived	19.8	0.0739	14.9	53	11.5	7.6	14.7
sol-gel-derived	1.7	0.0065	46	33.8	3.9	2.6	43.2
precipitation-derived	41.2	0.2020	26.9	67.6	2.1	1.4	80.2

^a Error of measurement = 10%. ^b Only catalyst supports were measured. ^c Calculated from the Barrett–Joyner–Halenda (BJH) method. ^d Determined from XRD line broadening. ^e Determined from CO chemisorption. Fraction of Pd active sites = $S_f \times (V_{\text{ads}}/V_g) \times (6.02 \times 10^{23})$, where V_{ads} the volume adsorbed, V_g the molar volume of gas at standard temperature and pressure (STP), and S_f the stoichiometry factor for CO on Pd. Error of measurement = $\pm 5\%$. ^f Based on $D = [\text{fraction of Pd active sites} \times (\text{MW}/\%M) \times 100\%] / (6.02 \times 10^{23})$, where D is the fractional metal dispersion, MW the molecular weight of the metal, and %M the percentage of metal. ^g Based on $d \text{ (nm)} = (1.12/D)^{40}$.

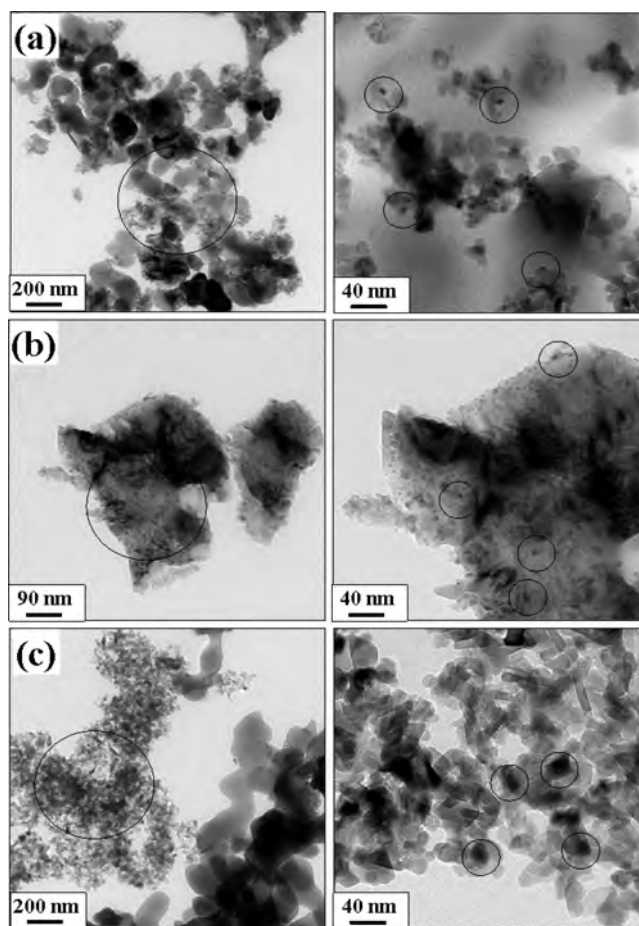
Table 2. Consumption of Hydrogen in TPR, and the Amount of Ethylene and CO Desorption

Pd/Al ₂ O ₃ catalyst	Temperature at Maximum (°C)						H ₂ consumption (μmol) ^a	amount of ethyl ene desorption (μmol) ^a	amount of CO desorption (μmol) ^a
	Peak 1			Peak 2		Peak 3			
	H ₂ -TPR ^b	C ₂ H ₄ -TPD ^c	CO-TPD ^d	C ₂ H ₄ -TPD ^c	CO-TPD ^d	C ₂ H ₄ -TPD ^c			
solvothermal-derived	60	90	90	240	230	420	658	131	76
sol-gel-derived	65	100	90	280	230	500	488	75	10
precipitation-derived	70	100	90	260	250	440	610	122	33

^a Measured using the same weight of catalysts. ^b Based on H₂-TPR results. ^c Based on C₂H₄-TPD results. ^d Based on CO-TPD results.

**Figure 3.** Pore size distribution results of the α -Al₂O₃ supports from (a) solvothermal, (b) sol-gel, and (c) precipitation methods.**Figure 4.** N₂ adsorption isotherms.

The reduction behaviors and reducibility of catalysts were studied by the TPR technique. The TPR profiles of Pd/ α -Al₂O₃ catalysts are shown in Figure 6. All the TPR profiles showed a single reduction peak in the range of 60–70 °C, which corresponded to the reduction of PdO to palladium metal.^{31–33} This peak was shifted to higher temperature for the catalysts that were supported on sol-gel- and precipitation-derived α -Al₂O₃ by ~ 10 °C. The lower reduction temperature of the TPR profile suggested that PdO/Pd supported on the solvothermal-derived α -Al₂O₃ facilitated reduction at lower temperature. The average oxidation states of palladium were calculated

**Figure 5.** TEM image of the palladium supported by α -Al₂O₃ from (a) solvothermal, (b) sol-gel, and (c) precipitation methods. Characteristic palladium is shown within the circles in the micrographs.

according to the amount of H₂ consumption, and the results are given in Table 2. The solvothermal Pd/Al₂O₃ possessed the highest fraction of Pd active sites, probably because it had the smallest PdO/Pd sizes produced, as determined by TEM measurement.

Ethylene-temperature-programmed desorption (C₂H₄-TPD) was performed to obtain information about the ethylene adsorp-

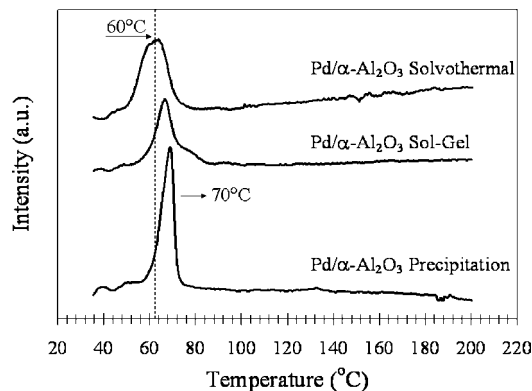


Figure 6. H₂-TPR profiles for the various Pd/α-Al₂O₃ catalysts.

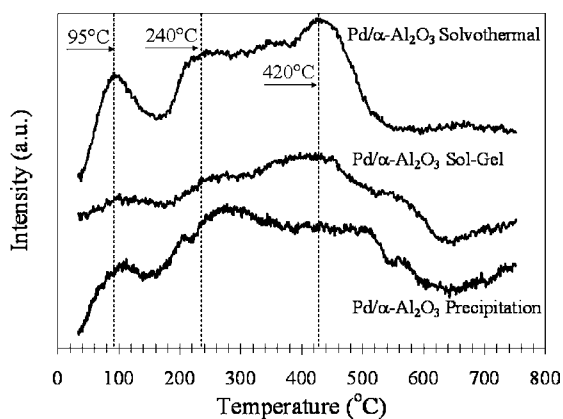


Figure 7. C₂H₄-TPD profiles for the various Pd/α-Al₂O₃ catalysts.

tion behavior on the catalyst surface, and the results are shown in Figure 7. We observed the peak locations and found that it appeared at different temperature ranges, depending on the characteristic modes of the ethylene adsorbed on the surface. All of the catalysts showed that the three major peaks had differences in their temperature positions and peak intensities. According to Shin et al.,^{34,35} the first peak, at ~95 °C, was assigned to π -bonded ethylene, which was weakly adsorbed and, consequently, desorbed without decomposition. The peak at ~240 °C was due to di- σ -bonded ethylene, which undergoes decomposition, followed by the recombination of the surface hydrocarbon species with hydrogen to produced ethylene as well as ethane. The last peak, at ~420 °C, was the CH₃ group, because the CH₃ signal was due to the decomposition of C₂ hydrocarbons that were adsorbed on the catalyst (tentatively, ethane or ethylene).^{36,37}

It is generally accepted that ethylene adsorption is dependent on palladium particle size; it adsorbs more strongly on larger palladium particles. The results in this study follow the same trend in the literature. The low-temperature ethylene desorption peak decreased and slightly shifted to higher temperature as the palladium particle size increased from 14.7 to 80.2 nm for the α-Al₂O₃ supports prepared by solvothermal, sol-gel, and precipitation, respectively. According to Shaikhutdinov et al.,³⁸ adsorption of π -bond ethylene occurs at low temperature and then desorbs when the temperature increases without hydrogenation reaction. Small palladium particles favor such a process, whereas, on larger palladium particles, a fraction of ethylene molecules adsorbs as di- σ -bonded ethylene, which can either desorb near room temperature or dehydrogenate, producing surface species such as ethylidyne and atomic hydrogen. The formation of these surface species is believed to be the origin

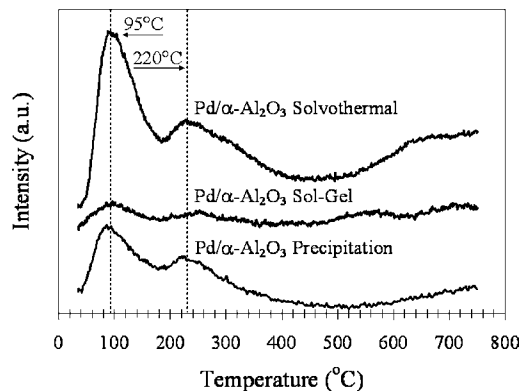


Figure 8. CO-TPD profiles for the various Pd/α-Al₂O₃ catalysts.

for ethane production and carbon deposits during acetylene hydrogenation.

The CO temperature-programmed desorption (CO-TPD) behavior for the palladium catalysts supported on Al₂O₃ from different preparation methods is shown in Figure 8. Two desorption peaks, one with strong intensity at ca. 95 °C and another small peak located at ca. 220 °C, were observed for all the catalysts, which could be attributed to CO adsorption on two adsorptive site groups. The first group gave the strong peak, ranging from 95 to 180 °C, which was weak CO species over the catalyst. The second one was characteristic of the strong chemisorbed CO molecules. The amount of chemisorbed CO (see Table 2) on Pd/α-Al₂O₃ (solvothermal-derived support) was 7 and 2 times greater than those on the Pd/α-Al₂O₃ sol-gel-derived support and the Pd/α-Al₂O₃ precipitation-derived support, respectively. The difference may be related to different geometry states of the adsorptive sites on catalysts that may have occurred from the different support configurations of the Pd/α-Al₂O₃ catalysts. Moreover, it has been reported that the activation energy of CO desorption decreased as the size of the palladium particles decreased.³⁹ The results from this study also show that the Pd/Al₂O₃ solvothermal-derived support with the smallest palladium particle size facilitated CO desorption. The atomic structures of CO and ethylene were similar, in terms of the double bond, which consisted of a π -bond and a σ -bond; thus, both the C₂H₄-TPD and CO-TPD results show the same trend.

3.3. Catalytic Performance in Selective Acetylene Hydrogenation. The effect of nanocrystalline porosity of α-Al₂O₃ obtained from various preparation methods on the catalytic properties of Pd/α-Al₂O₃ was investigated in selective acetylene hydrogenation. The catalyst performances are shown by the plots of acetylene conversion × ethylene selectivity versus the GHSV value in Figure 9. Ethylene yield (%) clearly was improved in the following order of Pd/α-Al₂O₃ catalysts:

Pd/solvothermal-derived α-Al₂O₃ > Pd/sol-gel-derived α-Al₂O₃ > Pd/precipitation-derived α-Al₂O₃

Among the three catalyst systems, the Pd/solvothermal-derived α-Al₂O₃ showed better performance than catalysts supported on the other α-Al₂O₃ supports. Based on our characterization results, Pd/solvothermal-derived α-Al₂O₃ had the appropriate total pore volume, the highest fraction of Pd active sites, and the highest metal dispersion of Pd on Al₂O₃ support; it also facilitated the reduction of PdO at lower temperature, which promoted acetylene conversion. Moreover, the TPD profiles of Pd/solvothermal-derived α-Al₂O₃ suggested that the amount of ethylene adsorbed at low temperature on the catalyst surface

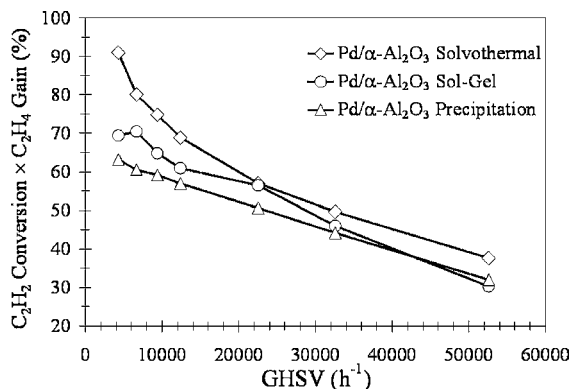


Figure 9. Performance of Pd/ α -Al₂O₃ catalysts in selective acetylene hydrogenation.

was highest, which was important for the improvement of ethylene gain, especially at high acetylene conversions.

4. Conclusions

Nanocrystalline porosity of α -Al₂O₃ powders was varied by changing the preparation methods. While the sol-gel method yielded the smallest crystallite size of α -Al₂O₃ with little pore volume and surface area, a mesopore structure with an average pore size of 15–27 nm was obtained via the solvothermal and precipitation methods. Suitable properties of the solvothermal-derived α -Al₂O₃, such as high surface area and narrow pore size distribution, were determined to result in the best catalyst performance of Pd/ α -Al₂O₃ catalysts in the selective hydrogenation of acetylene. The solvothermal-derived α -Al₂O₃ not only provided the highest percentage of palladium dispersion and smallest palladium particle size, but it also facilitated H₂ reduction at low temperature and the desorption of ethylene and CO.

Acknowledgment

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Effect of Fe-modified α -Al₂O₃ on the properties of Pd/ α -Al₂O₃ catalysts in selective acetylene hydrogenation

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Abstract The use of nanocrystalline Fe-modified α -Al₂O₃ prepared by sol–gel and solvothermal method as supports for Pd catalysts resulted in an improved catalyst performance in selective acetylene hydrogenation. Moreover, the amount of coke deposits was reduced due to lower acidity of the Fe-modified α -Al₂O₃ supports.

Keywords Fe-modified Al₂O₃ · Selective acetylene hydrogenation

Introduction

Selective hydrogenation of acetylene using supported Pd-based catalysts is an important process in the polyethylene industry because acetylene contaminant in ethylene feedstock poisons the polymerization catalyst. It is of particular challenge to produce an effective catalyst that can remove trace amounts of acetylene in ethylene feedstock while ethylene remains inactive during hydrogenation to prevent ethylene loss. Because Pd catalysts have poor selectivity at high acetylene conversion and oligomer formation on the catalysts, which lessens the catalyst lifetime, promotion with a second component such as Ag [1, 2], Si [3], K [4], Au [5], and TiO₂ [6] has often been employed in order to improve the catalyst performance. Besides Pd/Al₂O₃, new, efficient catalyst systems for selective hydrogenation of acetylene have been continually developed including Pd on nano-sized TiO₂ [7–10] and zeolite-supported Pd–Ag catalysts [11, 12].

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Recently, our studies showed that the use of nanocrystalline α -Al₂O₃ prepared by sol-gel and solvothermal method as supports for Pd catalysts yielded superior catalyst performance compared to those on commercial α -Al₂O₃ [13]. Moreover, modification of α -Al₂O₃ with a second metal such as Ni [14] and Zn [15] has been shown to result in significant improvement of Pd/ α -Al₂O₃ catalyst properties in selective acetylene hydrogenation in terms of both acetylene conversion and selectivity to ethylene. Formation of NiAl₂O₄ or ZnAl₂O₄ spinels dramatically decreased the acidity of the alumina supports hence the catalysts showed less deactivation by coke formation.

The present paper is our follow-up effort to produce a highly effective catalyst for purification of ethylene feed stream in polyethylene production. The effect of Fe-modified α -Al₂O₃ on the properties of Pd/ α -Al₂O₃ catalyst in selective acetylene hydrogenation is focused. The Fe-substituted alumina is interesting as a catalyst support due to its improved stability and high resistance to oxidation [16, 17]. The catalyst performances were correlated with the catalyst characterization results from N₂ physisorption, CO chemisorption, X-ray diffraction (XRD), ammonia temperature program desorption (NH₃-TPD), and thermal gravimetric and differential temperature analysis (TG/DTA).

Experimental

Preparation of α -Al₂O₃ and Fe-modified α -Al₂O₃

The nanocrystalline α -Al₂O₃ was prepared by solvothermal and sol-gel method according to that of Panpranot and co-workers [13]. The iron precursors used for the preparation of Fe-modified α -Al₂O₃ by solvothermal and sol-gel method were iron (II) acetylacetonate ((C₅H₈O₂)₃Fe) and ferric nitrate nonahydrate (FeN₃O₉·9H₂O), respectively. The Pd/Fe-modified α -Al₂O₃ catalysts were prepared by incipient wetness impregnation of support with a desired amount of an aqueous solution of palladium (II) nitrate hydrate (Aldrich) to obtain the final Pd loading of ca. 0.3 wt%. The catalysts were dried overnight at 110 °C and then calcined in N₂ flow (60 cm³/min) with a heating rate of 10 °C/min until the temperature reached 500 °C and then in air flow (100 cm³/min) at 500 °C for 2 h.

Catalyst characterization

X-ray diffraction patterns were recorded between 20° and 80° (2 θ) with a SIEMENS D5000 X-ray diffractometer using Cu K α radiation with a Ni filter. Specific surface areas were measured using nitrogen adsorption with a Micromeritic Chemisorb 2750 system. Prior to measurements, the samples were degassed at 200 °C for 2 h. Metal active sites were measured using CO chemisorption technique at room temperature in a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software. Before chemisorption measurement, the sample was reduced in a H₂ flow at 150 °C for 2 h then cooled down to ambient temperature in a He flow. NH₃-TPD was also performed in the Micromeritic Chemisorb 2750

automated system attached with ChemiSoft TPx software. The distribution of palladium on catalyst supports were characterized using a JEOL 2010 transmission electron microscope operated at 2,000 kV. Thermal gravimetric analysis (TGA) thermograms were performed using a SDT Analyzer Model Q600 from TA Instruments, USA.

Reaction study

The selective hydrogenation of acetylene was performed in a quartz tube reactor. Prior to the start of the reaction, the catalyst was reduced in H₂ at 150 °C for 2 h. Then the reactor was purged with argon and cooled down to the reaction temperature. The feed gas was composed of 1.5% C₂H₂, 1.7% H₂, and balanced C₂H₄ (TIG Co., Ltd.). The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). Acetylene conversion as used herein is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene.

Results and discussion

The XRD patterns of Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ are shown in Fig. 1. For all the samples, the characteristic peaks of α -Al₂O₃ were evident while the diffraction lines of iron, iron oxides, iron aluminate, palladium or palladium oxide

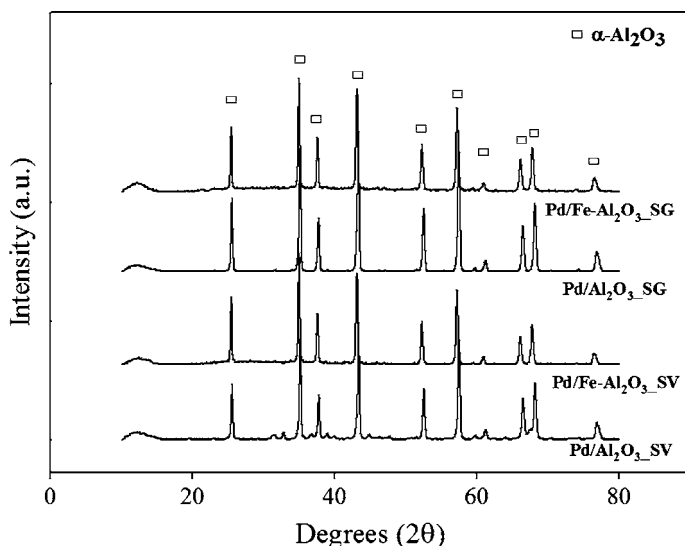


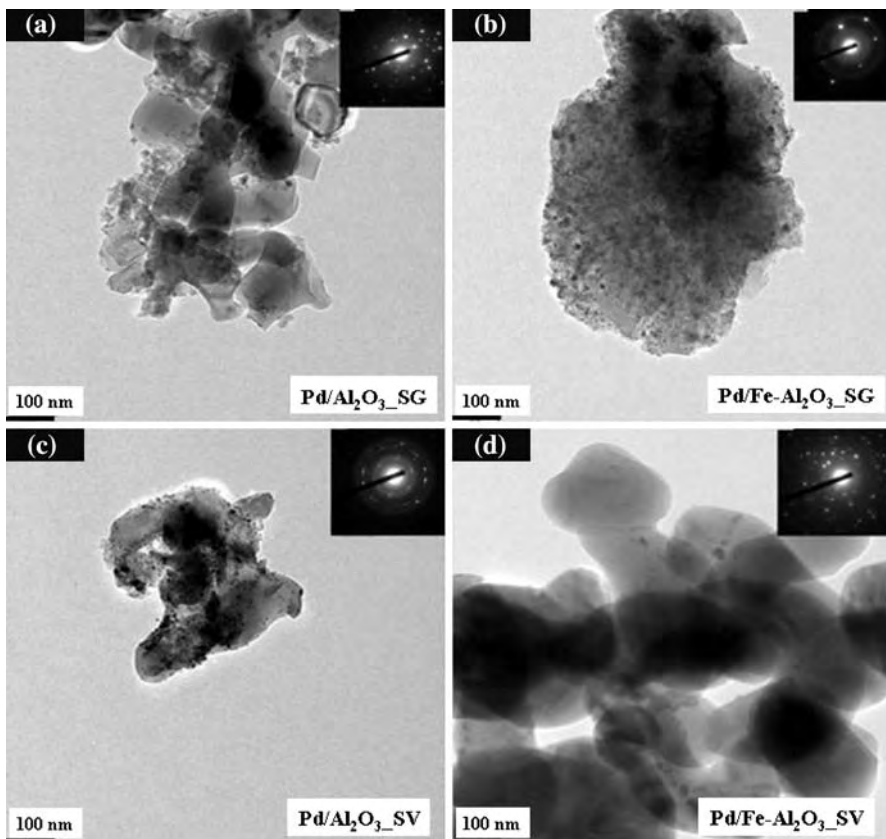
Fig. 1 XRD patterns of the Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ prepared by sol-gel (SG) and solvothermal (SV) methods

Table 1 Physicochemical properties of Pd/Al₂O₃ and Pd/Fe-Al₂O₃ catalysts

	BET surface area (m ² /g)	Avg. crystallite size ^a (nm)	CO chemisorption ($\times 10^{17}$ site/g cat.)	% Pd dispersion	d_p Pd ⁰ (nm)
Pd/Al ₂ O ₃ _SG	1.0	46	10.0	8.4	13
Pd/Fe-Al ₂ O ₃ _SG	1.4	62	4.1	2.7	42
Pd/Al ₂ O ₃ _SV	5.1	52	11.0	7.2	16
Pd/Fe-Al ₂ O ₃ _SV	3.9	63	7.8	5.1	22

^a Average crystallite size of α -Al₂O₃ supports determined from XRD results using Scherrer equation

were not apparent due probably to the very low amount present. The average crystallite sizes of α -Al₂O₃ were calculated from the full width at half maximum of the XRD peaks at $2\theta = 43^\circ$ using the Scherrer equation; the results are shown in Table 1. The average crystallite sizes of α -Al₂O₃ and Fe-modified α -Al₂O₃ prepared by sol-gel and solvothermal method were ranged between 46 and 63 nm. The corresponding surface areas of the catalysts were 1–5 m²/g which were quite low

**Fig. 2** TEM micrographs of Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ catalysts

probably due to high agglomeration of these nanocrystalline particles during calcination at high temperature. In a previous study, we have shown that sol-gel Al₂O₃ possessed much less pore volume than the samples prepared by the solvothermal method, as a consequence lower surface area was obtained [15].

Figure 2 shows the TEM micrographs with SAED patterns of Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ prepared by sol-gel and solvothermal methods. Palladium particles/clusters with average particle size ≤ 10 nm were found to be deposited on both of the alumina supports. The metal active sites, the Pd dispersion, and the average Pd metal particle sizes were also determined from CO chemisorption experiment and are summarized in Table 1. The technique is based on the assumption that only one CO molecule adsorbed on one metal active site and CO did not chemisorb on Al₂O₃ support [18]. It is clearly seen that when the catalysts were supported on Fe-modified α -Al₂O₃, Pd dispersion decreased. The larger crystallite size of α -Al₂O₃ resulted in larger Pd particle size being formed and lower Pd dispersion. Moreover, Pd catalyst supported on Fe-modified α -Al₂O₃ prepared by sol-gel method showed lower Pd dispersion than that prepared by solvothermal due probably to more agglomeration of the α -Al₂O₃ support as also noticed from TEM measurements.

NH₃ temperature program desorption is a commonly used technique for the titration of surface acid sites [19]. The strength of an acid site can be related to the corresponding desorption temperature, while the total amount of ammonia desorption after saturation coverage permits quantification of the number of acid sites at the surface. The temperature-programmed desorption profiles for the nanocrystalline α -Al₂O₃ and Fe-modified α -Al₂O₃ supports are shown in Fig. 3. It was found that modification of Al₂O₃ with small amounts of Fe considerably changed its acid properties, i.e., reduction in the number of strong acid sites [20].

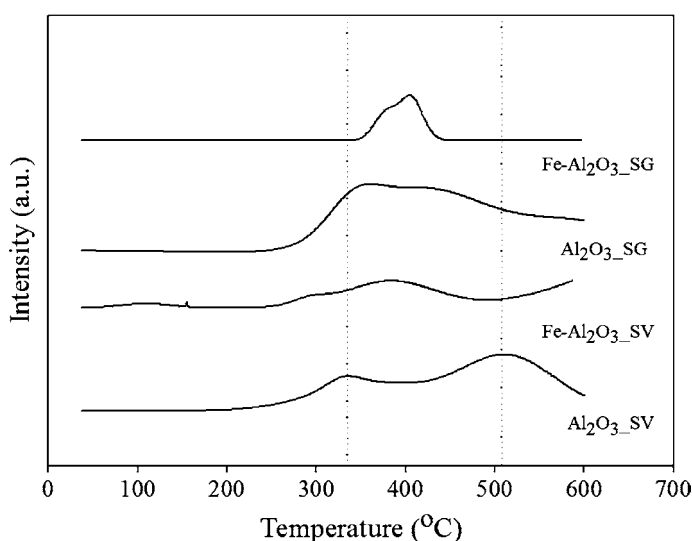


Fig. 3 NH₃ temperature program desorption profiles for α -Al₂O₃ and Fe-modified α -Al₂O₃ supports

The catalytic properties of Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ catalysts were evaluated in the selective hydrogenation of acetylene using a fixed bed flow reactor with a GHSV of 16,901 h⁻¹. A study of the temperature dependence of acetylene conversion and selectivity toward ethylene on Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ catalysts is shown in Fig. 4 in the temperature range between 40 and 100 °C. In all cases, acetylene conversion increases with increasing temperature while ethylene selectivity decreases due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction. Ethylene selectivity at relatively high acetylene conversion (>80%) improved in the order: Pd/Fe-modified

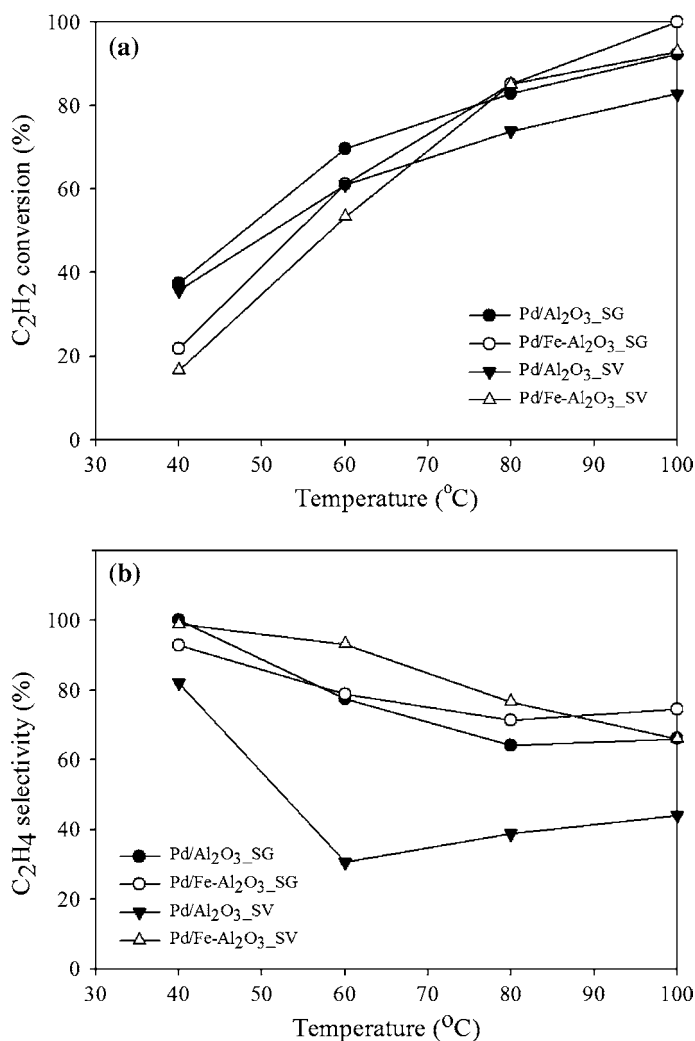


Fig. 4 Temperature dependence of the catalytic performance of Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ catalysts; **a** % conversion of C₂H₂, **b** % selectivity of C₂H₄

α -Al₂O₃-sol-gel > Pd/Fe-modified α -Al₂O₃-solvothetmal \approx Pd/ α -Al₂O₃-sol-gel > Pd/ α -Al₂O₃-solvothetmal. It was also found that acetylene hydrogenation activity depended on Pd particle size in which the activity increased with increasing Pd particle size. A similar trend has been observed for supported Pd catalysts in other selective hydrogenation reactions [21–24].

After reaction, the amounts of carbonaceous deposits on the catalyst samples were measured by thermal gravimetric analysis and the results are shown in Fig. 5. The weight loss at around 200–400 °C was due to oxidation of the carbonaceous deposited on the surface of used catalysts [25]. As shown by the exothermic peaks in

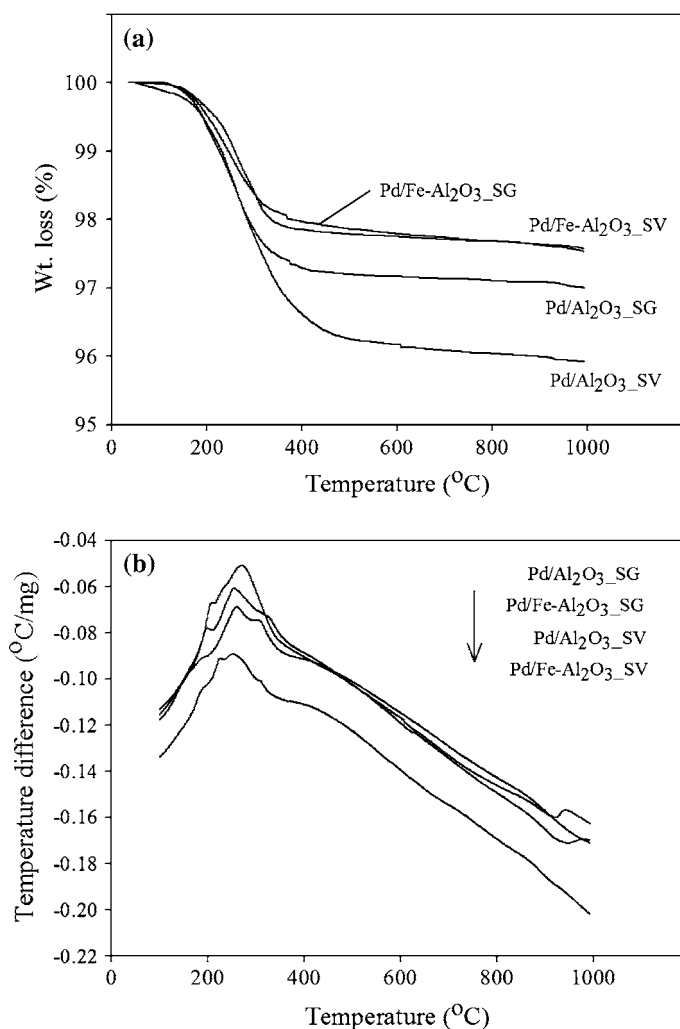


Fig. 5 Thermal gravimetric and differential temperature analysis (TG/DTA) of Pd/ α -Al₂O₃ and Pd/Fe-modified α -Al₂O₃ catalysts after reaction; **a** in terms of temperature (°C) and weight loss (%), **b** in terms of temperature (°C) and temperature difference (°C/mg)

Fig. 5b, the type of coke species occurred during reaction was probably “soft coke” similar to those suggested by Xiangjing et al. [26]. Based on TGA results, the amount of coke deposits on the catalysts on Fe-modified α -Al₂O₃ prepared by sol-gel or solvothermal method was lower than those on the unmodified ones. The results were in good agreement with acidity of the Al₂O₃ supports measured from NH₃ TPD technique.

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Synthesis of nanocrystalline alumina by thermal decomposition of aluminum isopropoxide in 1-butanol and their applications as cobalt catalyst support

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Abstract—Nanocrystalline alumina powders were prepared by thermal decomposition of aluminum isopropoxide (AIP) in 1-butanol at 300 °C for 2 h and employed as cobalt catalyst supports. The crystallization of alumina was found to be influenced by the concentration of AIP in the solution. At low AIP content, wrinkled sheets-like structure of γ - Al_2O_3 was formed, while at high AIP concentrations, fine spherical particles of χ - Al_2O_3 were obtained. It was found that using these fine particles alumina as cobalt catalyst supports resulted in much higher amounts of cobalt active sites measured by H_2 chemisorption and higher CO hydrogenation activities.

Key words: Nanocrystalline Alumina, Thermal Decomposition, Cobalt Catalyst, Solvothermal Method, CO Hydrogenation

INTRODUCTION

Alumina powders are very interesting crystalline materials with broad applicability as adsorbents, coatings, soft abrasives, ceramic tools, fillers, wear-resistant ceramics, catalysts, and catalyst supports [1,2]. Because of their fine particle size, high surface area, high melting point (above 2,000 °C), high purity, good adsorbent, and high catalytic activity, they have been employed in a wide range of large-scale technological processes [3,4].

Various transition aluminas (α , γ , χ , δ , η and θ) have been prepared by different methods, such as sol-gel synthesis [5,6], hydrothermal synthesis [7], microwave synthesis [8], emulsion evaporation [9], plasma technique [10], and solvothermal synthesis [11-18]. Among these methods, solvothermal synthesis attracts the most attention because it gives the products with small uniform morphology, well-controlled chemical composition, and narrow size distribution. Furthermore, the desired shape and size of particles can be produced by controlling process conditions such as solute concentration, reaction temperature, reaction time, and the type of solvent [19,20]. For example, Berntsen et al. [21] described a simple route to high surface area nanostructured MoS_2 based on the decomposition of cluster-based precursor $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot x\text{H}_2\text{O}$ in toluene at 380 °C. It was found that solvothermal decomposition resulted in nanostructured material distinct from that obtained by decomposition of the precursor in sealed quartz tubes at the same temperature. Wang et al. [22] prepared nanocrystalline titania in alcohols under solvothermal conditions at 100 °C for 24 h. The selection of crystal structures, grain sizes, and morphologies was achieved by simply varying the alcohols and other reaction conditions.

Alumina prepared by the solvothermal method is considered high thermal stability. In our recent works [23-26], nanocrystalline transition alumina with micro spherical particles and high thermal stabil-

ity has been synthesized by decomposition of aluminum isopropoxide (AIP) under solvothermal conditions. The mechanism of the process involves the formation of amorphous complexes before further decomposition takes place. Inoue et al. [27] prepared silica-modified alumina by the reaction of AIP and tetraethyl orthosilicate (TEOS) in 1,4-butanediol at 300 °C. The products were found to maintain large surface areas after calcination at high temperature.

In this study, the influence of concentration of aluminum isopropoxide in 1-butanol used in the preparation of nanocrystalline alumina by solvothermal method on the properties of alumina powders and alumina supported cobalt catalysts was investigated by using various characterization techniques such as XRD, BET analysis, TEM, SEM, EDX, H_2 chemisorption, and temperature-programmed reduction. The catalytic activity of the catalysts was tested in carbon monoxide hydrogenation at 220 °C and atmospheric pressure.

EXPERIMENTAL

1. Catalyst Preparation

1-1. Preparation of Nanocrystalline Al_2O_3

A selected amount of aluminum isopropoxide (Aldrich) (10-35 g) was suspended in 100 ml of 1-butanol (Ajax Finechem) in a test tube, which was then placed in a 300 ml autoclave. In the gap between the test tube and the autoclave wall, 30 ml of 1-butanol was added. The atmosphere inside the autoclave was purged completely with nitrogen. The mixture was heated to 300 °C at a heating rate of 2.5 °C/min and was kept at that temperature for 2 h. After cooling to room temperature, the resulting powders were collected after repeated washing with acetone by centrifugation. They were then air-dried. The calcination of the products was carried out in a box furnace by heating up to 600 °C at a rate of 10 °C/min and held at that temperature for 1 h.

1-2. Preparation of Al_2O_3 -Supported Co Catalysts

The $\text{Co}/\text{Al}_2\text{O}_3$ catalysts were prepared by incipient wetness impregnation of Al_2O_3 with a desired amount of an aqueous solution

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of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Aldrich). The final loading of the catalysts was determined by atomic absorption spectroscopy (Varian Spectra A800) to be ca. 10 wt% cobalt. The catalysts were dried at 110°C for 24 h and calcined in air at 300°C for 2 h using a ramp rate of $1^\circ\text{C}/\text{min}$.

2. Catalyst Nomenclature

In this study, alumina and alumina-supported cobalt catalysts are referred to as Al-x and Co/Al-x, where x is the amount (g) of AIP used in the preparation of alumina powders. For example, Al-10 and Co/Al-10 refer to Al_2O_3 and Co/ Al_2O_3 catalyst prepared with 10 g AIP.

3. Catalyst Characterization

XRD patterns of the samples were collected with a SIEMENS D-5000 X-ray diffractometer with Cu K_α radiation ($\lambda=1.54439 \text{ \AA}$). The spectra were scanned at a rate of $0.04^\circ/\text{step}$ from $2\theta=15^\circ$ to 80° . BET surface areas were calculated by using the BET-single point method at liquid N_2 temperature. Transmission electron microscopy (TEM) was performed with a JEOL JEM1220. SEM and EDX were performed with a JEOL JSM-35CF scanning electron microscope in the back scattering electron (BSE) mode at 20 kV. EDX was performed by using Link Isis 300 software. Static H_2 chemisorption was carried out on the reduced cobalt catalyst samples at 100°C according to the method described by Reuel and Bartholomew [28] by using a Micromeritics Pulse Chemisorb 2700 system. Prior to H_2 chemisorption, the catalyst samples were reduced at 350°C in flowing H_2 for 3 h. Temperature-programmed reduction (TPR) was performed by using an in-house system. Approximately 0.1 g of the catalyst was placed in the middle of a stainless steel reactor. A temperature ramp from 35 to 600°C at a ramp rate $5^\circ\text{C}/\text{min}$ and the reduction gas 5% H_2 in Ar were used. A thermal conductivity detector (TCD) was used to determine the amount of hydrogen consumed. A cold trap was placed before the detector to remove water produced during the reduction. The hydrogen consumption was calibrated by using TPR of silver oxide (Ag_2O) at the same conditions.

4. Reaction

CO hydrogenation was carried out in a fixed-bed quartz reactor under differential reaction conditions ($<10\%$ conversion) at 220°C , 1 atm total pressure, and $\text{H}_2/\text{CO}=10/1$. The total flow rate of $\text{H}_2/\text{CO}/\text{Ar}$ was 80/8/32 cc/min. Typically, 0.1 g of the catalyst sample was reduced *in situ* in flowing H_2 (50 cc/min) at 350°C for 3 h prior to CO hydrogenation. After the startup, samples were taken in 1-h interval and analyzed by gas chromatography. Steady state was reached within 6 h in all cases.

RESULTS AND DISCUSSION

1. Effect of AIP Concentration on the Properties of Al_2O_3

Fig. 1 shows the XRD patterns of various alumina powders obtained from thermal decomposition of AIP in 1-butanol after calcination at 600°C for 1 h. XRD patterns of Al_2O_3 show strong diffraction peaks at 31° , 33° , 38° , 43° , 47.5° , and 68° (according to the JCPDSs database). It was found that when lower amounts of AIP were used, only γ -alumina was formed as seen by the XRD characteristic peaks at $2\theta=33^\circ$ according to the JCPDSs database. The XRD characteristic peaks of χ -alumina were observed at $2\theta=42.5^\circ$ for the ones prepared with AIP 25 and 35 g. The intensity of χ -alumina peaks became stronger with increasing amount of AIP content. It

is indicated that increasing AIP content during the synthesis resulted in formation of mixed phase between γ -alumina and χ -alumina. The crystallization process of alumina was probably affected by the amounts of AIP in 1-butanol.

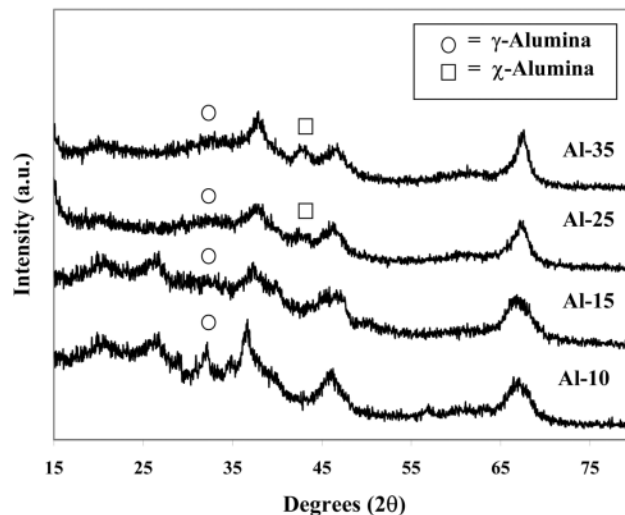


Fig. 1. XRD patterns of various nanocrystalline alumina prepared by the reaction of AIP in 1-butanol at 300°C for 2 h (after calcinations at 600°C for 1 h).

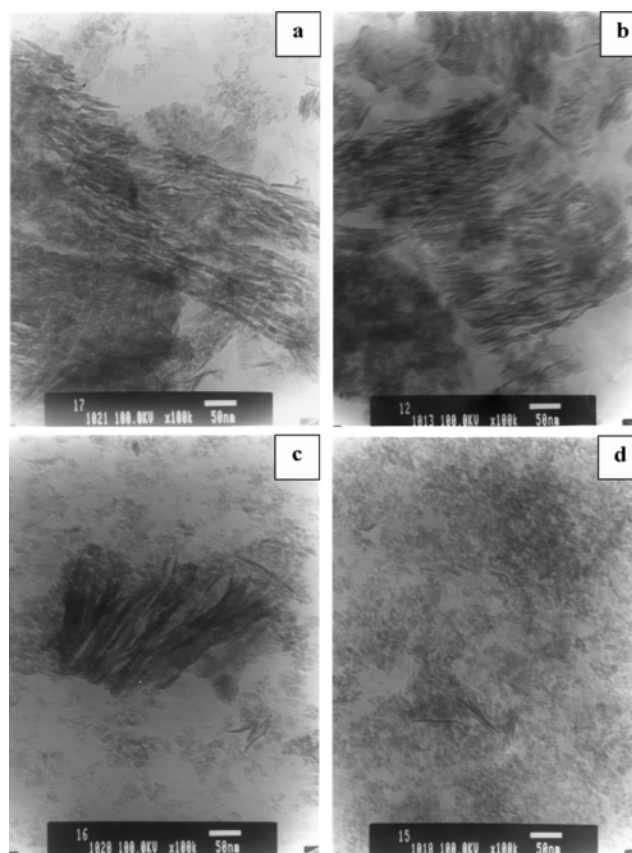


Fig. 2. TEM images of alumina obtained by the reaction of AIP in 1-butanol at 300°C for 2 h with different amounts of AIP (a) Al-10 (b) Al-15 (c) Al-25 (d) Al-35.

Table 1. The physical and chemical properties of Al₂O₃ supports

Samples	Amounts of AIP (g)	Surface area (m ² /g) ^a	Bulk density (g/cm ³) ^a	Morphology
Al-10	10	70	0.3824	Wrinkled sheets
Al-15	15	120	0.3858	High amount of wrinkled sheets
Al-25	25	139	0.3928	Wrinkled sheets and small amount of spherical particles
Al-35	35	145	0.5358	Small amount of wrinkled sheets and high amount of spherical particles

^aError of measurement=±5%

TEM images of alumina powders prepared with different amounts of AIP are shown in Fig. 2. For the ones prepared with lower amounts of AIP, Al-10 and Al-15, the wrinkled sheets morphology was observed. They were found to be similar to those obtained from the formation of γ -alumina by decomposition of glycol or alkyl derivatives on boehmite [26,27]. As the amounts of AIP increased, the wrinkled sheets morphology became less apparent and spherical particles were observed. The presence of spherical particles was probably due to the formation of χ -alumina, which is normally formed by thermal decomposition reaction of AIP in inert organic solvents at 300 °C [23-26]. TEM results were in good agreement with the XRD patterns that a mixture of γ -alumina and χ -alumina was observed when AIP concentration increased.

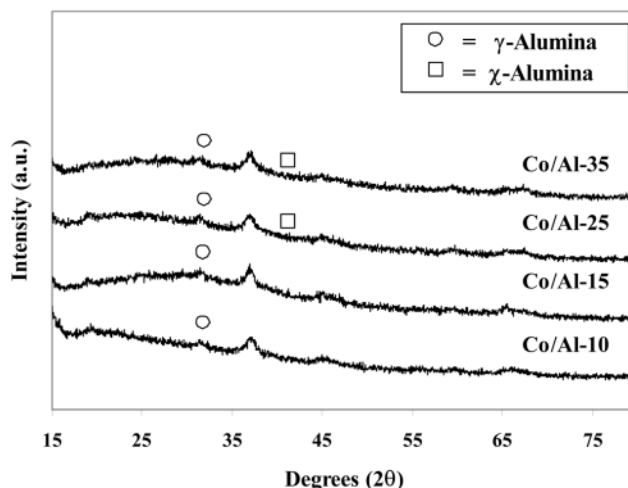
The physical properties of the alumina products are summarized in Table 1. The BET surface areas increased with increasing AIP concentration as a result of morphology changing from wrinkled sheets structure to small spherical particles. BET surface area of the Al-35 (145 m²/g) was found to be twice of that of Al-10 (70 m²/g). Similar trend was observed for the bulk density of the alumina powders. The bulk density increased with increasing AIP contents.

Mechanism of thermal decomposition of AIP in alcohol has been proposed in our previous works [23,26] involving three competitive reactions. First, AIP reacted with 1-butanol yielding aluminum butoxide, which decomposed further to give the alkyl (butyl) derivative of boehmite. Second, 1-butanol can be dehydrated to give water which then hydrolyzes aluminum isopropoxide or butoxide yielding pseudoboehmite. Finally, the direct decomposition of aluminum alkoxide in organic solvent, which proceeded slowest, gave χ -alumina. In the present work, at low AIP content, boehmite was probably the main product and γ -alumina was obtained after calcination at 600 °C for 1 h. The morphology of the boehmite products obtained via solvothermal reaction was wrinkled sheets [23,26], which was also similar to those of γ -alumina decomposed from. However, when the amounts of AIP in 1-butanol increased, formation of χ -alumina from direct decomposition of AIP in the solvent occurred as the main reaction.

2. Characteristics of Co/Al₂O₃ Catalysts

The XRD patterns of cobalt catalysts supported on alumina prepared with various amounts of AIP are shown in Fig. 3. The XRD patterns of the Co/Al₂O₃ catalysts were not significantly different from those of alumina supports. No XRD peaks of Co₃O₄ or other Co compounds were detected. This indicates that cobalt was present in a highly dispersed form on alumina even for cobalt loading as high as 10 wt% [29].

SEM and EDX were performed in order to study the morphol-

**Fig. 3. XRD patterns of Co/Al₂O₃ catalysts with different amounts of AIP.**

ogy and elemental distribution of the catalyst samples, respectively. Typical SEM micrographs of Co/Al₂O₃ catalysts are shown in Fig. 4. There was no significant change in morphology of the catalyst samples due to the effect of AIP concentrations in 1-butanol used in the preparation process. The white or light spots observed in all figures can be attributed to the cobalt patches distributed on the external surface of catalyst granules. Fig. 5 shows the SEM micrographs and the EDX mapping of the cross-sectioned Co/Al-35 catalyst granule. The distribution of cobalt was found to be well dispersed throughout the catalyst granule.

The relative amounts of active surface cobalt on the catalyst samples were calculated from H₂ chemisorption experiments at 100 °C according to Reuel and Bartholomew [28]. It is known that only surface cobalt metal atoms are active for CO hydrogenation, not its oxide or carbide [30]. The H₂ chemisorption results are reported in Table 2. The amounts of H₂ chemisorption increased from 0.90 to 20.65 μmol/g cat., with increasing amount of AIP in 1-butanol used in the preparation of the alumina supports from 10 to 35 g. It is likely that the increase in the relative amounts of active cobalt metals was due to the formation of the small spherical particles of χ -alumina. As also seen in the Table 2, the amount of H₂ chemisorption of Co/Com-Al (13.38 μmol/g cat.), prepared from the commercial γ -alumina which the crystal shape of alumina was spherical (the results was not shown), was better than solvothermal-made Co/ γ -alumina (0.90 μmol/g cat.) but lower than Co/ χ -alumina (20.65 μmol/g cat.).

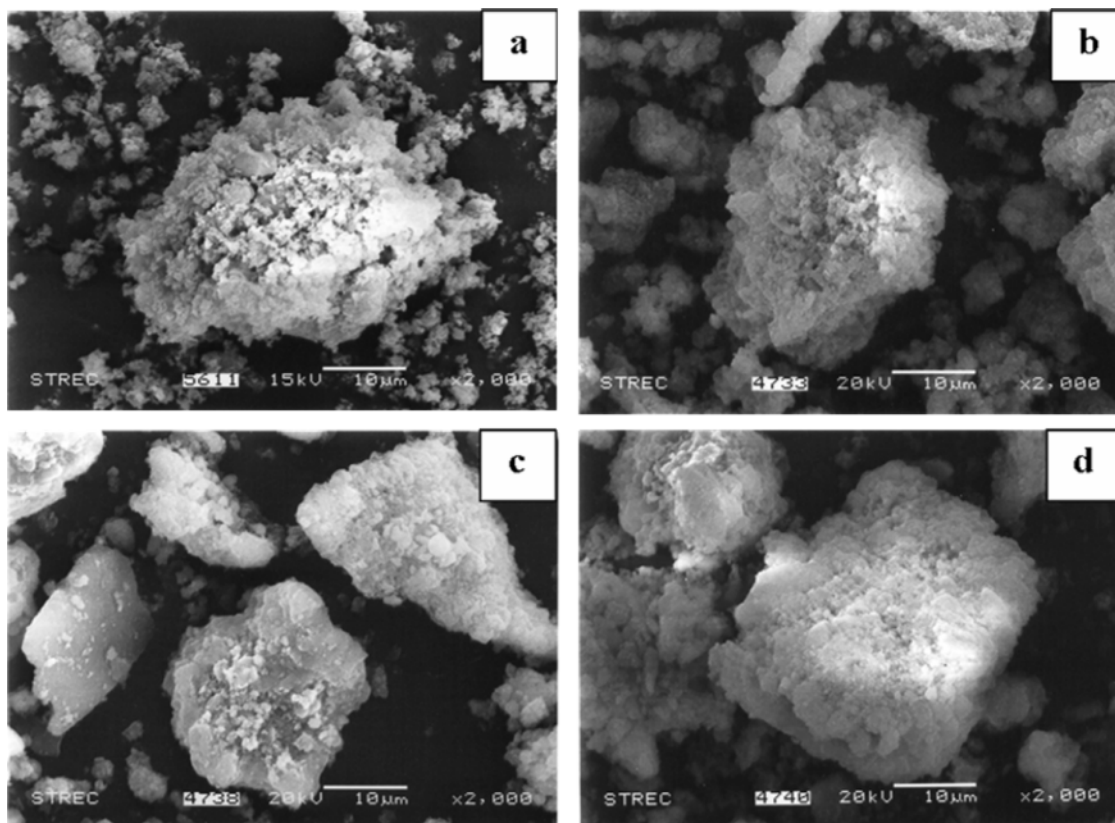


Fig. 4. SEM micrographs of (a) Co/Al-10, (b) Co/Al-15, (c) Co/Al-25, and (d) Co/Al-35.

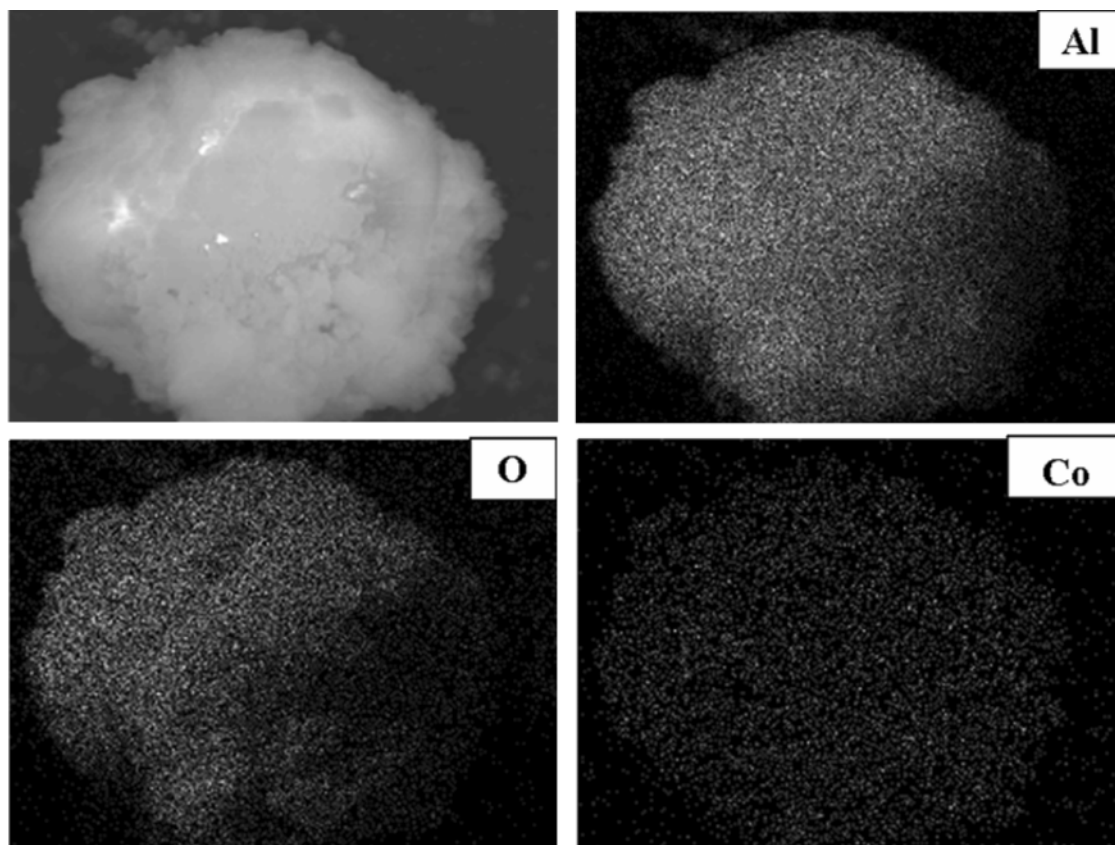


Fig. 5. SEM micrograph and EDX mapping of cross-sectioned Co/Al-35 catalyst granule.

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It was again confirmed that the spherical morphology of the alumina support is important in achieving a higher amount of active cobalt metal.

3. Reduction and Catalytic Behaviors of Co/Al₂O₃ Catalysts

Temperature program reduction (TPR) is a powerful tool for studying the reduction behavior of the catalysts. The TPR profiles of various nanocrystalline alumina supported cobalt catalysts are shown in Fig. 6. All the catalyst samples exhibited two main reduction peaks which could be assigned to the two-step reduction of Co₃O₄: first reduction of Co₃O₄ to CoO and then the subsequent reduction of CoO to Co⁰ [31]. The two reduction steps may not always be ob-

served as separate peaks in TPR profile [32], as seen in the Co/Al-35 sample. A wide range of variables such as metal particle size and metal-support interaction have an influence on the reduction behavior of cobalt catalysts resulting in the observation of different locations of the TPR peaks. The TPR profiles for all the catalysts except Co/Al-35 appeared to be not significantly different, suggesting that the AIP content had little impact on the interaction of cobalt and alumina supports. Thus, high dispersion of cobalt obtained on Co/Al-35 was rather to be due to the formation of small spherical particles alumina and not to the change in reducibility of the catalysts.

CO hydrogenation reaction was carried out as a test reaction to determine the catalytic activity of the catalyst samples. The results are shown in Table 3. It is clearly seen that alumina prepared with higher amounts of AIP in 1-butanol resulted in much higher CO hydrogenation activities and CH₄ selectivities. The reaction results confirm the amount of surface cobalt metals measured by H₂ chemisorption.

CONCLUSIONS

Nanocrystalline alumina powders were prepared by thermal decomposition of AIP in 1-butanol with various AIP contents. The concentration of AIP in 1-butanol had a significant impact on the properties of alumina and alumina supported cobalt catalysts. Increasing amounts of AIP in the solution resulted in the transformation of wrinkled sheet γ -alumina to fine spherical particles of χ -alumina. It also gave rise to the cobalt active sites and CO hydrogenation activities when employed as supports for preparation of Co/Al₂O₃ catalysts.

ACKNOWLEDGMENTS

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Table 2. The characteristics and H₂ chemisorption of cobalt catalyst

Catalyst samples	Surface area (m ² /g) ^a	Amount of H ₂ chemisorption (μmol/g cat.) ^a
Co/Al-10	61	0.90
Co/Al-15	87	2.29
Co/Al-25	108	7.58
Co/Al-35	114	20.65
Co/Com-Al*	145	13.38

^aError=±5%, as determined directly.

*Commercial γ -alumina, BET surface area of alumina 230 m²/g.

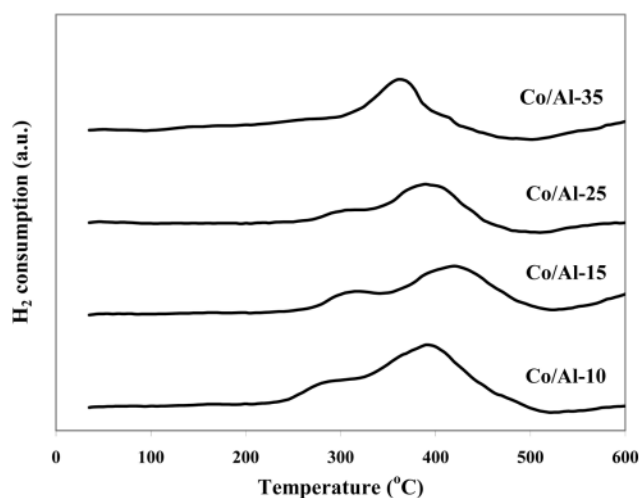


Fig. 6. TPR profiles of the catalyst samples.

Table 3. Reaction rate and selectivity for CO hydrogenation on catalyst samples

Catalyst samples	CO conversion (%) ^a		Rate ($\times 10^2$ gCH ₂ gcat ⁻¹ h ⁻¹) ^b		CH ₄ selectivity (%)	
	Initial ^c	SS ^d	Initial	SS	Initial	SS
Co/Al-10	1.92	0.54	5.76	1.62	13	11
Co/Al-15	2.63	0.75	7.89	2.25	49	47
Co/Al-25	5.45	3.02	16.35	9.06	56	54
Co/Al-35	8.49	4.03	25.47	12.09	70	67

^aCO hydrogenation was carried out at 220 °C, 1 atm, and H₂/CO/Ar=80/8/32.

^bError±5%, as determined directly.

^cAfter 20 min of reaction.

^dAfter 6 h of reaction.

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Copper-modified alumina as a support for iron Fischer–Tropsch synthesis catalysts

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Abstract

In the present study, the effect of Cu-modified Al_2O_3 on the properties of Al_2O_3 -supported Fe catalysts in the Fischer–Tropsch synthesis was investigated. Ten weight percent Cu was first impregnated into γ -alumina to produce Cu-modified Al_2O_3 supports; then 20 wt.% of Fe and (in some cases) 1 wt.% Cu were added to the supports by the sequential impregnation method. Two different pretreatment methods (drying or drying and calcining) were employed after each metal impregnation. It was found that the use of Cu-modified Al_2O_3 supports increased significantly the overall activity of the Fe/ Al_2O_3 catalysts. Addition of 1% Cu as a reduction promoter to the Cu-modified supported Fe catalysts was not necessary since it did not further enhance the activity of the catalysts. There were no changes in FT product selectivity, chain growth probability (α), or olefin selectivity due to any effect of the Cu-modified Al_2O_3 or Cu-promotion. However, the more calcination steps used during preparation, the higher the catalyst activity obtained. Cu-modification of the alumina most probably diminished the interaction/reaction of the Fe with the support, thereby improving its chemisorption and catalytic properties.

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Keywords: Iron catalysts; Alumina-supported catalysts; Copper modification; Fischer–Tropsch synthesis

1. Introduction

Due to depletion of oil reserves and increased cost of petroleum, alternative methods for synthesizing hydrocarbon fuels such as the Fischer–Tropsch synthesis (FTS) have again received considerable attention. FTS is an important technology in the production of liquid fuels and chemicals from syngas derived from coal, natural gas, or other carbon-containing materials. Several metal catalysts can be used for the FTS, however, only iron and cobalt catalysts appear to be economically feasible on an industrial scale [1]. Co catalysts yield mainly straight-chain hydrocarbons [2–4] while Fe catalysts are more useful when the H_2/CO ratio is low (because of the water–gas-shift activity of Fe) or for the production of alkenes, oxygenates, and branched hydrocarbons, which

depends on the promoters and process conditions employed [2,5]. Many inorganic oxides such as Al_2O_3 [6–9], SiO_2 [10], TiO_2 [7,11] and ZrO_2 [7,12] have been studied as supports for Fe catalysts. However, Fe can easily react with the supports to form compounds [10,12,13] and is often difficult to reduce when highly dispersed on refractory oxides. For example, Zhang et al. [10] investigated the iron–silica interaction of a silica-supported iron FTS catalyst and found that nanoparticles of iron oxide mixtures existed in the as-prepared catalyst while wüstite and iron silicate were the main phases after reduction. The formation of these nanoparticles and the presence of metastable phases resulted in lower FTS activity and production of more gaseous hydrocarbons. Thus, the use of supported Fe catalysts has been limited and bulk Fe catalysts usually show superior properties [2,14,15].

Development of highly active supported Fe catalysts, however, would be useful since it could reduce catalyst density and make catalyst application in fluidized/slurry reactors easier. Most of the studies reported have attempted to improve catalyst

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performance by promoting with additives such as K [11,16,17], Mn [11,18], Cr [11], Ru [19], and Pd [16–20]. Cu is usually present in bulk Fe catalysts as a reduction promoter [19,21–23]. It facilitates reduction of iron oxide to metallic iron during hydrogen activation by lowering the reduction temperature which, in turn, reduces sintering of the metallic iron that is formed [24]. However, to the best of our knowledge, the effect of Cu to modify the metal oxide support for supported iron catalyst in FTS has never been reported. Cu is more interesting than many other transition metals since it does not alloy with Fe. This means there is less chance that desired Fe catalytic properties would be altered.

The purpose of this study was to investigate the effect of Cu-modified Al_2O_3 on the properties of Al_2O_3 -supported Fe catalysts. A series of Cu-modified alumina supported Fe catalysts were prepared by the sequential impregnation method followed by different pretreatments (either drying or drying and calcining). The catalysts were then characterized by N_2 physisorption, CO chemisorption, X-ray diffraction, scanning electron microscopy, and FTS.

2. Experimental

2.1. Catalyst preparation

For preparation of the reference 1% Cu on $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst, a solution of iron(III) nitrate nonahydrate (Alfa Aesar) was first impregnated into the $\gamma\text{-Al}_2\text{O}_3$ support (Johnson Matthey, specific surface area of $100\text{ m}^2/\text{g}$) using the incipient wetness method to give a final catalyst composition of ca. 20 wt.% Fe. The impregnated catalyst was dried at $110\text{ }^\circ\text{C}$ for 24 h followed by calcination in air at $350\text{ }^\circ\text{C}$ for 3 h. Then, 1 wt.% Cu was impregnated into the sample using a solution of copper(II) nitrate trihydrate (Acros Organics) and incipient wetness (IW). The catalyst was dried at $110\text{ }^\circ\text{C}$ for 24 h and then calcined again in air at $460\text{ }^\circ\text{C}$ for 3 h.

The 10% Cu-modified Al_2O_3 supports were prepared by the incipient wetness impregnation of the $\gamma\text{-Al}_2\text{O}_3$ with a solution of copper(II) nitrate trihydrate. The samples were dried at $110\text{ }^\circ\text{C}$ for 24 h and then calcined (in some cases) in air with ramping of the temperature at $10\text{ }^\circ\text{C}/\text{min}$ up to $300\text{ }^\circ\text{C}$ and

holding for 1 h. The temperature was thereafter increased by $10\text{ }^\circ\text{C}/\text{min}$ up to $500\text{ }^\circ\text{C}$ and held for 6 h. Then a solution of iron(III) nitrate nonahydrate was used to impregnate (by IW) the Cu-modified Al_2O_3 supports to produce 20 wt.% Fe catalysts followed by drying and where indicated calcining at $350\text{ }^\circ\text{C}$. A solution of copper(II) nitrate trihydrate was finally impregnated (by IW) where indicated to produce 1 wt.% Cu, followed by drying and in some cases calcining at $460\text{ }^\circ\text{C}$.

2.2. Catalyst nomenclature

The catalyst nomenclature, the compositions, and the preparation conditions of the various Al_2O_3 supported Fe catalysts are given in Table 1. The Fe catalysts prepared basically had three metal components in addition to the Al_2O_3 support. The base catalyst was 1% Cu promoted 20% $\text{Fe}/\text{Al}_2\text{O}_3$. All the other catalysts were prepared on 10% Cu-modified Al_2O_3 supports. The catalysts were either dried (D) or dried and calcined (C) after each metal loading step. The nomenclature used for these catalysts consists of five components. For examples, the base catalyst is referred to as “1-0-*CC”, where the first number “1” referred to 1% Cu promoted 20% $\text{Fe}/\text{Al}_2\text{O}_3$ and the second number “0” referred to 0% Cu added to the Al_2O_3 support. The symbol and the letters “*CC” indicate the pretreatment used in each metal loading step. The asterisk (*) means that there was no pretreatment for the first stage since no Cu was added to the Al_2O_3 support in this sample but the catalysts were dried and calcined after Fe and Cu loadings. The catalyst designated “1-10-DDC” indicates that it was 1% Cu promoted 20% Fe catalyst on 10% Cu-modified Al_2O_3 support. The Cu-modified Al_2O_3 support was dried only (designated by the first D) but not calcined prior to Fe impregnation. The 20% Fe on 10% Cu-modified Al_2O_3 was then dried again (designated by the second D) but not calcined prior to the addition of 1% Cu. After the final impregnation step, the catalyst was then dried and calcined (designated by the third C).

2.3. Reaction

Steady-state FTS reaction rates and selectivities were measured in a stainless steel fixed-bed reactor under differential

Table 1
Catalyst nomenclatures and the preparation conditions

Catalyst	Metal loading (wt.%)			Pretreatment after each metal impregnation		
	Cu	Fe	Cu on Al_2O_3	1st (10% Cu on Al_2O_3)	2nd (20% Fe)	3rd (1% Cu)
1-0-*CC ^a	1	20	0	None	C	C ^b
1-10-CCC	1	20	10	C	C	C
1-10-CDC	1	20	10	C	D ^c	C
1-10-DDC	1	20	10	D	D	C
1-10-DDD	1	20	10	D	D	D
0-10-CC*	0	20	10	C	C	None
0-10-CD*	0	20	10	C	D	None
0-10-DC*	0	20	10	D	C	None

^a 1% Cu-promoted 20% $\text{Fe}/\text{Al}_2\text{O}_3$ is the reference catalyst.

^b C: dried in air at $110\text{ }^\circ\text{C}$ for 24 h followed by calcination in air at desired temperature and holding time for each metal.

^c D: dried in air at $110\text{ }^\circ\text{C}$ for 24 h.

reaction conditions at 280 °C and 1.8 atm total pressure. The H₂/CO ratio used was 2/1. Typically, 0.1 g of the catalyst sample was pretreated *in situ* in flowing H₂ (50 ml/min) at 460 °C for 16 h prior to reaction. After pretreatment the reaction mixture containing 5 ml/min of CO, 10 ml/min of H₂, and 45 ml/min of He was then introduced into the reactor at 280 °C. The system pressure used was 1.8 atm. Product samples were taken at 1.5-h intervals and analyzed by gas chromatography. Analysis of hydrocarbons was carried out with a AT-Q 30 m × 0.53 mm Heliflex capillary column using a flame ionization detector. Analysis of CO and CO₂ were performed in a Carbosphere 80/100 6 ft × 1/8 in. × 0.085 in. SS packed column using a thermal conductivity detector. Steady-state was reached within 6 h in all cases.

2.4. Catalyst characterization

The BET surface area, pore volume, and average pore size were measured by N₂ physisorption at liquid N₂ temperature (−196 °C) using a Micromeritics ASAP 2020 automated system. The samples were degassed under vacuum at 100 °C for 1 h and then the temperature was increased by 10 °C/min to 300 °C and the samples were held at that temperature for 2 h prior to each measurement. X-ray diffraction patterns of the catalysts were collected with a Scintag 2000 X-ray diffractometer, using monochromatized Cu K α radiation (40 kV, 40 mA), a Ge detector, and a step scan mode. The samples were scanned at a scan rate of 0.04° (2 θ) per second from 2 θ = 10° to 80°. SEM and EDX were carried out using a JEOL JSM-35CF scanning electron microscope in the back scattering electron (BSE) mode at 20 kV. EDX was performed using Link Isis 300 software. Pulse CO chemisorption was measured for the catalyst samples at 50 °C. Approximately, 0.1 g of catalyst was put in a quartz tube, placed in a temperature-controlled oven, and connected to a thermal conductivity detector (TCD). The carrier gas used was helium. Prior to CO chemisorption, the catalyst samples were pretreated in flowing (50 ml/min) H₂ at 460 °C for 16 h with a ramping rate of 10 °C/min. Afterwards,

the sample was purged with helium for 20 min and finally cooled down to 50 °C. Carbon monoxide was pulsed at 50 °C over the reduced catalyst until the TCD signal was constant. Temperature-programmed reduction (TPR) was performed to study the reduction behaviors of the catalysts using a Micromeritics Pulse Chemisorb 2750 system. Approximately 0.1 g of the catalyst was placed in the quartz tube. A temperature ramp from 35 to 800 °C at a ramp rate 5 °C/min and the reduction gas 10% H₂ in Ar were used. A thermal conductivity detector (TCD) was used to determine the amount of hydrogen consumed. A cold trap was placed before the detector to remove water produced during the reduction.

3. Results and discussion

The catalytic activities and selectivities for Fischer–Tropsch synthesis of the various Cu-modified Fe/Al₂O₃ catalysts are shown in Table 2. It can be seen that all the catalysts with Cu-modified Al₂O₃ supports exhibited higher hydrocarbon formation rates than the base Cu-promoted Fe/Al₂O₃ catalyst (1-0-CC), regardless of the addition of 1% Cu as a promoter. The steady-state rates for CO₂ formation were also higher for the catalysts prepared with Cu-modified Al₂O₃ supports. For a similar catalyst system (1% Cu-promoted or non-promoted Fe/Cu-modified Al₂O₃ catalysts), the more calcination steps used during preparation, the higher the FTS activity. Hence, among the catalysts studied, the 1-10-CCC catalyst gave the highest hydrocarbon formation activity. Neither the addition of 10% Cu to the Al₂O₃ support nor the pretreatment during preparation appeared to have much effect on the FTS product selectivity, the Anderson–Schulz–Flory (ASF) chain growth probability (α), or the olefin selectivity, at least under the reaction conditions used. No oxygenated hydrocarbon products were observed in this study due to such compounds not being major products and to the fact that differential conversion was used (<10%). The reaction results are consistent with those reported by Coville and co-workers [25] that Cu promotion enhances activity of supported Fe

Table 2
FTS reaction rate and selectivity

Catalyst	Metal loading (wt.%)			SS rate of CO ₂ formation ^{a,b} ($\mu\text{mol/g cat./s}$)	SS rate of total HC formation ^{a,b} ($\mu\text{mol of CO converted/g cat./s}$)	TOF (s ^{−1}) ^c	% Selectivity ^b							% Olefin (C ₂ –C ₄) ^b	α (C ₃ –C ₆) ^b
	Cu	Fe	Cu on Al ₂ O ₃				C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇₊		
1-0-CC	1	20	0	Nil	0.50	0.42	41.0	29.1	20.5	6.4	2.0	0.7	0.2	67	0.33
1-10-CCC	1	20	10	0.31	0.90	0.04	45.5	26.1	19.4	6.2	1.8	0.8	0.2	55	0.35
1-10-CDC	1	20	10	0.34	0.86	0.08	49.8	25.6	17.9	4.3	1.6	0.6	0.2	54	0.32
1-10-DDC	1	20	10	0.35	0.71	0.10	45.9	26.4	19.1	6.0	1.8	0.6	0.2	58	0.31
1-10-DDD	1	20	10	0.32	0.63	0.63	44.5	26.9	19.3	6.1	1.9	0.9	0.4	61	0.35
0-10-CC*	–	20	10	0.30	0.89	0.06	46.5	25.9	19.2	5.5	1.8	0.8	0.2	58	0.34
0-10-CD*	–	20	10	0.24	0.74	0.15	44.6	26.7	19.8	6.1	1.8	0.8	0.2	63	0.34
0-10-DC*	–	20	10	0.07 ^d	0.81	0.12	43.4	27.0	20.1	6.4	2.0	0.9	0.3	58	0.35

^a FTS reaction was carried out at 280 °C, 1.8 atm total pressure, and H₂/CO ratio used = 2/1. Rate of hydrocarbon formation is in $\mu\text{mol of CO converted/g cat./s}$. The reaction reached steady-state product formation before 6 h TOS, so all steady-state data is for that TOS.

^b Error of measurement = $\pm 5\%$ as determined directly.

^c Based on pulse CO chemisorption (see Table 3). Error of measurement = $\pm 10\%$.

^d Repeatability for two times. Error of measurement = $\pm 2\%$ as determined directly.

catalysts but does not have an effect on FT product selectivity. The results from this study reveal that the effect of the Cu-modified Al_2O_3 support on the catalytic properties of $\text{Fe}/\text{Al}_2\text{O}_3$ catalysts is similar in nature to the addition of Cu as a second metal promoter. Moreover, the catalyst that had never been calcined in any preparation step (1-10-DDD) exhibited the lowest FTS activity among the various Fe catalysts prepared with the Cu-modified Al_2O_3 support. Therefore, the calcination step appears to be very important in producing highly active catalysts.

Some physicochemical properties of the Al_2O_3 support and the various Al_2O_3 supported Fe catalysts are shown in Table 3. It was found that BET surface areas, pore volumes, and pore sizes of the 1% Cu promoted Fe on Cu-modified Al_2O_3 catalysts prepared with calcination pretreatment after the last metal impregnation (all of the 1–10 catalysts except 1-10-DDD) were in the range of 107–113 m^2/g and were not significant different from the base 1-0-*CC catalyst (115 m^2/g). On the other hand, for the 0–10 catalysts (the catalysts without 1% Cu as a second metal promoter) and the catalysts prepared with only drying after the last metal impregnation (prior to reduction), the BET surface areas were higher (130–147 m^2/g) with 0-10-CD* showed the highest BET surface area. Since the average pore sizes and pore volumes of all the catalysts were smaller than those of the alumina support, some of the active metal probably was deposited in the pores of the alumina. XRD patterns of the Al_2O_3 , the 10 wt.% $\text{Cu}/\text{Al}_2\text{O}_3$ (dried and calcined), and the various catalysts are shown in Fig. 1. The $\gamma\text{-Al}_2\text{O}_3$ exhibited strong diffraction peaks at $2\theta = 31^\circ, 33^\circ, 38^\circ, 39.7^\circ, 43^\circ, 46^\circ$, and 68° (based on the JCPDS database). For the 10% $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst, it was found that Cu was in the form of CuO, as indicated by its characteristic peaks at $2\theta = 35.5^\circ$ and 39° . It has been reported that interaction between CuO and Al_2O_3 occurs readily at calcination temperatures close to 600°C , yielding CuAl_2O_4 [26]. Moreover, the extent of solid–solid interaction between oxides involved in aluminate formation increases on increasing the calcination temperature from 600 to 800°C . It is likely that in this study CuAl_2O_4 was not formed at the calcination temperature used (460°C) since no XRD peaks for CuAl_2O_4 were detected. The XRD patterns for all the supported Fe catalysts do not show any characteristic

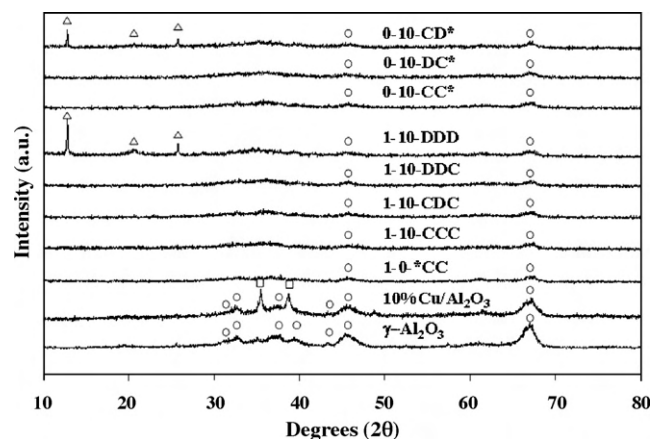


Fig. 1. XRD patterns of the $\gamma\text{-Al}_2\text{O}_3$ support, the 10 wt.% $\text{Cu}/\text{Al}_2\text{O}_3$ support (dried and calcined), the Al_2O_3 -supported Fe catalysts and Cu-modified Al_2O_3 -supported Fe catalysts. (○) $\gamma\text{-Al}_2\text{O}_3$; (□) CuO; (△) Nitrate species.

peaks of Fe_2O_3 or any other Fe compound suggesting that Fe was present in a highly dispersed form. Except for the catalysts that were only dried after the last metal impregnation, all the catalysts exhibited XRD patterns similar to the base catalyst where only the major peaks for $\gamma\text{-Al}_2\text{O}_3$ were found. For the 1-10-DDD and 0-10-CD* catalysts which were only dried after the last metal impregnation, additional diffraction peaks at $2\theta = 12.9^\circ, 20.9^\circ$, and 25.8° can be seen in the XRD patterns. These peaks are attributed to the presence of residual Fe nitrate of Cu nitrate in the catalysts. These catalysts were less active than those prepared with calcination pretreatment after impregnation of the metal(s), perhaps due to a greater difficulty in reducing the Fe oxide to Fe metal during reduction of the catalysts with H_2 .

SEM and EDX were also performed in order to study the morphology and elemental distribution of the catalyst samples. The alumina and Cu-modified alumina supports consisted of irregular shaped particles/granules formed by agglomeration of nanocrystalline alumina (results not shown). There were no differences in the cluster size and morphology of the various alumina-supported Fe catalysts, as seen in Fig. 2. An SEM micrograph with EDX elemental mapping (for Al, O, Fe, and Cu) of the 1-10-CCC catalyst is shown in Fig. 3. It can be seen

Table 3
Catalyst characteristics

Catalyst	Metal loading (wt.%)			BET surface area ($\text{m}^2/\text{g cat.}$) ^a	Average pore volume ($\text{cm}^3/\text{g cat.}$) ^a	Average pore size (nm) ^a	CO chemisorption ($\mu\text{mol/g cat.}$) ^b
	Cu	Fe	Cu on Al_2O_3				
$\gamma\text{-Al}_2\text{O}_3$	0	0	0	100.0	0.68	27.2	–
1-0-*CC	1	20	0	114.8	0.37	12.9	1.2
1-10-CCC	1	20	10	107.4	0.36	13.4	24.8
1-10-CDC	1	20	10	113.1	0.35	12.5	11.2
1-10-DDC	1	20	10	108.6	0.35	12.9	6.9
1-10-DDD	1	20	10	145.7	0.35	9.7	1.0
0-10-CC*	0	20	10	130.4	0.36	11.0	15.2
0-10-CD*	0	20	10	146.7	0.32	8.8	4.8
0-10-DC*	0	20	10	130.4	0.35	10.8	6.8

^a Using N_2 physisorption at 77 K. Error of measurement = $\pm 10\%$.

^b Error of measurement = $\pm 5\%$.

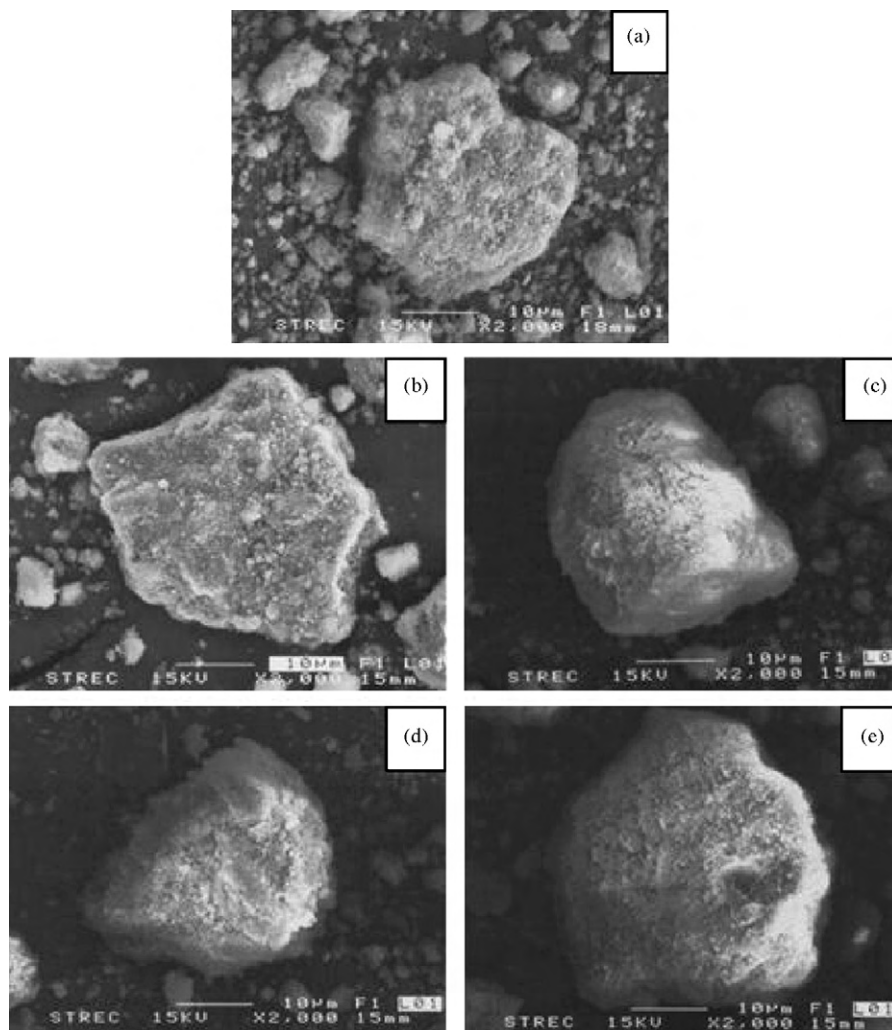


Fig. 2. SEM micrographs of the catalysts. (a) 1-0-CC, (b) 1-10-CCC, (c) 1-10-DDC, (d) 1-10-DDD and (e) 0-10-CC*.

that all of elements in the catalyst were well dispersed and distributed throughout the catalyst granules. Similar results were also obtained for other Cu-modified alumina-supported Fe catalysts.

The reduction behavior of the catalysts was studied by H_2 temperature program reduction (TPR). The TPR profiles of the Fe/Al_2O_3 catalyst and the variously Cu-modified Fe/Al_2O_3 catalysts are shown in Fig. 4. TPR profile of the alumina support (not shown) exhibited no reduction peak under the TPR conditions used. For the Fe/Al_2O_3 catalyst, only one reduction peak located at ca. 165–400 °C (maximum at 265 °C) was observed. TPR profiles for the Cu-modified Fe/Al_2O_3 catalysts were similar to that of Fe/Al_2O_3 with only a single reduction peak being observed. The reduction peaks of the Cu-modified Fe/Al_2O_3 catalysts (except 1-10-DDD and 0-10-CD*) were located at ca. 105–345 °C (maximum at 230 °C). While, the reduction peak of the 1-10-DDD and 0-10-CD* catalysts were located at ca. 200–400 °C (maximum at 330 °C). The maximum in the reduction peak at ca. 265 °C for the Fe/Al_2O_3 catalyst was shifted about 35 °C lower when there was a presence of Cu in the alumina support as seen for the Cu-modified Fe/Al_2O_3 catalysts (except 1-10-DDD and 0-10-CD*). The shift of the reduction

peak maximum to a lower temperature indicates a greater ease of reduction that can be due in part to a weaker interaction between iron and alumina. For the Cu-modified Fe/Al_2O_3 catalysts with drying pretreatment after the final impregnation (1-10-DDD and 0-10-CD*), the TPR peak maximum was about 65 °C higher (at ca. 330 °C). The shift of a reduction peak to higher temperature suggests a stronger interaction between iron and the alumina support. It can be seen that the reduction temperature decreased significantly for the Cu-modified alumina supported iron catalysts with calcining pretreatments after the final impregnation step. However, the one prepared with only a drying pretreatment after the final impregnation resulted in an increased reduction temperature. This may be due in large part to the presence of residual nitrate species in the catalysts.

Pulse CO chemisorption was performed in order to determine the relative amounts of active iron on the catalyst samples. The results are shown in Table 3. The amounts of CO chemisorption on the Cu-modified Fe/Al_2O_3 catalysts varied in the range of 1.0–24.8 $\mu\text{mol/g cat.}$ and were higher than that of the Fe/Al_2O_3 base catalyst. The presence of the Cu-modified alumina support resulted in an increase in the relative amounts of surface-exposed active iron metal. Each additional calcina-

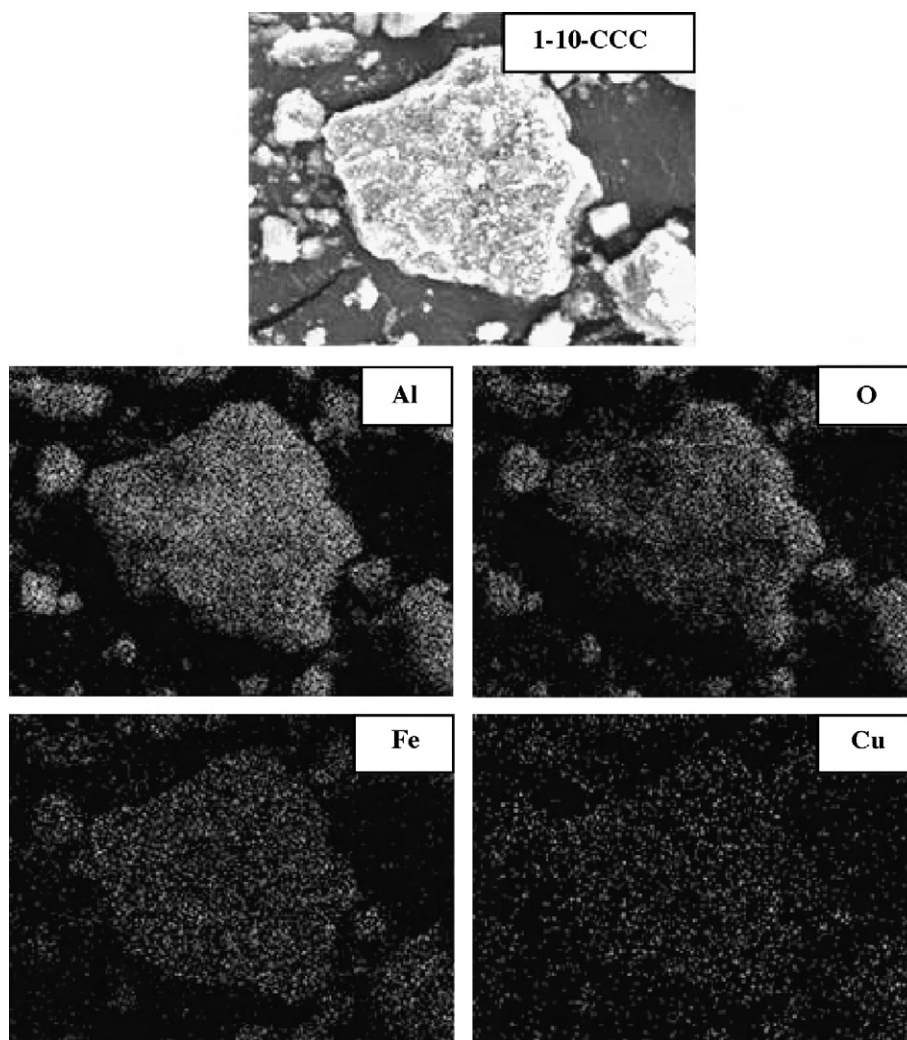


Fig. 3. SEM micrograph and EDX mapping of a cross-sectioned 1-10-CCC catalyst granule.

tion led to increased CO chemisorption, as shown in Fig. 5 for the Cu-modified Fe/Al₂O₃ catalysts. The CO chemisorption results suggest an increased Fe dispersion after multiple calcinations. However, CO is also known to adsorb somewhat on Cu oxide surfaces [27,28]; thus, some of the increase in CO

chemisorption may have been due to CO adsorbing on Cu oxide entities/particles on the catalyst surface.

Fig. 6 shows the effect of the number of calcinations on the steady-state hydrocarbon synthesis rate. It can be seen that there was a significant increase in the steady-state hydrocarbon

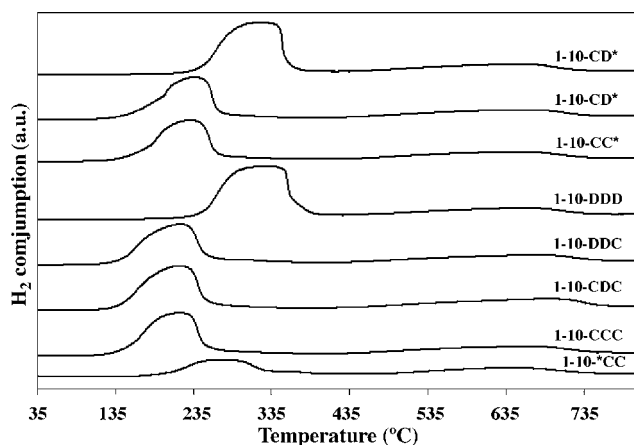


Fig. 4. TPR profiles of the catalyst samples.

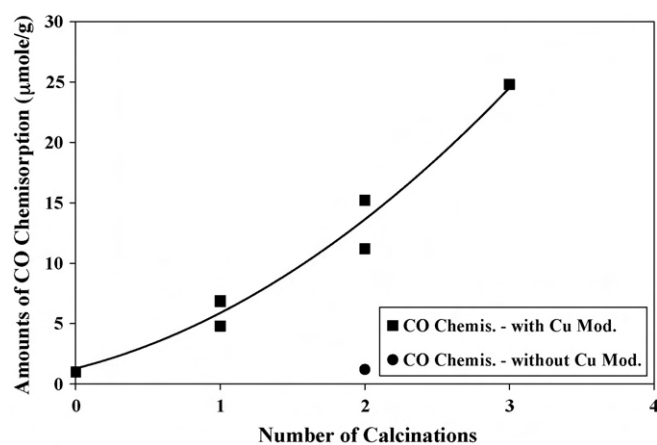


Fig. 5. Effect of number of calcinations on CO chemisorption.

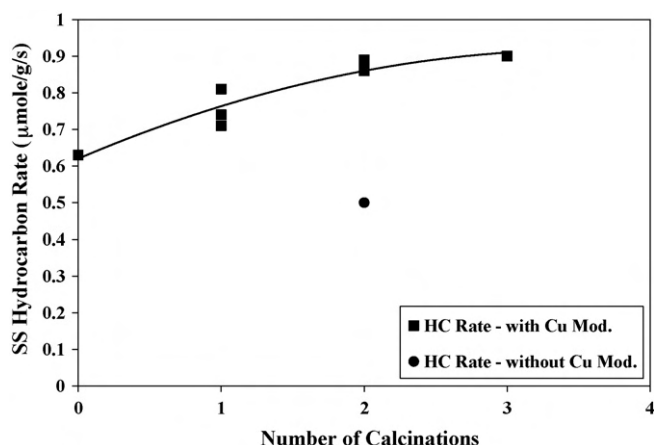


Fig. 6. Effect of number of calcinations on steady-state of total hydrocarbon rate.

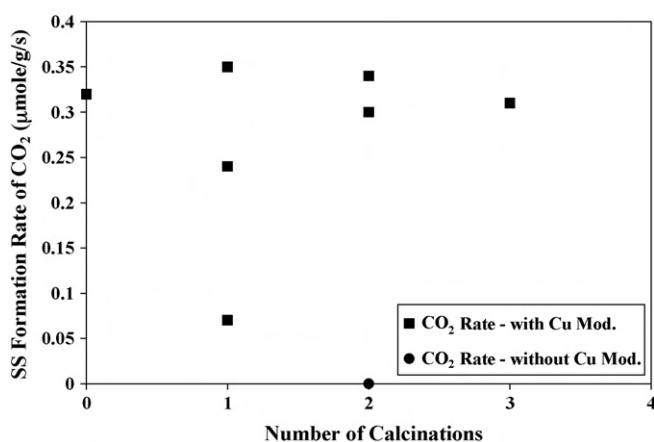


Fig. 7. Effect of number of calcinations on steady-state formation rate of CO₂.

synthesis rate with the number of calcinations. However, there was little (or no) effect of calcinations on the rate of CO₂ formation, although Cu-modification significantly increased water-gas-shift reaction on the catalysts (Fig. 7). The relationship between the steady-state hydrocarbon synthesis rate and CO chemisorption is illustrated in Fig. 8. It can be observed that while the rate of hydrocarbon formation

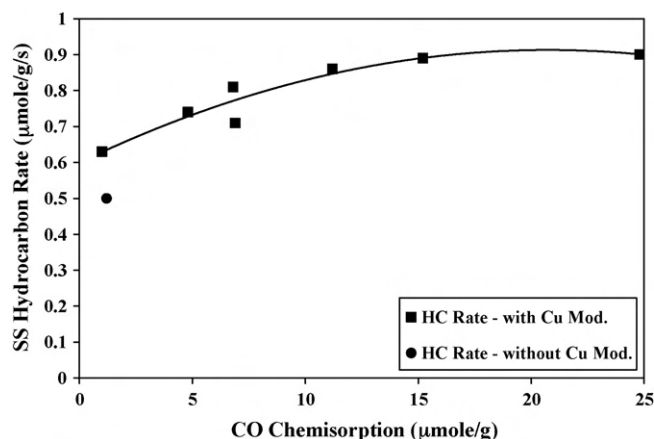


Fig. 8. Steady-state hydrocarbon synthesis rate vs. CO chemisorption.

increased with CO chemisorption, there was only a weak dependence, supporting the suggestion given above that some of the additional CO chemisorption took place on Cu oxide entities. The results of this study, however, clearly indicate that the number of calcinations during preparation is an important variable besides Cu-modification of the support in affecting the hydrogenation activity of Fe/Al₂O₃ catalysts. Multiple calcinations can perhaps (a) decrease the contamination of the surface by nitrate species, (b) increase Fe reducibility, and/or (c) produce larger Fe particles which are easier to reduce (although this is not able to be verified by XRD).

4. Conclusions

This study explored the effect of copper-modified alumina on the activity and selectivity of alumina-supported iron catalysts for the FTS reaction. It was found that the Fe catalysts supported on 10 wt.% Cu-modified alumina exhibited significantly higher activities than those of a 1 wt.% Cu-promoted Fe/Al₂O₃ catalyst. There was, however, little effect on FT product selectivity, chain growth probability (α), or olefin selectivity. Moreover, calcination after impregnation of each metal during catalyst preparation is important for producing highly active catalysts. It is likely that Cu-modification acts to restrict interaction of Fe with the alumina support, known to decrease the activity of Fe for FTS. Use of the Cu-modified support increased both the CO chemisorption and the ease of reduction provided the catalyst was calcined after preparation.

Acknowledgments

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Effect of mixed γ - and χ -crystalline phases in nanocrystalline Al_2O_3 on the dispersion of cobalt on Al_2O_3

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Abstract

This paper reports the results of a study into the effect of mixed γ and crystalline phases in Al_2O_3 on the characteristics and catalytic activities for CO hydrogenation of $\text{Co}/\text{Al}_2\text{O}_3$ catalysts. The catalysts were characterized by X-ray diffraction, N_2 physisorption, transmission electron microscopy, and H_2 chemisorption. Increasing Co loading from 5 to 20 wt% for the mixed phase Al_2O_3 -supported Co catalysts resulted in a constant increase in both the number of cobalt metal active sites and the hydrogenation activities. However, for those supported on γ - Al_2O_3 , Co dispersion increased up to 15 wt%Co and declined at 20 wt%Co loading. It is suggested that the spherical-shape like morphology of the χ -phase Al_2O_3 prevented agglomeration of Co particles, especially at high Co loadings.
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Keywords: Nanocrystalline alumina; Crystalline phase; Cobalt catalyst; CO hydrogenation; χ -Alumina; γ -Alumina

1. Introduction

Alumina is one of the most common commercial carriers used to disperse catalytic materials because of its excellent thermal stability, high mechanical resistance, and wide range of chemical, physical, and catalytic properties. In general, acidic, high surface area alumina hydrates are produced at relatively low temperatures by precipitation from either acidic or basic solutions and then are transformed to “transition” β -, γ -, η -, χ -, κ -, δ -, α -, and α - Al_2O_3 by dehydration and treatment at high temperatures [1].

Despite a wide range of crystalline structures, only γ - and α - Al_2O_3 have been studied often as catalyst supports. Typically, γ - Al_2O_3 provides a better dispersion of catalytically active metals than α - Al_2O_3 due to its higher surface

area. Only a few publications have reported the effect of other crystalline phases of alumina on the properties of alumina-supported catalysts. For example, Chary et al. [2] reported that dispersion of vanadium oxide on alumina as well as its catalytic activities in partial oxidation decreased with increasing calcination temperature due to the transformation of γ -alumina into θ -alumina, δ -alumina, and α -alumina phases. Recently, Moya et al. [3] studied silver nanoparticles supported on α -, η -, and δ - Al_2O_3 prepared by a colloidal processing route. It was found that silver particle sizes varied between 1 and 100 nm depending on the alumina phase. To our knowledge, the effect of mixed γ - and χ - Al_2O_3 phases on the properties of Al_2O_3 as a catalyst support has never been reported.

In this study, nanocrystalline transition Al_2O_3 (γ - Al_2O_3 and mixed γ - and χ - Al_2O_3) were synthesized by decomposition of aluminum isopropoxide (AIP) under solvothermal conditions. The advantages of the solvothermal method are

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that it gives products with uniform morphology, well-controlled chemical composition, and narrow particle size distribution [4–8]. Furthermore, desired shapes and sizes of particles can be tailored by controlling process conditions such as solute concentration, reaction temperature, reaction time, and the type of solvent [9,10]. The effects of mixed crystalline phases of Al_2O_3 on the dispersion of cobalt on Al_2O_3 and the resulting catalytic activity for CO hydrogenation were investigated.

2. Experimental

2.1. Preparation of alumina

Nanocrystalline transition Al_2O_3 was prepared by the solvothermal method according to the procedure described in Ref. [11]. The desired amount of aluminum isopropoxide (AIP) (Aldrich) (10, 15, 25, or 35 g) was suspended in 100 ml of 1-butanol (Ajax Finechem) in a beaker, which was then placed in a 300 ml autoclave. In the gap between the beaker and the autoclave wall, 30 ml of 1-butanol was added. After the atmosphere inside the autoclave was purged completely with nitrogen, the mixture was heated to 300 °C at a heating rate of 2.5 °C/min and was kept at that temperature for 2 h. After cooling to room temperature, the resulting powders were collected after repeated washing with acetone and were then air-dried. The calcination of the products was carried out in a box furnace by heating up to 600 °C at a rate of 10 °C/min and held at that temperature for 1 h.

2.2. Catalyst preparation

The Al_2O_3 -supported cobalt catalysts with different Co loadings (5, 10, 15, and 20 wt%) cobalt were prepared by incipient wetness impregnation of alumina with a desired amount of an aqueous solution of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Aldrich). After impregnation, the catalysts were dried at 110 °C for 24 h and calcined in air at 300 °C for 2 h using a ramp rate of 1 °C/min.

2.3. Catalyst characterization

X-ray diffraction patterns of the samples were collected using a SIEMENS D-5000 X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a rate of 0.04°/step from $2\theta = 15^\circ$ to 80° . The composition of each crystalline phase has been calculated from the calibration of X-ray diffraction peak areas of the mixtures between each pure phase (physically mixed). BET surface areas of the sample were calculated using the BET-single point method at liquid N_2 temperature. Transmission electron microscopy was performed to study the morphologies of the catalyst samples and the dispersion of cobalt oxide species on the alumina supports using a JEOL JEM 1230. The number of surface cobalt metal atoms was determined by pulse H_2 chemi-

sorption at 100 °C on the reduced cobalt catalysts based on the static method described by Reuel and Bartholomew [12] using a Micromeritics Pulse Chemisorb 2750 system. Prior to H_2 chemisorption, the catalyst samples were reduced at 350 °C in flowing H_2 for 3 h. The X-ray photoelectron spectroscopy (XPS) analysis was performed using an AMICUS photoelectron spectrometer equipped with a $\text{MgK}\alpha$ X-ray as a primary excitation and a KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV.

2.4. Reaction study

CO hydrogenation was carried out at 220 °C and 1 atm total pressure in a fixed-bed quartz reactor under differential reaction conditions. The H_2/CO ratio used was 10/1. Typically, 0.1 g of the catalyst sample was reduced *in situ* in flowing H_2 (50 cc/min) at 350 °C for 3 h prior to reaction. After the start up, samples were taken at 1-h intervals and analyzed by gas chromatography. Steady state was reached within 6 h in all cases.

3. Results and Discussion

In this study, nanocrystalline alumina powders were prepared by thermal decomposition of AIP in 1-butanol with various AIP content. XRD patterns of these alumina samples after calcination at 600 °C for 1 h are shown in Fig. 1. The XRD patterns of transition Al_2O_3 were observed at degree $2\theta = 31^\circ, 33^\circ, 38^\circ, 43^\circ, 47.5^\circ$, and 68° . It was found that when lower amounts of AIP were used (10 and 15 g in 100 cm³ of 1-butanol), only $\gamma\text{-Al}_2\text{O}_3$ was formed by calcination, as seen by the XRD characteristic peaks at $2\theta = 33^\circ$ according to the JCPDSs database.

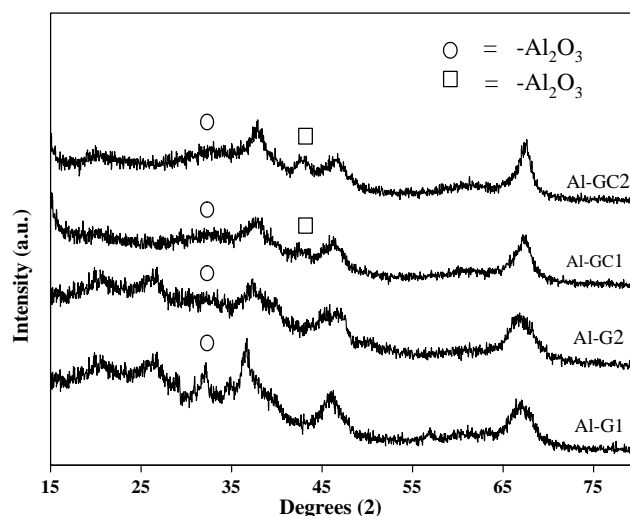


Fig. 1. XRD patterns of the various nanocrystalline alumina prepared by the reaction of AIP in 1-butanol at 300 °C for 2 h (after calcination at 600 °C for 1 h).

Table 1
Properties of the various nanocrystalline Al_2O_3 samples prepared by the reaction of AIP in 1-butanol at 300 °C for 2 h

Samples	Amounts of AIP (g)	Amounts of χ -phase (%)	Surface area (m^2/g) ^a	Bulk density (g/cm^3) ^a	Morphology [27]
Al-G1	10	–	70	0.38	Wrinkled sheets
Al-G2	15	–	120	0.38	High amount of wrinkled sheets
Al-GC1	25	33	139	0.39	Wrinkled sheets and small amount of spherical particles
Al-GC2	35	57	145	0.53	Small amount of wrinkled sheets and high amount of spherical particles
Al-C ^b	25	100	180	0.56	Spherical particles

^a Error of measurement = 5%.

^b Pure χ - Al_2O_3 .

These γ - Al_2O_3 samples are denoted hereafter as Al-G1 and Al-G2, respectively. The XRD characteristic peak of χ -alumina was observed at $2\theta = 42.5^\circ$ for the supports prepared with higher amounts of AIP (25 and 35 g in 100 cm^3 1-butanol). The mixed γ - and χ -crystalline phase samples containing χ -phase of ca. 33% and 57% were denoted as Al-GC1 and Al-GC2, respectively. Pure χ -alumina prepared by reaction of AIP in toluene was used as the reference sample and denoted as Al-C. The intensity of χ - Al_2O_3 peaks became stronger with increasing amount of AIP content during preparation, indicating that increasing AIP content during the solvothermal synthesis resulted in formation of alumina giving rise to mixed phases of γ - Al_2O_3 and χ - Al_2O_3 after calcination. The physical properties of the various Al_2O_3 samples are shown in Table 1. The BET surface area of the Al-GC2 ($145 \text{ m}^2/\text{g}$) was found to be twice of that of Al-G1 ($70 \text{ m}^2/\text{g}$). A similar trend was observed for the bulk density of the Al_2O_3 powders. The bulk density increased with increasing amount of AIP used during preparation (from $0.38 \text{ g}/\text{cm}^3$ to $0.54 \text{ g}/\text{cm}^3$). The BET surface areas also increased with increasing AIP concentration, probably as a result of morphology changing from a wrinkled sheet structure to small spherical particles (see Fig. 3). These results were confirmed by Al-C with highest BET surface area ($180 \text{ m}^2/\text{g}$), highest bulk density ($0.56 \text{ g}/\text{cm}^3$) and complete spherical particle morphologies. From results such as these, it has been proposed that for preparation with low AIP contents, boehmite is the main product resulting in γ -alumina after calcination at 600°C for 1 h. The morphology of the boehmite products obtained via the solvothermal reaction has been shown to be wrinkled sheets [13,14]. The precursor to spherical-shaped χ - Al_2O_3 was formed by direct decomposition of AIP in the solvent and appeared to increase with increasing AIP concentration.

Fig. 2 shows the IR spectra of alumina supports after calcination at 600°C for 1 h. The IR peaks assigned to OH stretching were observed at around 3730 and broad peak between 3200 and 3600 cm^{-1} . According to Peri's model [15], the features at 3791 , 3730 , and 3678 cm^{-1} are assigned to surface isolated hydroxyl groups. The broader peak at 3589 cm^{-1} is due to the vibration of associated

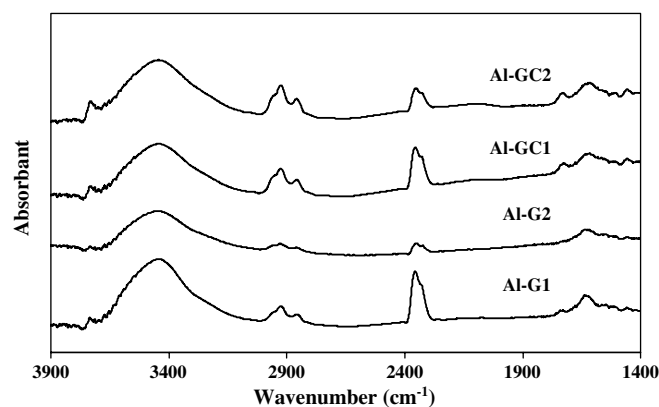


Fig. 2. IR spectra of various alumina supports.

hydroxyl groups of aluminum oxide. The spectra which assigned to OH groups of all samples were nearly identical. Therefore, the amounts and nature of OH groups of all supports were essentially same.

The nanocrystalline γ - Al_2O_3 and mixed γ - and χ - Al_2O_3 were then employed as catalyst supports for Co catalysts. The $\text{Co}/\text{Al}_2\text{O}_3$ catalysts were prepared using the incipient wetness impregnation method with cobalt loadings of 5, 10, 15, and 20 wt% in order to investigate the effect of mixed crystalline phases of Al_2O_3 on the dispersion of Co and its catalytic activity for CO hydrogenation. The XRD patterns of the various $\text{Co}/\text{Al}_2\text{O}_3$ catalysts after calcination at 300°C were not significantly different from those of the Al_2O_3 supports (results not shown). No XRD characteristic peaks of Co_3O_4 and/or other Co compounds were detected for all the catalyst samples. This suggests that the crystallite size of cobalt oxide on Al_2O_3 was probably below the lower limit for XRD detectability (3–5 nm). Such results also indicate that cobalt oxide species were present in a highly dispersed form on these nanocrystalline Al_2O_3 even for cobalt loadings as high as 20 wt%.

The morphology and distribution of cobalt oxide particles on the Al_2O_3 supports were investigated by transmission electron microscopy (TEM). The typical TEM micrographs of 20 wt% of cobalt on alumina supports

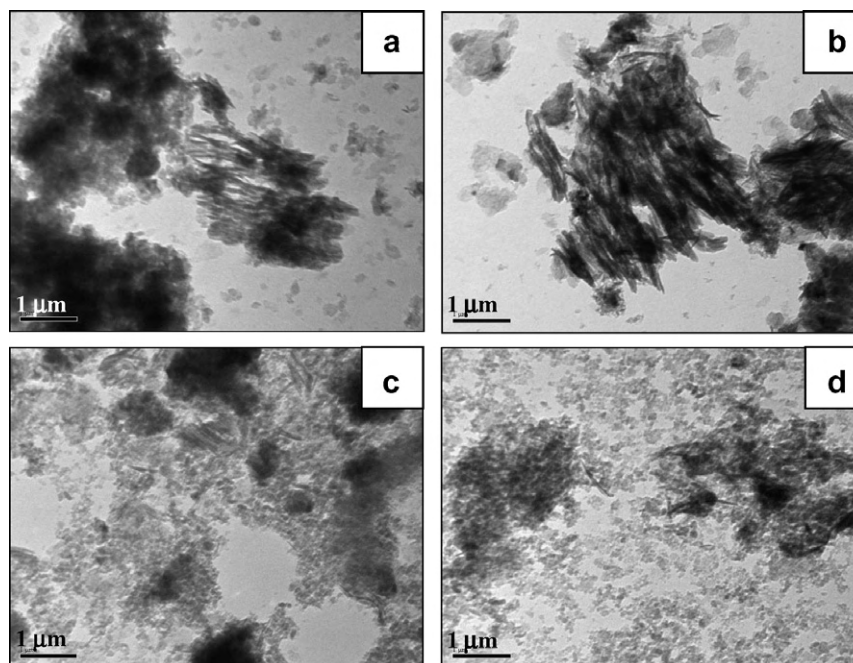


Fig. 3. TEM micrographs of the various 20 wt%Co/Al₂O₃ catalysts (a) 20Co/Al-G1 (b) 20Co/Al-G2 (c) 20Co/Al-GC1 (d) 20Co/Al-GC2.

containing different compositions of γ and χ phases are shown in Fig. 3. In all the TEM figures, the darker spots on the catalyst granules represent a high concentration of cobalt and its compounds while the lighter areas indicate the support with minimal or no cobalt present. It was found that the wrinkled sheets-like structure of γ -Al₂O₃ was maintained after impregnation and calcination for both 20Co/Al-G1 and 20Co/Al-G2 catalysts (Figs. 2a and b). The mixed structure between spherical particles of χ -Al₂O₃ and wrinkled sheets of γ -Al₂O₃ were also observed for 20Co/Al-GC1 and 20Co/Al-GC2 samples (Figs. 2c and d). However, cobalt oxide species appeared to be more agglomerated on the γ -Al₂O₃ supports than on the mixed γ - and χ -ones as shown by the appearance of larger cobalt oxide particles/granules.

Static H₂ chemisorption on the reduced cobalt catalyst was used to determine the number of active surface cobalt metal atoms [16]. The H₂ chemisorption results for all the

catalyst samples are reported in Table 2. The overall dispersion of reduced Co and crystal size of Co⁰ in the catalyst samples based on the H₂ chemisorption results is also given. In order to distinguish the effect of mixed γ - and χ -crystalline phases of Al₂O₃ and the effect of BET surface area, we also report the H₂ chemisorption results in terms of the amount of H₂ chemisorption per total specific surface area of the catalyst (see Fig. 4). For the Co/Al-G1 and Co/Al-G2 catalysts in which the Al₂O₃ contained only the γ -phase, the number of active surface cobalt metal atoms per unit surface area increased with increasing Co loading up to 15 wt%. Further increase of the amount of Co loading to 20 wt% resulted in both a lower cobalt dispersion and fewer exposed surface cobalt metal atoms (Table 2), even taking into account BET surface area (Fig. 4). This is typical for supported Co Fischer–Tropsch catalysts. Dispersion usually decreases with increasing Co loading beyond a certain point [17–

Table 2
H₂ chemisorption results

Catalyst samples	Amounts of H ₂ chemisorption ($\mu\text{mol/g cat.}$) ^a				%Co dispersion ^b				dp Co ⁰ (nm) (96.2/D%)			
	5%Co	10%Co	15%Co	20%Co	5%Co	10%Co	15%Co	20%Co	5%Co	10%Co	15%Co	20%Co
Co/Al-G1	0	0.9	9.2	3.3	0	0.1	0.7	0.2	0	962	137	481
Co/Al-G2	0.9	2.3	14.9	10.9	0.2	0.3	1.2	0.6	481	321	80	160
Co/Al-GC1	5.6	7.6	18.9	19.5	1.1	1.1	1.5	1.5	87	87	64	64
Co/Al-GC2	5.8	20.7	21.4	24.6	1.3	1.7	1.7	1.8	74	57	57	53
Co/Al-C ^c	–	–	16.8	–	–	–	1.3	–	–	–	74	–

^a Error = ± 5 %, as determined directly.

^b %Co dispersion = $[2 \times (\text{total H}_2 \text{ chemisorption/g cat.}) / (\text{no. of } \mu\text{mol of Co total/g cat.})] \times 100\%$

^c Co/Al₂O₃ prepared from pure χ -Al₂O₃ support.

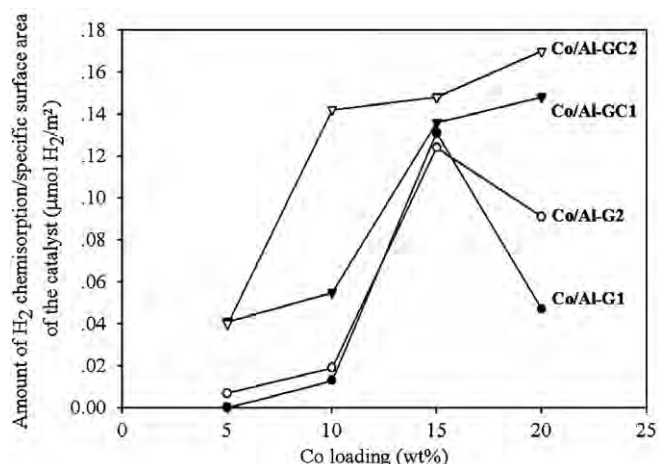


Fig. 4. The amount of H₂ chemisorption/specific surface area of the Co/Al₂O₃ catalysts as a function of cobalt loading.

21]. On the contrary, the amounts of H₂ chemisorption per unit surface area of the mixed γ - and χ -crystalline phases Al₂O₃ supported Co catalysts (Co/Al-GC1 and Co/Al-GC2) constantly increased with increasing Co loading from 5 to 20 wt% (Table 2, Fig. 4). To study the effect of phase composition on active sites of Co catalyst, 15%Co/pure χ -alumina catalyst was characterized to compare with 15%Co deposited on pure γ -Al₂O₃ and mix phase supports. The amounts of H₂ chemisorption increased from 9.2 to 21.4 μ mol/g catalyst as the χ -phase contents increased from 0% to 57%. While the amounts of H₂ chemisorption of Co/pure χ -alumina catalyst ranged around 16.8 μ mol/g catalyst. It is suggested that the presence of χ -phase in γ -Al₂O₃ may prevent agglomeration of Co particles especially at high Co loadings, resulting in the maintenance of high Co dispersion. Because of its sur-

face sensitivity, XPS is used to identify the surface compositions of the catalysts as well as the interaction between Co and the alumina supports. The results are given in Table 3. It was found that the ratio of Al/O atomic concentration was slightly increased while that of Co/Al decreased with the presence of χ -phase in γ -Al₂O₃ suggesting higher dispersion of Co on the mixed phase Al₂O₃ supports. There was also a slight shift of Co 2p binding energy to higher values for the 15Co/Al-GC1 and 15Co/Al-GC2 catalysts compared to those supported on γ -Al₂O₃ (Al-G1 and Al-G2). Such results suggest stronger interaction between Co and the mixed phases γ - and χ -Al₂O₃.

CO hydrogenation was carried out in a fixed-bed quartz reactor under differential reaction conditions in order to determine the catalytic activity of the catalyst samples. The reaction results in terms of CO conversion, hydrogenation rate, and the turnover frequency (TOF) per exposed Co atom calculated using the hydrogen chemisorption data are given in Table 4. The catalytic activities increased with increasing Co loading in general (at least to 15 wt%Co). For a similar Co loading, Co catalysts supported on the mixed crystalline phases Al₂O₃ exhibited higher CO hydrogenation activities compared to those supported on the ones containing only γ -phase Al₂O₃. The TOFs of the cobalt catalysts in which the Al₂O₃ support contained only the γ -phase decreased with increasing Co loading, suggesting perhaps an underestimation of exposed Co metal atoms by H₂ chemisorption. However, the TOFs for the mixed crystalline phases Al₂O₃ did not significantly change regardless of cobalt loading percentage. The reaction results are in a good agreement with the H₂ chemisorption results since CO hydrogenation is usually considered to be a structure insensitive reaction [22–26]. Thus, higher dispersion of Co yields higher hydrogenation activity.

Table 3
Surface compositions based on XPS results for 15 wt%Co/Al₂O₃ catalysts

Sample	Binding energy (eV)			Atomic concentration (%)	
	Co 2p	O 1s	Al 2s	Al/O	Co/Al
15Co/Al-G1	782.4	533.1	120.9	0.29	0.026
15Co/Al-G2	782.4	533.1	120.6	0.33	0.027
15Co/Al-GC1	782.8	533.1	121.0	0.34	0.015
15Co/Al-GC2	782.9	532.9	120.3	0.40	0.019

Table 4
Reaction rate for CO hydrogenation on Co/Al₂O₃ catalysts

Catalyst samples	CO conversion (%) ^a				Rate (μ mol g cat ⁻¹ s ⁻¹) ^b				TOF(s ⁻¹) ^{b,c}			
	5%Co	10%Co	15%Co	20%Co	5%Co	10%Co	15%Co	20%Co	5%Co	10%Co	15%Co	20%Co
Co/Al-G1	0.5	1.9	8.8	2.1	0.3	1.1	5.2	1.3	–	0.6	0.3	0.2
Co/Al-G2	1.1	2.6	10.0	4.0	0.7	1.6	6.0	2.4	0.4	0.3	0.2	0.1
Co/Al-GC1	2.9	5.5	10.2	7.3	1.7	3.3	6.1	4.3	0.2	0.2	0.2	0.1
Co/Al-GC2	4.0	8.5	10.6	10.7	2.4	5.1	6.3	6.3	0.2	0.1	0.1	0.2

^a CO hydrogenation was carried out at 220 °C, 1 atm, and H₂/CO/Ar = 80/8/32.

^b Error of measurement = $\pm 5\%$ as determined directly.

^c Based on H₂ chemisorption.

4. Conclusions

Nanocrystalline γ -Al₂O₃ and mixed γ - and χ -Al₂O₃ were obtained by decomposition of AIP in 1-butanol by varying the amounts of AIP used under the solvothermal conditions. For a similar Co loading, the presence of χ -phase in γ -Al₂O₃ support resulted in higher dispersion of Co as

well as higher CO hydrogenation activities of the Co/Al₂O₃ catalysts. It is suggested that the spherical-shape like morphology of the χ -phase Al₂O₃ provide better stability of the Co particles, especially for those with high Co loadings.

Acknowledgment

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Dependence of Quenching Process on the Photocatalytic Activity of Solvothermal-Derived TiO₂ with Various Crystallite Sizes

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In the present work, the effect of quenching on surface defect and photocatalytic activity of the solvothermal-derived nanocrystalline TiO₂ with average crystallite sizes between 9 and 13 nm was extensively studied. On the basis of CO₂-TPD (TPD = temperature-programmed desorption) and XPS (XPS = X-ray photoelectron spectroscopy) results, it was found that the amount of Ti³⁺ surface defects and photocatalytic activities of the prepared TiO₂ depended strongly on the type of quenching media used in the following order: H₂O₂-RT > H₂O₂-373K > H₂O-RT > H₂O-373K > air-RT > air-373K, where RT = room temperature. However, the TiO₂ sample that was slowly cooled after calcination (the nonquenched sample) also possessed a significant amount of Ti³⁺ surface defects and high photocatalytic activity to a degree similar to that quenched in H₂O-RT. The effect of quenching was more pronounced on the smaller crystallite size TiO₂ than on the larger ones due probably to its higher surface energy so that oxygen atoms were released more easily.

1. Introduction

Titanium(IV) dioxide or titania (TiO₂) has been the focus of many research interests during the past decade due to its scientific and technological importance. It is a low-cost, widely available, nontoxic, and biocompatible substance that is widely used in domestic applications (e.g., increasing paint durability, cleaning wastewaters, etc.).^{1–2} It has been demonstrated to be useful in various areas because of its versatile properties such as catalytic activity,³ photocatalytic activity for pollutant removal,⁴ good stability toward adverse environment,⁵ sensitivity to humidity and gas,⁶ dielectric character,⁷ photoelectrochemical conversion,⁸ nonlinear optics,⁹ and photoluminescence.¹⁰ TiO₂ has been an important component for cosmetics, pigments, filter coating, gas and humidity sensors, dielectric ceramics, catalyst support, solar cells, and so on.¹¹ Its performance in these applications depends to a large extent on its physical and chemical properties which are related to the synthetic conditions. These conditions dictate the properties such as crystal structure, morphology, grain size, thermal stability, and surface structure of the TiO₂ products.

The photocatalytic activity of TiO₂ is greatly influenced by its crystal structure, particle size, surface area, incident light intensity, and porosity. Among these factors, crystal structure and crystallinity of TiO₂ are considered the important factors. Amorphous titania has negligible photocatalytic activity because of the recombination between the pair of photoexcited electron and hole in the amorphous structure.¹² Anatase crystalline TiO₂ is generally accepted to have significant photocatalytic activity. However, much effort indicates that rutile TiO₂ and metal-doped rutile TiO₂ also exhibit high photocatalytic activity especially under visible light irradiation.^{13–15} With the decrease in particle size of powder to nanometer scale, the catalytic activity of titania is enhanced because the optical band gap is widened due to surface defect^{16,17} and an increased in surface area.^{18,19}

Many methods have been proposed to synthesize nanocrystalline TiO₂ in anatase polymorph such as sol–gel²⁰ and

hydrothermal method.²¹ Although the sol–gel method is widely used to prepare nanosized TiO₂, calcination of the gel inevitably causes the grain growth and reduction in the specific surface area of the TiO₂ particles and even induces phase transformation. Solvothermal synthesis, in which chemical reactions can occur in aqueous or organic media under the self-produced pressure at low temperature (usually lower than 250 °C), can solve those problems encountered during the sol–gel process.²² This method has been used to successfully synthesize various types of nanosized metal oxides with large surface area, high crystallinity, and high thermal stability.^{23–24}

In the present work, nanocrystalline TiO₂ powders with various crystallite sizes (9–13 nm) were prepared by the solvothermal method using titanium butoxide as the precursor. Then the TiO₂ products were subjected to a rapid quenching process in various quenching media such as air, water, and hydrogen peroxide at two different temperatures (303 and 373 K). The quenching process has shown to result in a variety of surface defects, strains, and reconstructions of materials.²⁵ It is believed that surface defects on the TiO₂ samples as well as their photocatalytic activity can be modified by rapid quenching process. The properties of TiO₂ samples were characterized using various analytical methods such as X-ray diffraction (XRD), N₂ physisorption, CO₂-temperature programmed desorption (CO₂-TPD), and X-ray photoelectron spectroscopy (XPS). Photocatalytic activity of the TiO₂ was tested in gas-phase decomposition of ethylene under UV irradiation.

2. Experimental Section

2.1. Preparation of Nanocrystalline TiO₂. Nanocrystalline TiO₂ was prepared using the solvothermal method according to that of Payakgul et al.²⁶ using titanium(IV) *n*-butoxide (TNB) as starting material. In general, an amount of 15–25 g of TNB was suspended in 100 cm³ of toluene in a test tube, which was then placed in a 300 cm³ autoclave. The gap between the test tube and the autoclave wall was filled with 30 cm³ of the same solvent used in the test tube. The autoclave was purged completely by nitrogen before heating up to the desired temperature, in the range of 573–593 K at a rate of 2.5 K/min.

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Table 1. Phase Compositions and Structural Properties of the TiO₂ Synthesized by Solvothermal Method after Quenching in Various Media

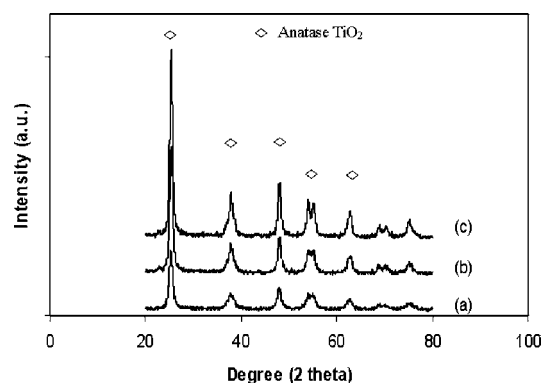
synthesis conditions	quenching medium	crystallite size (nm)	S_{BET} (m ² /g)	sample nomenclature
TNB, 15 g	air at 373 K	8.6	96	9A
toluene, 100 mL	air at RT*	9.4	94	9B
temp, 573 K	H ₂ O at 373 K	9.0	99	9C
holding time, 30 min	H ₂ O at RT	8.9	104	9D
	H ₂ O ₂ at 373 K	10.0	92	9E
	H ₂ O ₂ at RT	10.5	91	9F
TNB, 25 g	air at 373 K	9.6	85	11A
toluene, 100 mL	air at RT	10.6	93	11B
temp, 573 K	H ₂ O at 373 K	10.4	95	11C
holding time, 2 h	H ₂ O at RT	10.5	112	11D
	H ₂ O ₂ at 373 K	13.2	90	11E
	H ₂ O ₂ at RT	13.3	94	11F
TNB, 15 g	air at 373 K	10.4	60	13A
toluene, 100 mL	Air at RT	13.4	67	13B
temp, 593 K	H ₂ O at 373 K	13.4	67	13C
holding time, 6 h	H ₂ O at RT	13.2	69	13D
	H ₂ O ₂ at 373 K	14.6	61	13E
	H ₂ O ₂ at RT	14.7	63	13F

Autogenously pressure during the reaction gradually increased as the temperature was raised. Once the prescribed temperature was reached, the temperature was held constant for 0.5–6 h. After the system was cooled down, the resulting powders were repeatedly washed with methanol and dried in air.

2.2. Quenching Process. Prior to quenching, the synthesized TiO₂ was dried in air atmosphere at 573 K with a heating rate of 10 K/min for 1 h, and then it was taken out and immediately quenched in various quenching media. In this study, both liquid-phase and gas-phase media were employed. For quenching in gas-phase media, air at room temperature and 373 K were used (samples A and B). For quenching in liquid-phase media, hydrogen peroxide at room temperature and 373 K (samples C and D) and water at room temperature and 373 K (samples E and F) were used. After the samples were quenched in the media for 30 min, all the TiO₂ samples were dried in air at room temperature and stored in a desiccator.

2.3. Characterization. The XRD patterns of the TiO₂ samples were recorded using a SIEMENS D5000 X-ray diffractometer using Cu K α radiation with a Ni filter in the range of 20–80° 2 θ . The crystallite size of TiO₂ was determined from half-height width of the 101 diffraction peak of anatase using the Scherrer equation. The specific surface area (S_{BET}) was calculated using BET single-point method on the basis of nitrogen (N₂) uptake measured at 77 K in a Micromeritics ASAP 2000. Temperature-programmed desorption using CO₂ as a probe molecule was performed to determine the Ti³⁺ site existing on the surface of TiO₂ particle.²⁷ It was carried out using 0.05 g of a TiO₂ sample. TiO₂ was dosed by 1 vol % CO₂ in helium for 1 h and then desorbed from 143 to 273 K with the rate of 21.5 K/min. The XPS measurement was carried out using an AMICUS photoelectron spectrometer equipped with an Mg K α X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. All the binding energies were referenced to the C 1s peak at 285.0 eV of the surface adventitious carbon.

2.4. Photocatalytic Activity Measurement. Catalytic decomposition of ethylene was carried out in order to determine photocatalytic activity of the TiO₂ using a horizontal quartz fixed bed reactor. High purity grade air containing 0.1 vol % ethylene was continuously fed at a constant flow rate with a gas hourly space velocity (GHSV) of 120 h⁻¹. An air stream with 0.1 vol % ethylene was first passed through the reactor without irradiation until reaching gas–solid adsorption equilibrium.

**Figure 1.** The XRD patterns of the various TiO₂ samples after quenching in air at room temperature: (a) 9 nm, (b) 11 nm, (c) 13 nm.

Then, UV light was irradiated on the surface of the catalyst using a 500 W mercury lamp (Philips, HPL-N). The outlet gas was taken every 30 min. Its composition was analyzed using a Shimadzu GC-14B gas chromatograph equipped with the flame-ionized detector until the reaction reached steady state.

3. Results and Discussion

3.1. Structure and Surface Properties of TiO₂ Quenched in Different Media. In this study, the effects of quenching medium as well as quenching temperature on the properties of nanocrystalline TiO₂ synthesized by solvothermal method are extensively investigated. Quenching process was applied as a postsynthesis treatment with the aims being to create more defects on the TiO₂ surface and, as a consequence, improve their photocatalytic activities. Physical properties of the various TiO₂ such as the BET surface areas and the average TiO₂ crystallite sizes after quenching in different media are shown in Table 1. Due to the different preparation conditions, the TiO₂ samples possessed different crystallite sizes and specific surface areas. The average crystallite size of TiO₂ samples increased from 9 to 13 nm as the BET surface area of the TiO₂ samples decreased from ca. 95 to 65 m²/g. Quenching treatment, however, did not significantly alter the specific surface area and the average crystallite size of the TiO₂. The anatase TiO₂ crystalline phase was preserved after quenching. All the TiO₂ samples consisted of only pure anatase phase TiO₂ (major XRD peaks at 25.36, 37.82, and 48.18° 2 θ). XRD patterns of the TiO₂ with various crystallite sizes after quenching in air at room temperature are shown in Figure 1. The crystallite sizes of the TiO₂ from XRD are in good agreement with those observed from the TEM micrographs of the samples (Figure 2).

The surface structure of TiO₂ was characterized by temperature-programmed desorption of CO₂. All the TiO₂ samples exhibited two main desorption peaks at temperatures ca. 145 and 170 K which could be attributed to adsorption of CO₂ on two different structures of TiO₂ surface.²⁷ For example, the CO₂-TPD profiles of TiO₂ samples with average crystallite size of 11 nm after quenching in various media are shown in Figure 3. The desorption peak at ca. 145 K was attributed to CO₂ molecules binding to the regular five-coordinate Ti⁴⁺ site which was considered as the perfected TiO₂ structure. The second peak at ca. 170 K has been considered as desorption of CO₂ molecules binding to Ti³⁺ defect sites of TiO₂. On the basis of the CO₂-TPD results, it was found that, for a given TiO₂ crystallite size, the peak areas for CO₂ desorption at ca. 170 K (representing the amount of Ti³⁺ defective sites) depended on the type of quenching media employed in the following order: air at 373 K < air at RT < H₂O at 373 K < H₂O at RT < H₂O₂ at 373

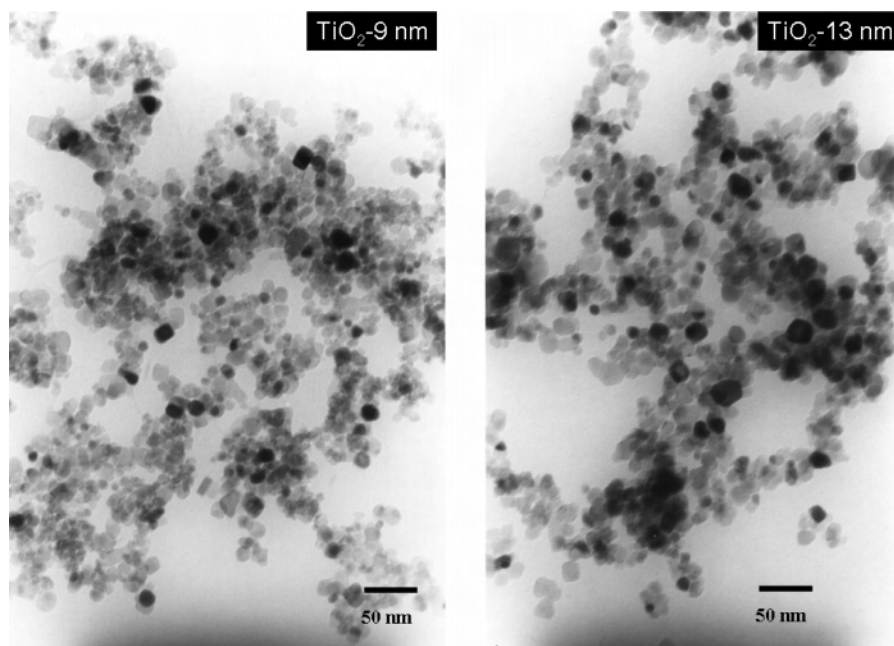


Figure 2. TEM micrographs of TiO₂-9 nm and TiO₂-13 nm (nonquenched).

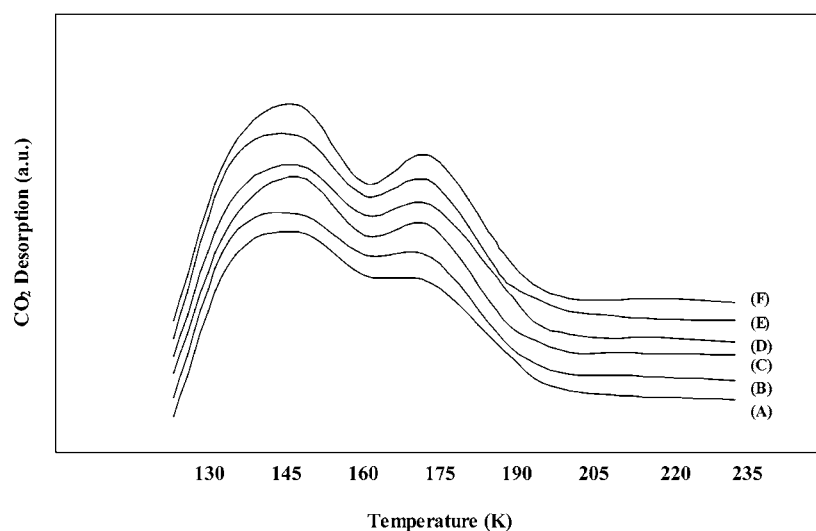


Figure 3. CO₂-temperature-programmed desorption results of the TiO₂-11 nm quenched in different media: (A) air at 373 K, (B) air at RT, (C) H₂O at 373 K, (D) H₂O at RT, (E) H₂O₂ at 373 K, and (F) H₂O₂ at RT (RT = room temperature).

K < H₂O₂ at RT. It is known that quenching treatment of a metal can create nucleation of dislocations, surface defect, and concentration of stress on the metal surface.²⁸ The results in this study have shown that quenching process can be applied as a postsynthesis treatment for controlling the amount of surface defects on nanocrystalline TiO₂. The Ti³⁺/Ti⁴⁺ ratios calculated from CO₂-TPD results of the various quenched TiO₂ samples and the nonquenched one are illustrated in Figure 4. It was found that the nonquenched sample also possessed a significant amount of Ti³⁺ to a degree similar to that quenched in H₂O at room temperature. However, when compared with the TiO₂ sample quenched in H₂O₂ and H₂O, it is noticed that the TiO₂ sample quenched in liquid-phase media that contained more -OH group in molecules exhibited higher Ti³⁺/Ti⁴⁺ and higher photocatalytic activity. Recently, Xiao-Quan et al.²⁹ reported that the trapping site of photogenerated holes or the surface -OH is also an important factor affecting photocatalytic reaction besides the surface Ti³⁺.

The presence of Ti³⁺ on the TiO₂ samples was also studied by X-ray photoelectron spectroscopy. For example, high-resolution XPS spectra of Ti 2p and O 1s recorded from the TiO₂ samples quenched in H₂O₂ at room temperature are shown in Figure 5. The Ti 2p spectrum can be fitted with Gaussian-Lorentzian functions into two spin-orbit components at binding energies of 457.2, and 459.2 eV, corresponding to Ti₂O₃ (Ti³⁺) and TiO₂ (Ti⁴⁺) fractions on the TiO₂ surface, respectively. The component binding energy values are in agreement with those reported in the literature.³⁰ The O 1s peak is often believed to be composed of three to five different oxygen species such as Ti-O bonds in TiO₂ and Ti₂O₃, hydroxyl groups, C-O bonds, and adsorbed H₂O. It is shown that the O 1s peak is asymmetric, suggesting that at least three peaks related to three different chemical states of oxygen are present. The binding energies of each individual component are 530.8 (Ti⁴⁺-O), 531.8 (Ti³⁺-O), and 533.3 eV (O-H).³¹⁻³² The shapes of the XPS spectra of Ti 2p and O 1s for all the TiO₂ samples are quite similar,

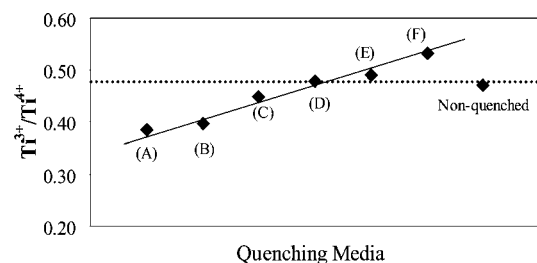


Figure 4. Ti^{3+}/Ti^{4+} ratios calculated from CO_2 -TPD results of the TiO_2 -11 nm quenched in different media: (A) air at 373 K, (B) air at RT, (C) H_2O at 373 K, (D) H_2O at RT, (E) H_2O_2 at 373 K, and (F) H_2O_2 at RT (RT = room temperature).

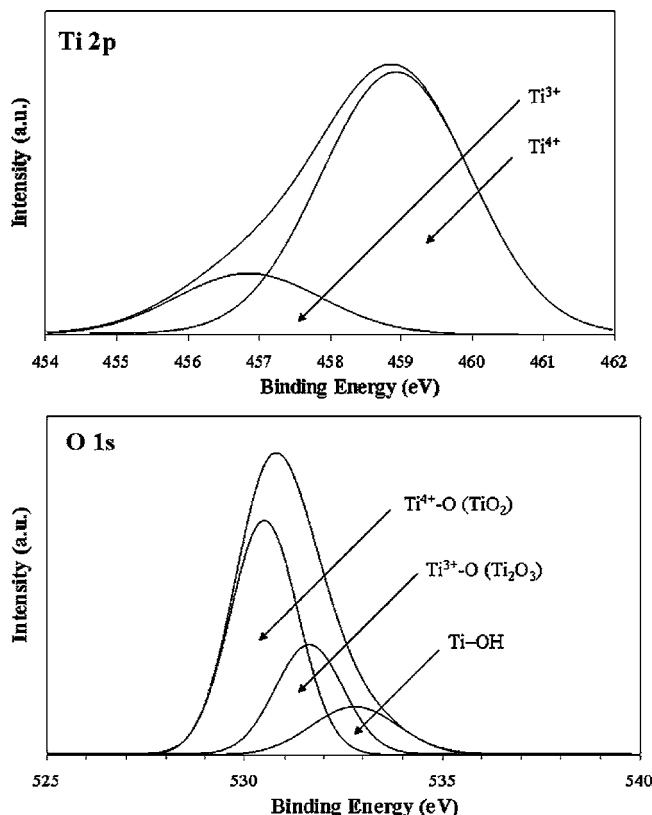


Figure 5. XPS spectra of Ti 2p and O 1s for TiO_2 -11 nm quenched in H_2O_2 at room temperature.

and it was found that the amount of surface Ti^{3+} sites increased in a trend similar to those observed from CO_2 -TPD results.

In photocatalysis, defect sites on the surface of TiO_2 are known as adsorption sites,^{33,34} electronic promoters,³⁵ or electron traps.^{36,37} In general, light irradiation of TiO_2 powder with photon energy larger than the band gap energy produces electrons (e^-) and holes (h^+) in the conduction band and the valence band, respectively.^{38,39} These electrons and holes are thought to have the respective abilities to reduce and oxidize chemical species adsorbed on the surface of TiO_2 particles. For a photocatalyst to be most efficient, different interfacial electron processes involving e^- and h^+ must compete effectively with the major deactivation processes involving e^- - h^+ recombination. Surface Ti^{3+} defect sites (oxygen vacancies) are the sites that oxygen adsorption occurs as well as that the photogenerated electrons are trapped,^{40–42} so they are effective sites for interface electron transferring. The relationship between the amount of Ti^{3+} defects on TiO_2 surface and their photocatalytic activities has been reported by many authors.^{43–46}

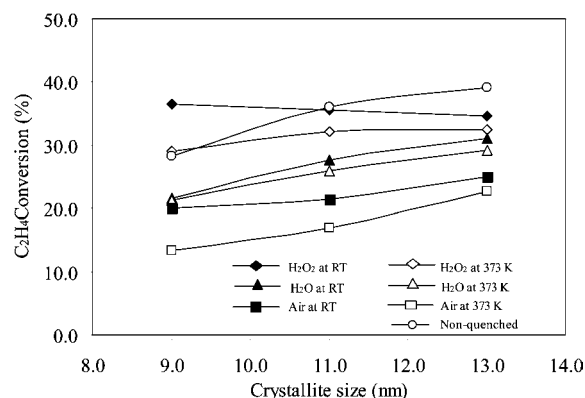


Figure 6. Results of the photocatalytic activities of TiO_2 samples quenched in different media.

3.2. Photocatalytic Activity of the TiO_2 Quenched in Different Media

Photocatalytic activities of the TiO_2 samples with various crystallite sizes after quenching in different media were evaluated in the decomposition of ethylene in gas-phase and the results are shown in Figure 6. Ethylene conversions at steady state (after 180 min of run) for the quenched TiO_2 samples with various crystallite sizes were ranged from ca. 20–37%, while that of TiO_2 Degussa P25 under similar reaction conditions gave ca. 30% ethylene conversion. It was found that, for a given TiO_2 crystallite size, ethylene conversions were strongly dependent on the quenching media and were found to be in the following order: H_2O_2 at RT > H_2O_2 at 373 K > H_2O at RT > H_2O at 373 K > air at RT > air at 373 K. Such results were in good agreement with the amount of Ti^{3+} surface defect on the TiO_2 samples in which those with higher amounts of Ti^{3+} surface defect exhibited higher photocatalytic activities for ethylene decomposition. For a similar quenching medium, the TiO_2 quenched at low temperature resulted in a larger amount of Ti^{3+} and exhibited higher photocatalytic activity compared to those quenched at high temperature. This can probably be explained by a thermal shock effect that a large difference in temperature of the TiO_2 surface and quenching medium can create more surface defects. However, compared to the TiO_2 sample that was slowly cooled down after calcination (the nonquenched sample), only the smaller crystallite size TiO_2 (TiO_2 , 9 nm) that quenched in H_2O_2 exhibited higher photocatalytic activities. The effect of quenching was less pronounced on the larger TiO_2 crystallite size and the nonquenched samples showed higher activities.

4. Conclusions

The surface properties and photocatalytic activities of nano-sized TiO_2 powders synthesized by solvothermal method with various crystallite sizes (9–13 nm) were significantly influenced by quenching media and quenching conditions. For the use of similar quenching media, the TiO_2 quenched in a low-temperature medium has been shown to result in more Ti^{3+} surface defects on the TiO_2 surface and consequently higher photocatalytic activity than those quenched in a high-temperature one. The amount of Ti^{3+} and photocatalytic activity of the quenched samples depended on the type of quenching medium in the following order: H_2O_2 > H_2O > air. Compared to the nonquenched sample (the one slowly cooled after calcination), quenching in H_2O_2 has shown to result in higher Ti^{3+} and photocatalytic activity of the TiO_2 with small crystallite size (9 nm). There was less effect of quenching on larger crystallite size TiO_2 .

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