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รายงานวิจัยฉบับสมบูรณ์

โครงการ การเตรียม วิเคราะห์ลักษณะ และประสิทธิภาพของตัวเร่งปฏิกิริยาโลหะผสมที่ประกอบด้วยแพลทินัมและโลหะอื่น

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สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา
และสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานฉบับนี้เป็นของผู้วิจัย สกอ. และ สกว. ไม่จำเป็นต้องเห็นด้วยเสมอไป)

สารบัญ

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บทคัดย่อ

โครงการวิจัยนี้ มีจุดประสงค์เพื่อเตรียมตัวรองรับตัวเร่งปฏิกิริยาโดยใช้ซิลิกาจากแกลบ จากนั้นนำไปเป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาแพลทินัมและโลหะอื่น และนำไปทดสอบการเร่งปฏิกิริยาของสารประกอบไฮโดรคาร์บอน ผลการดำเนินงานที่ประสบความสำเร็จคือได้สังเคราะห์ตัวรองรับซีโอไลต์เอกซ์ ซีโอไลต์วาย วัสดุมีโซพอร์ MCM-41 ซึ่งนำไปเติมอะลูมิเนียมให้เป็น Al-MCM-41 และได้วิเคราะห์ลักษณะเชิงกายภาพและเคมีของวัสดุเหล่านี้ แล้วนำไปเป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาโลหะ ได้เตรียมตัวเร่งปฏิกิริยาแพลทินัม-โคบอลต์บนซีโอไลต์วาย (Pt-Co/Y) และ แพลทินัม-เหล็กบน MCM-41 (Pt-Fe/MCM-41) ส่วนซีโอไลต์เอกซ์ไม่ได้นำมาใช้ประโยชน์ต่อ เนื่องจากไม่เสถียร โครงสร้างถูกทำลายระหว่างการเตรียมตัวเร่งปฏิกิริยาจากปฏิกิริยาไฮโดรไลซิส

การนำ Pt-Co/Y ไปทดสอบการเร่งปฏิกิริยาระหว่างไฮโดรเจนกับบิวเทน เพื่อให้แตกตัวเป็นสารประกอบไฮโดรคาร์บอนโมเลกุลเล็ก (Butane hydrogenolysis) นั้นยังไม่ประสบความสำเร็จเนื่องจากเกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยาจากการจับของโค้กบนผิวหน้า ส่วนตัวเร่งปฏิกิริยา Pt-Fe/MCM-41 และ Pt-Fe/Al-MCM-41เมื่อนำไปทดสอบปฏิกิริยาการเติมหมู่ไฮดรอกซิลของโทลูอีน (Toluene hydroxylation) พบว่าตัวเร่งปฏิกิริยาได้ โดยประสิทธิภาพการเร่งปฏิกิริยาขึ้นกับเวลาและปริมาณ Al ที่เติม ผลิตภัณฑ์ของปฏิกิริยาคือเคดาคอลและไฮโดรควิโนน

คำหลัก bimetallic catalyst, MCM-41, ซีโอไลต์เอกซ์ ซีโอไลต์วาย

Abstract

The goal of this research was to prepare catalytic support materials from rice husk silica for bimetallic catalysts containing platinum and other metals. These catalysts were tested for reactions of hydrocarbon compounds. The successes of the project included the synthesis of zeolite X, Y, mesoporous MCM-41, and aluminium-modified MCM-41 (Al-MCM-41) which were characterized by physical and chemical methods. The zeolite Y was used as a support for platinum-cobalt catalysts (Pt-Co/Y) and the Al-MCM-41 was used as a support for platinum-iron catalysts (Pt-Fe/MCM-41). However, zeolite X was not used as a support because its structure collapsed during the catalysts preparation due to hydrolysis.

Pt-Co/Y Catalysts were tested for butane hydrogenolysis but not successful due to catalysts deactivation from coking. The Pt-Fe/MCM-41 and Pt-Fe/Al-MCM-41 catalysts were found to be active for toluene hydroxylation. The activities depended on time and Al amount added. The products from this reaction were chetechol and hydroquinone.

คำหลัก bimetallic catalyst, MCM-41, zeolite X, zeolite Y

Executive Summary

รหัสโครงการ	MRG4780147
ชื่อโครงการ	(ไทย) การเตรียม วิเคราะห์ลักษณะ และประสิทธิภาพของตัวเร่งปฏิกิริยาโลหะผสมที่ประกอบด้วยแพลทินัมและโลหะอื่น (English) Preparation, characterization and catalytic testing of bimetallic catalyst containing platinum and other metals
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โครงการวิจัยนี้ มีจุดประสงค์เพื่อเตรียมตัวรองรับตัวเร่งปฏิกิริยาโดยใช้ซิลิกาจากแกลบ จากนั้นนำไปเป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาแพลทินัมและโลหะอื่น และนำไปทดสอบการเร่งปฏิกิริยาของสารประกอบไฮโดรคาร์บอน ผลการดำเนินงานที่ประสบความสำเร็จคือได้สังเคราะห์ตัวรองรับซีโอไลต์เอกซ์ ซีโอไลต์วาย วัสดุมีโซพอร์ MCM-41 ซึ่งนำไปเติมอะลูมิเนียมให้เป็น Al-MCM-41 และได้วิเคราะห์ลักษณะเชิงกายภาพและเคมีของวัสดุเหล่านี้ แล้วนำไปเป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาโลหะ ได้เตรียมตัวเร่งปฏิกิริยาแพลทินัม-โคบอลต์บนซีโอไลต์วาย (Pt-Co/Y) และ แพลทินัม-เหล็กบน MCM-41 (Pt-Fe/MCM-41) ส่วนซีโอไลต์เอกซ์ไม่ได้นำมาใช้ประโยชน์ต่อ เนื่องจากไม่เสถียร โครงสร้างถูกทำลายระหว่างการเตรียมตัวเร่งปฏิกิริยาจากปฏิกิริยาไฮโดรไลซิส

การนำ Pt-Co/Y ไปทดสอบการเร่งปฏิกิริยาระหว่างไฮโดรเจนกับบิวเทน เพื่อให้แตกตัวเป็นสารประกอบไฮโดรคาร์บอนโมเลกุลเล็ก (Butane hydrogenolysis) นั้นยังไม่ประสบความสำเร็จเนื่องจากเกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยาจากการจับของโค้กบนผิวหน้า ส่วนตัวเร่งปฏิกิริยา Pt-Fe/MCM-41 และ Pt-Fe/Al-MCM-41เมื่อนำไปทดสอบปฏิกิริยาการเติมหมู่ไฮดรอกซิลของโทลูอีน (Toluene hydroxylation) พบว่าตัวเร่งปฏิกิริยาได้ โดยประสิทธิภาพการเร่งปฏิกิริยาขึ้นกับเวลาและปริมาณ Al ที่เติม ผลิตภัณฑ์ของปฏิกิริยาคือเคดาคอลและไฮโดรควิโนน

Output ของโครงการนี้ได้แก่ การส่งบทความเพื่อตีพิมพ์ในวารสารระดับนานาชาติ คือ Korean Journal of Chemical Enginnering 1 เรื่อง (ได้แก้ไขตาม reviewer แล้วและอยู่ในระหว่างการพิจารณาขั้นต่อไป) บทความตีพิมพ์ในวารสารในประเทศ คือ Suranaree Journal of Science and Technolgy 1 เรื่อง นอกจากนี้ยังมีการนำเสนอผลงานวิจัยในระดับนานาชาติ 2 เรื่อง และในระดับประเทศอีก 5 เรื่อง

เนื้อหางานวิจัย

1. วัตถุประสงค์

1. เพื่อเตรียมซิลิกาจากแกลบ และวิเคราะห์ความบริสุทธิ์และลักษณะ
2. เพื่อสังเคราะห์ตัวรองรับสำหรับตัวเร่งปฏิกิริยา ได้แก่ ซีโอไลต์เอกซ์ และซีโอไลต์วาย โดยใช้ซิลิกาจากแกลบ และวิเคราะห์ลักษณะของซีโอไลต์ดังกล่าว ด้วยเทคนิคต่าง ๆ เช่น X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning electron microscopy (SEM) และ Brunnauer-Emmette-Teller (BET)
3. เพื่อเตรียมตัวเร่งปฏิกิริยาแพลทินัม-โคบอลต์บนซีโอไลต์วาย (Pt-Co/Y) เพื่อทดสอบการเร่งปฏิกิริยา Butane hydrogenolysis
4. เพื่อเตรียมตัวเร่งปฏิกิริยาแพลทินัม-เหล็กบน MCM-41 (Pt-Fe/MCM-41)เพื่อทดสอบการเร่งปฏิกิริยา Toluene hydroxylation

2. วิธีการทดลอง

2.1 การเตรียมซิลิกาจากแกลบและการวิเคราะห์ลักษณะ

Rice husk was washed thoroughly with water to remove the adhering soil and dust and dried at 100 °C overnight. The dried rice husk then was refluxed in 3M HCl solution for 6 h, filtered and washed repeatedly with water until the filtrate was neutral and dried in an oven at 100 °C overnight. Finally, the refluxed rice husk was pyrolyzed in a hot air furnace muffle (Carbolite, CWF1200) at 550 °C for 3 h to remove the organic contents to obtain the white rice husk silica (RHS).

The chemical compositions of RHS in the form of oxides were analyzed by energy dispersive XRF (EDS Oxford Instrument ED 2000) with an array of 16 anodes analyzing crystals and Rh X-ray tube as a target with a vacuum medium.

2.2 การสังเคราะห์ซีโอไลต์เอกซ์และการวิเคราะห์ลักษณะ

The LSX synthesis was synthesized by hydrothermal method with an initial batch composition of 5.5 Na_2O : 1.65 K_2O : Al_2O_3 : 2.2 SiO_2 : 122 H_2O prepared from sodium silicate and sodium aluminate solution with a method modified from that described by Kühl (2001). The sodium silicate solution was prepared by slowly adding RHS into 100 mL of 14 % wt NaOH solution under stirring until a homogeneous solution was obtained. In the LSX synthetic procedure, sodium aluminate was dissolved in deionized water and slowly added into a solution containing KOH and NaOH. The new solution was mixed with diluted sodium silicate solution. The resulting mixture was transferred into a polypropylene bottle, capped and sealed with paraffin film. Aging and crystallization were carried out at 70 °C for 3 h without stirring, then adjusted to 100 °C for 2 h to complete crystallization; the sample was cooled down to room temperature and washed with water and 0.01 N NaOH solution, and dried at 110–125 °C overnight. The obtained product was zeolite LSX in the form of Na and K cations and was designated as NaK- LSX throughout this article.

Phase and crystallinity of RHS and NaK-LSX were confirmed by powder XRD (Bruker AXS diffractometer D5005) with nickel filter Cu K_α radiation scanning from 4 to 50° at a rate of 0.05 °/s with current 35 kV and 35 mA.

Functional groups within the NaK-LSX structure were identified by FT-IR (Spectrum GX, Perkin-Elmer) using KBr as a medium. IR spectra were scanned in the range of 4,000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The specific surface areas (BET), pore volumes, and pore sizes of NaK-LSX were determined from a nitrogen adsorption isotherm by a Quantachrome (NOVA 1200e) gas adsorption analyzer at liquid nitrogen temperature. The sample was degassed at 300 °C for 3 h before the measurement.

Crystallite size and morphology of NaK-LSX were studied by SEM (JEOL JSM-6400) with applied potential 10 - 20 kV.

Particle size distribution of NaK-LSX was determined by DPSA (Malvern Instruments, Mastersizer 2000) with the sample dispersed in distilled water and analyzed by He-Ne laser. The standard volume percentiles at 10, 50, and 90, or denoted as d(0.1), d(0.5), and d(0.9), respectively, were recorded from the analysis and used to calculate the width of the distribution.

Finally, NaK-LSX was exchanged to NH_4-LSX by stirring in NH_4NO_3 for 18 h. After filtration and drying, the obtained NH_4-LSX product was calcined at 400 °C to convert to H-LSX. Thermal stabilities of NH_4-LSX were investigated by TGA on a Simultaneous Differential Thermal Analysis (SDT 2690) by heating from room temperature to 1000 °C with a heating rate of 10 °C/min in nitrogen flow (100 ml/min). The phases of both materials were also analyzed by XRD.

2.3 การสังเคราะห์ซีโอไลต์วายและการวิเคราะห์ลักษณะ

The zeolite NaY was synthesized from a seed gel and feedstock gel with a procedure modified from that described elsewhere (Ginter, 2001). The major difference between seed gel and feedstock gel is that the feedstock gel was prepared and used immediately without aging. Briefly, the seed gel with a molar ratio of $10.67Na_2O:Al_2O_3:10SiO_2:180H_2O$ was prepared by adding Na_2SiO_3 solution to the solution of $NaAlO_2$. The mixture was stirred until homogeneous and transferred into a polypropylene (PP) bottle, capped, and aged at room temperature for 24 h.

The feedstock gel with molar ratio $4.30Na_2O:Al_2O_3:10SiO_2:180H_2O$ was prepared in similar fashion to that of the seed gel except that it was used immediately without aging.

The NaY synthesis was carried out by a slow addition of the seed gel into the feedstock gel under stirring. The mixture was transferred into a PP bottle, capped, and crystallized at 90 °C. This study compared two synthetic routes for NaY. The first route was "one-step" synthesis in which the mixture of seed gel and feedstock gel was mixed and taken directly to crystallization at 90 °C for 24 h. The second route was a "two-step" synthesis in which the seed gel and the feedstock gel were mixed and aged at room temperature for 24 h and crystallized at 90 °C at various time (22 – 72 h). After the crystallization, the samples were cooled down to room temperature. The solid product was separated by filtration, washed thoroughly with distilled water, and dried at 110 °C.

2.4 การสังเคราะห์ MCM-41 และ Al-MCM-41 และการวิเคราะห์ลักษณะ

Siliceous MCM-41 is synthesized from a gel having a molar composition of $4SiO_2:1Na_2O:1CTABr:0.29H_2SO_4:400H_2O$. SiO_2 (3 g) is dissolved in a solution containing NaOH (6 g) in distilled water. The solution is then mixed with a solution of CTABr (4.5 g) in distilled water 90 mL until a clear solution is obtained. The pH of the gel mixture is adjusted to 11 with H_2SO_4 then the gel mixture is stirred for 2 h and finally the mixture is transferred into a Teflon-lined autoclave and kept at 100 °C under static conditions for 3 day. The solid material obtained is separated by centrifugation at 3000 rpm for 30 min. and washed well with distilled water, until the solid shows a neutral pH then dried in air at 100 °C overnight. Finally the resulting material is calcined at 540 °C for 6 h, at a heating ramp of 10 °C /min. MCM-41 is characterized by various techniques including XRD, XRF, TEM, BET surface area and FT-IR.

Al-MCM-41-Post samples are also prepared by grafting method. Siliceous MCM-41 is heated to remove water in an oven at 100 °C overnight. $NaAlO_2$ solution is added to MCM-41 with Si/Al ratios 100, 75, 50 and 25 in a propylene bottle and the mixture is stirred vigorously for 30 min. The solid material obtained is separated by centrifugation at 3000 rpm for 30 min and washed well with distilled water, until the filtrate shows a neutral pH then dried in air at 100 °C overnight. Finally the resulting material is calcined at 540 °C for 6 h, at a heating ramp of 10 °C /min.

2.5 การเตรียมตัวเร่งปฏิกิริยา Pt-Co/NaY การทดสอบการเร่งปฏิกิริยา Butane hydrogenolysis

Pt monometallic catalysts on zeolites Y (Pt/Y) are prepared by incipient wetness impregnation with aqueous solutions of H_2PtCl_4. Co monometallic catalysts on zeolite Y (Co/Y) is also prepared by impregnation with aqueous solutions of $CoCl_2$. 6 H_2O.

Bimetallic Pt-Co/Y catalysts are prepared by conventional wet impregnation technique, sequential impregnation method and co-impregnation method by using H_2PtCl_4 and $CoCl_2$ as precursors.

The catalytic testing is conducted in a tubular flow reactor (Fig. 1). The catalysts are loaded into tubular micro-reactor and reduced under H_2 at 450 ^{o}C for 2 hours and cooled under N_2 flow to 200 ^{o}C. A gas reaction mixture containing C_4H_{10}, H_2 and He with mole ratio of 1:2:5 is flowed into the micro-reactor and carry out the reaction is carried out at 200 ^{o}C. The composition of effluent gas is analyzed by on-line GC equipped with thermal conductivity detector.

2.6 การเตรียมตัวเร่งปฏิกิริยา PtFe/Al-MCM-41 และการทดสอบการเร่งปฏิกิริยา Phenol hydroxylation

The 0.5 wt.% of platinum and 5 wt% of iron catalyst supported on MCM-41 and Al-MCM-41 was prepared by co-impregnation with $FeCl_3$ and $H_2PtCl_6.6H_2O$ solution the materials was dried at 100 °C overnight and calcined at 300 °C for 2 h, with a heating rate of 10 °C /min. The catalysts obtained were 0.5Pt5Fe/MCM-41, 0.5Pt5Fe/75AlMCM-41, 0.5Pt5Fe/50AlMCM-41 and 0.5Pt5Fe/25AlMCM-41 where the number 75, 50 and 25 were Si/Al ratio. The catalysts were characterized by temperature programmed-reduction (TPR).

The catalytic testing for phenol hydroxylation, the catalyst, phenol and H_2O_2 solution (30% w/v) were mixed (phenol/H_2O_2 mole ratio = 3) in a two-necked round bottle (250 ml) equipped with a magnetic stirrer and a reflux condenser. The reaction was carried out at 60 °C for 1 h and the catalyst was separated by centrifugation. The product was analyzed by a gas chromatograph (Shimadzu GC14-A) equipped with a capillary column (ID-BP1 3.0 um, 30 m x 0.53 mm), a flame ionization detector (FID) and the injector and column temperatures were 250 °C and 190 °C, respectively.

3. ผลการทดลองและวิจารณ์ผลการทดลอง

3.1 ผลการวิเคราะห์ลักษณะซิลิกาจากแกลบ

The chemical compositions of RHS in the form of oxides are shown in Table 1. The major component was SiO_2 along with small amounts of Al_2O_3, K_2O, CaO and Fe_2O_3. The purity of RHS was sufficient to use as a silica source for the synthesis of NaK-LSX.

Table 1. RHS components determined by XRF

Components	(%wt)
SiO_2	97.96
Al_2O_3	00.56
K_2O	00.06
CaO	00.98
Fe_2O_3	00.02

The powder XRD pattern of RHS is shown in Figure 1. Only a broad peak at approximately 22 degrees which was a characteristic of amorphous silica was observed. This phase was more suitable for the NaK-LSX synthesis than the crystalline form because it could be dissolved to form sodium silicate more easily. A longer time would be needed in the synthesis with crystalline silica.

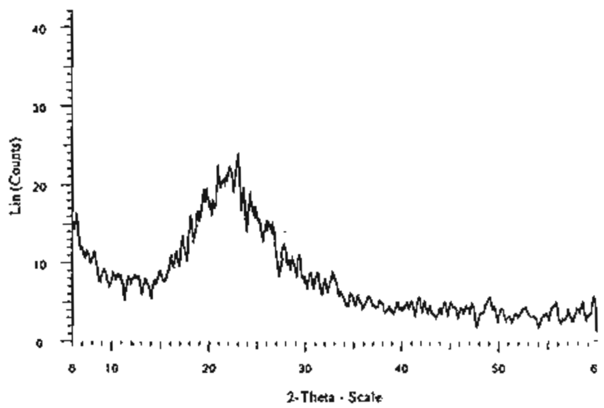

Figure 1 Powder XRD pattern of RHS

3.2 ผลการสังเคราะห์ซีโอไลต์เอกซ์และการวิเคราะห์ลักษณะ

3.2.1 Characterization of NaK-LSX by XRD

The formation of the NaK-LSX framework synthesized from RHS was confirmed by XRD comparing with standard NaX (Figure 2). The sample gave peaks at positions similar to that of the standard NaX, indicating the formation of the faujasite structure, and the sharp peaks indicated high crystallinity. The relative crystallinitiy to the standard NaX was calculated and the obtained value was approximately 100%:

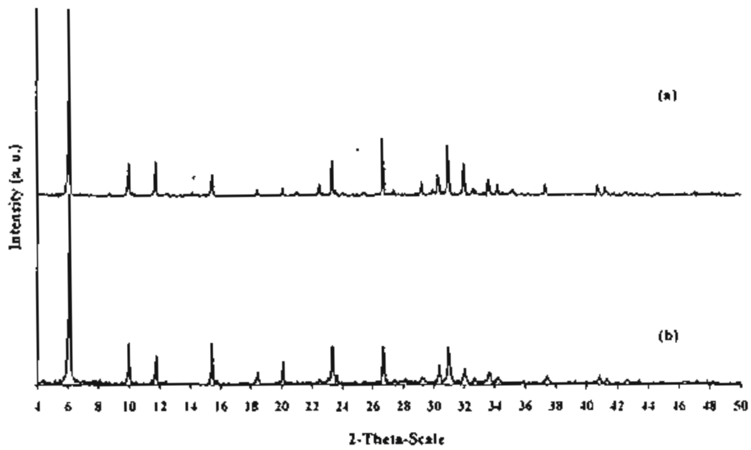

Figure 2 XRD spectrum of (a) NaK-LSX synthesized from RHS and (b) standard NaX

The details of peak positions, d-spacing and relative intensity of NaK-LSX and standard NaX are presented in Table 2. Although all the XRD peaks of NaK-LSX were similar to those of the standard NaX, the sequence of intensities were different. This was not surprising because our sample contains both Na and K cations, while the standard only has the Na cation. It was previously reported that the sequence of peak intensities depended strongly on type of cations (Joshi *et al.*, 2002; Esposito *et al.*, 2004) and the presence of K^+ attenuated them. Moreover, the lower Si/Al ratio enhanced the line intensities (Kühl, 1987).

Table 2. Peak positions, d-spacing and relative intensity of NaK-LSX and standard NaX

2θ	d	Relative intensities	
		Standard NaX	Synthesized LSX
6.10	14.48	100.00	100.00
15.43	5.74	22.70	13.10
9.99	8.85	22.40	17.30
26.70	3.34	22.10	29.40
23.32	3.81	21.00	20.00
30.10	2.88	20.40	26.20
11.73	7.54	16.40	17.80
20.09	4.42	12.60	6.90
30.36	2.94	11.21	13.10
32.03	2.79	8.62	17.30
18.43	4.81	7.18	4.20
34.24	2.62	4.89	6.20

3.2.2 Characterization of NaK-LSX by FTIR

The synthesized NaK-LSX was characterized by FTIR to identify functional groups in the structure. Figure 3 shows a strong peak at 950 cm^{-1} which was assigned to an asymmetric T—O stretching. In general, T—O is a tetrahedral atom referred to the framework of Si, Al composition and may shift to a lower frequency with an increase of the number of tetrahedral Al atoms (Lee *et al.*, 2006). Bands in the region 773 cm^{-1}, 690 cm^{-1} and 571 – 460 cm^{-1} were attributed mainly to the symmetric stretching, double ring and T—O bending vibrations, respectively. Lee *et al.* (2006) and Sang *et al.* (2006) reported that a band at 600 – 500 cm^{-1} is related to the topological arrangement of secondary units of structure in zeolites that contain the double 4 and 6 rings external linkage peak associated with the FAU structure and also observed in all the zeolite structures. The band with a peak at 3,487 was assigned to OH stretching and the vibration at 1,638 cm^{-1} was referred to bending vibration of adsorbed water molecule (Dyer *et al.*, 2004).

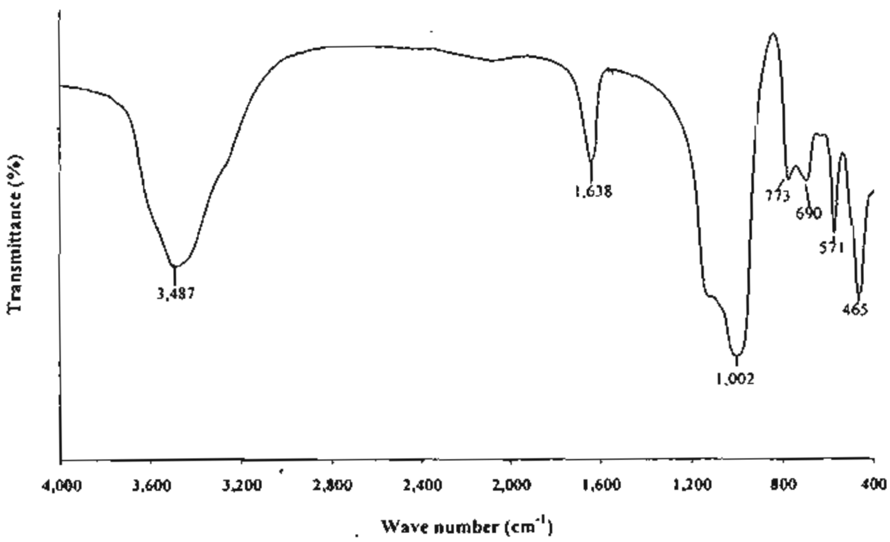

Figure 3 IR spectrum of zeolite NaK-LSX synthesized from RHS

3.2.3 Surface Analysis of NaK-LSX by BET

The N_2 adsorption isotherm of NaK-LSX is shown in Figure 4. It was type I based on IUPAC's classification with a large nitrogen uptake at low pressure and the desorption almost overlapping with the adsorption. The step increased in N_2 adsorption with an increased relative pressure, P/P_0 and N_2 adsorbed amount reaching 127 cm^3/g at P/P_0 = 0.048 suggesting the pressure of an appreciable amount of micropore on the

NaK-LSX surface. This result was common for the zeolite structure as explained by Langmi *et al.* (2005) that zeolite X has a very open framework and the entries to internal pores are not restricted by a large cation. Moreover, the effect of a cation on the surface area and pore structure show that the ion-exchange processes could induce enormous changes in surface and pore structure and these ions inhibited the movement of nitrogen molecule into pores or the so-called pore blocking effect, resulting in the decrease in surface area (Langmi *et al.*, 2003; Rakoczy and Traa, 2003; Huang *et al.*, 2004).

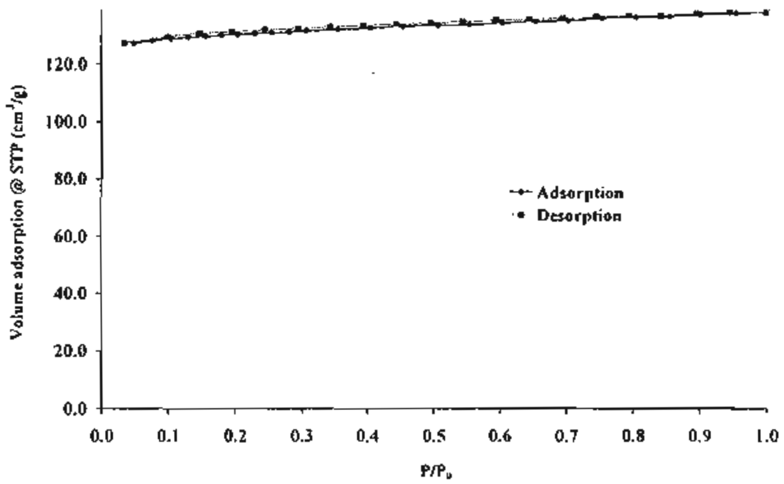

Figure 4 N_2 adsorption-desorption isotherm at 77 K on the synthesized NaK-LSX

Figure 5 shows cumulative pore volume and pore size distributions of NaK-LSX from N_2 adsorption. The pore diameter of NaK-LSX, shown in Figure 5(a), was calculated by the HK method and showed a narrow pore width between 0.3 – 1.9 nm with pore volume of 0.195 – 0.201 cm^3/g. Nevertheless, the curves of pore size distribution evaluated from desorption data by utilizing the BJH model shown in Figure 5(b) exhibited a narrow pore size distribution ranging from 1.3 nm – 30.0 nm with the highest pore size at 1.7 nm. However, a shoulder peak distribution is dominant and it was probably from interconnected surface pores of LSX (Chang *et al.*, 2005 and Lee *et al.* (2006).

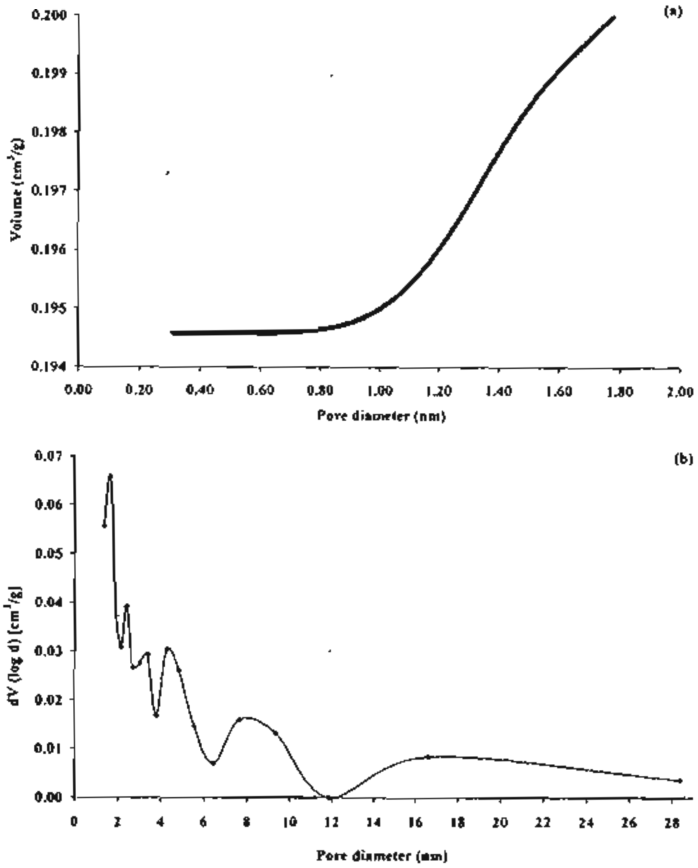

Figure 5 (a) HK cumulative pore volume and (b) BJH pore size distribution of NaK-LSX zeolite, where V is the cumulative pore volume (cm^3/g)

Table 3 shows results from a nitrogen adsorption study including the BET surface areas, pore volumes, and average pore diameters of NaK-LSX. The BET surface area and pore volume of NaK-LSX form RHS was interesting as it supported material for catalysis preparation or other application. (Langmi *et al.*, 2005)

Table 3 Textural properties of synthesized NaK-LSX zeolite

Textual Properties	Value	Unit
BET surface area[a]	391.4	(m^2/g)
External surface area[b]	361.0	(m^2/g)
Micro pore surface area[b]	355.3	(m^2/g)
Langmuir surface area[c]	577.1	(m^2/g)
Pore volume of micro pore[d]	0.19	(cm^3/g)
Micro pore diameter[e]	13.58	(nm)

[a]Multipoint BET analysis, [b]BJH analysis (t-method), [d]t-method, [e]DA method

3.2.4 Morphology of NaK-LSX Studied by SEM

Shape and size of NaK-LSX particles synthesized from RHS were studied by SEM and images are displayed in Figure 6 with magnification of 1,500 (a) and 25,000 (b). In the image with the smaller magnification, the solid product contained a mixture of multi-faceted spherulite crystals with a particle diameter approximately 6 – 10 μm along with round amorphous particles with a particle diameter approximately 0.2 – 5.0 μm. The multi-faceted spherulite particles were composed of polycrystal particles with different sizes along with small particles. Because some particles apparently connected with other particles, (Figure 5a), the particle size distribution was expected to be large as it was confirmed by DPSA (see next section). The particles in Figure 6(a) were distributed in the range of 0.3 – 10 μm with the largest contribution in the 0.3 – 2.0 μm range.

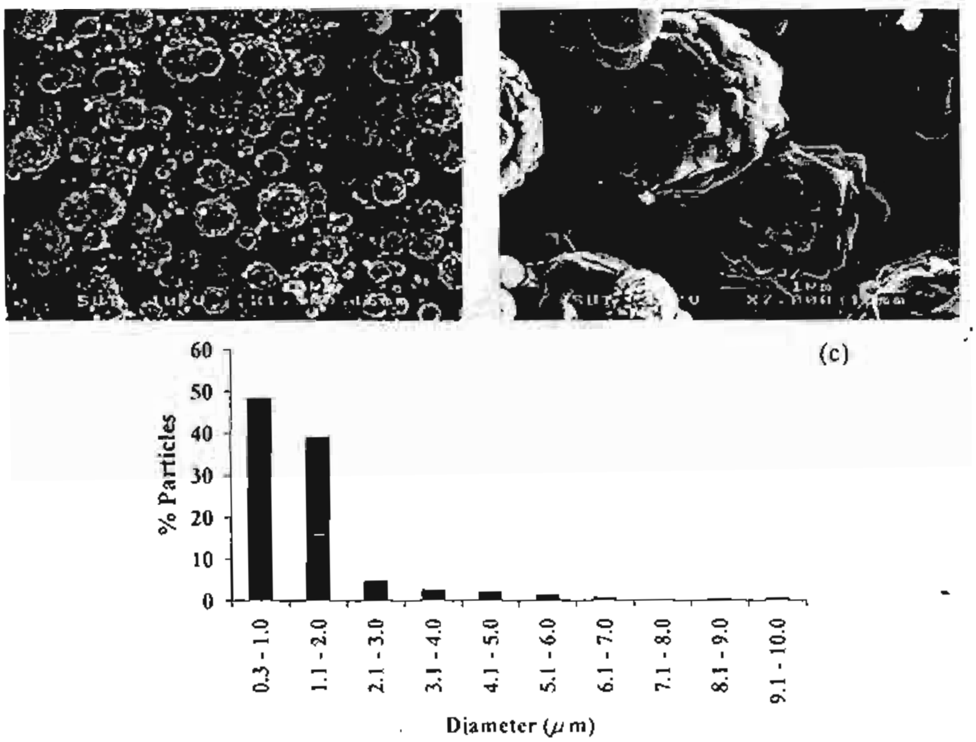

Figure 6 SEM images of synthesized Na-LSX with magnification of (a) 1,500 and (b) 25,000, respectively, and (c) particle size distribution measured from all particles in (a)

3.2.5 Particle Size Distribution of NaK-LSX by DPSA

The particle size distribution of Na-LSX was also investigated with DPSA and the results are presented as a histogram in Figure 7. The sizes were classified as oversize (area a) and undersize (area b), and the histogram plot and frequency curves are (c). The histogram plot shows the percentage of volume of particles, and the height of the histogram bars (left hand scale) was at 15.0 – 17.5 μm as for the majority of particles. The peak frequency curve provided the apparent tail in particle size analysis and shows the dominantly single modal distributions at 5 – 50 μm. Note that the results from DPSA were the size and distribution of bulk particles which might be composed of several small particles clustered together, and thus were different from the results from SEM which displayed images of isolate particles. Because the shape of samples as seen in SEM varied from a spherical shape to multi-faceted spherulite, that caused a different light scattering or diffraction effect based on the angularity of the crystals and their hydrodynamic behavior suspension (Cundy and Cox, 2005).

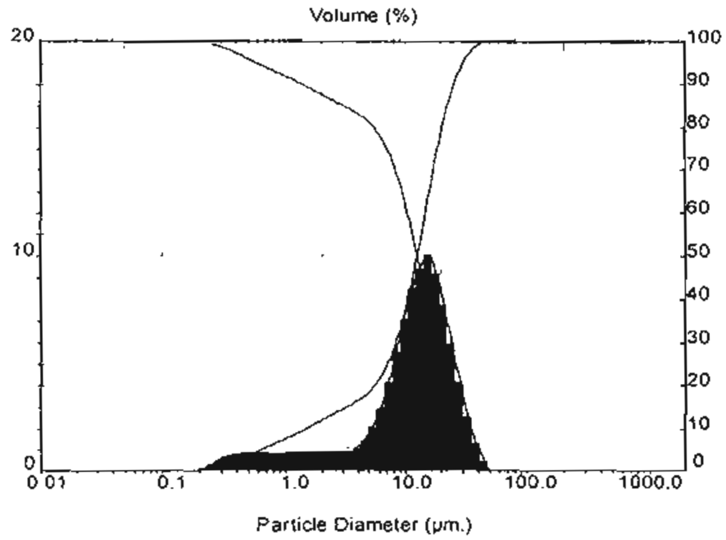

Figure 7 Particle size distribution of NaK-LSX synthesized from RHS; (a) percentage of sample below a certain size of particle, (b) percentage of sample above a certain size of particle and (c) histogram plot and frequency curve of particle Characterization and Thermal Stability of NH_4-LSX from Ion Exchange of NaK-LSX

3.3 ผลการสังเคราะห์ซีโอไลต์วายและการวิเคราะห์ลักษณะ

3.3.1 Comparison between One-step and Two-step Routes in NaY Synthesis

In this work, two synthetic routes for NaY synthesis were compared, namely, one-step and two-step. The products from both routes were characterized by XRD comparing with the pattern of standard NaY. As shown in Fig. 8, two-step route gave XRD pattern which was characteristic of NaY and all peaks were similar to those of the standard NaY. Thus, the product from two-step route contained NaY in pure phase. In contrast, the product from one-step route gave XRD peaks which were characteristic of both NaY and NaP. It was reported that aging time was essential for synthesis of NaY (with Si/Al ratio 1.8) from kaolin [13]. The process with no aging time resulted in the formation of NaP. From this observation, the suitable method for the NaY synthesis from RHS was two-step route and aging time of 24 h was sufficient to produce NaY in pure phase.

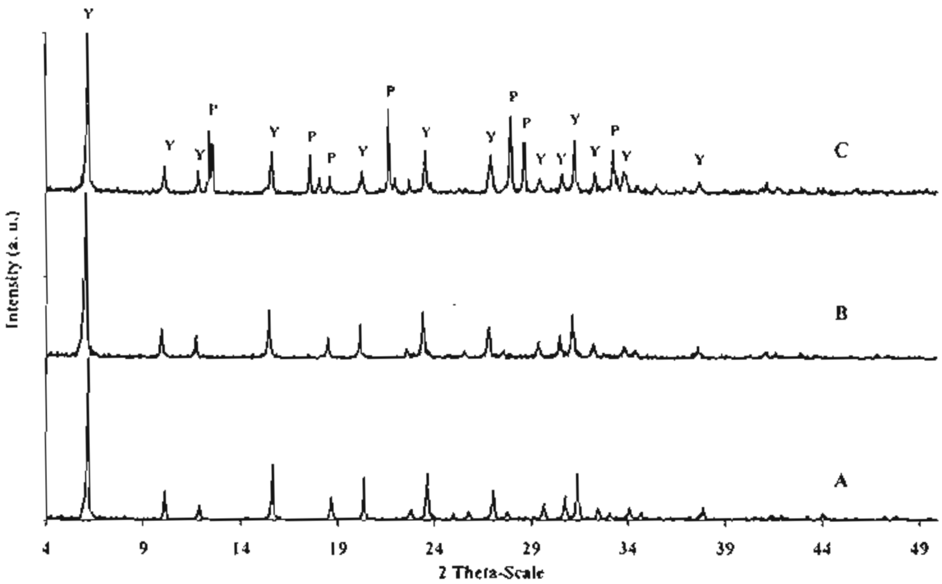

Figure 8 Normalized XRD spectrum of NaY from one-step and two-step synthesis (A) standard Y zeolite, (B) two-step, (C) one-step; (Y = NaY and P = NaP)

The mixed intermediate phase of NaY and NaP could be formed after mixing the seed gel and the feedstock gel with equilibrium in favor of NaY intermediate at room temperature, thus aging time was required. The presence of mixed phase during crystal growth was also found in the synthesis of MFI-Type zeolites and it was reported to be dependent on the degree of crystallization that proposed on the basis of the appearance of stable silicate species and the role of OH- ions during the induction period (Oh *et al.*, 2001).

3.3.2 Crystallization Time in Two-step Route

In the synthesis of NaY by two-step route, the crystallization time was varied from 22 to 72 h and the results were displayed in Fig.9. All spectra were normalized relative to the most intense peak and the crystallinity was compared from line broadening. In standard method (Ginter, 2001), the crystallization time was recommended to be 22 h with no more than 2 additional h. Thus, the crystallization time was carried out at both 22 and 24 h and the product obtained from both periods displayed only spectrum characterizing NaY (Fig.3, spectrum A and B, respectively). The spectrum of NaY from

24 h before normalization (not shown) exhibited sharper peaks with higher intensity than that from 22 h indicating that the optimum crystallization time for the synthesis of zeolite NaY with RHS was 24 h. The relative crystallinity of NaY with 22 h crystallization time was approximately 73% compared to that with 24 h.

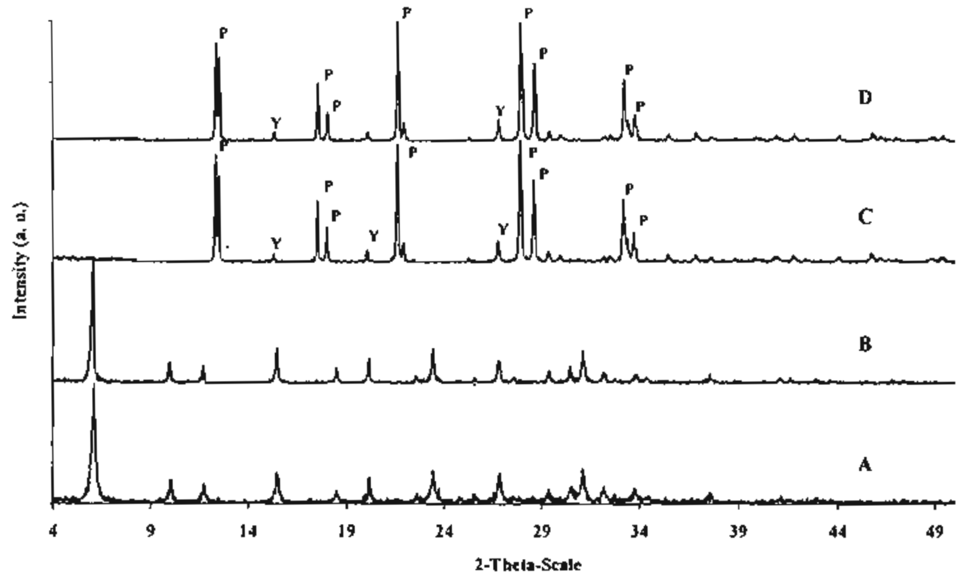

Figure 9 Normalized XRD spectrum of NaY from two-step synthesis crystallized at (A) 22, (B) 24, (C) 48, and (D) 72 h ; (Y = NaY and P = NaP)

After 24 h, additional peaks in XRD spectrum which were characteristic of zeolite NaP started to appear. The intensity of NaP peaks increased with crystallization time while that of the peaks of NaY decreased. The peaks of NaP were dominant at 48 and 72 h and the peaks of NaY were still observed with low intensity (Fig.9, spectrum C and D) indicating that longer time was required to complete the transformation of NaY to NaP. The synthesis of NaP in pure phase from commercial silica suspension was reported with crystallization time of 5 days (Albert *et al.*, 1998).

3.3.3 Textural Properties of NaY

Table 2 lists the BET surface areas, pore volumes, and average pore diameters of zeolite Y with different synthesis routes and crystallization times. The BET surface area of the product from one-step route was lower than that of the two-step route because of the presence of zeolite P which was a less porous phase. The presence of zeolite P was confirmed by XRD in Fig. 2 as mentioned above.

Table 4 Textural properties of synthesized zeolite Y from one- and two-step route

Sample	BET area (m^2/g)	Vp (cm^3/g)	Dp (nm)
One-step	382.10	0.194	2.693
Two-step			
22 h	440.10	0.220	2.565
24 h	625.10	0.320	2.547
48 h	12.71	0.002	2.593
72 h	31.13	0.006	3.820

Vp = pore volume, Dp = pore diameter

In the two-step route, the only product observed from crystallization time of 22 and 24 h was NaY. The product from crystallization time of 24 h had surface area of 625.10 m^2/g which was higher than that obtained from crystallization time of 22 h that was 440.10 m^2/g. This confirmed that crystallization for 24 h allowed more complete formation of NaY. The surface area of the products from crystallization of 48 and 72 h were much lower because the major products were zeolite P which was a less porous phase.

3.3.4 Morphology of NaY by SEM

The SEM micrograph of NaY synthesized from RHS at optimum conditions, two-step route and 24 h crystallization time, with magnification of x20000 is displayed in Fig. 10. The particles were uniform in size and some crystals apparently fused together to form agglomerate particles. The particle size of isolate crystal from SEM micrograph was approximately 1 μm.

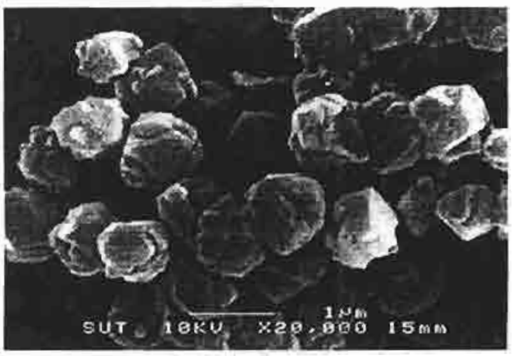

Figure 10 SEM image of zeolite Y synthesized from RHS with magnification of x20000

As mentioned earlier that NaY underwent transformation to NaP completely after crystallization for 72 h. The morphology of NaP was also studied by SEM. As exhibited in Fig. 5, the crystal shape of NaP was apparently different from that of NaY

(Fig.10). The shape of crystals was spherulitic particles of approximately 6-8 μm. Most crystals had cracks through the center and virtually similar, but much larger than that of zeolite P prepared from commercial silicate (Albert, et al., 1998).

3.3.5 Particle Size Distribution of NaY by DPSA

The result from DPSA analysis was the particle size distribution and the statistics of distribution calculated from the results using the derived diameters, an internationally agreed method of defining the mean and other moments of particles size British Standards; BS2955:1993. The percentage of volume sample that was under a certain particle size band (% under) at 10, 50, and 90% were 0.66, 6.18, and 25.93 μm, respectively. The width of distribution was 4.09 μm. The particle size distribution in all range by DPSA was displayed in a histogram in Fig. 11 revealing that the obtained products were not homogeneous in size. The average particle size from DPSA was approximately 15 μm. This average was different from the size of isolate crystals from SEM because several crystals fused together to from large particles. This information showed homogeneity of zeolite particles which could be of use for designing the application of the material.

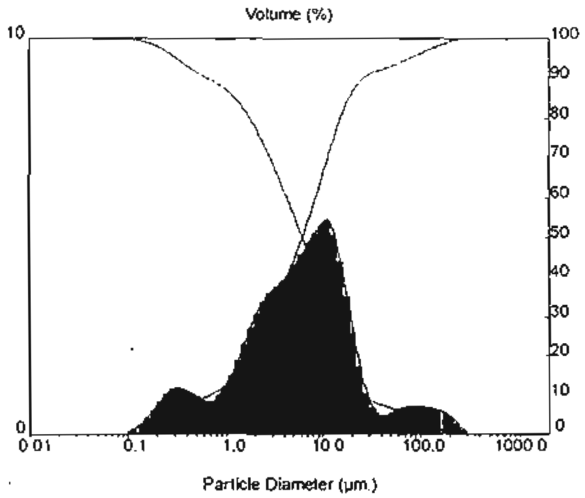

Figure 11 Particle size distribution of zeolite Y synthesized from RHS analyzed by DPSA

3.4 ผลการสังเคราะห์ MCM-41 และการวิเคราะห์ลักษณะ

The XRD patterns of the calcined MCM-41 and Al-MCM-41 are displayed in Fig. 12. The MCM-41 showed a strong peak at 2.5 and small peaks at 4, and 4.5

corresponding to the (100), (110), and (200) planes of a hexagonal lattice, respectively. Only the (100) peak was observed in all Al-MCM-41 indicating that the structure was slightly changed after Al grafting. The peak positions shifted slightly to lower value as aluminum was incorporated and the intensities decreased indicating changes in crystallinity. The widths of the strongest peak of Al-MCM-41 samples were broader than that MCM-41 and the differences in peak area were compared to estimate the relative crystallinity. As shown in the second column in Table 1, the crystallinity of Al-MCM-41 decreased as aluminum was incorporated.

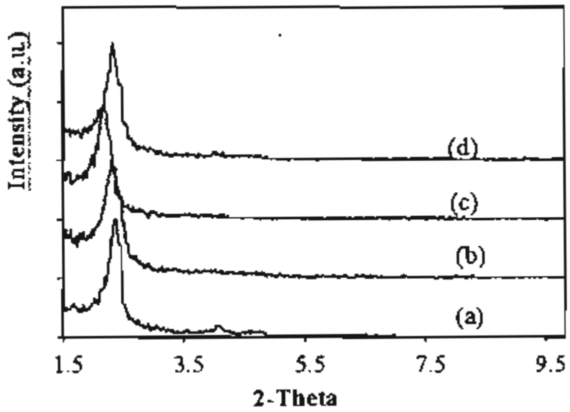

Figure 12 Normalized XRD patterns of (a) MCM-41, (b)-(d) Al-MCM-41 with Si/Al ratio of (b) 75, (c) 50 and (d) 25

The N_2 adsorption isotherms of MCM-41 and Al-MCM-41 samples with Si/Al ratio of 75, 50 and 25 are shown in Fig 13. All isotherms corresponded to type IV which was typical for mesoporous materials. At the beginning, the adsorbed amount increased quickly and concaved to the P/P_0 axis due to adsorption on external surface and form monolayer. The adsorbed amounts of all Al-MCM-41 samples were lower than that of MCM-41 indicating that their surface areas decreased after Al grafting. As shown in the second column in Table 1, the surface area of MCM-41 was 1,230 m^2/g and those of all Al-MCM-41 decreased to the range 740-870 m^2/g.

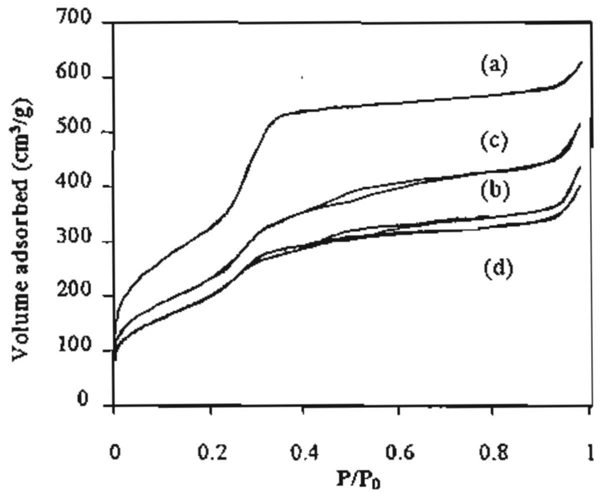

Figure 13 N_2 adsorption isotherm of (a) MCM-41, (b)-(d) Al-MCM-41 with Si/Al ratio of (b) 75, (c) 50 and (d) 25

At the 0.2-0.4 range of P/P_0, the N_2 increased again before reaching nearly constant volume. This range corresponded to nitrogen adsorption in the mesopores of MCM-41 and Al-MCM-41. However, the adsorption in this range for Al-MCM-41did not increased sharply as in MCM-41 indicating that some mesopores might collapse during the Al-grafting. This change could be an explanation to the significant decrease of surface area.

In addition to the relative crystallinity and BET surface area, Table 1 also showed the concentration of Si and Al in the MCM-41 and Al-MCM-41 determined from XRF. MCM-41 contained a small amount of Al because Al originally presented in the silica obtained from rice husk. Upon rafting, the concentration of Al increased and the acidity from ammonia adsorption was expected to have a similar trend to the Al concentration.

Results derived from the ammonia adsorption of the calcined samples are listed in the last column of Table 5. The acidity from ammonia adsorption was lower than the concentration of Al from XRF for all materials indicating that only some portion of Al were present at the surface and accessible for adsorption. The acidity values of Al-MCM-41 was in the range of 0.20 – 0.25 mmol/g compared to 0.17 mmol/g of the un-grafted MCM-41.

Table 5 Composition, surface area and acidity of MCM-41 and Al-MCM-41

Sample	Relative crystallinity	BET surface area (m^2/g)	Concentration of Si from XRF (mmol/g)	Concentration of Al from XRF (mmol/g)	Acidity from NH_3 adsorption (mmol/g)
MCM-41	100.00	1231.4641	34.30	0.28	0.17
75AlMCM-41	81.20	741.3508	35.22	0.52	0.22
50AlMCM-41	51.56	864.8746	34.92	0.81	0.25
25AlMCM-41	76.82	746.7049	34.22	0.66	0.22

3.4 ผลการทดสอบการเร่งปฏิกิริยา Butane hydrogenolysis ด้วยตัวเร่งปฏิกิริยา Pt-Co/NaY

การทดสอบปฏิกิริยา Butane hydrogenolysis ยังไม่ประสบความสำเร็จ เนื่องจากสภาวะที่ศึกษาเกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยาอย่างรวดเร็ว เนื่องจากการสะสมของคาร์บอนที่ผิวหน้าของตัวเร่งปฏิกิริยา (Coking) เนื่องจากการแตกตัวของสารตั้งต้นอย่างรวดเร็วพร้อมกับการเกิดพอลิเมอไรเซชันของคาร์บอน นอกจากนี้เครื่องมือที่ใช้ ได้แก่ชุดควบคุมการไหลของแก๊ส (Mass flow controller) ชำรุด และต้องใช้เวลาในการซ่อมนาน ซึ่งการวิจัยในส่วนนี้ต้องหาทุนวิจัยอื่นมาสนับสนุนเพิ่มเติม เพราะสารตั้งต้นและแก๊สมาตรฐานมีราคาแพง จึงไม่สามารถทำการวิจัยในส่วนนี้ให้เสร็จตามที่ได้ตั้งเป้าหมายไว้

3.5 ผลการทดสอบการเร่งปฏิกิริยา Phenol hydroxylation ด้วยตัวเร่งปฏิกิริยา Pt-Fe/Al-MCM-41

The hydroxylation activities of 0.5Pt5Fe on MCM-41 and Al-MCM-41 at various reaction times are presented in Fig.14. The phenol conversion increased remarkably in the time range of 0–1 h. The detail of conversion and selectivity are included in Table 5. The activities were in this order: 0.5Pt5Fe/75Si/Al-MCM-41 < 0.5Pt5Fe/50Si/Al-MCM-41 < 0.5Pt5Fe/25Si/Al-MCM-41. After 2 h, the conversion became nearly constant during the 4 h testing period.

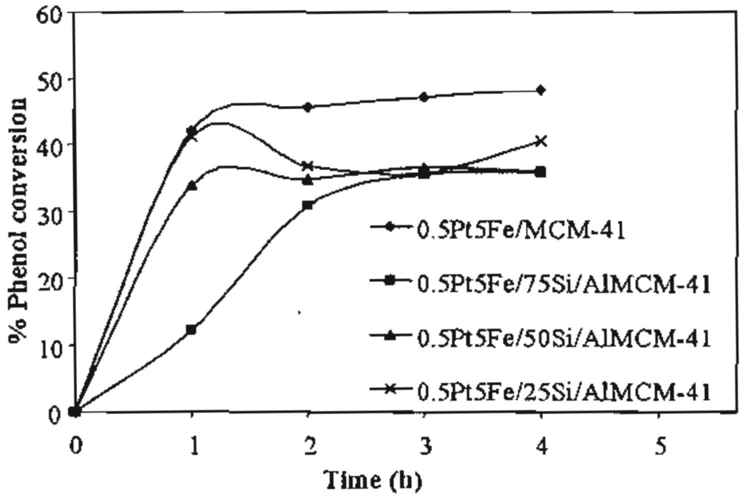

Figure 14 Phenol hydroxylation activity (H_2O_2/phenol = 1/3 at 70 °C and amount of catalysts 0.05 g.)

The table 2 showed the performance of other Pt-Fe bimetalic catalysts for phenol hydroxylation reaction. The reaction was carried out with fixed amount of H_2O_2 and phenol in 1:3 at 70 °C for 1 h and amount of catalysts 0.05 g. The 5Fe0.5Pt/MCM-41 showed the highest phenol conversion 42 % because MCM-41 had high surface and good dispersion of platinum and iron. For the bimetallic catalysts on Al-MCM-41 with Si/Al ratio of 75, 50 and 25 were 12, 34 and 41%, respectively, but the selectivity of chetechol were 73, 53 and 51% and selectivity of hydroquinone were 26, 47, 49%, respectively. The selectivity of hydroquinone seemed to increase as acidity of Al-MCM-41 increased. The phenol conversion showed higher conversion than either Fe-NaY, Co-NaY Fe-Co-NaY catalyst catalyst reported in literatures (Park, et al., 2006).

Table 5 Catalytic activities of various catalysts in phenol hydroxylation with conditions: phenol/H_2O_2 ratio = 3/1, reaction temperature = 70 °C, reaction time = 1 h.

Catalyst	% phenol conversion	Selectivity of chetechol	Selectivity of hydroquinone
0.5Pt 5Fe/MCM-41	42.20	52.35	47.64
0.5Pt 5Fe/75AlMCM-41	12.23	73.44	26.56
0.5Pt 5Fe/50AlMCM-41	34.04	52.61	47.39
0.5Pt 5Fe/25AlMCM-41	41.31	50.76	49.24

The table 2 showed the performance of other Pt-Fe bimetalic catalysts for phenol hydroxylation reaction. The reaction was carried out with fixed amount of H_2O_2 and phenol in 1:3 at 70 °C for 1 h and amount of catalysts 0.05 g. The 5Fe0.5Pt/MCM-41 showed the highest phenol conversion 42 % because MCM-41 had high surface and good dispersion of platinum and iron. For the bimetallic catalysts on Al-MCM-41 with Si/Al ratio of 75, 50 and 25 were 12, 34 and 41%, respectively, but the selectivity of chetechol were 73, 53 and 51% and selectivity of hydroquinone were 26, 47, 49%, respectively. The selectivity of hydroquinone seemed to increase as acidity of Al-MCM-41 increased. The phenol conversion showed higher conversion than either Fe-NaY, Co-NaY Fe-Co-NaY catalyst catalyst reported in literatures [16].

สรุป

งานวิจัยนี้ได้สังเคราะห์ตัวรองรับซีโอไลต์เอกซ์ ซีโอไลต์วาย วัสดุมีโซพอร์ MCM-41 ซึ่งนำไปเติมอะลูมิเนียม ให้เป็น Al-MCM-41 และได้วิเคราะห์ลักษณะเชิงกายภาพและเคมีของวัสดุเหล่านี้ แล้วนำไปเป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาโลหะ ได้เตรียมตัวเร่งปฏิกิริยาแพลทินัม-โคบอลต์บนซีโอไลต์วาย (Pt-Co/Y) และ แพลทินัม-เหล็กบน MCM-41 (Pt-Fe/MCM-41) ส่วนซีโอไลต์เอกซ์ไม่ได้นำมาใช้ประโยชน์ต่อ เนื่องจากไม่เสถียร โครงสร้างถูกทำลายระหว่างการเตรียมตัวเร่งปฏิกิริยาจากปฏิกิริยาไฮโดรไลซิส

การนำ Pt-Co/Y ไปทดสอบการเร่งปฏิกิริยาระหว่างไฮโดรเจนกับบิวเทน เพื่อให้แตกตัวเป็นสารประกอบไฮโดรคาร์บอนโมเลกุลเล็ก (Butane hydrogenolysis) นั้นยังไม่ประสบความสำเร็จเนื่องจากเกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยาจากการจับของโค้กบนผิวหน้า ส่วนตัวเร่งปฏิกิริยา Pt-Fe/MCM-41 และ Pt-Fe/Al-MCM-41เมื่อนำไปทดสอบปฏิกิริยาการเติมหมู่ไฮดรอกซิลของโทลูอีน (Toluene hydroxylation) พบว่าตัวเร่งปฏิกิริยาได้ โดยประสิทธิภาพการเร่งปฏิกิริยาขึ้นกับเวลาและปริมาณ Al ที่เติม ผลิตภัณฑ์ของปฏิกิริยาคือเคตาคอลและไฮโดรควิโนน

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ข้อเสนอแนะสำหรับงานวิจัยในอนาคต

Output จากโครงการวิจัยที่ได้รับจากทุน สกอ. และ สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

ได้ส่งบทความ เรื่อง Synthesis and Characterization of Zeolite NaY from Rice Husk Silica เพื่อตีพิมพ์ในวารสาร Korean Journal of Chemical Engineering ตั้งแต่ เดือน เมษายน 2550 และได้รับการตอบรับแบบ "Acceptable with major revision" ดังเอกสารแนบ ซึ่งได้ดำเนินการแก้ไขและส่งบทความฉบับแก้ไขแล้ว ตั้งแต่วันที่ สิงหาคม 2550 ขณะนี้รอผลการดำเนินการ

2. ผลงานอื่น ๆ

2.1 ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ

ได้ส่งบทความ เรื่อง Synthesis and Characterization of Zeolite LSX from Rice Husk Silica เพื่อตีพิมพ์ในวารสารเทคโนโลยีสุรนารี ได้รับการตอบรับแล้ว ดังเอกสารแนบ

2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.1 การเสนอผลงานในการประชุมนานาชาติ

1. การเสนอแบบ Oral Presentation เรื่อง Synthesis and Characterization of Na-LSX and NaY Zeolites from Rice Husk Silica โดย Pongtanawat Khemthong และ Jatuporn Wittayakun ชื่องานประชุม Regional Symposium on Chemical Engineering (RSCE 2006) 3-5 ธันวาคม 2549 ประเทศสิงคโปร์
2. การเสนอแบบ Oral Presentation เรื่อง Bimetallic platinum-iron catalysts on Al-MCM-41 supports: supports and catalyst characterization and catalytic activity for phenol hydroxylation โดย <u>Jitlada Chumee,</u> Nurak Grisdanurak, Arthit Neramittagapong and Jatuporn Wittayakun ชื่องานประชุม Regional Symposium on Chemical Engineering (RSCE 2006) 4-5 ธันวาคม 2550 ประเทศอินโดนีเซีย (ได้รับการตอบรับแล้ว ตามเอกสารแนบ)

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

1. การนำเสนอแบบ Oral presentation เรื่อง การเตรียมและวิเคราะห์ลักษณะ ของ MCM-41 และ Al-MCM-41 โดยใช้ซิลิกาจากแกลบข้าว (Preparation and characterization of MCM-41 and Al-MCM-41 from rice husk silica) โดย จิตรลดา ชูมี และ จตุพร วิทยาคุณ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549
2. การนำเสนอแบบ Oral presentation เรื่อง การสังเคราะห์วิเคราะห์ลักษณะของซีโอไลต์วาย โดยใช้ซิลิกาจากแกลบข้าว (Synthesis and characterization of

zeolite Y from rice husk silica) โดย พงษ์ธนวัฒน์ เข็มทอง และ จตุพร วิทยาคุณ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549

3. การนำเสนอแบบ Poster presentation เรื่องการเพิ่มประสิทธิภาพการเร่งปฏิกิริยาของ MCM-41 ที่สังเคราะห์โดยใช้ซิลิกาจากแกลบด้วยการเพิ่มโลหะไทเทเนียม (Enhancement of catalytic performance of MCM041 from rice husk silica by addition of titanium) โดย สุรชัย อาจกล้า จตุพร วิทยาคุณ และ นุรักษ์ กฤษดานุรักษ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549
4. การนำเสนอแบบบรรยายเรื่อง Synthesis of zeolite Y and Al-MCM-41 from rice husk silica as catalytic support materials โดย Wittayakun, J., Khemthong, P. Chume, J., Grisdanurak, N. ชื่องาน การประชุม นักวิจัยรุ่นใหม่...พบ...เมธีวิจัยอาวุโส สกว. 12-14 ตุลาคม 2549 เพชรบุรี
5. การนำเสนอแบบโปสเตอร์เรื่อง Preparation and characterization of catalyst support using silica source from rice husk โดย Wittayakun, J., Khemthong, P. Chume, J., Grisdanurak, N. ชื่องาน การประชุม นักวิจัยรุ่นใหม่...พบ...เมธีวิจัยอาวุโส สกว. 12-14 ตุลาคม 2548 เพชรบุรี

ภาคผนวก

1. ต้นฉบับผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

บทความที่แก้ไขแล้ว เรื่อง Synthesis and Characterization of Zeolite NaY from Rice Husk Silica ที่ส่งตีพิมพ์ในวารสาร Korean Journal of Chemical Engineering และเอกสารการตอบรับ (อยู่ระหว่างรอผลการพิจารณาขั้นสุดท้าย)

2. ผลงานอื่น ๆ

2.1 ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ

ต้นฉบับบทความ เรื่อง Synthesis and Characterization of Zeolite LSX from Rice Husk Silica ที่ได้รับตอบรับให้ตีพิมพ์ในวารสารเทคโนโลยีสุรนารี พร้อมเอกสารการตอบรับ

2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.1 การเสนอผลงานในการประชุมนานาชาติ

1. บทความที่ได้นำเสนอแบบ Oral presentation เรื่อง Synthesis and Characterization of Na-LSX and NaY Zeolites from Rice Husk Silica โดย Pongtanawat Khemthong และ Jatuporn Wittayakun ชื่องานประชุม Regional Symposium on Chemical Engineering (RSCE 2006) 3-5 ธันวาคม 2549 ประเทศสิงคโปร์
2. บทความที่ได้รับตอบรับให้นำเสนอแบบ Oral Presentation เรื่อง Bimetallic platinum-iron catalysts on Al-MCM-41 supports: supports and catalyst characterization and catalytic activity for phenol hydroxylation โดย Jitlada Chumee, Nurak Grisdanurak, Arthit Neramittagapong and Jatuporn Wittayakun ชื่องานประชุม Regional Symposium on Chemical Engineering (RSCE 2006) 4-5 ธันวาคม 2550 ประเทศอินโดนีเซีย (ได้รับการตอบรับแล้วตามเอกสารแนบ)

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

1. บทคัดย่อ การนำเสนอแบบ Oral presentation เรื่อง การเตรียมและวิเคราะห์ลักษณะ ของ MCM-41 และ Al-MCM-41 โดยใช้ซิลิกาจากแกลบข้าว (Preparation and characterization of MCM-41 and Al-MCM-41 from rice husk silica) โดย จิตรลดา ชูมี และ จตุพร วิทยาคุณ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ์ ตุลาคม 2549

2. บทคัดย่อ การนำเสนอแบบ Oral presentation เรื่อง การสังเคราะห์วิเคราะห์ลักษณะของซีโอไลต์วาย โดยใช้ซิลิกาจากแกลบข้าว (Synthesis and characterization of zeolite Y from rice husk silica) โดย พงษ์ธนวัฒน์ เข็มทอง และ จตุพร วิทยาคุณ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549
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5. บทคัดย่อ การนำเสนอแบบโปสเตอร์เรื่อง Preparation and characterization of catalyst support using silica source from rice husk โดย Wittayakun, J., Khemthong, P. Chume, J., Grisdanurak, N. ชื่องาน การประชุมนักวิจัยรุ่นใหม่ ...พบ...เมธีวิจัยอาวุโส สกว. 13-15 ตุลาคม 2548 เพชรบุรี

1. ต้นฉบับผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

บทความที่แก้ไขแล้ว เรื่อง Synthesis and Characterization of Zeolite NaY from Rice Husk Silica ที่ส่งตีพิมพ์ในวารสาร Korean Journal of Chemical Engineering และเอกสารการตอบรับ (อยู่ระหว่างรอผลการพิจารณาขั้นสุดท้าย)

From: KIChE <kmh@kiche.or.kr>
To: jatuporn@sut.ac.th
Date: 07/26/2007 01:12 PM
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Journal: The Korean Journal of Chemical Engineering
Specific Area: Materials, Polymer, Fluidization, Particle Technology
Title: Synthesis and Characterization of Zeolite NaY from Rice Husk Silica
Authors : Jatuporn Wittayakun (Suranaree University Of Technology)
Article No: KJ2007-100
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Manuscript History

Submission

Article No.: **KJ2007-100** (2007-04-18)

Title: Synthesis and Characterization of Zeolite NaY from Rice Husk Silica

Status: 1st Revision requested (Accept with major revision)

Author: Jatuporn Wittayakun (Suranaree University Of Technology)

Reviews & Revisions

Review History

Review	Reviewer	Assigned	Due	Reviewed	Recommendation
1st Review	Reviewer 1	2007-04-20	2007-05-04	2007-04-30	Acceptable with a major revision, please reformulate the article
	Reviewer 2	2007-04-20	2007-05-04	2007-07-25	Acceptable with a major revision, please reformulate the article

Revision History

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ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
มหาวิทยาลัยธรรมศาสตร์ ปทุมธานี

6 กันยายน 2550

เรื่อง แสดงความประสงค์ไม่ใส่ชื่อในผลงานตีพิมพ์ ทุนสนับสนุนการวิจัย ตามสัญญาเลขที่ MRG4780147

เรียน ฝ่ายวิชาการ สำนักงานกองทุนสนับสนุนการวิจัย

ตามที่กระผมได้รับเป็นนักวิจัยพี่เลี้ยงแก่ รองศาสตราจารย์ ดร. จตุพร วิทยาคุณ ในทุนพัฒนาศักยภาพในการทำงานวิจัยของอาจารย์รุ่นใหม่ ประจำปี 2547 จากสำนักงานคณะกรรมการอุดมศึกษา (สกอ.) และสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) โครงการ "การเตรียม วิเคราะห์ลักษณะ และประสิทธิภาพของตัวเร่งปฏิกิริยาโลหะผสมที่ประกอบด้วยแพลทินัมและโลหะอื่น" ตามสัญญาเลขที่ MRG4780147 ซึ่ง ได้ส่งบทความเรื่อง Synthesis and Characterization of Na-LSX and NaY Zeolites from Rice Husk Silica เพื่อตีพิมพ์ในวารสาร Korean Journal of Chemical Engineering แต่ไม่มีชื่อของกระผมปรากฏในชื่อเจ้าของผลงานนั้น กระผมขอเรียนชี้แจงว่ากระผมเป็นผู้แจ้งความประสงค์แก่ รองศาสตราจารย์ ดร. จตุพร ไม่ให้ใส่ชื่อของกระผมในผลงานตีพิมพ์นี้ เนื่องจากกระผมเห็นว่าการให้คำปรึกษา ไม่จำเป็นต้องใส่ชื่อ อย่างไรก็ตามกระผมและรองศาสตราจารย์ ดร. จตุพรมีงานวิจัยร่วมกัน และคาดว่าจะมีผลงานตีพิมพ์อื่น ๆ ที่มีชื่อของทั้งสองคนในอนาคตอันใกล้นี้

จึงเรียนมาเพื่อทราบ และโปรดพิจารณาให้ รองศาสตราจารย์ ดร. จตุพร วิทยาคุณ ปิดโครงการวิจัยนี้ได้ โดยไม่ต้องมีชื่อของกระผมในผลงานตีพิมพ์

ขอแสดงความนับถือ

(รองศาสตราจารย์ ดร. นุรักษ์ กฤษดานุรักษ์)
นักวิจัยพี่เลี้ยง

Synthesis and Characterization of Zeolite NaY from Rice Husk Silica

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Abstract–Rice husk silica (RHS) in amorphous phase with 98% purity was prepared from a waste rice husk from rice milling by leaching with hydrochloric acid and calcination. The RHS was used effectively as a silica source for the synthesis of zeolite Y in sodium form (NaY). The zeolite in pure phase was obtained from a two-step synthetic route in which the starting gels were mixed, aged for 24 h at room temperature and crystallized for 24 h at 90 °C. The diameter of single crystal particle from scanning electron microscope was approximately 1.0 μm whereas the average particle diameter from laser diffraction particle size analyzer was approximately 10 μm because of the agglomeration of small crystals. Longer crytallization time in this route resulted in a mixed phase containing NaY and zeolite P in sodium form (NaP). In addition, one-step synthetic route (no aging) was studied and the product was also a mixed phase zeolite.

Key words: Rice husk silica, Zeolite Y, NaY, Two-step route, One-step route, Zeolite P

INTRODUCTION

Rice husk which is often considered as a solid waste from rice milling contains approximately 70% of organic compounds and 30% of hydrate silica (SiO_2) [1, 2]. In general, the rice husk can be used as a cheap energy source through combustion or for other purposes as low value material. When the rice husk is leached with mineral acid and calcined in air, white powder rice husk silica (RHS) is obtained. The RHS with high silica purity is suitable as a silica source for the production of inorganic materials such as silicon carbide and silicon nitride [3, 4]. In a research field related to catalysis, RHS was used as a silica source for the synthesis of microporous materials such as zeolites [5 – 8] and mesoporous silica such as MCM-41 [9]. In this work, RHS was successfully used as a silica source for the synthesis of zeolite Linde type Y in sodium form (NaY).

Zeolites are microporous crystalline aluminosilicates composed of tetrahedral TO_4 units (T = Si or Al) linked together by sharing oxygen atoms. The general formula of zeolites is $M_a^{n+}[Si_xAl_yO_z]\cdot mH_2O$ where M^{n+} is extra-framework cation, $[Si_xAl_yO_z]$ is zeolite framework, and mH_2O is water molecules in sorbed phase [10]. Zeolites have several interesting properties that can be related to various applications such as solid acidity, ion-exchange capability, adsorption/release capability, and molecular-level pores. Zeolite NaY, the main focus in this work, is in the faujasite (FAU) family with a framework containing double 6 rings linked through sodalite cages that generate supercages with average pore diameter of 7.4 Å. There are several applications of FAU zeolites such as fluid cracking catalysts and sorbents for volatile organic removal [11].

The goal of this research was to use the RHS as silica source in the synthesis of NaY with the formula $Na_{56}[Al_{56}Si_{136}O_{384}]\cdot 250H_2O$. Two different synthetic routes, one-step and two-step, and crystallization time were investigated. The NaY products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area analysis (BET), and laser diffraction particle size analyzer (DPSA).

EXPERIMENTAL

1. Materials for RHS Extraction and NaY Syntheses

Rice husk was obtained from a local rice mill in Lampang Province, Thailand. Chemicals for RHS extraction and NaY synthesis were hydrochloric acid (37%wt HCl Carlo-Erba), sodium aluminate (~ 55-56% of $NaAlO_2$, Riedel-de Haën), sodium hydroxide (97%wt NaOH, Carlo-Erba), and potassium hydroxide (85%wt KOH, Ajax Fine Chem). Standard zeolites were NaY with Si/Al molar ratio 5.7 (JRC with Tosoh Crop) and NaP (Fluka).

2. Silica Extraction from Rice Husk

Rice husk was washed thoroughly with water to remove the adhering soil and dust and dried at 100 °C overnight. The dried rice husk was refluxed in 3M HCl solution for 3 h, filtered and washed repeatedly with water until the filtrate was neutral. After the acid treatment, the rice husk was dried at 100 °C overnight and pyrolyzed in a furnace muffle (Carbolite) at 550 °C for 6 h to remove the organic contents. The obtained product, RHS, was characterized by X-ray fluorescence (XRF) and powder XRD.

3. Synthesis of Zeolite NaY

The zeolite NaY was synthesized from a seed gel and feedstock gel with a procedure modified from that described elsewhere [12]. The major difference between seed gel and feedstock gel is that the feedstock gel was prepared and used immediately without aging. Briefly, the seed gel with a molar ratio of $10.67Na_2O{:}Al_2O_3{:}10SiO_2{:}180H_2O$ was prepared by adding Na_2SiO_3 solution to the solution of $NaAlO_2$. The mixture was stirred until homogeneous and transferred into a polypropylene (PP) bottle, capped, and aged at room temperature for 24 h.

The feedstock gel with molar ratio $4.30Na_2O:Al_2O_3:10SiO_2:180H_2O$ was prepared in similar fashion to that of the seed gel except that it was used immediately without aging.

The NaY synthesis was carried out by a slow addition of the seed gel into the feedstock gel under stirring. The mixture was transferred into a PP bottle, capped, and crystallized at 90 °C. This study compared two synthetic routes for NaY. The first route was "one-step" synthesis in which the mixture of seed gel and feedstock gel was mixed and taken directly to crystallization at 90 °C for 24 h. The second route was a "two-step" synthesis in which the seed gel and the feedstock gel were mixed and aged at room temperature for 24 h and crystallized at 90°C at various time (22 – 72 h). After the crystallization, the samples were cooled down to room temperature. The solid product was separated by filtration, washed thoroughly with distilled water, and dried at 110 °C.

4. Characterization of RHS and NaY

The chemical compositions of RHS, calculated as major oxides, were analyzed by energy dispersive XRF (EDS Oxford Instrument ED 2000) with array of 16 anodes analyzing crystals and Rh X-ray tube as target with a vacuum medium. The specific surface areas (BET), pore volumes, and pore sizes of NaY were determined by a Quantachrome (NOVA 1200e) gas adsorption analyzer and the nitrogen adsorption isotherms were obtained at liquid nitrogen temperature. The sample was degassed at 300 °C for 3 h before the measurement.

Phase and crystallinity of the RHS and the synthesized NaY were confirmed by powder XRD (Bruker AXS diffractometer D5005) with nickel filter Cu K_α radiation scanning from 4 to 50° at a rate of 0.05 degree/s. The intensity of peak at 22.5° was chosen for the crystallinity comparison. Morphology of the synthesized NaY was studied by SEM (JEOL JSM-6400) with applied potential 10 kV. Particle size distribution was determined by DPSA (Malvern Instruments, Mastersizer 2000) with the sample dispersed in distilled water and analyzed by He-Ne laser. The standard volume percentiles at 10, 50, and 90% denoted as d(0.1), d(0.5), and d(0.9), respectively, were recorded from the analysis and used to calculate the width of the distribution. The width was calculated from the equation below:

$$\frac{d(0.9)-d(0.1)}{d(0.5)}$$

RESULTS AND DISCUSSION

1. RHS Characterization

The chemical compositions of RHS in the form of stable oxides were shown in Table 1. The major component was SiO_2 with purity approximately 98%wt along with small amounts of other inorganic oxides including Al_2O_3, K_2O, CaO, and Fe_2O_3. The silica purity was sufficient to use as a silica source for the synthesis of NaY. The silica purity of the RHS from acid-leached rice husk in this study was higher than that of the rice husk ash (RHA) obtained directly from rice husk combustion without leaching [7]. However, the RHA silica was still suitable for the synthesis of zeolites such as zeolite beta and zeolite ZSM-5 [6, 7]. In general, RHA from pyrolysis of rice husk at high temperature contains silica in crystalline form [5] which takes a long time to dissolve in NaOH solution to form water glass for zeolite synthesis.

From the XRD pattern of RHS in Fig.1, only a broad peak with 2θ at 22 degree which was a characteristic of amorphous silica was observed. This form of silica is suitable for zeolite synthesis because it dissolves easily in NaOH solution to form sodium silicate.

2. Comparison between One-step and Two-step Routes

In this work, two synthetic routes for NaY synthesis were compared, namely, one-step and two-step. The products from both routes were characterized by XRD comparing with the pattern of standard NaY. As shown in Fig.2, two-step route gave XRD pattern which was characteristic of NaY and all peaks were similar to those of the standard NaY. Thus, the product from two-step route contained NaY in pure phase. In contrast, the product from one-step route gave XRD peaks which were characteristic of both NaY and NaP. It was reported that aging time was essential for synthesis of NaY (with Si/Al ratio 1.8) from kaolin [13]. The process with no aging time resulted in the formation of NaP. From this observation, the suitable method for the NaY synthesis from RHS was two-step route and aging time of 24 h was sufficient to produce NaY in pure phase.

The mixed intermediate phase of NaY and NaP could be formed after mixing the seed gel and the feedstock gel with equilibrium in favor of NaY intermediate at room temperature, thus aging time was required. The presence of mixed phase during crystal growth was also found in the synthesis of MFI-Type zeolites and it was reported to be dependent on the degree of crystallization that proposed on the basis of the appearance of stable silicate species and the role of OH- ions during the induction period [14].

3. Crystallization Time in Two-step Route

In the synthesis of NaY by two-step route, the crystallization time was varied from 22 to 72 h and the results were displayed in Fig.3. All spectra were normalized relative to the most intense peak and the crystallinity was compared from line broadening. In standard method [11], the crystallization time was recommended to be 22 h with no more than 2 additional h. Thus, the crystallization time was carried out at both 22 and 24 h and the product obtained from both periods displayed only spectrum characterizing NaY (Fig.3, spectrum A and B, respectively). The spectrum of NaY from 24 h before normalization (not shown) exhibited sharper peaks with higher intensity than that from 22 h indicating that the optimum crystallization time for the synthesis of zeolite NaY with RHS was 24 h. The relative crystallinity of NaY with 22 h crystallization time was approximately 73% compared to that with 24 h.

After 24 h, additional peaks in XRD spectrum which were characteristic of zeolite NaP started to appear. The intensity of NaP peaks increased with crystallization time while that of the peaks of NaY decreased. The peaks of NaP were dominant at 48 and 72 h and the peaks of NaY were still observed with low intensity (Fig.3, spectrum C and D) indicating that longer time was required to complete the transformation of NaY to NaP. The synthesis of NaP in pure phase from commercial silica suspension was reported with crystallization time of 5 days [15].

4. Textural Properties of NaY

Table 2 lists the BET surface areas, pore volumes, and average pore diameters of zeolite Y with different synthesis routes and crystallization times. The BET surface area of the product from one-step route was lower than that of the two-step route because of the presence of zeolite P which was a less porous phase. The presence of zeolite P was confirmed by XRD in Fig. 2 as mentioned above.

In the two-step route, the only product observed from crystallization time of 22 and 24 h was NaY. The product from crystallization time of 24 h had surface area of 625.10 m^2/g which was higher than that obtained from crystallization time of 22 h that was 440.10 m^2/g. This confirmed that crystallization for 24 h allowed more complete formation of NaY. The surface area of the products from crystallization of 48 and 72 h were much lower because the major products were zeolite P which was a less porous phase.

5. Morphology of NaY by SEM

The SEM micrograph of NaY synthesized from RHS at optimum conditions, two-step route and 24 h crystallization time, with magnification of x20000 is displayed in Fig.4. The particles were uniform in size and some crystals apparently fused together to form agglomerate particles. The particle size of isolate crystal from SEM micrograph was approximately 1 μm.

As mentioned earlier that NaY underwent transformation to NaP completely after crystallization for 72 h. The morphology of NaP was also studied by SEM. As exhibited in Fig.5, the crystal shape of NaP was apparently different from that of NaY (Fig.4). The shape of crystals was spherulitic particles of approximately 6-8 μm. Most crystals had cracks through the center and virtually similar, but much larger than that of zeolite P prepared from commercial silicate [15].

6. Particle Size Distribution of NaY by DPSA

The result from DPSA analysis was the particle size distribution and the statistics of distribution calculated from the results using the derived diameters, an internationally agreed method of defining the mean and other moments of particles size [16] British Standards; BS2955:1993. The percentage of volume sample that was under a certain particle size band (% under) at 10, 50, and 90% were 0.66, 6.18, and 25.93 μm, respectively. The width of distribution was 4.09 μm. The particle size distribution in all range by DPSA was displayed in a histogram in Fig. 6 revealing that the obtained products were not homogeneous in size. The average particle size from DPSA was approximately 15 μm. This average was different from the size of isolate crystals from SEM because several crystals fused together to from large particles. This information showed homogeneity of zeolite particles which could be of use for designing the application of the material.

CONCLUSIONS

RHS in amorphous phase with 98% purity was prepared by leaching rice husk with HCl acid and calcinination; and used as silica source for the synthesis of zeolite NaY. The NaY in pure phase was obtained from two-step synthetic route in which starting gels were mixed, aged for 24 h at room temperature and crystallized for 24 h at 90 °C. The diameter of single crystal from scanning electron microscope was approximately 0.6 – 1.0 μm whereas the average diameter of zeolite particles from laser diffraction particle size analyzer were approximately 10 μm. When the crystallization time was longer than 24 h, NaY slowly transformed to zeolite NaP.

ACKNOWLEDGEMENTS

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Table 1. Chemical components of RHS determined by XRF

Component	(%wt.)
Al_2O_3	00.56
SiO_2	97.96
K_2O	00.06
CaO	00.98
Fe_2O_3	00.02

Table 2. Textural properties of synthesized zeolite Y from one- and two-step route

Sample	BET area (m^2/g)	Vp (cm^3/g)	Dp (nm)
One-step	382.10	0.194	2.693
Two-step			
22 h	440.10	0.220	2.565
24 h	625.10	0.320	2.547
48 h	12.71	0.002	2.593
72 h	31.13	0.006	3.820

Vp = pore volume, Dp = pore diameter

List of Figures

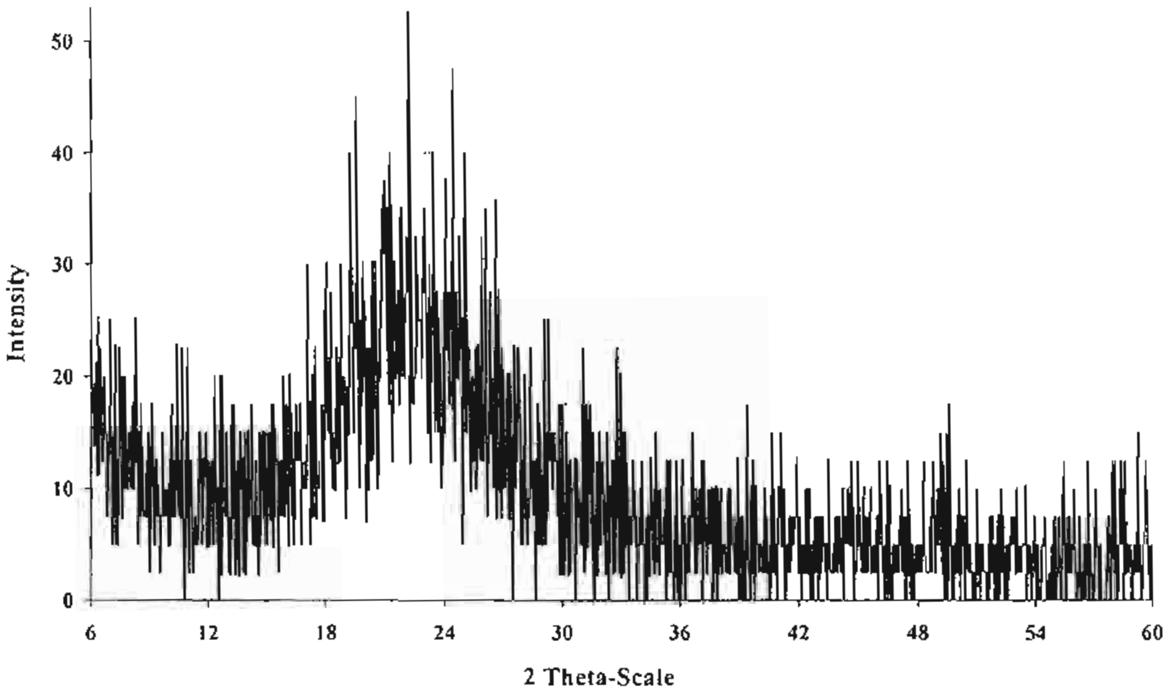

Fig. 1. XRD pattern of RHS.

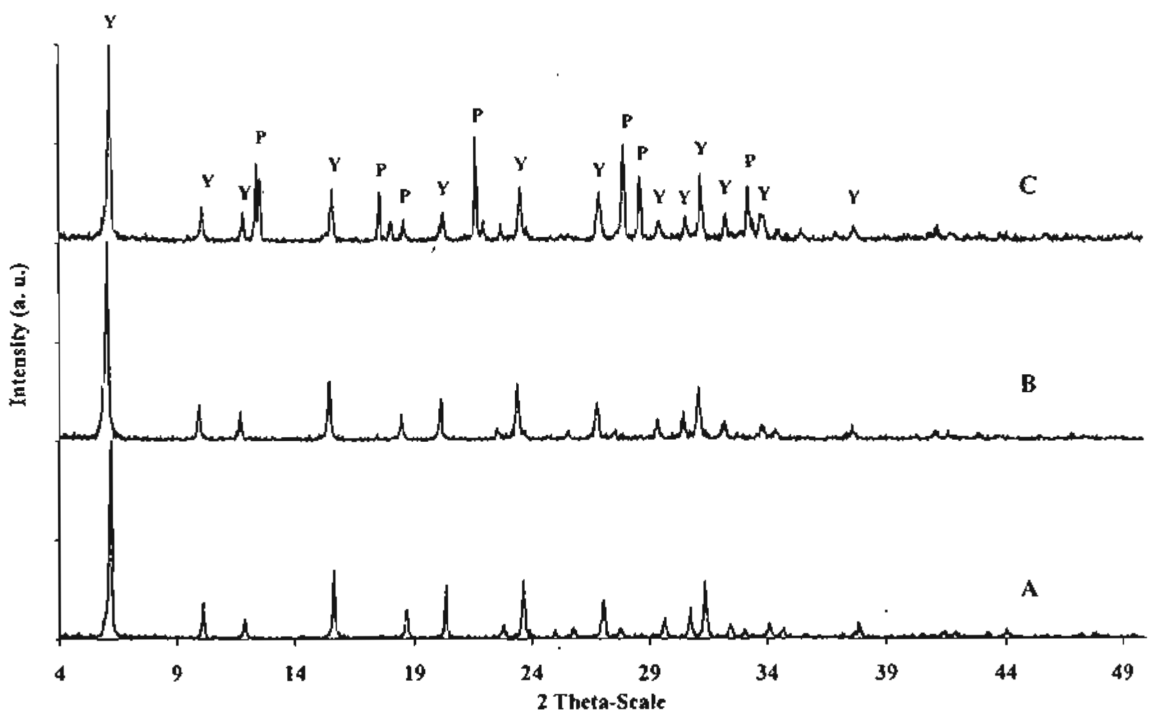

Fig. 2. Normalized XRD spectrum of NaY from one-step and two-step synthesis (A) standard Y zeolite, (B) two-step, (C) one-step; (Y = NaY and P = NaP).

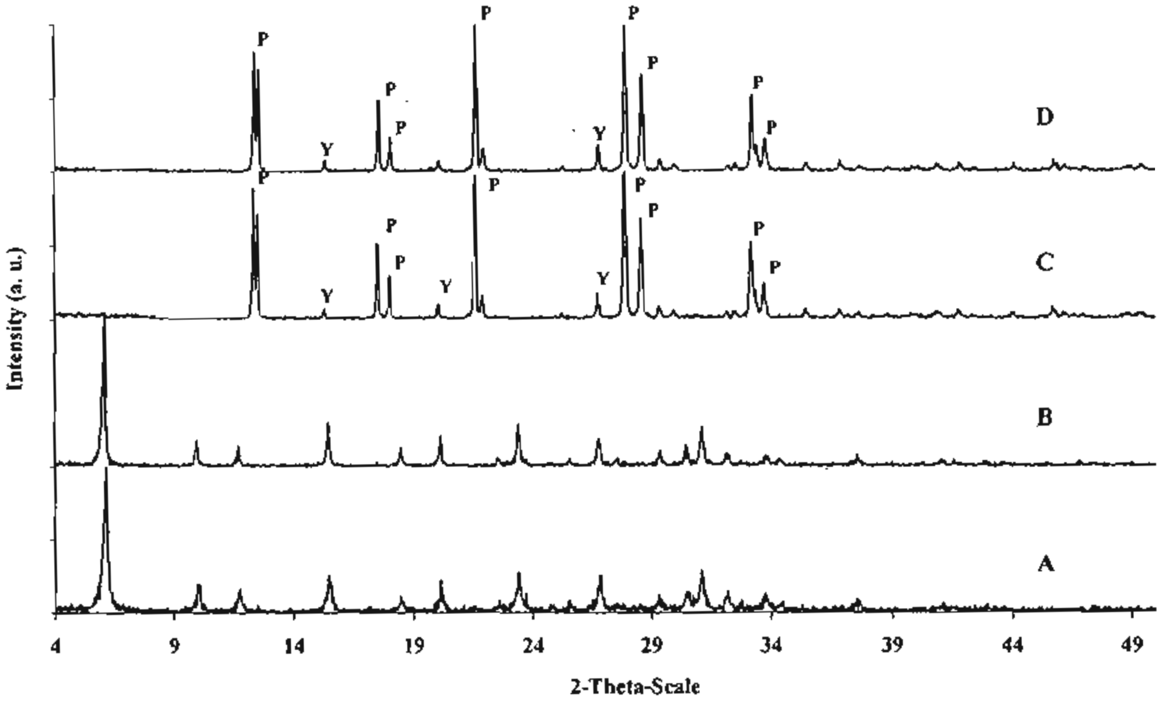

Fig. 3. Normalized XRD spectrum of NaY from two-step synthesis crystallized at (A) 22, (B) 24, (C) 48, and (D) 72 h ; (Y = NaY and P = NaP).

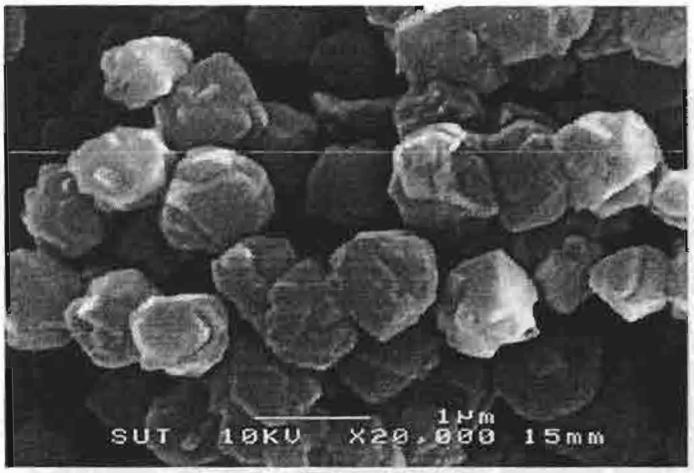

Fig. 4. SEM image of zeolite Y synthesized from RHS with magnification of x20000.

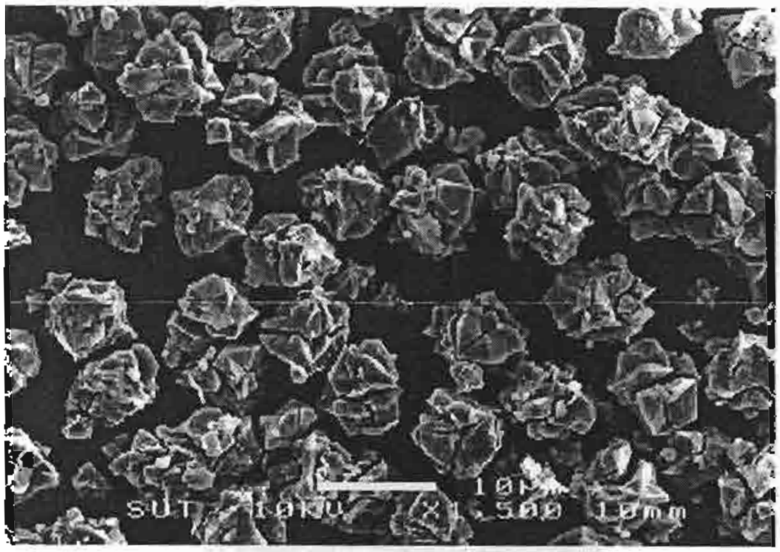

Fig. 5. SEM image of zeolite NaP with magnification of x1500.

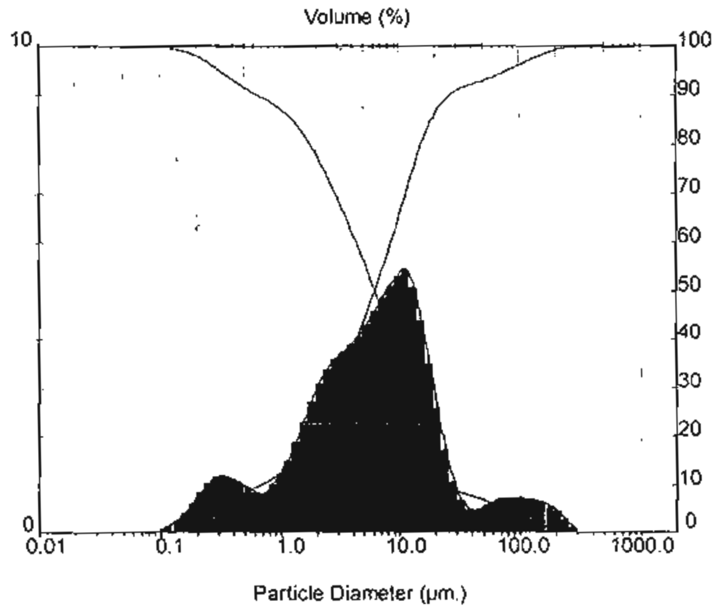

Fig. 6. Particle size distribution of zeolite Y synthesized from RHS analyzed by DPSA.

2. ผลงานอื่น ๆ

2.1 ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ

ต้นฉบับบทความ เรื่อง Synthesis and Characterization of Zeolite LSX from Rice Husk Silica ที่ได้รับตอบรับให้ตีพิมพ์ในวารสารเทคโนโลยีสุรนารี พร้อมเอกสารการตอบรับ

บันทึกข้อความ

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ที่ 5621/ 723 วันที่ 16 AUG 2007

เรื่อง Letter of acceptance.

Dear Associate Professor Dr. Jatuporn Wittayakun,

I am pleased to inform you that your article entitled "SYNTHESIS AND CHARACTERIZATION OF ZEOLITE LSC FROM RICE HUSK SILICA" has been accepted to be published in Suranaree Journal of Science and Technology. The galley proof will be later sent to you for the final corrections.

Thank you for publishing with Suranaree Journal of Science and Technology.

Sincerely,

J. Yongsawatdigul

Jirawat Yongsawatdigul, Ph.D.

Associate Professor

Editor

SYNTHESIS AND CHARACTERIZATION OF ZEOLITE LSX FROM RICE HUSK SILICA

Pongtanawat Khemthong, Sanchai Prayoonpokarach and Jatuporn Wittayakun*

Abstract

Silica powder with approximately 98% purity was extracted from rice husk (RH), converted to a sodium silicate solution, and used as a silica source for the synthesis of low silica type X (LSX) by hydrothermal process. The synthesized zeolite in the form of Na and K cations, referred to as NaK-LSX, was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), which confirmed the success of the synthesis. Images from scanning electron microscopy (SEM) of NaK-LSX displayed multi-faceted spherulite particles composed of polycrystal particles with different sizes along with small amorphous particles. The particle size distribution of NaK-LSX from a laser diffraction particle size analyzer (DPSA) was in the range of 0.2 – 50 μm and nitrogen adsorption indicated a surface area around 400 m^2/g. The structure of LSX did not change after the ion-exchange to produce an ammonium form but collapsed after subsequent calcination.

Keywords: Rice husk silica, NaK-LSX, zeolite, hydrothermal

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Introduction

The composition of rice husks varies with geological location. Mainly it contains organic substance and approximately 20% wt of silica (SiO_2) and after combustion the white ash contains approximately over 90% wt of SiO_2 (Williams and Nugranad, 2000; Park, 2003; Hamdan *et al.*, 1997; Kapur, 1985; Huang *et al.*, 2001). There are impurities in rice husk ash such as oxides of alkali metal which could be removed by leaching rice husk with acids before calcination; such a method could improve the purity of rice husk silica (RHS) to 96 – 99 % wt. (Williams and Nugranad, 2000; Sun and Gong, 2001; Chorkendorff *et al.*, 2003; Liou, 2004; Prasetyoko *et al.*, 2005). With high purity, RHS has potential as a silica source for the production of silicon-based inorganic materials such as silicon carbide (SiC); silicon nitride (SiN); mesoporous silica including MCM-41 and MCM-48; and zeolites (Wang *et al.*, 1998; Huang *et al.*, 2001; Sun and Gong, 2001; Grisdanurak *et al.*, 2003, Mohamed, 2004; Katsuki *et al*, 2005; Prasetyoko *et al.*, 2005). This study focuses on using RHS as a silica source for the synthesis of low silica zeolite type X (LSX).

Zeolites are microporous crystalline aluminosilicates in which the structural framework contains tetrahedral TO_4 units (T = Si or Al) linked together by oxygen sharing (Corma, 2001). The general formula of zeolite is $M_a^{n+}[Si_xAl_yO_z]\cdot mH_2O$ where M_a^{n+} are extra-framework cations; $[Si_xAl_yO_z]$ is the zeolite framework; and mH_2O are sorbed water molecules (Roberie *et al.*, 2001). Zeolites are related to several industrial applications, for example they are catalysts in fluid cracking, sorbents in volatile organic removal (Cundy *et al.*, 2005), a solid-state hydrogen storage medium (Langmi *et al.*, 2005; Li and Yang, 2006), and an internal side space for synthesis of transition-metal encapsulation (Salavati-Niasari *et al.*, 2006).

Zeolite LSX is in the faujasite (FAU) family with a framework containing double 6 rings linked through sodalite cages that generate supercages with pore diameters of 7.4 Å.

The typical Si/Al ratio of LSX is in the range of 1–1.5. It belongs to the space group F_{3m} (Auerbach *et al.*, 2003) and has a large number of extra-framework cations. LSX can be synthesized from a variety of silica sources including natural clay such as kaolinite, oil shale ash, and commercial silicates (Chandrasekhar and Pramada, 2001a, 2002b; Machado and Miotto, 2005). There are no reports on the synthesis of LSX with a silica source from rice husk.

Here we report the synthesis of zeolite LSX with the formula $Na_{73}K_{22}[Si_{97}Al_{95}O_{384}]\cdot 212H_2O$ (Esposito *et al.*, 2004) by using RHS as a silica source and characterization by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), surface area analysis (BET), scanning electron microscopy (SEM), and laser diffraction particle size analyzer (DPSA). Its stability after ion exchange to ammonium and proton forms (NH_4-LSX and H-LSX, respectively) was studied by thermogravimetric analysis (TGA).

Experimental

Materials for RHS Extraction and Zeolite Synthesis

Hydrochloric acid (37% HCl, Carlo-Erba), sodium silicate solution (Na_2SiO_3; 28.7% SiO_2, 8.9% Na_2O, Panreac, N Brand clarified), sodium aluminate (~ 55 – 56% of $NaAlO_2$, Riedel-de Haën), sodium hydroxide (97% NaOH, Carlo-Erba), potassium hydroxide (85% KOH; Ajax Fine Chem), ammonium nitrate (99.0% NH_4NO_3, J. T. Baker), and rice husk for RHS (local rice mill in Lampang, Thailand).

Silica Extraction from Rice Husk

Rice husk was washed thoroughly with water to remove the adhering soil and dust and dried at 100°C overnight. The dried rice husk then was refluxed in 3M HCl solution for 6 h, filtered and washed repeatedly with water until the filtrate was neutral and dried in an oven at 100°C overnight. Finally, the refluxed rice husk was pyrolyzed in a hot air furnace muffle (Carbolite, CWF1200) at 550°C for 3 h to remove the organic contents to obtain the white RHS.

Synthesis of Zeolite LSX

The LSX synthesis was synthesized by hydrothermal method with an initial batch composition of 5.5 Na_2O : 1.65 K_2O : Al_2O_3 : 2.2 SiO_2 : 122 H_2O prepared from sodium silicate and sodium aluminate solution with a method modified from that described by Kühl (2001). The sodium silicate solution was prepared by slowly adding RHS into 100 mL of 14 % wt NaOH solution under stirring until a homogeneous solution was obtained. In the LSX synthetic procedure, sodium aluminate was dissolved in deionized water and slowly added into a solution containing KOH and NaOH. The new solution was mixed with diluted sodium silicate solution. The resulting mixture was transferred into a polypropylene bottle, capped and sealed with paraffin film. Aging and crystallization were carried out at 70°C for 3 h without stirring, then adjusted to 100°C for 2 h to complete crystallization; the sample was cooled down to room temperature and washed with water and 0.01 N NaOH solution, and dried at 110–125°C overnight. The obtained product was zeolite LSX in the form of Na and K cations and was designated as NaK- LSX throughout this article.

Characterization of RHS and NaK- LSX

The chemical compositions of RHS in the form of oxides were analyzed by energy dispersive XRF (EDS Oxford Instrument ED 2000) with an array of 16 anodes analyzing crystals and Rh X-ray tube as a target with a vacuum medium.

Phase and crystallinity of RHS and NaK-LSX were confirmed by powder XRD (Bruker AXS diffractometer D5005) with nickel filter Cu K_α radiation scanning from 4 to 50° at a rate of 0.05 °/s with current 35 kV and 35 mA.

Functional groups within the NaK-LSX structure were identified by FT-IR (Spectrum GX, Perkin-Elmer) using KBr as a medium. IR spectra were scanned in the range of 4,000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The specific surface areas (BET), pore volumes, and pore sizes of NaK-LSX were determined from a nitrogen adsorption isotherm by a Quantachrome (NOVA 1200e) gas adsorption analyzer at liquid nitrogen temperature. The sample was degassed at 300°C for 3 h before the measurement.

Crystallite size and morphology of NaK-LSX were studied by SEM (JEOL JSM-6400) with applied potential 10 - 20 kV.

Particle size distribution of NaK-LSX was determined by DPSA (Malvern Instruments, Mastersizer 2000) with the sample dispersed in distilled water and analyzed by He-Ne laser. The standard volume percentiles at 10, 50, and 90, or denoted as d(0.1), d(0.5), and d(0.9), respectively, were recorded from the analysis and used to calculate the width of the distribution. The width was calculated from the equation below:

$$\frac{d(0.9)-d(0.1)}{d(0.5)}$$

Finally, NaK-LSX was exchanged to NH_4-LSX by stirring in NH_4NO_3 for 18 h. After filtration and drying, the obtained NH_4-LSX product was calcined at 400°C to convert to H-LSX. Thermal stabilities of NH_4-LSX were investigated by TGA on a Simultaneous Differential Thermal Analysis (SDT 2690) by heating from room temperature to 1000°C with a heating rate of 10 °C/min in nitrogen flow (100 ml/min). The phases of both materials were also analyzed by XRD.

Results and Discussion

RHS Characterization

The chemical compositions of RHS in the form of oxides are shown in Table 1. The major component was SiO_2 along with small amounts of Al_2O_3, K_2O, CaO and Fe_2O_3. The purity of RHS was sufficient to use as a silica source for the synthesis of NaK-LSX. The purity from this study was higher than that of rice husk ash (RHA) obtained from combustion without leaching which was less than 95% (Kapur, 1985; Williams and Nugranad, 2000; Huang *et al.*, 2001; Liou, 2004). However, that silica from RHA was still suitable for the synthesis of several porous materials such as MCM-41, zeolite beta, zeolite ZSM-5 and zeolite Y (Sun and Gong, 2001; Grisdanurak *et al.*, 2003; Khemthong and Wittayakun, 2006a, 2006b; Prasetyoko *et al.*, 2006).

The powder XRD pattern of RHS is shown in Figure 1. Only a broad peak at approximately 22 degrees which was a characteristic of amorphous silica was observed. This phase was more suitable for the NaK-LSX synthesis than the crystalline form because it could be dissolved to form sodium silicate more easily. A longer time would be needed in the synthesis with crystalline silica (Hamdan *et al.*, 1997).

Characterization of NaK-LSX by XRD

The formation of the NaK-LSX framework synthesized from RHS was confirmed by XRD comparing with standard NaX (Figure 2). The sample gave peaks at positions similar to that of the standard NaX, indicating the formation of the faujasite structure, and the sharp peaks indicated high crystallinity. The relative crystallinitiy to the standard NaX was calculated in the equation below (Gosh *et al.*, 1994; Tangkawanit and Rangsriwatananon, 2004) and the obtained value was approximately 100%:

$$\%\text{Crystallinity} = \left(\frac{\sum^{12} \text{intensity of XRD peak of product}}{\sum^{12} \text{intensity of XRD peak of standard zeolite NaX}} \right) \times 100.$$

The details of peak positions, d-spacing and relative intensity of NaK-LSX and standard NaX are presented in Table 2. Although all the XRD peaks of NaK-LSX were similar to those of the standard NaX, the sequence of intensities were different. This was not surprising because our sample contains both Na and K cations, while the standard only has the Na cation. It was previously reported that the sequence of peak intensities depended strongly on type of cations (Joshi *et al.*, 2002; Esposito *et al.*, 2004) and the presence of K^+ attenuated them. Moreover, the lower Si/Al ratio enhanced the line intensities (Kühl, 1987).

Characterization of NaK-LSX by FTIR

The synthesized NaK-LSX was characterized by FTIR to identify functional groups in the structure. Figure 3 shows a strong peak at 950 cm^{-1} which was assigned to an asymmetric T–O stretching. In general, T–O is a tetrahedral atom referred to the framework of Si, Al composition and may shift to a lower frequency with an increase of the number of tetrahedral Al atoms (Lee *et al.*, 2006). Bands in the region 773 cm^{-1}, 690 cm^{-1} and 571 – 460 cm^{-1} were attributed mainly to the symmetric stretching, double ring and T–O bending vibrations, respectively. Lee *et al.* (2006) and Sang *et al.* (2006) reported that a band at 600 – 500 cm^{-1} is related to the topological arrangement of secondary units of structure in zeolites that contain the double 4 and 6 rings external linkage peak associated with the FAU structure and also observed in all the zeolite structures. The band with a peak at 3,487 was assigned to OH stretching and the vibration at 1,638 cm^{-1} was referred to bending vibration of adsorbed water molecule (Dyer *et al.*, 2004).

Surface Analysis of NaK-LSX by BET

The N_2 adsorption isotherm of NaK-LSX is shown in Figure 4. It was type I based on IUPAC's classification with a large nitrogen uptake at low pressure and the desorption almost overlapping with the adsorption. The step increased in N_2 adsorption with an increased relative pressure, P/P_0 and N_2 adsorbed amount reaching 127 cm^3/g at P/P_0 = 0.048 suggesting the pressure of an appreciable amount of micropore on the NaK-LSX surface. This result was common for the zeolite structure as explained by Langmi *et al.* (2005) that zeolite X has a very open framework and the entries to internal pores are not restricted by a large cation. Moreover, the effect of a cation on the surface area and pore structure show that the ion-exchange processes could induce enormous changes in surface and pore structure and these ions inhibited the movement of nitrogen molecule into pores or the so-called pore blocking effect, resulting in the decrease in surface area (Langmi *et al.*, 2003; Rakoczy and Traa, 2003; Huang *et al.*, 2004).

Figure 5 shows cumulative pore volume and pore size distributions of NaK-LSX from N_2 adsorption. The pore diameter of NaK-LSX, shown in Figure 5(a), was calculated by the HK method and showed a narrow pore width between 0.3 – 1.9 nm with pore volume of 0.195 – 0.201 cm^3/g. Nevertheless, the curves of pore size distribution evaluated from desorption data by utilizing the BJH model shown in Figure 5(b) exhibited a narrow pore size distribution ranging from 1.3 nm – 30.0 nm with the highest pore size at 1.7 nm. However, a shoulder peak distribution is dominant and it was probably from interconnected surface pores of LSX (Chang *et al.*, 2005 and Lee *et al.* (2006).

Table 3 shows results from a nitrogen adsorption study including the BET surface areas, pore volumes, and average pore diameters of NaK-LSX. The BET surface area and pore volume of NaK-LSX form RHS was interesting as it supported material for catalysis preparation or other application. (Langmi *et al.*, 2005)

Morphology of NaK-LSX Studied by SEM

Shape and size of NaK-LSX particles synthesized from RHS were studied by SEM and images are displayed in Figure 6 with magnification of 1,500 (a) and 25,000 (b). In the image with the smaller magnification, the solid product contained a mixture of multi-faceted spherulite crystals with a particle diameter approximately 6 – 10 μm along with round amorphous particles with a particle diameter approximately 0.2 – 5.0 μm. The multi-faceted spherulite particles were composed of polycrystal particles with different sizes along with small particles. Because some particles apparently connected with other particles, (Figure 5a), the particle size distribution was expected to be large as it was confirmed by DPSA (see next section). The particles in Figure 6(a) were distributed in the range of 0.3 – 10 μm with the largest contribution in the 0.3 – 2.0 μm range.

Particle Size Distribution of NaK-LSX by DPSA

The particle size distribution of Na-LSX was also investigated with DPSA and the results are presented as a histogram in Figure 7. The sizes were classified as oversize (area a) and undersize (area b), and the histogram plot and frequency curves are (c). The histogram plot shows the percentage of volume of particles, and the height of the histogram bars (left hand scale) was at 15.0 – 17.5 μm as for the majority of particles. The peak frequency curve provided the apparent tail in particle size analysis and shows the dominantly single modal distributions at 5 – 50 μm. Note that the results from DPSA were the size and distribution of bulk particles which might be composed of several small particles clustered together, and thus were different from the results from SEM which displayed images of isolate particles. Because the shape of samples as seen in SEM varied from a spherical shape to multi-faceted spherulite, that caused a different light scattering or diffraction effect based on the angularity of the crystals and their hydrodynamic behavior suspension (Cundy and Cox, 2005).

Only the important part of the DPSA data was summarized in Table 3 because there were too many numbers in the full data. The particle size distribution of NaK-LSX at volume percentiles of 10 was above 1.43 μm, while that of 50 was 12.35 μm and that of 90 was below 24 μm. The large particle size distribution of zeolite X was common as Lee *et al.* (2006) reported that uniformly sized NaX was difficult to synthesize in a large single phase crystal because crystal nuclei grew rapidly during the crystallization period and might transfer into zeolite NaP which was a more stable phase.

Characterization and Thermal Stability of NH_4-LSX from Ion Exchange of NaK-LSX

LSX in ammonium form (NH_4-LSX) was prepared by ion exchange of NaK-LSX with a NH_4NO_3 solution and characterized by powder XRD. As shown in Figure 8(b), the resulting material still had all peaks positioned similarly to that of the standard NaX. The sequence of intensities was different from the standard NaX because of the difference in cation type as discussed earlier. The NH_4-LSX was also studied by SEM and the micrograph is displayed in Figure 9. Compared with the NaK-LSX in Figure 6(a), the exchanged zeolite contained more crystalline particles and the amorphous particles might be removed with a basic solution during the exchange and wash process.

In general, zeolite in proton form can be obtained by calcination of ammonium form which releases ammonia. Thus, NH_4-LSX was calcined at 400°C for 3 h and the resulting material was characterized by XRD. As shown in Figure 8 (spectrum c), the characteristic peaks of zeolite X were no longer observed indicating the collapse of the NH_4-LSX structure to an amorphous form upon calcination. From this result, we investigated the thermal stability of NH_4-LSX by thermal analysis.

The thermal stability of NH_4-LSX was studied by thermal analysis. The results in Figure 10 demonstrated weight loss of NH_4-LSX when the temperature was raised from room temperature to 1,000°C, along with the first derivative of weight loss. When NH_4LSX was heated, there were three ranges of weight loss. The first range, with approximately 17% weight loss below 200°C, was attributed to removal of adsorbed water (Chandrasekhar and Pramada, 2001; Joshi *et al.*, 2002; Huang *et al.*, 2004). The second region with approximately 10 % weight loss between 200°C and 300°C, was caused by the decomposition of NH_4^+ ion to ammonia and proton (Chandrasekhar and Pramada, 2001). The last region was a relatively small loss compared with the other two regions from 300°C to 650 °C, possibly caused by loss of the structural hydroxyl group. No further weight loss was observed at a higher temperature. In general at the temperature range of 900 – 1,018 °C, zeolite will be converted to mullite and glass phases (Chandrasekhar and Pramada, 2001; Esposito *et al.*, 2004).

Conclusions

RHS in amorphous phase with 98% purity was prepared by leaching rice husk with HCl acid and calcination, and used as a silica source for the synthesis of zeolite NaK-LSX. The formation of the zeolite structure was confirmed by XRD and FTIR. The NaK-LSX crystal morphology was multi-faceted spherulite particles as shown by SEM micrographs. The particle size distribution from DPSA shows a large scale in crystal size and size distribution. The BET surface area of the NaK-LSX was approximately 400 m^2/g. The ion-exchange with ammonium ions gives NH_4-LSX and the zeolite structure was still maintained after ion exchange. However, the structure collapsed after calciantion to convert to proton form.

Acknowledgement

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List of Tables

Table 1. RHS components determined by XRF

Components	(%wt)
SiO_2	97.96
Al_2O_3	00.56
K_2O	00.06
CaO	00.98
Fe_2O_3	00.02

Table 2. Peak positions, d-spacing and relative intensity of NaK-LSX and standard NaX

2θ	d	Relative intensities	
		Standard NaX	Synthesized LSX
6.10	14.48	100.00	100.00
15.43	5.74	22.70	13.10
9.99	8.85	22.40	17.30
26.70	3.34	22.10	29.40
23.32	3.81	21.00	20.00
30.10	2.88	20.40	26.20
11.73	7.54	16.40	17.80
20.09	4.42	12.60	6.90
30.36	2.94	11.21	13.10
32.03	2.79	8.62	17.30
18.43	4.81	7.18	4.20
34.24	2.62	4.89	6.20

Table 3. Textural properties of synthesized NaK-LSX zeolite

Textual Properties	**Value**	**Unit**
BET surface area[a]	391.4	(m^2/g)
External surface area[b]	361.0	(m^2/g)
Micro pore surface area[b]	355.3	(m^2/g)
Langmuir surface area[c]	577.1	(m^2/g)
Pore volume of micro pore[d]	0.19	(cm^3/g)
Micro pore diameter[e]	13.58	(nm)

[a]*Multipoint BET analysis,* [b]*BJH analysis (t-method),* [d]*t-method,* [e]*DA method*

Table 4. Percentile of NaK-LSX particle size distribution analyzed by DPSA

Statistic distribution of particle	Result (% volume)	Unit
d(0.1)	1.43	(μm)
d(0.5)	12.35	(μm)
d(0.9)	25.05	(μm)
Average diameter	13.23	(μm)
Span (width of distribution)	1.91	(μm)

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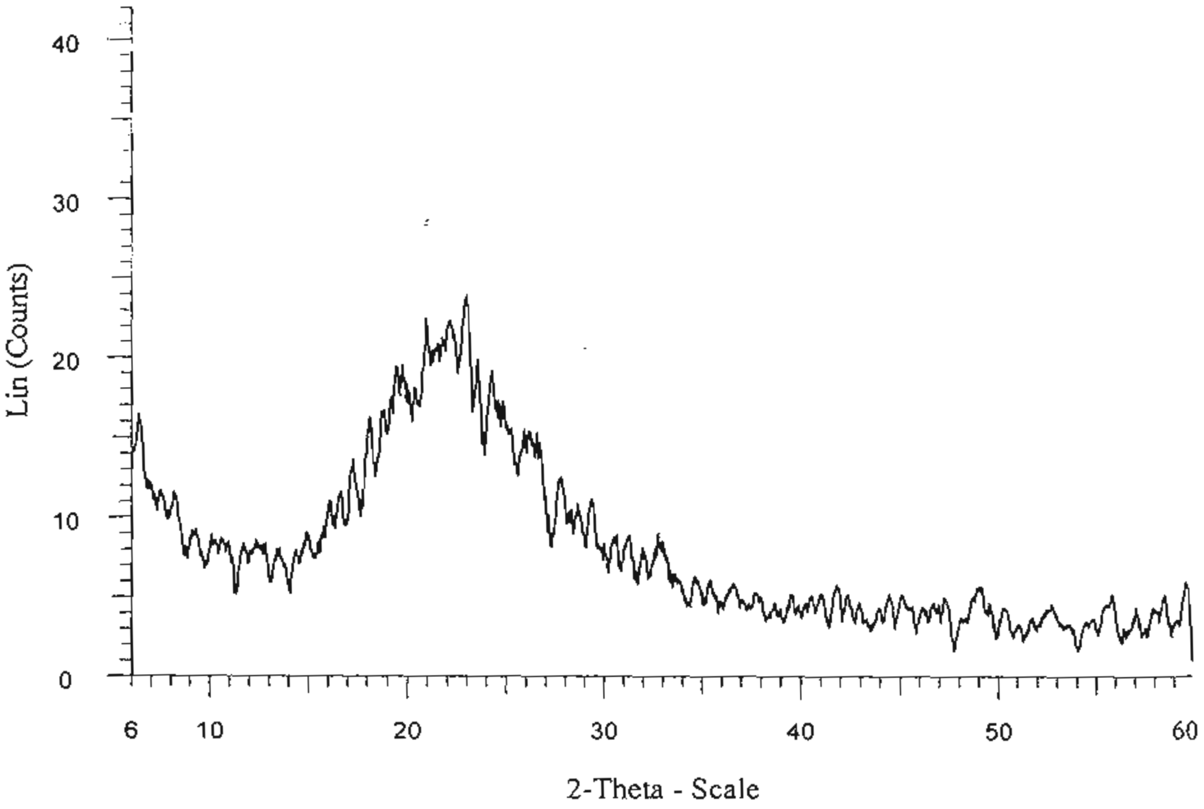

Figure 1. Powder XRD pattern of RHS

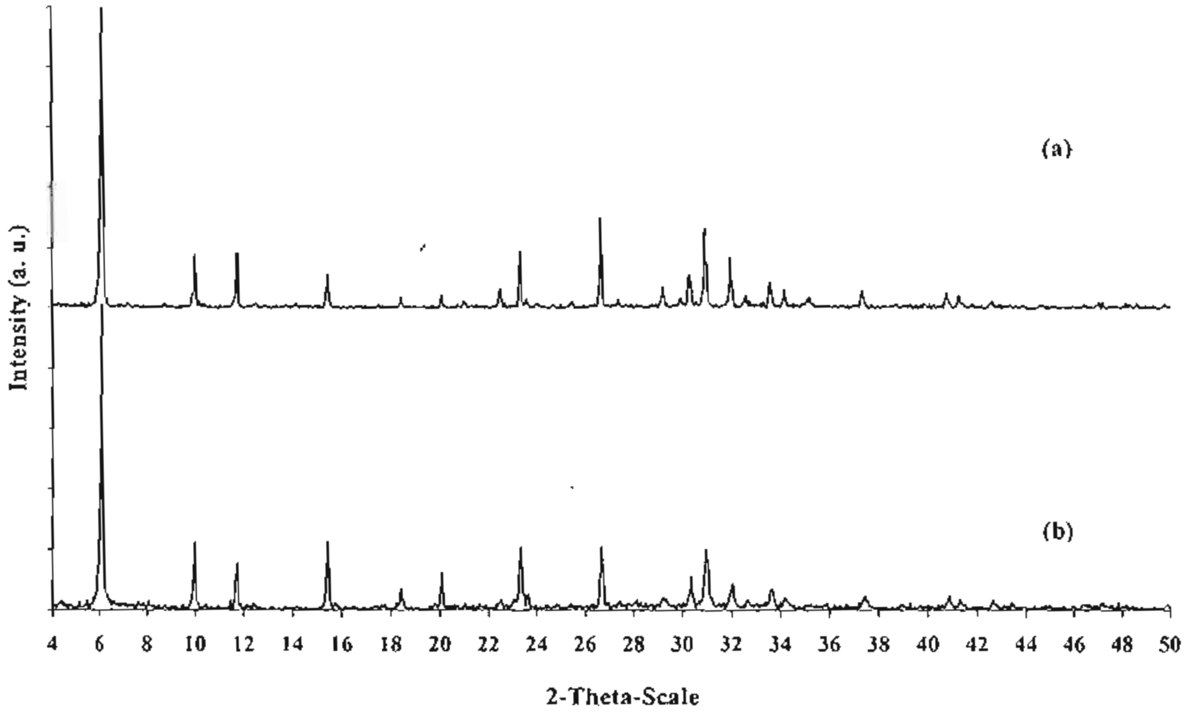

Figure 2. XRD spectrum of (a) NaK-LSX synthesized from RHS and (b) standard NaX

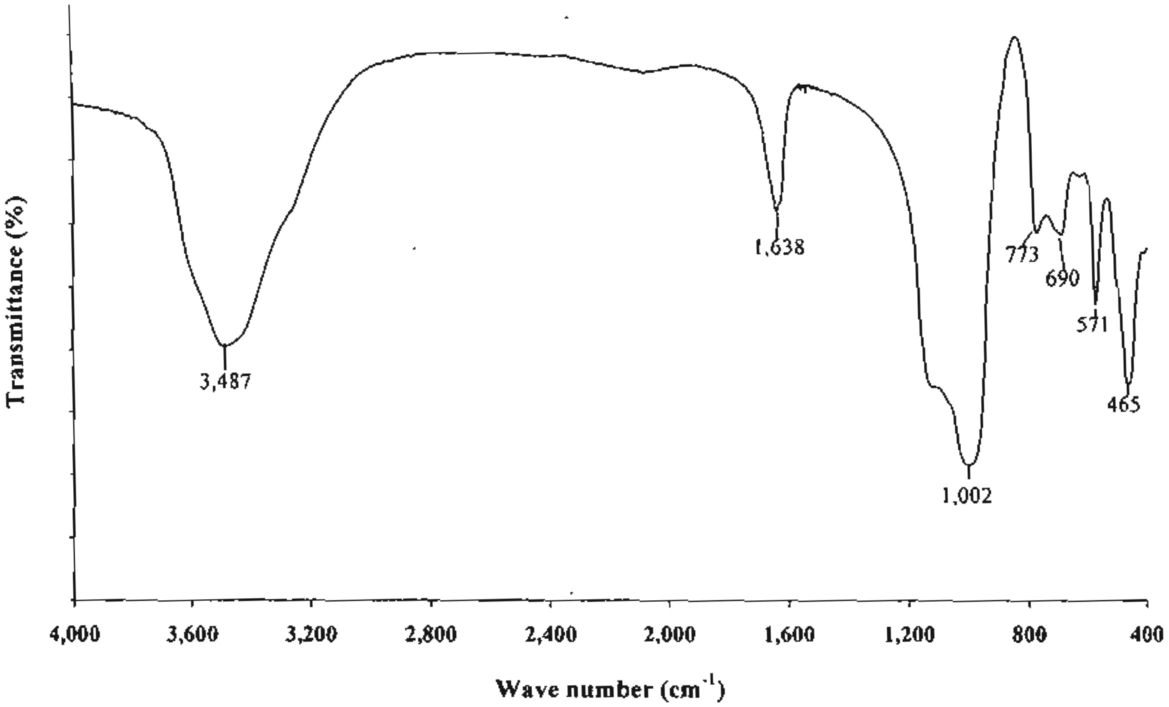

Figure 3. IR spectrum of zeolite NaK-LSX synthesized from RHS

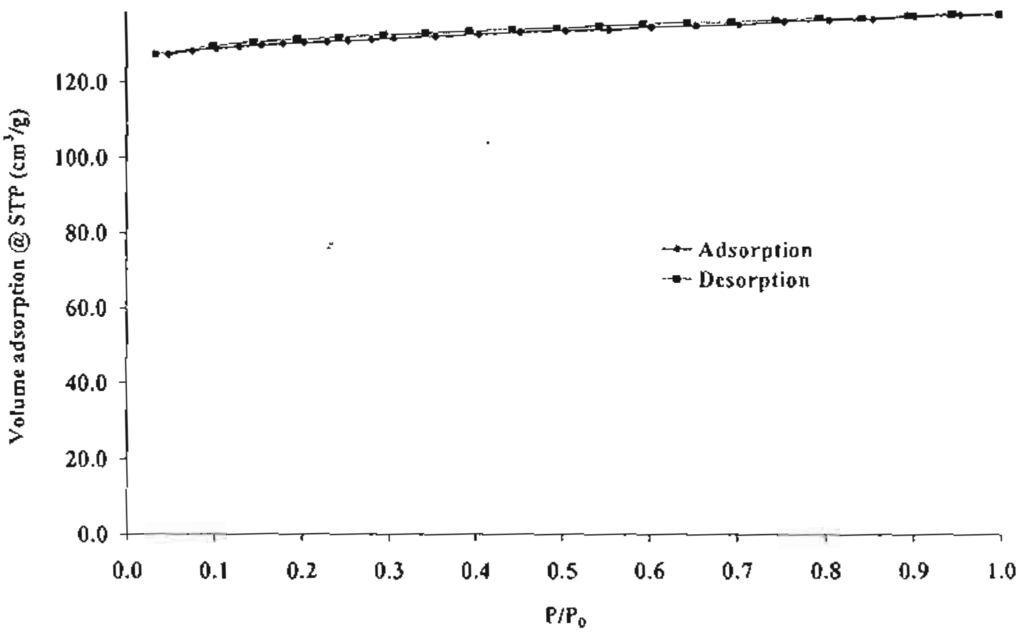

Figure 4. N_2 adsorption-desorption isotherm at 77 K on the synthesized NaK-LSX

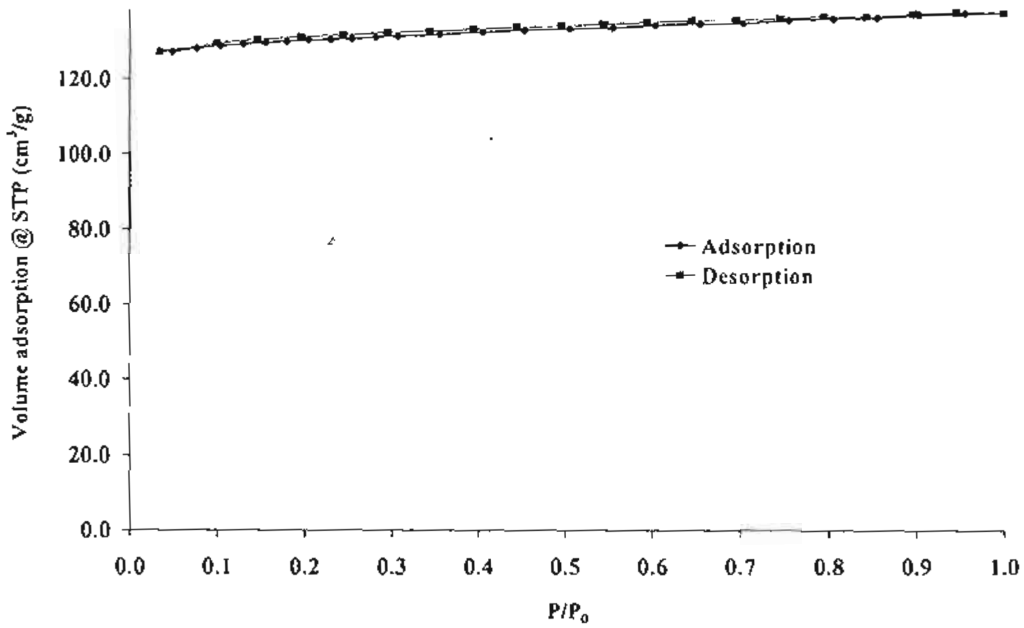

Figure 4. N_2 adsorption-desorption isotherm at 77 K on the synthesized NaK-LSX

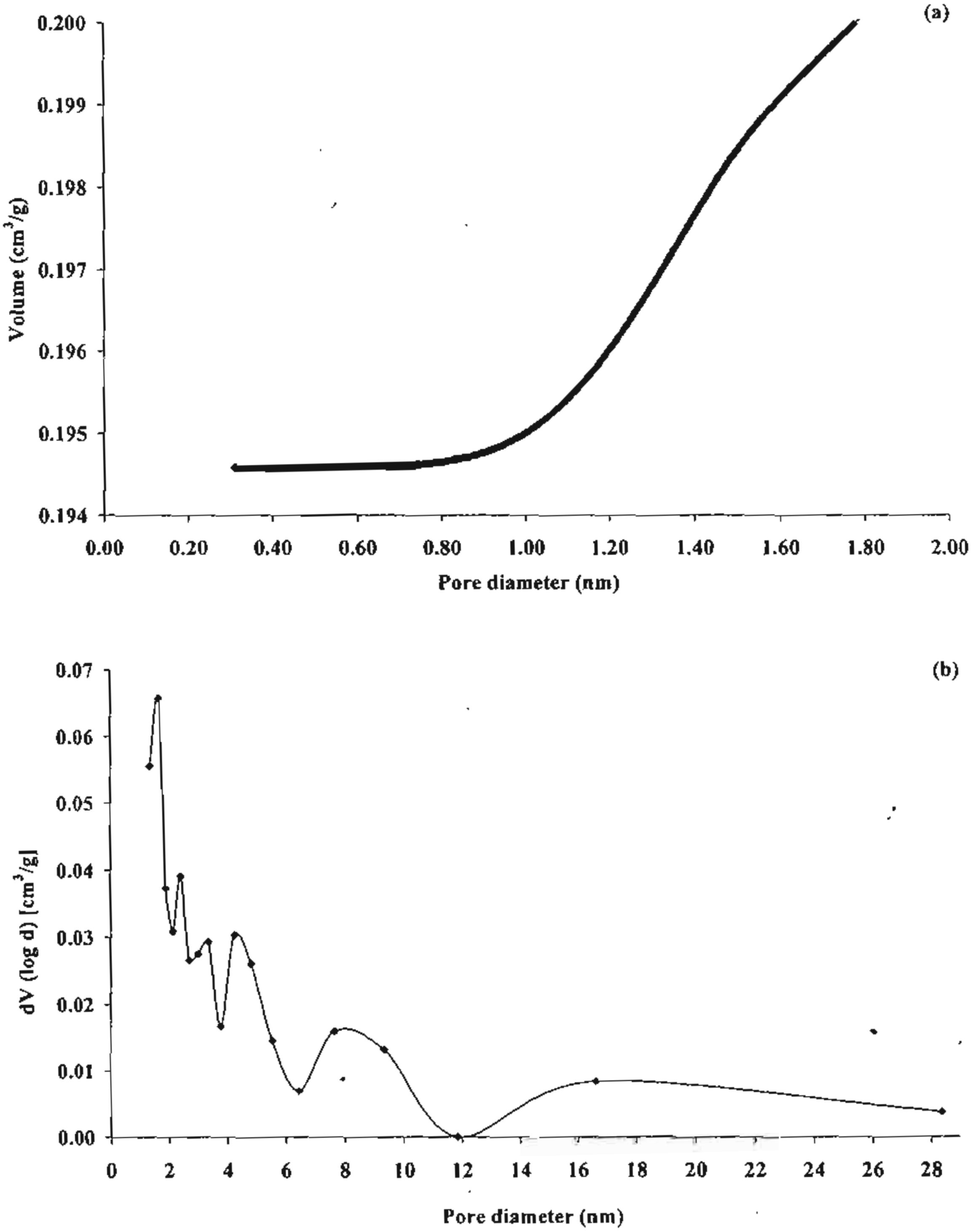

Figure 5. (a) HK cumulative pore volume and (b) BJH pore size distribution of NaK-LSX zeolite, where V is the cumulative pore volume (cm^3/g)

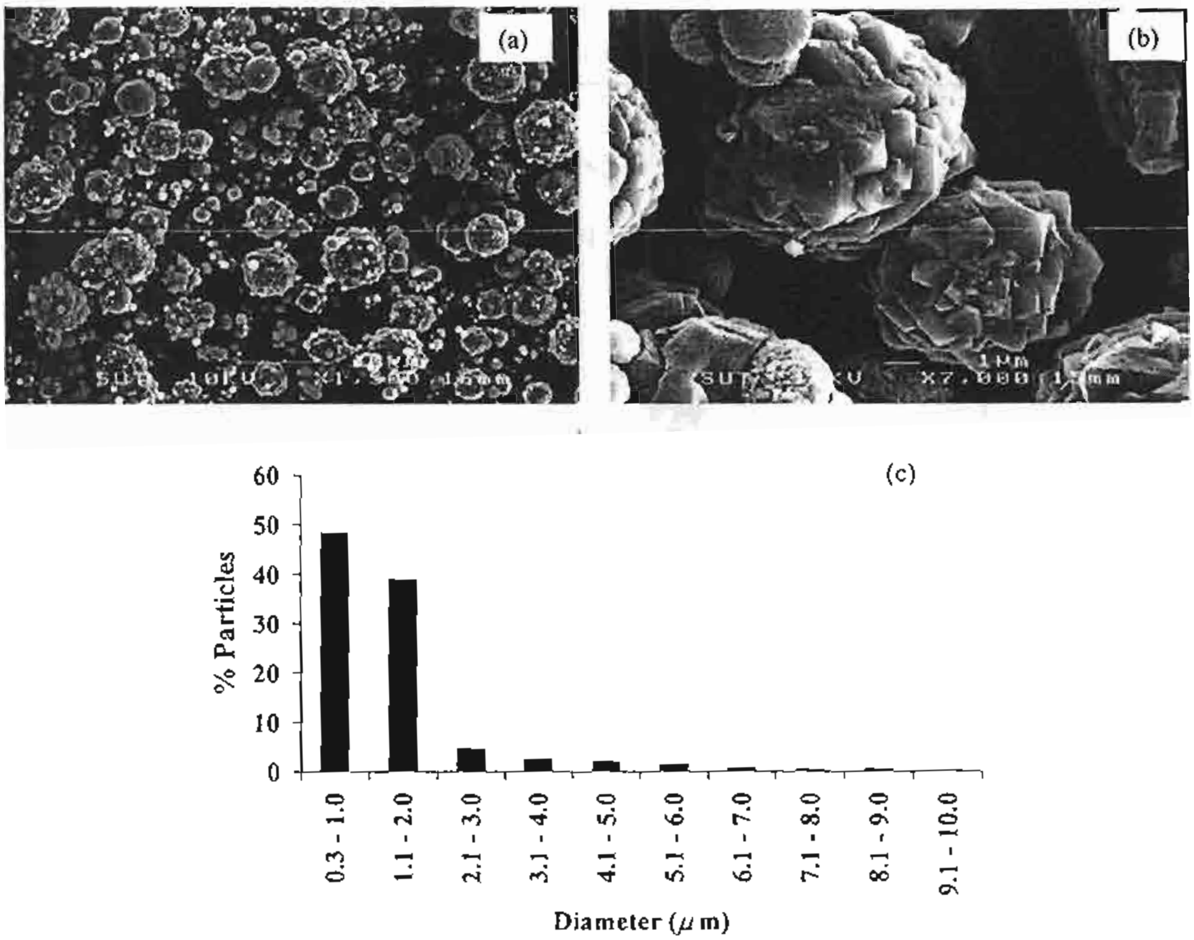

Figure 6. SEM images of synthesized Na-LSX with magnification of (a) 1,500 and (b) 25,000, respectively, and (c) particle size distribution measured from all particles in (a)

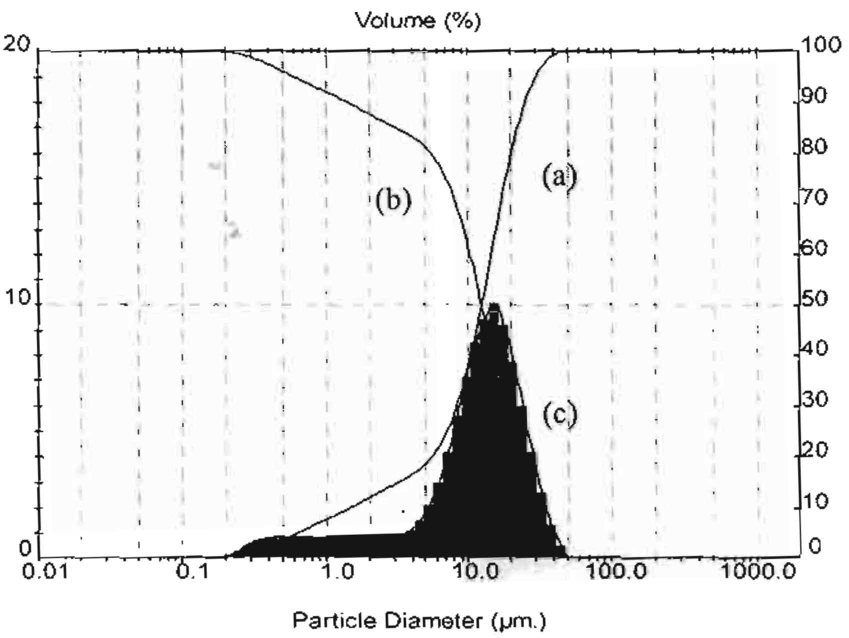

Figure 7. Particle size distribution of NaK-LSX synthesized from RHS; (a) percentage of sample below a certain size of particle, (b) percentage of sample above a certain size of particle and (c) histogram plot and frequency curve of particle

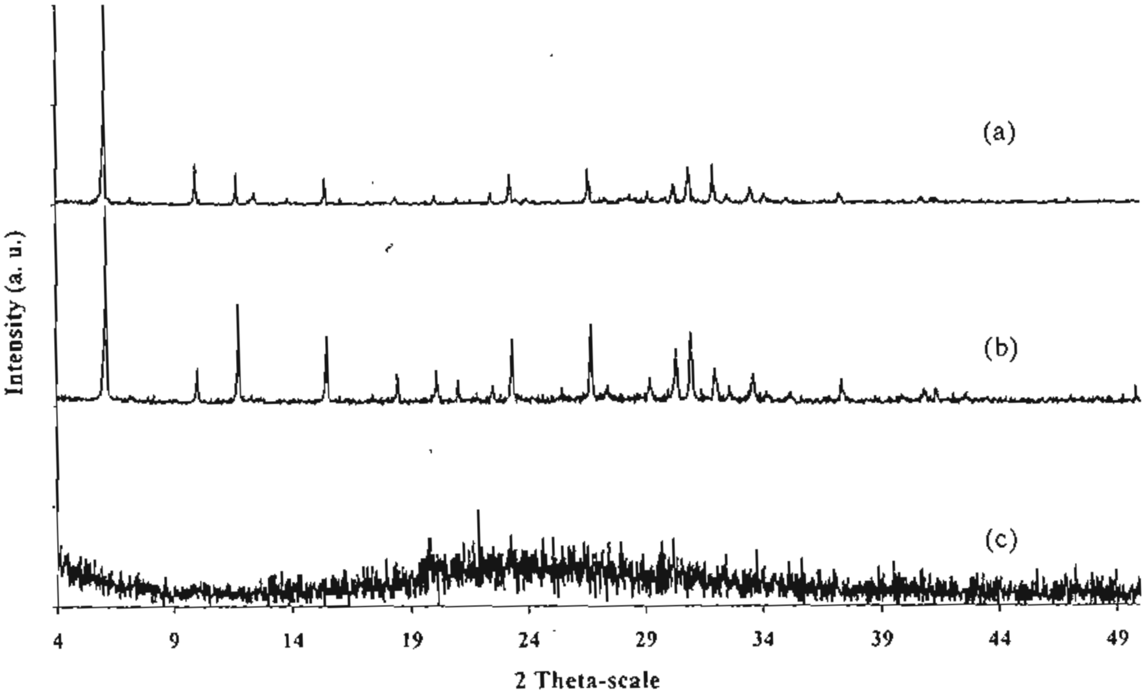

Figure 8. XRD patterns of (a) Na-LSX (b) NH_4-LSX, and (c) NH_4-LSX after calcination

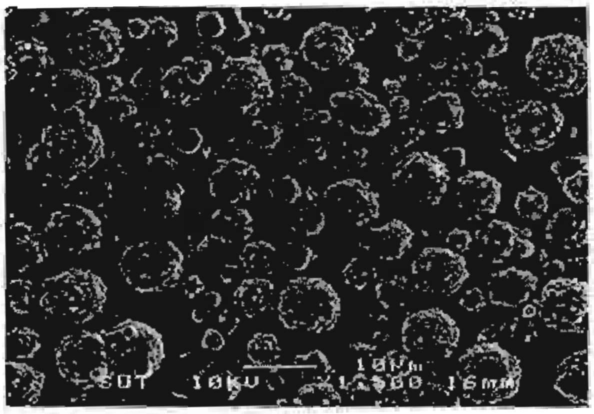

Figure 9. SEM images of NH_4-LSX with magnification of 1,500

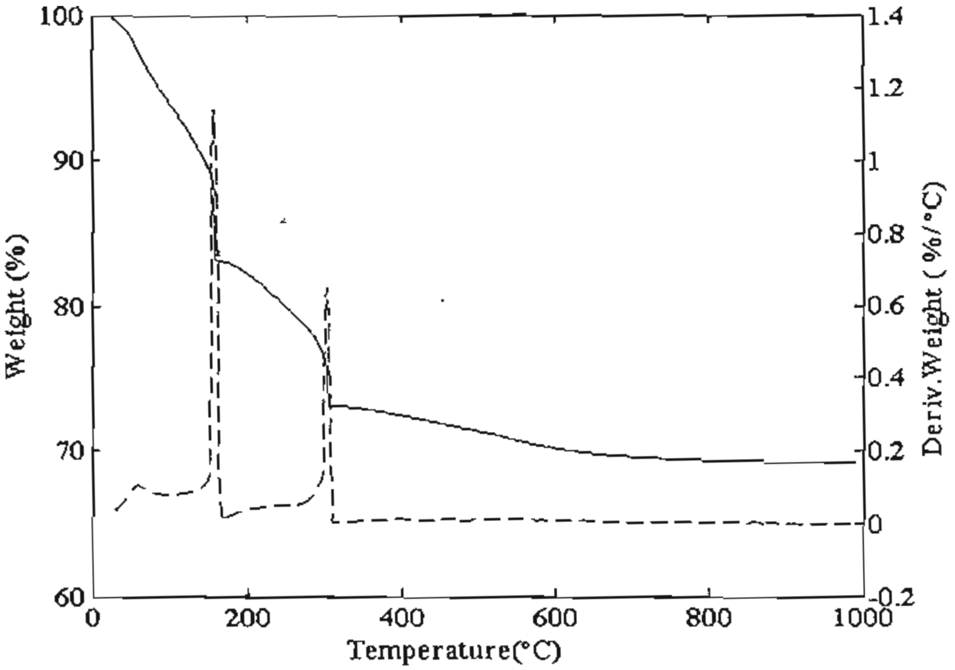

Figure 10. Thermoram of zeolite NH_4LSX (solid line is weight and dash line is first derivative of weight with respect to temperature)

2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.1 การเสนอผลงานในการประชุมนานาชาติ

1. บทความที่ได้นำเสนอแบบ Oral presentation เรื่อง Synthesis and Characterization of Na-LSX and NaY Zeolites from Rice Husk Silica โดย Pongtanawat Khemthong และ Jatuporn Wittayakun ชื่องานประชุม Regional Symposium on Chemical Engineering (RSCE 2006) 3-5 ธันวาคม 2549 ประเทศสิงคโปร์

Synthesis and Characterization of Na-LSX and NaY Zeolites from Rice Husk Silica

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Abstract
This paper focused on the utilization of rice husk silica to produced microporous material to use as metal catalyst support. Silica powder with approximately 99% pure was prepared from rice husk (RH) by refluxing in HCl and thermal decomposition. The obtained silica was then converted to sodium silicate solution and used as silica source for the syntheses of low silica type X (LSX) and Linde type Y zeolites by hydrothermal process. In addition to the RH silica (RHS), commercial sodium silicate was used as a silica source for zeolite syntheses with similar procedures to compare the effect of starting material on the zeolite properties. The yield of each zeolite was close to 100%. Zeolites from both silica sources were characterized by XRD, SEM, DPSA, and BET. The formation of zeolite frameworks from both sources were confirmed by XRD showing similar patterns to the reference database. It was observed that there was no significant difference in formation frameworks between these two silica sources. SEM micrographs of Na-LSX zeolites from both silica sources were not different in shape and size. In contrast, NaY prepared from commercial silica source had larger particle size than that prepared from RHS. Amorphous particles were also observed in all zeolite micrographs. The information to be reported at the symposium also includes the application of supported bimetallic catalyst as well as the structure of such type of catalyst.

Keywords: Hydrothermal synthesis; Y zeolite; LSX zeolite; Rice husk silica

1. Introduction
It is well know that RH is by-product of the rice milling process. The main compositions are organic compounds and hydrated silica (10-20% wt.). To obtain silica with high purity, HCl has been used as leaching agent in pre-treatment before combustion [1]. It is effective in substantially removing most of the metallic impurities producing silica with purity 96 – 99% [2]. After acid leaching, the silica produced is completely white in color and has high purity, also called rice husk silica. At present, RHS is the raw materials for the production of zeolites.

Zeolites are microporous crystalline material of aluminosilicates. They are attractive materials due to their solid acidity, ion-exchange capability, adsorption/release capability, and molecular-level pores. Zeolites are usually synthesized under conventionally hydrothermal condition from solutions of sodium aluminate, sodium silicate, or sodium hydroxide, and template. Among the zeolites that suitable properties for used in heterogeneous basic catalysis are low silica type X (LSX) and Y zeolites. Several types of zeolites including MOR, ZSM-5, ZSM-48, NaX, Beta, and FSM-16 have been successfully synthesized from RHS. In this work, RHA is raw material for the synthesis of Na-LSX and Na-Y zeolites which are used further as support materials for Pt-Co catalysts. The synthesis products were characterized by X-ray diffraction (XRD), BET surface area (BET), scanning electron microscopy (SEM), and diffraction particle size analyzer (DPSA).

2. Experimental
Rice husk was washed with water, dried, and leached with 3 M HCl acid for 6 h. The leached material was washed with deionized water, dried, and pyrolyzed in the hot air furnace (Carbolite) at 550°C for 6 h, to yield RHS. The chemical contents of RHS were analyzed by X-ray fluorescence spectroscopy (XRF). RHS was dissolved in 14% wt NaOH to produce sodium silicate solution, filtered to remove carbon residue, and used in zeolite syntheses. Each zeolite was synthesized by a method described in literature [3]. The formation of zeolite framework was confirmed by XRD with a filtered Cu K_α radiation with the 2θ scan range between 4°-50° with step size of 0.02°. Specific surface areas were measured according to the BET method by nitrogen adsorption. Particle size and size distribution of zeolite support was determined by DPSA with sample amount 10-30 mg dispersed in distilled water. The morphology of crystals was observed by SEM in JEOL, Model JSM-6400 with applied potential 10 kV.

3. Results and discussion

The chemical compositions of RHS by weight presented in the form of stable oxides and included 98.5% SiO_2, 0.68% Al_2O_3, 0.05 % K_2O, and 0.43 % CaO in average. It can be seen that the $[SiO_2]/[Al_2O_3]$ ratio was very high. Therefore, it was efficient and interested as silica source for zeolites synthesis.

Fig. 1 illustrates the XRD diffraction patterns obtained for Na-LSX and NaY samples synthesis at different silica source compared with zeolites X and Y standards. The spectrum was similar to that in reference confirming the formation of zeolite frameworks from both sources. XRD sharp peaks indicated that the zeolites had high crystallinity.

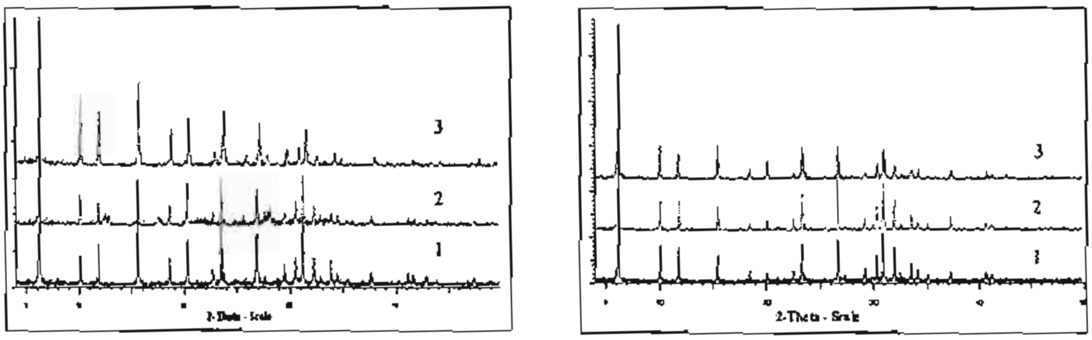

Fig. 1 Powder x-ray diffraction patterns of Na-LSX (left) and NaY (right) at various silica sources; [1] commercial silica source [2] rice husk silica source [3] standard zeolites

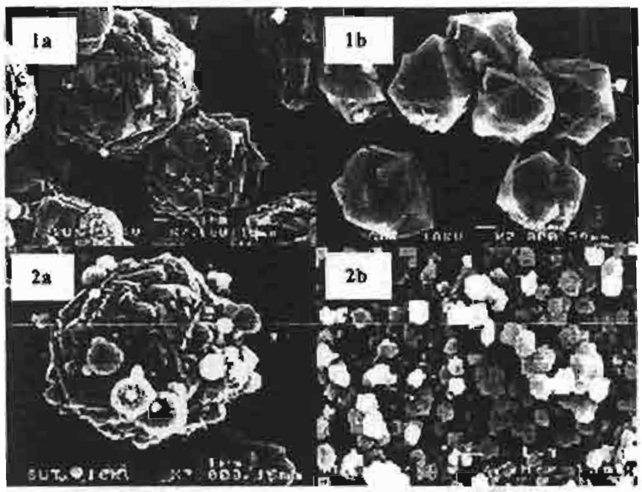

Fig.2. SEM image of (a) Na-LSX, (b) NaY ; [1] commercial silica source [2] rice husk silica source

The morphology of the crystal was shown in Fig. 2 As expected; SEM micrographs of Na-LSX zeolites from both silica sources (Fig. 1a and 2a, respectively) were not different in shape and size showing polycrystalline particles with some amorphous spheres. In contrast, SEM micrographs of NaY prepared from commercial silica source showed larger polycrystalline particles than that from RH silica (i.e., ~4-8 μm vs. ~1 μm). This result indicated that longer aging time is needed in the preparation of NaY from RH silica. In addition, amorphous particles were also observed in all zeolite micrographs.

4. Conclusion

The high purity silica from rice husk was successfully used as silica source for the syntheses of low silica type X and Linde type Y zeolites. The obtained zeolites were high crystallinities and suitable for used as support materials for Pt-Co catalysts.

Acknowledgement

The authors would like to thank Suranaree University of Technology (SUT) Research Fund and SUT scholarship for outstanding students and Thailand Research Fund (TRF) for providing financial support.

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2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.1 การเสนอผลงานในการประชุมนานาชาติ

2. บทความที่ได้รับตอบรับให้นำเสนอแบบ Oral Presentation เรื่อง Bimetallic platinum-iron catalysts on Al-MCM-41 supports: supports and catalyst characterization and catalytic activity for phenol hydroxylation โดย Jitlada Chumee, Nurak Grisdanurak, Arthit Neramittagapong and Jatuporn Wittayakun ชื่องานประชุม Regional Symposium on Chemical Engineering (RSCE 2006) 4-5 ธันวาคม 2550 ประเทศอินโดนีเซีย (ได้รับการตอบรับแล้วตามเอกสารแนบ)

BIMETALLIC PLATINUM–IRON CATALYSTS ON Al-MCM-41: SUPPORTS AND CATALYST CHARACTERIZATION AND CATALYTIC ACTIVITY FOR PHENOL HYDROXYLATION

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ABSTRACT

MCM-41 was synthesized by using silica from rice husk and further modified to increase acidity by adding Al with grafting method. The resulting aluminum-modified MCM-41 material denoted as Al-MCM-41, with Si/Al ratio of 75, 50 and 25 were characterized by XRD, TEM, BET and ammonia adsorption on TGA. XRD spectrums of the modified MCM-41 showed characteristic peaks at 2.5, 4, and 4.5 of the (100), (110), and (200) planes, respectively; and their TEM images exhibited well order structure. Surface areas of all Al-MCM-41 were approximately 700 m^2/g, lower than that of the parent which was 1,230 m^2/g. The increase of acidity after Al-addition was clearly observed by ammonia adsorption in which the acidity of Al-MCM-41 was in the range of 0.200 – 0.250 mmol/g compared to 0.166 mmol/g of the Al-free MCM-41. All Al-MCM-41 materials were used as supports for bimetallic platinum–iron catalysts, denoted as Pt-Fe/Al-MCM-41, with Pt and Fe amount of 0.5 and 5.0% by weight, respectively. Characterization by temperature-programmed reduction indicated that the presence of Al assisted the interaction between Pt and Fe indicated by the shift of reduction temperature of iron oxides to lower value. All catalysts were tested for phenol hydroxylation using H_2O_2 as an oxidant with the following conditions: phenol/H_2O_2 ratio = 3/1, reaction temperature = 70 °C, reaction time = 1 h. As the amount of Al in MCM-41 increased, the conversion increased whereas the selectivity decreased. The phenol conversions of the bimetallic catalysts on Al-MCM-41 with Si/Al ratio of 75, 50 and 25 were 12, 34 and 41%, respectively, but the selectivities for chetechol were 73, 53 and 51%, respectively.

Keywords: Al-MCM-41, rice husk, phenol hydroxylation, Pt-Fe/Al-MCM-41

I. INTRODUCTION

Rice husk is the milling byproduct of rice and could be considered as an agricultural waste [1]. The major constituents of rice husk are cellulose, lignin and ash varying with the variety, climate and geographic location of growth. The ash is largely composed of silica with small amounts of inorganic salts and silica with high purity can be obtained from rice husk by a simple acid-leaching procedure and calcination [2]. Thus, rice husk can be used as a silica source for a number of silicon compounds such as silicon carbide, silicon nitride, zeolite and mesoporous MCM-41[3]-[5]. This work will focus on using rice husk silica as a source for the synthesis of MCM-41 which was further modified to utilize as catalyst support materials.

Mesoporous MCM-41 is amorphous silica with a regular mesopore system (pore size 2-50 nm) which consists of an array of unidimensional and hexagonally shaped mesopores. MCM-41 has attracted considerable interest as a model substance of gas adsorption, catalyst support [6]. However, the surface of MCM-41 is only weakly acidic. Acidity modification of MCM-41 is necessary for the applications to acid-catalyzed reactions such as cracking, isomerization, alkylation and hydroxylation [6]-[8]. Brønsted acid sites could be generated through isomorphous substitution of Si by Al. There are two methods to introduce Al to MCM-41: direct sol–gel method (Pre) and post-synthetic grafting method (Post). The first method causes not only unfavorable hydrothermal structural deterioration but also produces very low concentration and strength of Brønsted acid sites even at high aluminum content. Therefore, post-synthesis modifications have been developed to maintain structural stability and to incorporate various metal elements easily into siliceous MCM-41 support. In this work, Al-MCM-41 was prepared by post methods and used as catalyst support for platinum and iron for phenol hydroxylation.

Phenol hydroxylation to produce dihydroxybenzenes is an important selective oxidation reaction in which the products, catechol and hydroquinone, are used in such diverse applications as photographic chemicals, antioxidants, flavoring agents, polymerization inhibitors and pharmaceuticals [10]. The process of phenol hydroxylation with 30% H_2O_2 would be a useful process in the future because of its simplicity and lack of pollution. Redox molecular sieves, which are promising materials for transformations of large organic molecules in liquid phase reactions, had emerged recently by incorporating various transition metal species such as platinum and iron [11]-[12]. In this work, the bimetallic platinum/iron supported on Al-MCM-41 will be used as catalysts in hydroxylation of phenol. The acid sites and pore size of Al-MCM-41 which is larger than that of zeolite (< 15 Å) is suitable for phenol. The % conversion of phenol and the reaction time of using the bimetallic catalyst will be investigated in this work.

II. EXPERIMENTAL

A. Chemicals

The chemical used for rice husk silica preparation is hydrochloric acid 37% (HCl, supplied by Carlo Erba). The chemicals for MCM-41 and Al-MCM-41 preparation are cetyltrimethylammonium bromide (CTABr, supplied by Fluka), sodium hydroxide, anhydrous pellet (NaOH, supplied by, Carlo Erba), sulphuric acid 96% (H_2SO_4, supplied by Carlo Erba), sodium aluminate anhydrous ($NaAlO_2$, supplied by Riedel-de Haen) and ammonium nitrate (NH_4NO_3 supplied by, Ajax).

The chemicals for catalyst preparation are iron(III)chloride hexahydrate ($FeCl_3.6H_2O$, supplied by Polskie Odczynniki Chemiczne and dihydrogen hexachlorplatinate(IV) 40% ($H_2PtCl_6.6H_2O$, supplied by Alfa).

The chemicals for catalyst testing are phenol (C_6H_5OH, supplied by BDH), hydrogenperoxide 30% (H_2O_2, supplied by Ajax), cetechol ($C_6H_6O_2$, supplied by Fluka) and hydroquinone ($C_6H_4(OH)_2$, supplied by Asia Pacific Speciality Chemicals).

B. Extraction of silica from rice husk

The rice husk silica (RHS) was prepared with a procedure similar to our previous work [4]. The purity of silica was 98.5% wt and its phase was amorphous.

C. MCM-41 and Al-MCM-41 preparation

Siliceous MCM-41 was synthesized with a method modified from literature [8]. Briefly, the starting gel with a molar composition of $4SiO_2$:1CTMABr:0.29H_2SO_4:400H_2O (CTMABr = cetyl trimethyl ammonium bromide) was prepared, and the gel pH was adjusted to 11 with H_2SO_4. Crystallization was done in a Teflon- lined autoclave at 100 °C in static condition for 3 days. The MCM-41 powder was separated by centrifugation, washed with distilled water, dried and calcined at 540 °C for 6 h to remove CTMABr template.

Al-MCM-41 supports with Si/Al ratio of 75, 50 and 25 were prepared from silicons MCM-41 and $NaAlO_2$ by grafting method [8]. The starting materials were mixed in a polypropylene bottle and stirred vigorously for 30 min. Then the solid powder was separated by centrifugation, dried at 100 °C oven 3h and calcined at 540 °C for 6 h.

Both MCM-41 and Al-MCM-41 were characterized by powder x-ray diffraction (XRD), X-ray fluorescence (XRF), transmission electron microscopy (TEM), N_2 adsorption-desorption (BET method) and ammonia adsorption on thermogravimetric analyzer (TGA).

D. Catalyst preparation and testing for phenol hydroxylation

The 0.5 wt.% of platinum and 5 wt% of iron catalyst supported on MCM-41 and Al-MCM-41 was prepared by co-impregnation with $FeCl_3$ and $H_2PtCl_6.6H_2O$ *solution the materials was dried at 100 °C overnight and calcined at 300 °C for* 2 h, with a heating rate of 10 °C /min. The catalysts obtained were 0.5Pt5Fe/MCM-41, 0.5Pt5Fe/75AlMCM-41, 0.5Pt5Fe/50AlMCM-41 and 0.5Pt5Fe/25AlMCM-41 where the number 75, 50 and 25 were Si/Al ratio. The catalysts were characterized by temperature programmed-reduction (TPR).

The catalytic testing for phenol hydroxylation, the catalyst, phenol and H_2O_2 solution (30% w/v) were mixed (phenol/H_2O_2 mole ratio = 3) in a two-necked round bottle (250 ml) equipped with a magnetic stirrer and a reflux condenser.. The reaction was carried out at 60 °C for 1 h and the catalyst was separated by centrifugation. The product was analyzed by a gas chromatograph (Shimadzu GC14-A) equipped with a capillary column (ID-BP1 3.0 um, 30 m × 0.53 mm), a flame ionization detector (FID) and the injector and column temperatures were 250°C and 190°C, respectively.

E. Supports and catalyst characterization

The XRD patterns were obtained using Cu Kα radiation on a Bruker axs D5005 diffractometer. The composition of mesoporous material samples was determined by XRF (Phillip, MagiX Pro). The arrangement of mesopores is investigated by TEM (JSM 6400). Physical characteristics of the sample are determined by N_2 adsorption-desorption isotherm at -196°C for relative pressure from 10^{-2} to 0.99 on an AUTOSORB-1 analyzer. Before measurement, each sample was degassed at 300°C for 3 h. The BET surface area was obtained from the N_2 adsorption data in the relative pressure range of 0.001-0.99. The pore size and pore volumes were calculated from the desorption branches of the isotherm using Barrett-Joyner-Halenda (BJH) method.

Ammonia adsorption to determine the amount of acidity of MCM-41 and Al-MCM-41 was carried out on a TGA, (NETZSCH, model STA 409PC) where the weight changes due to adsorption and desorption was measured directly from a microbalance. Each sample (approximately 120 mg) was pretreated by heating from room temperature to 300 °C in nitrogen flow (flow rate 30 mL/min and heating ramp rate of 10 °C/min) and held for 1 h to remove water. After cooling down to room temperature, the sample was exposed to ammonia in helium (20% and total flow rate 40 mL/min) until the maximum adsorption was obtained. Then it was purged with nitrogen (flow rate 30 mL/min) to remove physisobred ammonia until the weight becomes constant. The weight change ws used to calculate the acidity of material and the acidity unit is reported as mmol of ammonia per gram of material.

For the TPR measurement of PtFe catalyst, a catalyst sample with approximately 50 mg was packed on quartz wool catalyst bed in a quartz tube and placed in a furnace connected to temperature controller, gas flow and mass spectrometer. Before TPR measurement, the catalyst was pretreated by heating from room temperature to 300 °C in helium flow (flow rate 20 ml/min and ramp rate of 10 °C/min) and held for 1 h to remove water. After cooling down to room temperature, a gas mixture containing 5%H_2 in He was introduced with flow rate of 2 mL/min and the temperature was ramped again with the rate 5 °C/min from room temperature to 600 °C. The water from reduction was detected continuously by a mass spectrometer and plotted with temperature.

III. RESULTS AND DISCUSSION

A. Supports characterization by XRD, XRF, BET and ammonia adsorption

The XRD patterns of the calcined MCM-41 and Al-MCM-41 are displayed in Fig. 1. The MCM-41 showed a strong peak at 2.5 and small peaks at 4, and 4.5 corresponding to the (100), (110), and (200) planes of a hexagonal lattice, respectively. Only the (100) peak was observed in all Al-MCM-41 indicating that the structure was slightly changed after Al grafting. The peak positions shifted slightly to lower value as aluminum was incorporated and the intensities decreased indicating changes in crystallinity. The widths of the strongest peak of Al-MCM-41 samples were broader than that MCM-41 and the differences in peak area were compared to estimate the relative crystallinity. As shown in the second column in Table 1, the crystallinity of Al-MCM-41 decreased as aluminum was incorporated.

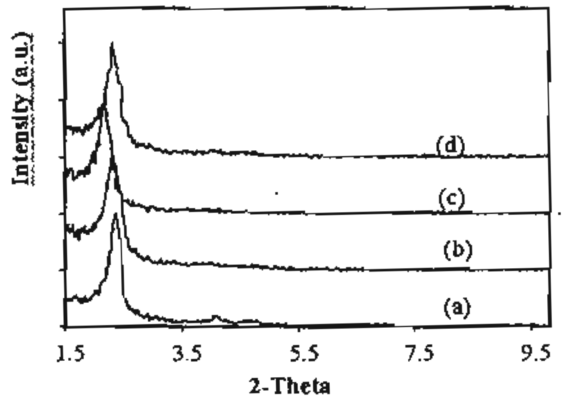

Fig. 1 Normalized XRD patterns of (a) MCM-41, (b)-(d) Al-MCM-41 with Si/Al ratio of (b) 75, (c) 50 and (d) 25

The N_2 adsorption isotherms of MCM-41 and Al-MCM-41 samples with Si/Al ratio of 75, 50 and 25 are shown in Fig 2. All isotherms corresponded to type IV which was typical for mesoporous materials. At the beginning, the adsorbed amount increased quickly and concaved to the P/P_0 axis due to adsorption on external surface and form monolayer. The adsorbed amounts of all Al-MCM-41 samples were lower than that of MCM-41 indicating that their surface areas decreased after Al grafting. As shown in the second column in Table 1, the surface area of MCM-41 was 1,230 m^2/g and those of all Al-MCM-41 decreased to the range 740-870 m^2/g.

At the 0.2-0.4 range of P/P_0, the N_2 increased again before reaching nearly constant volume. This range corresponded to nitrogen adsorption in the mesopores of MCM-41 and Al-MCM-41. However, the adsorption in this range for Al-MCM-41did not increased sharply as in MCM-41 indicating that some mesopores might collapse during the Al-grafting. This change could be an explanation to the significant decrease of surface area.

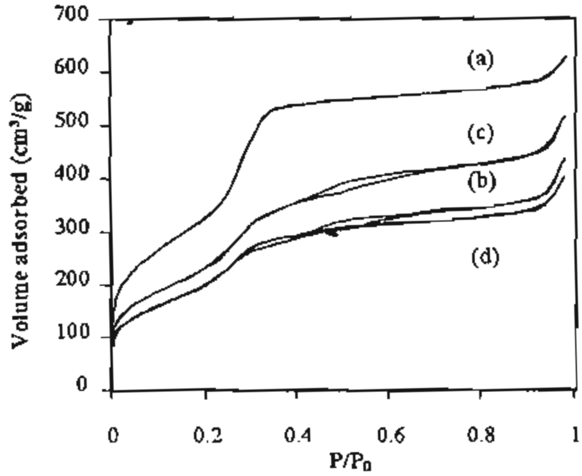

Fig. 2 N_2 adsorption isotherm of (a) MCM-41, (b)-(d) Al-MCM-41 with Si/Al ratio of (b) 75, (c) 50 and (d) 25

In addition to the relative crystallinity and BET surface area, Table 1 also showed the concentration of Si and Al in the MCM-41 and Al-MCM-41 determined from XRF. MCM-41 contained a small amount of Al because Al originally presented in the silica obtained from rice husk. Upon rafting, the concentration of Al increased and the acidity from ammonia adsorption was expected to have a similar trend to the Al concentration.

Results derived from the ammonia adsorption of the calcined samples are listed in the last column of Table 3. The acidity from ammonia adsorption was lower than the concentration of Al from XRF for all materials indicating that only some portion of Al were present at the surface and accessible for adsorption. The acidity values of Al-MCM-41 was in the range of 0.20 – 0.25 mmol/g compared to 0.17 mmol/g of the un-grafted MCM-41.

Table 1 Composition, surface area and acidity of MCM-41 and Al-MCM-41

Sample	Relative crystallinity	BET surface area (m^2/g)	Concentration of Si from XRF (mmol/g)	Concentration of Al from XRF (mmol/g)	Acidity from NH_3 adsorption (mmol/g)
MCM-41	100.00	1231.4641	34.30	0.28	0.17
75AlMCM-41	81.20	741.3508	35.22	0.52	0.22
50AlMCM-41	51.56	864.8746	34.92	0.81	0.25
25AlMCM-41	76.82	746.7049	34.22	0.66	0.22

B. Characterization of PtFe catalysts by TPR

The TPR results from bimetallic Pt-Fe catalysts supported on MCM-41 and Al-MCM-41 are shown in Figure 3. For Pt-Fe/MCM-41, there were two peaks, the first peak around 100 °C was assigned to the reduction of platinum and the second around 480 °C was assigned to the reduction of iron. The assignment was based on the fact that platinum oxides are more easily reduced than iron. For the Pt-Fe/Al-MCM-41, the reduction peaks of iron in all catalysts shifted to lower temperature with maximum around 380°C. It was possible that iron on these supports located near platinum. After platinum oxide was reduced, it became adsorption site for hydrogen and the adsorbed could easily migrate to reduce iron oxides, resulting in lower reduction temperature. Because this behavior was not observed on bimetallic catalyst on MCM-41, it was possible that the presence of Al on MCM-41 facilitate the interaction between platinum and iron.

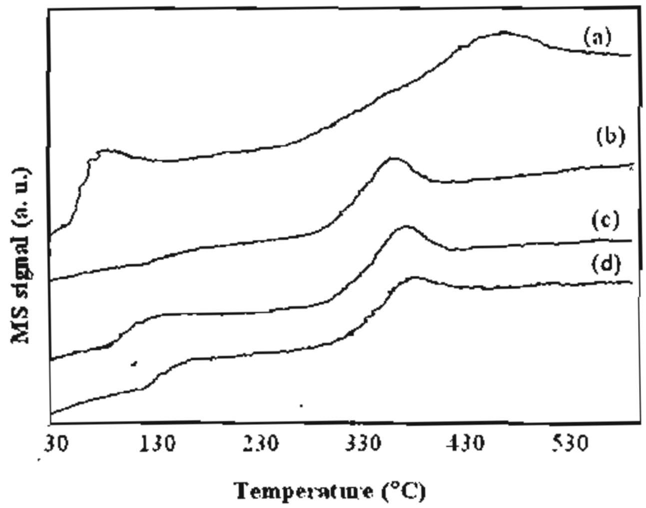

Fig. 3 Water production from temperature-programmed reduction of (a) 0.5Pt5Fe/ MCM-41, (b) 0.5Pt5Fe/75Si/Al-MCM-41, (c) 0.5Pt5Fe/50Si/Al-MCM-41 and (d) 0.5Pt5Fe/25Si/Al-MCM-41

C. Catalyst activity testing on phenol hydroxylation

The hydroxylation activities of 0.5Pt5Fe on MCM-41 and Al-MCM-41 at various reaction times are presented in Fig.4. The phenol conversion increased remarkably in the time range of 0–1 h. The detail of conversion and selectivity are included in Table 2. The activities were in this order: 0.5Pt5Fe/75Si/Al-MCM-41 < 0.5Pt5Fe/50Si/Al-MCM-41 < 0.5Pt5Fe/25Si/Al-MCM-41. After 2 h, the conversion became nearly constant during the 4 h testing period.

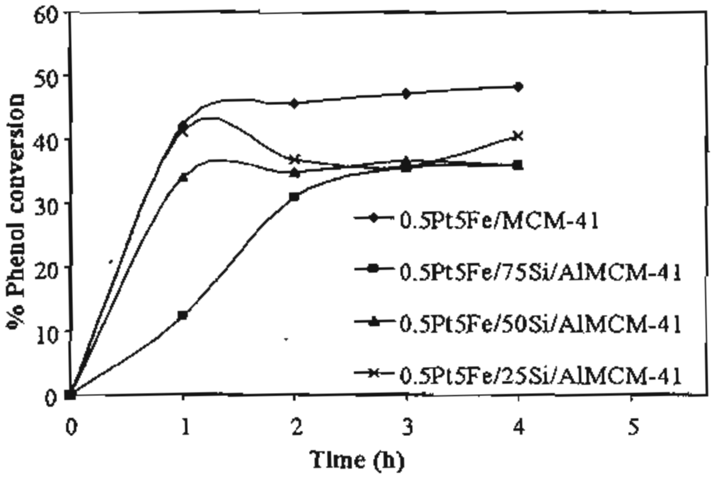

Fig. 4 Phenol hydroxylation activity (H_2O_2/phenol = 1/3 at 70 °C and amount of catalysts 0.05 g.)

Table 2 Catalytic activities of various catalysts in phenol hydroxylation with conditions: phenol/H_2O_2 ratio = 3/1, reaction temperature = 70 °C, reaction time = 1 h.

Catalyst	% phenol conversion	Selectivity of chetechol	Selectivity of hydroquinone
0.5Pt 5Fe/MCM-41	42.20	52.35	47.64
0.5Pt 5Fe/75AlMCM-41	12.23	73.44	26.56
0.5Pt 5Fe/50AlMCM-41	34.04	52.61	47.39
0.5Pt 5Fe/25AlMCM-41	41.31	50.76	49.24

The table 2 showed the performance of other Pt-Fe bimetalic catalysts for phenol hydroxylation reaction. The reaction was carried out with fixed amount of H_2O_2 and phenol in 1:3 at 70 °C for 1 h and amount of catalysts 0.05 g. The 5Fe0.5Pt/MCM-41 showed the highest phenol conversion 42 % because MCM-41 had high surface and good dispersion of platinum and iron. For the bimetallic catalysts on Al-MCM-41 with Si/Al ratio of 75, 50 and 25 were 12, 34 and 41%, respectively, but the selectivity of chetechol were 73, 53 and 51% and selectivity of hydroquinone were 26, 47, 49%, respectively. The selectivity of hydroquinone seemed to increase as acidity of Al-MCM-41 increased. The phenol conversion showed higher conversion than either Fe-NaY, Co-NaY Fe-Co-NaY catalyst catalyst reported in literatures [16].

IV. CONCLUSION

MCM-41 was prepared from rice husk silica and its acidity was improved by adding aluminum by grafting method. The aluminum addition was successful and the acidity of Al-MCM-41 samples was higher than that of MCM-41. Upon grafting, the surface area of Al-MCM-41 decreased but the mesoporous structure was still maintained. The prepared Al-MCM-41 materials were used as supports for bimetallic Pt-Fe catalysts and tested for hydroxylation of phenol. The acidity has effect to conversion and selectivity of hydroquinone. The selectivity of hydroquinone was increased as acidity of Al-MCM-41. The 5Fe0.5Pt/MCM-41 was shown highest phenol conversion 42 %, 5Fe0.5Pt/75MCM-41 was shown highest selectivity of chetechol 73 % and 5Fe0.5Pt/25MCM-41 was shown highest selectivity of hydroquinone 49 %.

ACKNOWLEDGMENT

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2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

1. บทคัดย่อ การนำเสนอแบบ Oral presentation เรื่อง การเตรียมและวิเคราะห์ลักษณะ ของ MCM-41 และ Al-MCM-41 โดยใช้ซิลิกาจากแกลบข้าว (Preparation and characterization of MCM-41 and Al-MCM-41 from rice husk silica) โดย จิดรลดา ชูมี และ จตุพร วิทยาคุณ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549

การเตรียม และ วิเคราะห์ลักษณะ ของ MCM-41 และ Al-MCM-41 โดยใช้ซิลิกาจากแกลบข้าว

PREPARATION AND CHARACTERIZATION OF MCM-41 AND Al-MCM-41 FROM RICE HUSK SILICA

จิตรลดา ชูมี, จตุพร วิทยาคุณ

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บทคัดย่อ: การเตรียมซิลิกา (SiO_2) จากแกลบข้าวทำได้โดยการรีฟลักซ์แกลบด้วย สารละลายกรดไฮโรคลอริก เข้มข้น 3 M ที่ 60 °C นาน 3 ชั่วโมง กรอง ล้าง อบให้แห้งแล้วนำไปให้ความร้อนที่ 500 °C นาน 6 ชั่วโมง จากนั้นนำเถ้าที่ที่ได้เป็นผงสีขาวไปวิเคราะห์ด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ (XRD) และฟลูออเรสเซนซ์ของรังสีเอกซ์ (XRF) ผลที่ได้แสดงว่าเถ้าแกลบประกอบด้วยซิลิกาอสัณฐาน มีความบริสุทธิ์ 98.5% และมีองค์ประกอบอนินทรีย์อื่นเพียงเล็กน้อย หลังจากนั้นนำซิลิกาที่ได้จากแกลบมาเตรียม MCM-41 ด้วยวิธีไฮโดรเทอร์มัล และทำการปรับแปลงโดยการเติมอะลูมิเนียมลงไปในของผสมที่เตรียมด้วยวิธีโซลเจลโดยตรง เพื่อเพิ่มความเป็นกรด ด้วยอัตราส่วนจำนวนโมล Si/Al เท่ากับ 100, 75, 50 และ 25 จากนั้นนำ MCM-41 และ Al-MCM-41 ไปวิเคราะห์ด้วยเครื่อง XRD กล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) และการวิเคราะห์เชิงความร้อน (TGA) แสดงให้เห็นว่าความเข้มของพีค XRD ของ MCM-41 และ Al-MCM-41 ลดลงเมื่อมีจำนวน Al เพิ่มขึ้น และโครงสร้างที่มีการจัดเรียงตัวแบบเฮกซะโกนัลเป็นลำดับสม่ำเสมอ

Abstract: Silica (SiO_2) was prepared from rice husk by refluxing with 3M hydrochloric solution at 60 °C for 3 h. The acid-leached husk was filtered, washed, dried and calcined at 500 °C for 6 h. The white ash powder was characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF). It was found that the ash contained of amorphous silica 98.5% and small amounts of inorganic compounds. After that the rice husk silica was used as silica source for the synthesis of MCM-41 by hydrothermal method and further modified by addition of aluminiun with Si/Al ratio of 100, 75, 50 and 25 to increase acidity with direct sol–gel methods. The MCM-41 and Al-MCM-41 were characterized by XRD, TEM, and TGA. The XRD peak intensity MCM-41 and Al-MCM-41 decreased with aluminum increased and MCM-41 showed an ordered structure characteristic of a regular hexagonal array.

Introduction:

Rice husk is byproduct of rice milling composed of cellulose, lignin and ash varying with the variety, climate and geographic location of growth. [1] The ash is largely composed of silica with small amounts of inorganic compounds. Pure silica can be obtained from rice husk by a simple acid-leaching procedure and calcination at 600°C under in atmosphere. HCl is most often used for acid leaching.[1, 2] Due to its high silica content RH has become a source for preparation a number of silicon compounds such as silicon carbide, silicon nitride, zeolite and mesoporous MCM-41. MCM-41 is amorphous silica consists of an array of unidimensional and hexagonally shaped. The pore size of the MCM-41 can be controlled from 1.5 to 10 nm by use of an appropriate surfactant as a template. Because of its uniform size and shape of mesopores as well as its thermal stability, MCM-41 has attracted considerable interest as a model substance of gas adsorption, catalyst supports. MCM-41 was prepared originally by hydrothermal reactions of silicate gels in the temperature range from 100-120 °C. [3] The surface of MCM-41 is only weakly acidic and the acidity could be generated through isomorphous substitution of Si by Al. Acidity modification of MCM-41 is necessary for the applications to acid-catalyzed reactions such as cracking, isomerization, alkylation and hydroxylation. [3, 4]

Methodology:

Extraction of silica from rice husk and characterization; The rice husk was washed thoroughly with water to remove adhering soil and dust and dried at 120 °C overnight. The water-rinsed rice husk and 3 M HCl solution in ratio 100 g : 500 mL were refluxed under stirring in a round-bottomed flask at 60 °C for 3 h. The mixture was filtered and the husk was washed with distilled water several times until the filtrate was free from acid. The acid-leached husk was then dried at at 120 °C overnight and calcined at 500 °C for 6 h, with a heating ramp of 10 °C /min. The silica from rice husk was characterized by XRD and XRF.

MCM-41 and Al-MCM-41 preparation and characterization; Pure siliceous MCM-41 was synthesized from a gel having a molar composition $4SiO_2$:$1Na_2O$:1CTMABr:$0.29H_2SO_4$:$400H_2O$, where CTMABr is cetyl trimethyl ammonium bromide. SiO_2 3 g was dissolved in a solution containing NaOH 6 g in distilled water. The solution is then mixed with a solution of CTMABr 4.5 g in distilled water 90 mL until a clear solution is obtained. The pH of the gel mixture was adjusted to 11 with H_2SO_4 then the gel mixture was stirred for 2 h and finally the mixture was transferred into a Teflon-lined autoclave and kept at 100 °C under static conditions for 3 day. The solid material obtained was separated by centrifugation at 3000 rpm for 30 min. and washed well with distilled water, until the solid shows a neutral pH then dried in air at 100 °C overnight. Finally the resulting material was calcined at 540 °C for 6 h, at a heating ramp of 10 °C /min. Al-MCM-41 were prepared by the same procedure with an addition of Al source ($NaAlO_2$) with Si/Al ratio = 100, 75, 50 and 25 to the preparation mixture. MCM-41 and Al-MCM-41 were characterized by various techniques including XRD, TEM and TGA.

Results, Discussion, and Conclusion: Rice husk silica is composed of amorphous silica 98.51% and small amounts of inorganic compounds. The XRD patterns of the calcined MCM-41 and Al-MCM-41 in Fig. 1 showed characteristic peaks that can be indexed on a hexagonal lattice. The intensity of the peaks decreased as aluminum was incorporated. TEM micrograph MCM-4 and Al-MCM-41 of the calcined can be clearly observed exhibits a well-ordered long-range structure in Fig. 2. TGA of MCM-4 and Al-MCM-41 showed thermal stability to 600 °C. Acidity modification of MCM-41 from rice husk silica can using in applications to acid-catalyzed reactions such as cracking, isomerization, alkylation and hydroxylation.

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Keywords: MCM-41, Al-MCM-41, rice husk

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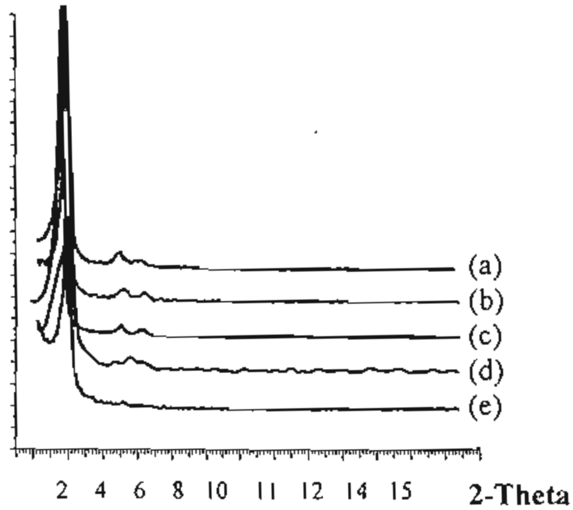

Fig. 1 XRD patterns of the calcined (a) MCM-41, (b)-(e) Al-MCM-41 with Si/Al ratio of (b) 100, (c) 75, (d) 50, and (e) 25

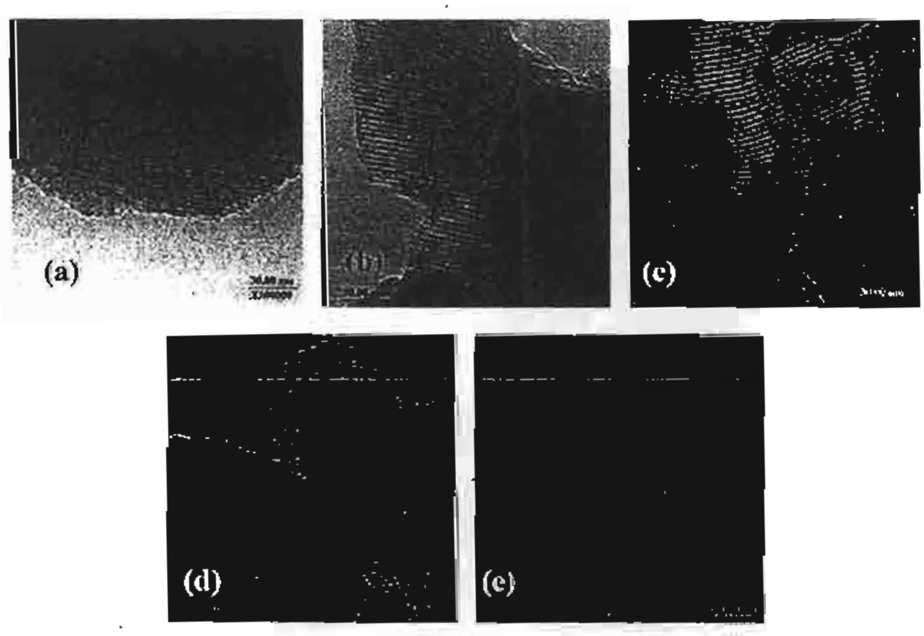

Fig. 2 TEM micrographs of the calcined (a) MCM-41, (b)-(e) Al-MCM-41 with Si/Al ratio of (b) 100, (c) 75, (d) 50, and (e) 25

2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

2. บทคัดย่อ การนำเสนอแบบ Oral presentation เรื่อง การสังเคราะห์วิเคราะห์ลักษณะของซีโอไลต์วาย โดยใช้ซิลิกาจากแกลบข้าว (Synthesis and characterization of zeolite Y from rice husk silica) โดย พงษ์ธนวัฒน์ เข็มทอง และ จตุพร วิทยาคุณ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549

การสังเคราะห์และการวิเคราะห์ลักษณะของซีโอไลต์วาย โดยใช้ซิลิกาจากแกลบข้าว

SYNTHESIS AND CHARACTERIZATION OF ZEOLITE Y FROM RICE HUSK SILICA

นายพงษ์ธนวัฒน์ เข็มทอง และ จตุพร วิทยาคุณ

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บทคัดย่อ: ซิลิกาที่สกัดได้จากแกลบข้าวมีความบริสุทธิ์ประมาณร้อยละ 98 โดยการนำมารีฟลักซ์ด้วยกรดไฮโดรคลอริก จากนั้นนำซิลิกาที่ได้ไปเปลี่ยนรูปเป็นสารละลายโซเดียมซิลิเกตเพื่อนำไปใช้เป็นแหล่งของซิลิกาในการสังเคราะห์ซีโอไลต์วายด้วยกระบวนการไฮโดรเทอร์มัล เปรียบเทียบลักษณะของซีโอไลต์ที่ได้กับซีโอไลต์ที่สังเคราะห์โดยใช้โซเดียมซิลิเกตเชิงการค้า และทำการวิเคราะห์ลักษณะซีโอไลต์ด้วยเครื่องวัดพื้นที่ผิว เครื่องวัดการเลี้ยวเบนของรังสีเอกซ์ กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ผลการวัดพื้นที่ผิวของโซเดียมซีโอไลต์วาย พบว่าเมื่อใช้แหล่งของซิลิกาจากแกลบข้าวมีพื้นที่ผิวเท่ากับ 655.58 ตารางเมตรต่อกรัม แต่เมื่อใช้แหล่งซิลิกาเชิงการค้าพบว่าพื้นที่ผิวที่ได้คือ 400.25 ตารางเมตรต่อกรัม การเกิดเป็นโซเดียมซีโอไลต์วายจากแหล่งของซิลิกาทั้งสองยืนยันโดยผลจาก เครื่องวัดการเลี้ยวเบนของรังสีเอกซ์ ซึ่งให้สเปคตรัมเหมือนกับสเปคตรัมอ้างอิง ส่วนผลจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด พบว่าเมื่อใช้แหล่งซิลิกาจากแกลบข้าวพบเพียงผลึกเดี่ยวของโซเดียมซีโอไลต์วาย ซึ่งมีขนาดอนุภาคประมาณ ~ 0.6 – 1 ไมโครเมตร ในขณะที่ซีโอไลต์วายที่เตรียมจากแหล่งซิลิกาทางการค้า พบว่ามีอนุภาคขนาด ~ 4-8 ไมโครเมตร และอนุภาคมีรูปร่าง 2 แบบดังนี้ ผลึกแบบออคตะฮีดรัลโดยมุมมีรอยตัดและผลึกคล้ายเข็มรวมตัวกันเป็นทรงกลม นอกจากนี้ยังปรากฏอนุภาคทรงกลมที่มีลักษณะเป็นอสัณฐาน

Abstract: Silica (SiO_2) powder was prepared from rice husk (RH) by refluxing with hydrochloric (HCl) acid and calcination in air. The resulting white solid which was analyzed by X-ray fluorescence spectrometry (XRF) contained approximately 98% wt SiO_2. The obtained silica was converted to sodium silicate (Na_2SiO_3) and used as silica source for the hydrothermal syntheses of Linde Type Y zeolite (Y). In addition to RH silica, commercial sodium silicate was used as a silica source for the zeolite syntheses with similar procedure in order to compare the effect of starting material to the zeolites properties. Zeolites from both silica sources were characterized by X-ray diffractometer (XRD), Brunauer –Emmentt-Teller analyzer (BET), and scanning electron microscope (SEM). The formation of zeolite frameworks were confirmed by XRD showing similar spectrum to the reference standard. Surface area from BET analysis of the zeolite from RHS was 655.58 m^2/g, while that from the commercial silica was 400.25 m^2/g. SEM micrographs of the zeolite prepared from RHS source showed only crystalline shape, but the Y zeolites that prepared from commercial silica were observed in two types of particle shapes: octahedral with beveled edge and ball of wool. However, needle amorphous agglomerates are also observed. The particles size of Y zeolite prepared from rice husk silica was ~0.6-1 μm, while that from commercial silica was ~4-8 μm.

Introduction: RH is an agricultural by-product; it contains organic materials as the major constituent and hydrate silicon, which produce high ash content [1]. The ash contains 87 – 98% SiO_2 and a small proportion of metallic elements [2]. Some of the advantages of rice husk silica are widely used in electronics, ceramic, and polymer material industries, thermal insulator and composite fillers [3]. The silica contents of rice husk ash are used as precursor species for alkaline hydrothermal conversion of rice husk ash into zeolite.

Zeolite is an attractive microporous crystalline material because of its solid acidity, ion-exchange capability, adsorption/release capability and molecular-level pores [4]. Important industrial application of zeolite is such as in catalyst and sorbents for removal of ions and molecules from wastewaters [5]. Zeolites are usually synthesized under hydrothermal conditions from solution of sodium aluminate, sodium silicate, or sodium hydroxide [6].

Because, silica in rice husk ash (RHA) formed by combustion below 800 °C was found to be sufficiently pure and in amorphous phase [7], this study explored the potential of RH silica as a raw material to produce Na_2SiO_3 for syntheses Linde type Y zeolites (NaY). The obtained products were characterized by XRD, SEM, and diffraction particle size analyzer.

Experimental: Rice husk was washed with water, dried, and leached with 3 M HCl acid (CARLO-ERBA) for 6 h. The leached material was washed with deionized water, dried, and pyrolyzed in the hot air furnace (Carbolite) at 550°C for 6 h, to yield rice husk silica (RHS). The chemical contents of RHS were analyzed by X-ray fluorescence spectroscopy (XRF; Oxford). RHS was dissolved in 14%wt. NaOH to produce Na_2SiO_3 solution, filtered to remove carbon residue, and used in zeolite syntheses. Each zeolite was synthesized by a method described in literature [8]. The formation of each zeolite product was confirmed by powder XRD (Bruker AXS diffractometer, Model D5005) using nickel filter Cu K_α radiation scanning from 4 to 50° at a rate of 0.05°/s with current 35 kV and 35 mA. SEM (JEOL, Model JSM-6400 with applied potential 10 kV) was used to determine particle size and nature of particle surface.

Results and discussion: From the XRF results, the components of rice husk ash included approximately 99 %wt SiO_2, 0.5 – 0.7 %wt Al_2O_3 and trace of other metal oxides. Therefore, it was efficient and interested as silica source for zeolites synthesis.

The diffraction patterns of the microporous zeolites NaY are shown in Fig. 1. The spectrum were similar to that in reference database [8] confirming the formation of zeolite frameworks from both sources. XRD sharp peaks indicated that the zeolites have high crystallinity.

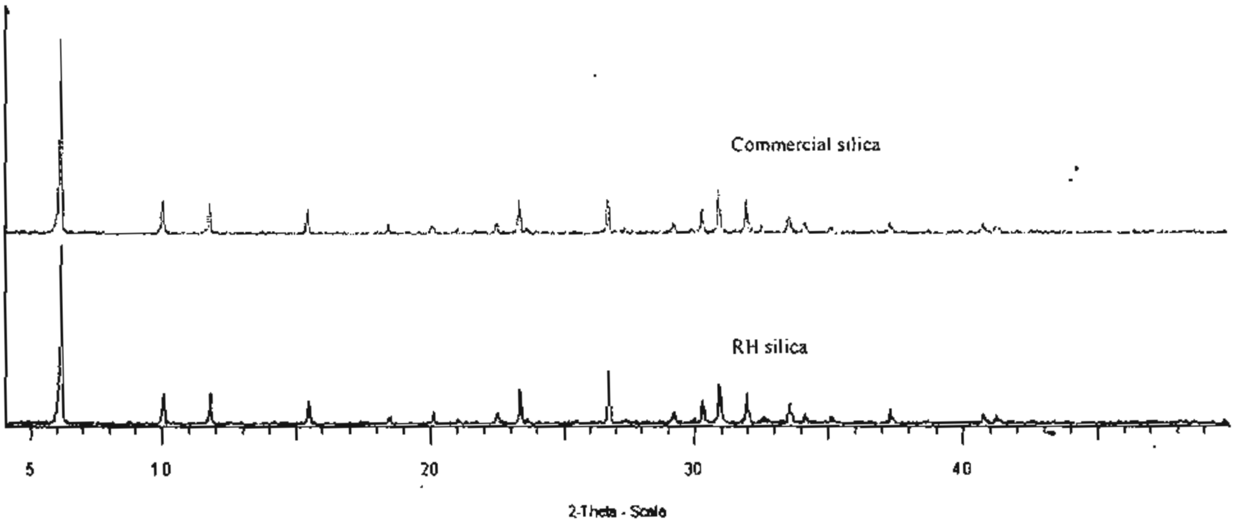

Fig. 1. XRD pattern of NaY from RHS and commercial silica source

SEM micrographs of NaY zeolites from RHS were not different in shape and size showing more usual octahedral crystals habit of NaY and corners has been modified to one with beveled edges (fig. 2). In contrast, SEM micrographs of NaY prepared from commercial silica source (fig. 3) showed larger particles than that from RHS (i.e., ~4-8 μm vs. ~1 μm). There are two types of particle shapes including polycrystalline or beveled octahedral (3b), ball of wool or also zeolites impurities. Nevertheless, needle agglomerates or amorphous zeolites (3c) are also observed. This result indicated that longer aging time is needed in the preparation of NaY from RH silica. In addition, amorphous particles were also observed in all zeolite micrographs.

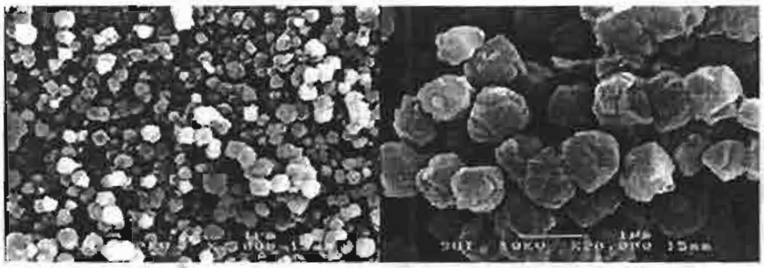

Fig.2. SEM image of NaY prepared from RHS source

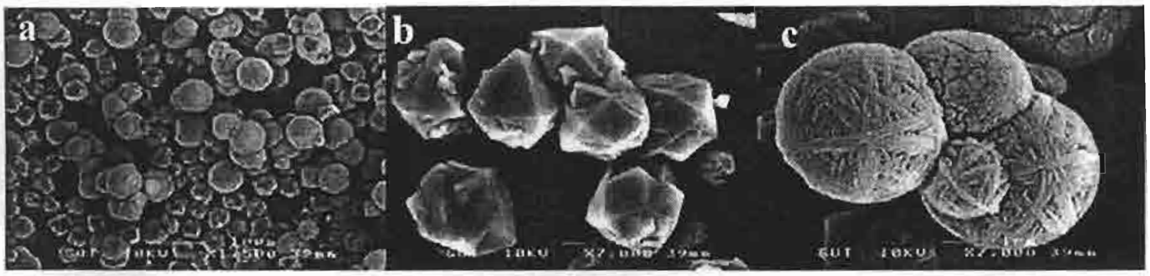

Fig.3. SEM image of NaY prepared from commercial silica source

Conclusions: The high purity silica from rice husk ash was successfully used as silica source for the syntheses of Linde type Y zeolite.

Acknowledgement

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Keywords: Rice husk Silica, Zeolite, NaY,

2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

3. บทคัดย่อ การนำเสนอแบบ Poster presentation เรื่องการเพิ่มประสิทธิภาพการเร่งฏิกิริยาของ MCM-41 ที่สังเคราะห์โดยใช้ซิลิกาจากแกลบด้วยการเพิ่มโลหะไทเทเนียม (Enhancement of catalytic performance of MCM041 from rice husk silica by addition of titanium) โดย สุรชัย อาจกล้า จตุพร วิทยาคุณ และนุรักษ์ กฤษดานุรักษ ชื่องาน การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 32 ศูนย์ประชุมแห่งชาติสิริกิติ ตุลาคม 2549

การเพิ่มประสิทธิภาพการเร่งปฏิกิริยาของ MCM-41 ที่สังเคราะห์โดยใช้ซิลิกาจากแกลบด้วยการเพิ่มโลหะไทเทเนียม

ENHANCEMENT OF CATALYTIC PERFORMANCE OF MCM-41 FROM RICE HUSK SILICA BY ADDITION OF TITANIUM

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บทคัดย่อ: วัสดุมีโซพอร์ MCM-41 ที่สังเคราะห์จากแกลบข้าว สามารถนำมาปรับแปลงให้มีความเหมาะสมต่อปฏิกิริยาทางเคมีด้วยการเติมโลหะทรานซิชันบางตัวลงไป สำหรับงานวิจัยนี้ได้เติมโลหะไทเทเนียมลงในโครงสร้างของ MCM-41 ด้วยวิธีสังเคราะห์แบบไฮโดรเทอร์มัล พบว่า Ti-MCM-41 ที่สังเคราะห์มีโครงสร้างแบบเฮกซะกอนัล เพื่อ XRD แสดงพีค (100), (110) และ (200) ที่ 2θ ต่ำกว่า 10 องศา โลหะทาเนียมที่เติมลงไปอยู่เป็นอะตอม ไม่มีเฟสออกไซด์เกิดขึ้น และตัวเร่งปฏิกิริยานี้ถูกปรับแปลงเพิ่มเติมด้วยการเติม KNO_3 และKOH ลงไปที่ผิวหน้าเพื่อไปใช้ในการเร่งปฏิกิริยาการสังเคราะห์ไบโอดีเซล ผลการทดลองจาก GC แสดงให้เห็นว่ามีเอสเทอร์ของกรด ปาล์มมิติก โอเลอิก และลิโนเลอิก เกิดขึ้นที่ retention time 30.59, 41.36 และ 45.40 นาที ตามลำดับ

Abstract: Mesoporous material, MCM-41, was synthesized by hydrothermal method from rice husk silica and modified further by adding titanium into its framework. The resultant solid product Ti-MCM-41 possessed high specific surface area and narrow pore size distribution. XRD pattern exhibited reflection of (100), (110) and (200) at 2θ lower than 10 degree and the form of loaded titanium was free-oxide titanium form. The Ti-MCM-41 was modified surface by KNO_3 and KOH and the resulting catalysts were designated as K/Ti-MCM-41 and K_2O/Ti-MCM-41, respectively. They were used to catalyze biodiesel production of palm olein oil and methanol via transesterification reaction. GC chromatograms showed that methyl palmitate, oleate and linoleate were clearly presented at retention time of 30.59, 41.36 and 45.40 min, respectively.

Introduction: This study began from extraction of silica from rice husk by acid leaching and calcinations. The obtained white powder resultant contains ~ 98% silica in an amorphous form with small amount of metallic impurities. This silica was utilized to synthesize mesoporous material, MCM-41 and the active acid sites were created by adding titanium into its framework, noted as Ti-MCM-41. Moreover, they were modified further by introducing KNO_3 and KOH onto surface, named K/Ti-MCM-41 and K_2O /MCM-41, respectively. K/Ti-MCM-41 and K_2O/MCM-41 were utilized to transesterification reaction for biodiesel production.

Methodology:

Preparation of Ti-MCM-41

Silica source for Ti-MCM-41 synthesis was extracted from rice husk by acid-leaching method with 3 M HCl followed by calcinations at 500 °C. The molar ratio of each composition in the MCM-41 gel mixture was SiO_2:0.25 CTABr: 0.0303 TBOT: 180 H_2O, where CTABr is cetyltrimethylammonium bromide. In general synthesis, CTABr 1.45 g was dissolved in 30.00 mL of deionization water. The mixture was stirred constantly further 4 hours to obtained clear solution, denoted as solution A. Then solution B was simultaneously prepared by the following procedure: 1.00 g of silica, 0.173 g of tetrabutyl orthotitanate (TBOT) and 2.00 g of NaOH were dissolved together in 15 mL deionization water and constantly stirred further 4 hours to obtained clear solution. Consequently, the solution A was poured to 100 mL teflon linen autoclave and solution B was gradually added dropwise for 20 minute. The pH of the mixture was adjusted to about 11.5 by slowly dropping 5 N H_2SO_4 until small particles agglomerate as a white sol-gel started to appear. The gel mixture was then transferred into a tleon-linen autoclave and annealed hydrothermically in an oven at 100 °C for 72 h to obtain the crystallized product. The product mixture was filtered and dried at 100 °C to remove water. Finally, Powder was ground and calcined at 540°C to remove the template. The product had Si/Ti = 35.

Preparation of K/Ti-MCM-41

K/Ti-MCM-41 was prepared by impregnation method adapted from Wenlei Xie et al [6]. Firstly, 0.20 g of Ti-MCM-41 was dried at 120 °C for 16 h. then 0.12 g KNO_3 was dissolved in 0.7 mL of deionized water. Slurry gel was vigorously stirred for 30 min. Finally, the mixture was calcined at 500°C for 5 h and (35%) K/TiMCM-41 was obtained.

Preparation of K_2O/Ti-MCM-41

Similar to K/Ti-MCM-41 preparation, K_2O/Ti-MCM-41 was prepared in the same condition. Firstly, 0.20 g of Ti-MCM-41 was dried at 120 °C for 16 h. then 0.53 g of KOH was dissolved in 0.7 mL of deionized water. Slurry gel was vigorously stirred for 30 min. Finally, mixture was calcined at 500°C for 5 h and (35%) K_2O/TiMCM-41 was obtained.

Catalytic performance for transesterification reaction

The prepared catalysts were used to test for biodiesel production. First, 100 g of oil was preheated to reaction temperature (70 °C) while appropriate amounts of methanol and catalyst were vigorous mixed together to produce metoxide anion. The reaction was carried out with a weight ratio of 4.5:6.0:0.3 (methanol: soybean: catalyst). Then, the mixture of methanol and catalyst was transferred to preheated oil and vigorously stirred for 8 h. During the period of reaction, pale yellowish liquid was formed and the viscosity was decreased significantly. After reaction completed, the pale yellowish solution was distillated to remove access amounts of methanol. Consequently, liquid product was centrifuged to separate fatty acid methyl ester from glycerol and solid catalyst. Then the ester was dried by molecular sieve anhydrous to obtained pure fatty acid methyl ester. Finally, a biodiesel product was characterized by gas chromatography with FID detector.

Results, discussion and conclusion

XRD patterns of MCM-41 and Ti-MCM-41 in Figure 1 exhibited a main reflection peak corresponding to the (1 0 0) plane at a low angle (around 2θ = 2.0–2.5). The other peaks had lower intensities, (110) and (200), occur below 2θ = 5.0. No diffractions were seen at higher angles that mean titanium loaded isolates from titanium oxide form. Intensity of (100) plane was decreased when titanium was loaded. In addition, the peak shifted to higher 2 θ due to an increase of the wall thickness.

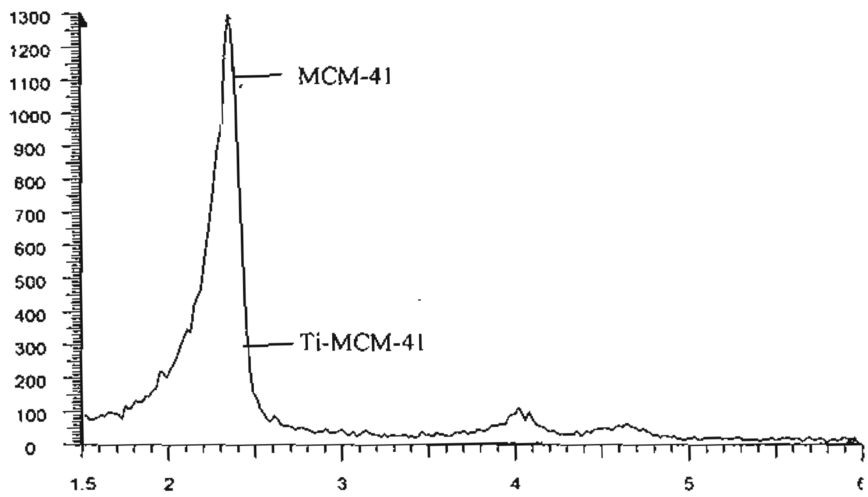

Figure 1. XRD patterns of MCM-41 and Ti-MCM-41 samples (Si/Ti = 35)

Biodiesel production

K/Ti-MCM-41 and K_2O/MCM-41 were used to catalyze biodiesel production. Chromatograms of CG showed peaks of methyl palmitate, oleate and linoleate at the retention time of 30.59, 41.36 and 45.40 min, respectively. Unfortunately, the biodiesel products at this step were still too low to calculate the yield. At present, the amount of Ti, K, and K_2O are varied for better conversion and the results will be presented at the conference. The problem may involve reversibility of transesterification reaction. Methyl palmitate, oleate and linoleate can revert to palmitic, oleic acid and linoleic acid, respectively. Another ongoing work to solve this problem is by performing the reactions of biodiesel in a continuous batch reactor in which the product can be collected and analyzed while the reaction reaches equilibrium.

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2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

4. บทคัดย่อ การนำเสนอแบบบรรยายเรื่อง Synthesis of zeolite Y and Al-MCM-41 from rice husk silica as catalytic support materials โดย Wittayakun, J., Khemthong, P. Chume, J., Grisdanurak, N. ชื่องาน การประชุมนักวิจัยรุ่นใหม่...พบ...เมธีวิจัยอาวุโส สกว. 12-14 ตุลาคม 2549 เพชรบุรี

Synthesis of zeolite Y and Al-MCM-41 from rice husk silica as catalytic support materials

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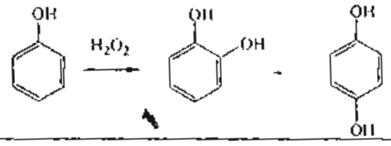
Abstract

Silica (SiO_2) powder was prepared from rice husk (RH) by refluxing with hydrochloric acid and calcination in air. The resulting white solid was analyzed by X-ray fluorescence spectrometry (XRF) containing approximately 98.5%wt SiO_2. The obtained silica was converted to sodium silicate (Na_2SiO_3) and used as silica source for the hydrothermal syntheses of zeolite Y. In addition to RH silica, commercial sodium silicate was used as a silica source for the zeolite syntheses with similar procedure in order to compare the effect of starting material to the zeolites properties. Zeolites from both silica sources were characterized by X-ray diffractometer (XRD), Brunauer-Emmentt-Teller analyzer (BET), and scanning electron microscope (SEM). The formation of zeolite frameworks was confirmed by XRD showing similar spectrum to the standard. Surface area from BET analysis of the zeolite from RH silica and from commercial silica was 655.58 and 400.25 m^2/g. SEM micrographs of the zeolite prepared from RH silica source showed only crystalline shape, but the Y zeolites that prepared from commercial silica were observed in three types of particle shapes, polycrystalline, wool balls and needle agglomerates. The particles size of Y zeolite prepared from rice husk silica was ~0.6-1 µm, while that from commercial silica was ~4-8 µm. The zeolite is used as support materials for platinum and cobalt catalysts which are currently tested for butane hydrogenolysis (equation below). Investigation on effect of reaction conditions and kinetics is underway.

$$2C_4H_{10} + H_2 \rightarrow C_3H_8 + C_2H_4 + CH_4 + H_2$$

In addition, the rice husk silica was used as silica source for the synthesis of MCM-41 by hydrothermal method and further modified by addition of aluminiun with Si/Al ratio of 100, 75, 50 and 25 to increase acidity with direct sol–gel methods. The MCM-41 and Al-MCM-41 were characterized by XRD, TEM, and TGA. The XRD peak intensity MCM-41 and Al-MCM-41 decreased with aluminum increased and MCM-41 showed an ordered structure characteristic of a regular hexagonal array. The Al-MCM-41 is used as support material for platinum and iron which are currently tested for phenol hydroxylation (shown below).



Keywords: zeolite Y, Al-MCM-41, bimetallic catalyst, platinum, cobalt, iron

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2.2 การเสนอผลงานในที่ประชุมวิชาการ

2.2.2 การเสนอผลงานในการประชุมระดับชาติ

5. บทคัดย่อ การนำเสนอแบบโปสเตอร์เรื่อง Preparation and characterization of catalyst support using silica source from rice husk โดย Wittayakun, J., Khemthong, P., Chume, J., Grisdanurak, N. ชื่องาน การประชุมนักวิจัยรุ่นใหม่ ...พบ...เมธีวิจัยอาวุโส สกว. 13-15 ตุลาคม 2548 เพชรบุรี

Preparation and characterization of catalyst support using silica souce from rice husk

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Abstract—Silica was produced from rice husk after being refluxed in hydrochloric acid, washed, and calcined at 500°C. The percentage of silica content of the resulting silica determined by X-ray Fluorescence Spectroscopy (XRF) was approximately 99%. The silica from rice husk was utilized to prepared catalyst supports including MCM-41 and zeolite Y. The success of the syntheses was confirmed by characterization with Powder X-ray Diffraction (XRD). The XRD patterns of both materials were similar to those reported in literatures. Further characterizations of both materials include the determination of Si/Al ratio by XRF and the measurement of surface area and pore size by adsorption method. These materials are being used as the support for bimetallic catalysts containing platinum which will be prepared by impregnation, ion exchange and adsorption. The catalysts will be characterized and tested for hydrogenation of light hydrocarbon compounds. The obtained results will be reported in the meeting.

Keywords—rice husk silica, MCM-41, zeolite Y, supported bimetallic catalyst, platinum

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