



รายงานวิจัยฉบับสมบูรณ์

โครงการ

"การศึกษาวิธีการสังเคราะห์ และการประยุกต์สารไทเทเนียมไดออกไซด์-ซิลิกอนไดออกไซด์เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

โดย นางสุจิตรา วงศ์เกษมจิตต์และคณะ

สัญญาเลขที่ BRG4680013

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เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย
(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกวาไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณสำนักงานกองทุนสนับสนุนการวิจัย ที่ได้ให้การสนับสนุนโครงการวิจัยนี้
ด้วยดีตลอดทั้งโครงการ

บทคัดย่อ

รหัสโครงการ : BRG4680013

ชื่อโครงการ : "การศึกษาวิธีการสังเคราะห์ และการประยุกต์สารไททาเนียมไดออกไซด์-ซิลิกอนไดออกไซด์เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

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งานวิจัยนี้ได้มีการสังเคราะห์สารประกอบโลหะอัลคอกไซด์คือ สารไททาเนียมไกลโคเลตและสารไททาเนียมไตรโอซิโพรพานอลามีนจากวัตถุดิบที่หาง่ายและราคาถูก ด้วยกระบวนการสังเคราะห์สารประกอบออกไซด์ขั้นตอนเดียวที่เรียกกันว่า Oxide One Pot Synthesis (OOPS) โดยสารที่สังเคราะห์ได้มีสมบัติที่เป็นเอกลักษณ์ที่มีความสำคัญมากในกระบวนการโซล-เจล จากการวิเคราะห์สารตัวอย่างด้วยเครื่อง XRD พบว่า สารที่ผ่านการเผาด้วยอุณหภูมิสูงจะมีการเปลี่ยนแปลงของโครงสร้างผลึกจากชนิดอนาเทส (anatase) เป็นรูไทต์ (rutile) ที่อุณหภูมิสูง ขณะที่อุณหภูมิ 300 องศาเซลเซียส สารไม่ก่อตัวเป็นโครงสร้างผลึก ในกระบวนการผลิตสารไททาเนียมที่มีผลึกระดับนาโนและมีรูพรุนขนาดกลางโดยกระบวนการโซล-เจลงั้น สารตั้งต้นที่ใช้เป็นไททาเนียมไกลโคเลตในสภาวะที่มีองค์ประกอบเป็นน้ำและกรด ผลการวิเคราะห์จากเครื่อง XRD พบโครงสร้างผลึกชนิดอนาเทสที่อุณหภูมิการเผาสารในช่วง 600-800 องศาเซลเซียส และมีพื้นที่ผิวสูงถึง 125 ตารางเมตรต่อกรัม ที่อัตราส่วนโดยปริมาตรระหว่างกรดไฮโดรคลอริกและน้ำเท่ากับ 0.28 ถ้าสารไททาเนียมที่เผาที่อุณหภูมิ 800 องศาเซลเซียส ผลึกไททาเนียมไดออกไซด์จะมีลักษณะเป็นทรงกลมที่มีขนาดเล็กประมาณ 1 ไมครอน จากการศึกษาทางด้านรีโอโลยีของสารไททาเนียมไกลโคเลตโดยวิธีการของวินเทอร์พบว่าเวลาในการเกิดเจลงั้น ขึ้นอยู่กับอัตราส่วนของกรดไฮโดรคลอริกและน้ำ ความแข็งแรงของเจลงั้นเพิ่มขึ้นเมื่ออัตราส่วนของกรดและน้ำสูงขึ้น ดังนั้น สามารถกล่าวได้ว่า การเพิ่มความเข้มข้นกรดจะส่งผลให้ความแข็งแรงของโครงสร้างเพิ่มขึ้นและไม่ก่อให้เกิดการยุบตัว จากการศึกษารีโอโลยีของไททาเนียมไกลโคเลตเจลที่อัตราส่วนโดยโมลของกรดไฮโดรคลอริกและสารอัลคอกไซด์เท่ากับ 0.8 0.9 1.0 และ 1.1 พบว่า เวลาในการเกิดเจลแปรผันตามอัตราส่วนโดยโมลของกรดและสารอัลคอกไซด์ รวมทั้งความแข็งแรงของเจลที่เตรียมได้ขึ้นอยู่กัอัตราส่วนของกรดเช่นกัน

ในงานวิจัยนี้ ยังได้ประสบความสำเร็จในการสังเคราะห์สารซีโอไลต์ชนิดทีเอส-วัน (TS-1) ที่มีปริมาณไททาเนียมในโครงสร้างของซีโอไลต์สูงโดยใช้วัสดุที่เสถียรต่อโมเลกุลของน้ำในอากาศ ได้แก่

สารไททาเนียมไกลโคเลตและโซลาเทรน และใช้คลื่นไมโครเวฟเป็นแหล่งให้ความร้อนในการทำปฏิกิริยา งานวิจัยนี้ได้มีการศึกษาผลกระทบจากปัจจัยที่ใช้ในการสังเคราะห์สาร ได้แก่ ปริมาณ TPA⁺ โซเดียมไฮดรอกไซด์ และน้ำ รวมทั้งสภาวะต่างๆ เช่น เวลาในการเกิดปฏิกิริยา อุณหภูมิในการทำปฏิกิริยา และเวลาที่ตั้งสารไว้ที่อุณหภูมิห้อง จากการศึกษาพบว่า ไททาเนียมสามารถเข้าทำปฏิกิริยาและเป็นองค์ประกอบในโครงสร้างของสารซีโอไลต์ได้ด้วยปริมาณสูง โดยมีปริมาณไททาเนียมส่วนน้อยที่แยกตัวออกจากโครงสร้างของสารซีโอไลต์ ซึ่งพบในตัวอย่างที่มีอัตราส่วนของซิลิกอน/ไททาเนียมเท่ากับ 5.0 จากการทดสอบความสามารถในการแตกสลายสาร 4-ไนโตรฟีนอลโดยใช้สารทีเอส-วันเป็นตัวเร่งปฏิกิริยาพบว่า ความสามารถในการแตกสลายสาร 4-ไนโตรฟีนอลสูงขึ้นตามปริมาณของไททาเนียมในโครงสร้างซีโอไลต์

นอกจากนั้น ได้มีการศึกษาการแตกสลายของสาร 4-ไนโตรฟีนอลโดยการเตรียมเป็นเยื่อเลือกผ่าน โดยมีสารไททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงกระจายอยู่ในพอลิเมอร์ชนิดต่างๆ ได้แก่ เซลลูโลสอะซิเตด โพลีอะคลิไนด์ ไนไตร และโพลีไวนิลแอลกอฮอล์ สารไททาเนียมไดออกไซด์ที่ใช้เป็นตัวเร่งปฏิกิริยานั้นเตรียมจากสารอัลคอกไซด์ชนิดไททาเนียมไตรไอโซโพรพานอลามีน จากการศึกษาพบว่า เยื่อเลือกผ่านที่เตรียมจากโพลีอะคลิไนด์นั้นเสถียรที่สุดและมีอัตราการไหลของสารผ่านพื้นที่ผิวเยื่อเลือกผ่านน้อยที่สุดด้วย การศึกษาความเสถียรและความสามารถในการเร่งปฏิกิริยาของสารไททาเนียมในเยื่อเลือกผ่านและทดสอบกับปฏิกิริยาการแตกสลายของ 4-ไนโตรฟีนอลพบว่า ที่ปริมาณการใส่สารไททาเนียมมากขึ้นส่งผลให้ความสามารถในการเร่งปฏิกิริยามากขึ้นด้วย

ผลงานวิจัยทั้งหมดนี้ ได้จดสิทธิบัตรภายในประเทศ 1 ฉบับ ตีพิมพ์ในวารสารนานาชาติ จำนวน 3 ฉบับคือ Journal of Mesoporous and Microporous Materials, Journal of Materials Chemistry and Physics และ Applied Organometallic Chemistry และตีพิมพ์ในวารสารภายในประเทศจำนวน 1 ฉบับ นอกจากนี้ ยังมีผลงานวิจัยที่ได้ไปเสนอในที่ประชุมวิชาการ ณ ประเทศอิตาลีอีก 1 เรื่อง

คำหลัก : ไททาเนียมไกลโคเลต, ไททาเนียมไตรไอโซโพรพานอลามีน, TS-1, การสลายตัวด้วยแสง, ซีโอไลต์

Abstract

Project Code: BRG4680013

Project Title: "Study of a synthetic method and application of TiO_2 - SiO_2 as mixed matrix membrane"

Investigator: Ms. Sujitra Wongkasemjit

The Petroleum and Petrochemical College, Chulalongkorn University

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Project Period : 3 Years

A much milder, simpler and more straightforward reaction to titanium glycolate and titanium triisopropanolamine products is successfully investigated using low cost starting materials via the oxide one pot synthesis (OOPS) process. XRD patterns of pyrolyzed products show the morphology change from anatase to rutile as increasing calcination temperature from 500° to 1100°C, while at 300°C totally amorphous phase is formed. The mesoporous nanocrystalline titanium dioxide was prepared via the sol-gel technique using titanium glycolate as precursor in 1M HCl solution at various HCl:H₂O ratios. XRD analysis indicates the anatase phase forms at calcination temperatures in the range 600°-800°C. The highest specific surface area (BET) obtained is 125 m²/g at the HCl:H₂O ratio of 0.28. The material calcined at 800°C is found to be consist primarily of spherical particles with diameters smaller than 1 μm . Application of the Winter rheological criteria for the gel point indicates that the gelation time increases with an increase of the HCl:H₂O volume ratio. The fractal dimension of the critical gel cluster decreases with acid ratio, whereas the gel strength increases with acid ratio. Thus, the increase of acidity leads to a less dense but stronger network structure. From the rheological study of different titania gelling systems using HCl:alkoxide molar ratios of 0.8, 0.9, 1.0 and 1.1, the viscoelastic properties are investigated. As evaluated by Winter et al., the gelation time increases as increasing HCl:alkoxide molar ratio. The gel strength increases as a function of acid ratio and the fractal dimension determined from the frequency scaling exponent of the modulus at the gel point indicates a tight structure at low acid ratio.

TS-1 with high Ti loading is successfully synthesized using moisture-stable precursors, viz. titanium glycolate and silatrane. The microwave instrument is used as a heating source for the synthesis. The effects of the compositions (TPA^+ , NaOH , H_2O) and conditions (aging time, reaction temperature, reaction time) are studied. The Si:Ti molar ratio and the ability of Ti incorporated into the zeolite framework are also studied. Small amount of extra-framework titanium dioxide is identified at 5.0 Si:Ti molar ratio. Photocatalytic decomposition (PCD) of 4-NP is used to test the activity of TS-1 samples and the results of all samples show high efficiency in PCD.

In addition, photocatalytic membranes are successfully prepared using an efficient, high surface area TiO_2 catalyst, dispersed into different polymeric matrices, viz. cellulose acetate, polyacrylonitrile and polyvinyl acetate. The catalyst is directly synthesized using titanium triisopropanolamine as the precursor. We find that polyacrylonitrile provides the most effective matrix, showing the highest stability and the lowest permeate flux. The amount of TiO_2 loaded in the membrane was varied between 1, 3 and 5 wt% to explore the activity and stability of membranes in the photocatalytic reaction of 4-NP. As expected, the higher the TiO_2 loading, the higher the resulting catalytic activity.

All the works described above have been nationally patented and published in three international journals, viz. Journal of Mesoporous and Microporous Materials, Journal of Materials Chemistry and Physics and Applied Organometallic Chemistry Journal, and one national journal. Moreover, there is also one proceeding presented in an international conference in Italy.

Key words: Titanium glycolate, Titanium triisopropanolamine, TS-1, Photocatalytic decomposition, Rheology

Executive Summary

1. Research Title

(English): "Study of a synthetic method and application of TiO_2 - SiO_2 as mixed matrix membrane"

(Thai): "การศึกษาวิธีการสังเคราะห์ และการประยุกต์สารไทเทเนียมไดออกไซด์-ซิลิกอนไดออกไซด์เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

2. Objectives

1. Study of a method for synthesizing and characterizing titanium glycolate and titanium triisopropanolamine precursors.
2. Study of the sol-gel process and viscoelastic property of titanium glycolate.
3. Study of the sol-gel process of mixed titanium glycolate and silatrane precursors.
4. Preparation of a mixed matrix membrane to study its photo-catalytic property, selectivity and permeability.

3. Project Output

National Patent

1. สุจิตรา วงศ์เกษมจิตต์ และนพวรรณ พรรณชัย เรื่อง "เยื่อแผ่นสำหรับย่อยสลายสารพิษและเชื้อโรคด้วยแสง" เลขที่คำขอ 103423 เมื่อวันที่ 19 สิงหาคม พ.ศ. 2548

International Publications

1. N. Phonthammachai, E. Gulari, A.M. Jamieson and S. Wongkasemjit*, "Photocatalytic Membrane of a Novel High Surface Area TiO_2 Synthesized from Titanium Triisopropanolamine Precursor", Appl. Organometal. Chem., In press (IF = 1.385)
2. N. Phonthammachai, M. Krissanasaeranee, E. Gulari, A. Jamieson and S. Wongkasemjit*, "Crystallization and Catalytic Activity of High Titanium Loaded TS-1 Zeolite", Materials Chemistry and Physics, 97, 458-467 (2006) (IF = 1.183).
3. N. Phonthammachai, T. Chairassameewong, E. Gulari, A. Jamieson and S. Wongkasemjit*, "Structural and Rheological Aspect of Mesoporous Nanocrystalline

TiO₂ via Sol-Gel Process and Its Rheological Study", Mesoporous and Microporous. Mater., 66/2-3, pp. 261-271 (2003). (IF = 3.355)

National Publication

4. N. Phonthammachai, T. Chairassameewong, E. Gulari, A. Jamieson and S. Wongkasemjit*, "Oxide One Pot Synthesis of a Novel Titanium Glycolate and Its Pyrolysis", J.Metals, Minerals and Materials, Chulalongkorn University, 12(1), 23-28 (2002).

International Proceeding

5. N. Phonthammachai, M. Krissanasaeranee, E. Gulari, A. Jamieson and S. Wongkasemjit*, "High Surface Area and Thermally Stable TiO₂ Synthesized Directly from Titanium Triisopropanolamine Precursor", Micro- and Mesoporous Mineral Phases Meeting, December 6-7, 2004, Rome, Italy

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- D. N. Phonthammachai, T. Chairassameewong, E. Gulari, A. Jamieson and S. Wongkasemjit, "Structural and Rheological Aspect of Mesoporous Nanocrystalline TiO_2 via Sol-Gel Process and Its Rheological Study", *Mesoporous and Microporous. Mater.*, 66/2-3, 261-271 (2003).113
- E. N. Phonthammachai, T. Chairassameewong, E. Gulari, A. Jamieson and S. Wongkasemjit, "Oxide One Pot Synthesis of a Novel Titanium Glycolate and Its Pyrolysis", *J. Metals, Minerals and Materials, Chulalongkorn University*, 12(1), 23-28 (2002).125
- F. N. Phonthammachai, M. Krissanasaeranee, E. Gulari, A. Jamieson and S. Wongkasemjit, "High Surface Area and Thermally Stable TiO_2 Synthesized Directly from Titanium Triisopropanolamine Precursor", *Micro- and Mesoporous Mineral Phases Meeting, December 6-7, 2004, Rome, Italy.*133

CHAPTER I

INTRODUCTION

Titanium dioxide (TiO_2) is widely used in the field of catalysis, as filters or adsorbents or membrane to remove organics from wastewaters (catalytic wet oxidation) and structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts. Transitional metal substituted zeolite frameworks have received considerable attention in recent years due to their catalytic activity in a number of important industrial processes. The titanium doped TS-1 zeolite with the MFI type framework is a well-known catalyst for the selective oxidation of many organic and inorganic compounds with H_2O_2 in mild conditions. The reaction is of interest since water is detrimental to conventional titania-silica catalysts and no environmentally undesirable side products are formed from hydrogen peroxide reactions.

Nowadays, industrial wastewater becomes more and more important problem due to increasing trend of many industries. With the same intention, many researchers have been studying to obtain the efficient wastewater treatment to mineralize all the toxic species present in the wastewater without leaving behind any hazardous residues and with low cost. There are many technologies developed for the wastewater treatment, such as, air stripping, granular activated carbon, biological degradation, chemical oxidation and heterogeneous photocatalysis, having been found to be effective for complete mineralization of many toxic, bacteria and bio-resistant organic compounds in wastewaters at such a milder experimental condition. TiO_2 is one of the famous catalysts for photocatalytic degradation due to its effective activity, chemical stability and non-toxic properties. A practical utilization of photocatalysis process generates the main drawback, involving expensive liquid-solid separation process due to the formation of milky dispersions after mixing the powder catalyst in water

Currently, this drawback has been solved by the use of highly dispersed fine particles in a porous material using TiO_2 membrane. Titania membranes attract a great attention in recent years due to their unique characteristics, such as high water flux, semiconducting properties, photocatalysis and chemical resistances over other membrane materials, such as silica and γ -alumina. Many different types of existing membranes consist of a variety of materials, such as, polymers, metals, mixed solid

oxides and porous inorganic materials. However, mixed matrix membrane (MMM), a microencapsulated membrane, becomes more interesting because of its high selectivity combined with an outstanding separation performance of the catalysts, the processing capabilities and low cost of polymers used as matrix.

The important factor to produce titania with good properties is the purity of metal alkoxide precursors. The titanium dioxide has most often been carried out using the titanium alkoxide, however, the synthesis of metal alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity because they contain an unsaturated Ti^{IV} center which is highly reactive to air and moisture, therefore the reaction must be carried out under inert gas. Another reason is that they used very expensive starting materials

From that worthy knowledge, it brings up an idea to study how to improve the special features, such as, its redox/oxidation properties and its high oxygen mobility. Key point is how to increase specific surface area with homogeneous distribution of pore size. Sol-gel processing has become one of the most successful techniques for preparing nanocrystalline metallic oxide materials. In general, this method involves the hydrolysis and polycondensation of a metal alkoxide, to ultimately yield hydroxide or oxide under well-specified reaction conditions. A gel is defined as a two- or multicomponent system of semisolid nature, rich in liquid and consisting of continuous solid and fluid phases of colloidal dimensions. It contains a stable cross-linked or entangled network structure infiltrated with liquid. The network structure is formed using chemical or physical gelation processes. Chemical gelation produces branched structures based on covalent bonds between the molecules and the network subunits, whereas the physical gelation is determined by forces (Van der Waals, electrostatic, hydrogen bonding) that generate reversible intermolecular associations. The key advantage of preparing metallic oxides by the sol-gel method is the possibility to control their microstructure and homogeneity. Furthermore, the product after sol-gel processing and sintering is easy to be prepared in different forms, such as, powder, monoliths, thin film and membranes. To obtain homogeneous nanoscale macromolecular oxide networks via sol-gel processing, control of hydrolysis is essential. The properties and nature of the product are controlled by the particular alkoxide used, the presence of acidic or basic additives, the solvent and various other processing conditions (e.g. temperature). The calcination temperature is also a key factor, too low a temperature

results in incomplete combustion and too high a temperature causes phase transformation.

Although much of the work done to characterize the sol-to-gel transition has used spectroscopic techniques, most of these techniques do not provide information about molecular weights. However, a precise experimental determination of the exact transition point is rather difficult because of its divergent nature. On the other hand, rheological measurements are sensitive to the structural and textural evolution of gels and are complementary to spectroscopic experiments. Oscillatory measurement has received great attention among researchers around the world because of its ability to assess and provide important information on the physical structure and rheological properties of materials without disturbing the material configuration. Knowledge of the evolution in rheological properties during sol-gel processing is a useful guide to the manufacturer when formulating dispersion to optimize the physical properties required in the final product. The shear rheology is an ideal tool for detecting the gel point, using the self-similarity of the structure, which implies that both linear viscoelastic moduli G' and G'' follow the same power law with frequency. It is generally accepted that polymeric materials as well as many dispersed particles are viscoelastic. Therefore, the steady shear measurement alone could not fully characterize the rheological behavior of these materials. Consequently, there is a growing need to carry out the rheological dynamic measurement, which can fully characterize both the viscous and the elastic components of the dispersions.

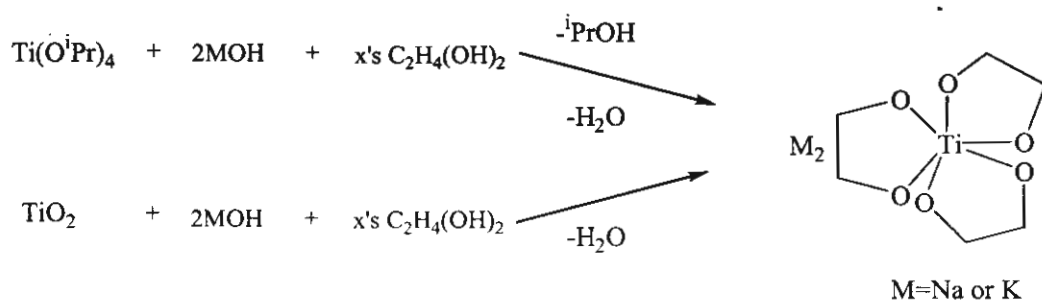
In this work titanium glycolate ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$) and titanium triisopropanol amine ($\text{Ti}(\text{OCHCH}_3\text{CH}_2)_2\text{N}(\text{CH}_2\text{CHCH}_3\text{OH})_2$) were synthesized using the Oxide One Pot Synthesis (OOPS) method and low cost starting materials. $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ is a novel crystalline complex with infinite one-dimensional chains and exhibits outstanding high stability not only in alcohol but also in water. The high surface area TiO_2 was prepared from the synthesized precursor using the sol-gel process followed by calcinations. The rheological properties of titania were measured at different conditions to study the gelation time and gel strength. The microwave treatment of titanium glycolate and silatrane precursors in basic solution was studied to prepare TS-1 zeolite with high percentage of titanium incorporated in the zeolite framework. The application of titania as a photocatalytic membrane reactor was studied by varying the types of polymer membrane and the amount of titanium loading.

CHAPTER II

LITERATURE SURVEY

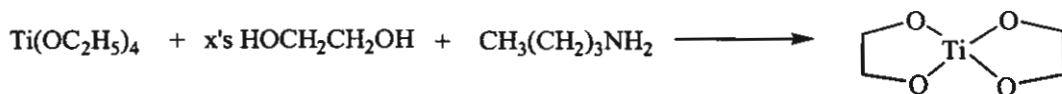
2.1 Synthesis of Metal Alkoxides

The metal alkoxide precursors for catalyst synthesis are of interest to study because of their remarkable ability as precursor for electroceramic materials. Apparently, the synthesis of new metal alkoxides possessing unique structures and properties is of great significance for the investigation of sol-gel process as well as the evolution of metal alkoxide chemistry. However, there are some disadvantages of metal alkoxides that make it difficult to study their structures and properties thoroughly, such as, the extreme moisture sensitivity and the tendency to form mixtures of structurally complex species upon hydrolysis. From these reasons, many literatures tried to improve the properties of metal alkoxide, such as, the synthesis of anionic titanium tris(glycolate) complex from reaction of titanium dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxide, as shown in scheme 2.1.¹



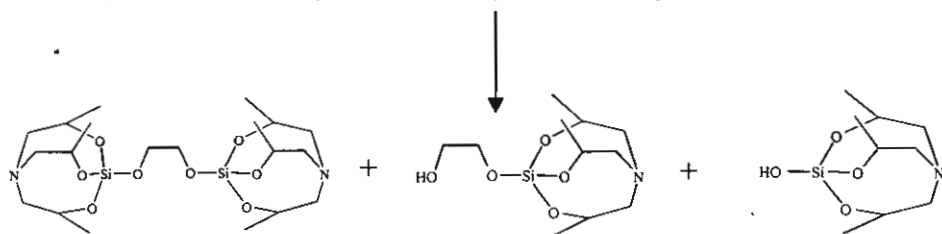
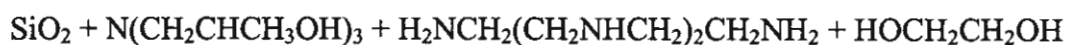
Scheme 2.1 The preparation of synthesized anionic titanium tris(glycolate) complex.

The hydrothermal reaction of titanium tetraethoxide, n-butylamine and glycol to obtain titanium glycolate complex was successful after the reaction at 160°-180°C for 5 days. The product exhibited outstanding high stability not only in alcohol, but also in water (scheme 2.2)².



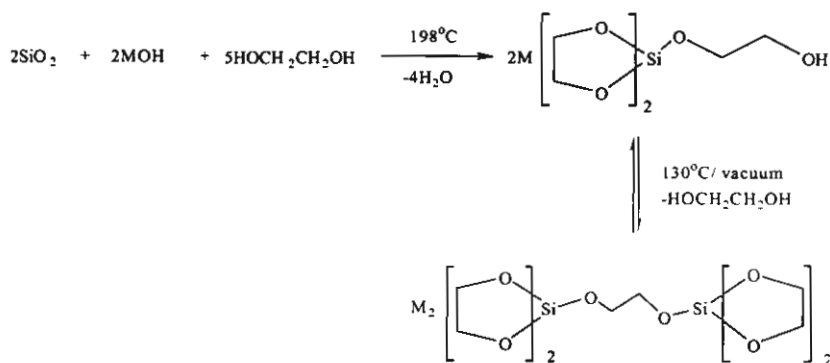
Scheme 2.2 The preparation of titanium glycolate complex by reacting titanium tetraethoxide with glycol.

The silatrane complex was synthesized by direct reaction of SiO_2 and triisopropanolamines. The precursor exhibited the outstanding high stability not only in alcohol but also in water and was synthesized from inexpensive starting materials as scheme 2.3³.



Scheme 2.3 The preparation of silatrane complexes by Wongasemjit's method.

The oxide one pot synthesis (OOPS) process was used to investigate a straightforward and low-cost route to produce alkoxide precursors by direct reactions of a stoichiometric mixture of silica and group I metal hydroxide with ethylene glycol, as shown in scheme 2.4⁴.



Scheme 2.4 The preparation of siloxane complex by the reaction of SiO_2 and glycol.

The synthesis of titanium tetraethoxide ($\text{Ti}(\text{OEt})_4$) and titanium tetrapropoxide ($\text{Ti}(\text{OPr}^n)_4$) was studied by the reaction of hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$, $n=0.15-1.23$) and dialkyl carbonates using various alkali-metal hydroxide catalysts (LiOH , NaOH , KOH and CsOH) as scheme 2.5. The reaction was carried out in autoclave at a heating rate of 90 Kh^{-1} . It was reported that use of sodium hydroxide gave the highest yield compared to the others⁵.



Scheme 2.5 The preparation of titanium tetraethoxide ($\text{Ti}(\text{OEt})_4$) and titanium tetrapropoxide ($\text{Ti}(\text{OPr})_4$).

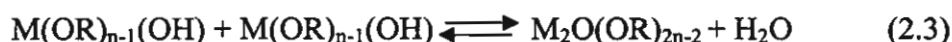
2.2 Sol-gel Process of Metal alkoxides

Sol-gel technique has been extensively used to prepare amorphous and crystalline materials. In general, the sol-gel process is the synthesis of an inorganic network at low temperatures by a chemical reaction in solution. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Generally, the precursor is dissolved in a suitable organic solvent in order to form a solution. The solvent must be carefully selected so that a solution with high concentration of the required component can be obtained. Metal oxide network formation involves the following steps:

1. precursor formation
2. hydrolysis to form solution (sol)
3. polycondensation
4. film and gel formation
5. organic pyrolysis by heat treatment
6. densification and crystallization by annealing process

There are two important reactions in polymeric gel formation. These reactions are partial hydrolysis, followed by condensation polymerization. Polymerization steps via hydrolysis and condensation reaction are illustrated, as follows⁶:



The M-O-M network product is formed by polycondensation reactions, as shown in Reactions 2.2 and 2.3 in which alcohol and water are produced as the by-

products. These reactions lead to a degree of gelation regarding to the appropriate amount of water. Other critical parameters usually considered are viscosity of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are employed to improve spin ability and coating ability. In addition, solution concentration, viscosity, surface tension of the solution and the deposition technique determine the film thickness and uniformity.

In general, the sol-gel process gives high surface area, pore structure, homogeneous property of the products, and moreover, it is a low-temperature method for converting metal alkoxide to metal oxide. There are many works investigated the sol-gel process using various types of precursors for certain properties.

Previously, the mesoporous nanocrystalline TiO_2 was prepared by a sol-gel technique using butanediol mixed with tetrapropylorthotitanate and aged in ambient temperature for 1-8 weeks. The highest surface area of $97 \text{ m}^2/\text{g}$ with diameter of 10 nm was obtained after calcination at 400°C for 2h. The aging time and calcination temperature influence the phase transformation of nanophase titanium dioxide which the phase transition of anatase to rutile began at 630°C and was complete at 730°C ⁷.

The forced hydrolysis of boiling reflux method of $\text{Ti}(\text{SO}_4)_2$ solution in the presence of a small amount of H_2SO_4 was used to prepare nanodispersed spherical TiO_2 . The particle size distribution was over 100 nm. The inhibition of H_2SO_4 to phase transformation causes the nucleation rate to slow down. When the concentration of H_2SO_4 continues to rise, the particle size increases and the production of TiO_2 powder is reduced dramatically⁸.

The MOCVD (molecular chemical vapor deposition) technology was used to synthesize nanosized anatase titania. The titanium tetrabutoxide was pyrolyzed in an oxygen-containing atmosphere and the average grain size ranging from 7.4 to 15.2 nm was observed. The preparation temperatures not only accelerate the nucleation rate, but also the particle growth rate. The smallest average grain size 7.4 nm and the highest surface area $180 \text{ m}^2/\text{g}$ were obtained at 700°C . The anatase-rutile transformation temperatures were about 700°C - 1000°C ⁹.

The hydrolysis of titanium tetraisopropoxide (TTIP) in the aqueous cores of water/NP-5/cyclohexane microemulsion was used to synthesize ultrafine titania particles. With increasing calcination temperature from 300° to 700°C , the specific

surface area of the TiO_2 particles decreased from 325.6 to 5.9 m^2/g , whereas the average pore radius increased from 1.4 to 25.1 nm. The particles calcined up to 300°C indicated that they are amorphous and upon increasing the temperature to 650°C, the rutile peaks appeared¹⁰.

The sol-hydrothermal method using titanium n-butoxide (TNB) precursor in various acidic media (HCl , HNO_3 , H_2SO_4 and CH_3COOH) was used to synthesize nanocrystalline titanium dioxide. The nanocrystals of pure rutile with size < 10 nm were obtained at higher HCl concentrations under mild conditions. The propensity of acidic medium for rutile formation is shown as follows: $\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HAc}$ ¹¹.

The mesoporous spherical titania particles were prepared via hydrolysis of pure titanium tetra-isopropoxide in n-heptane solution. Calcination of hydrolyzed product produced pure anatase at 400°-600°C and rutile at 800°C. The highest specific surface area of 132 m^2/g and pore size of 10 nm were obtained at 400°C which are higher than that of material calcined at 600°C (58.5 m^2/g) and much higher than that of the material calcined at 800°C (5.0 m^2/g)¹².

Nanosized titanium (IV) oxide in the anatase form was synthesized by hydrolysis of titanium n-butoxide in toluene with water at high temperature (150°-300 °C). The crystalline size of the anatase was gradually increased with reaction temperature and reaction time. The surface area of 71 m^2/g was received after calcination at 700 °C and the transformation temperature from anatase to rutile was at around 1000°C¹³.

2.3 Rheological Study of Metal Alkoxides

Chambon and Winter¹⁴ proposed a constitutive equation for linear viscoelasticity of incipient gels, which they called the gel equation.

$$\delta(t) = S \int_{-\infty}^t (t - t')^{-n} \gamma(t') dt' \quad (2.4)$$

where δ is the shear stress, γ is the rate of deformation tensor, n is the relaxation exponent and S is the gel strength parameter (with dimensions Pa.s^n), which depends on the cross-linking density and the molecular chain flexibility. A more general version of

this model has been developed, where the model proposed by Winter and Chambon¹⁴ constitutes a special case.

The storage modulus G' and the loss modulus G'' at the gel point both will follow similar power laws in frequency,

$$G' = G''/\tan \delta = S \omega^n \Gamma(1-n) \cos \delta \quad (2.5)$$

where $\Gamma(1-n)$ is the gamma function. The phase angle between stress (δ) and strain is independent of frequency but proportional to the relaxation exponent,

$$\delta = n \pi/2 \quad (2.6)$$

This result suggests that the power law behavior of the dynamic moduli can be expressed as

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad (2.7)$$

Theoretical models have been elaborated to rationalize values of the relaxation exponent in the physical accessible range $0 < n < 1$. In the theoretical advances, based on the fractal concept, the dynamic exponent n is associated with information about the molecular structure and connectivity of the incipient gel.

The structure may be described by a fractal dimension d_f , which is defined by $R^d_f \sim M$, where R is the radius of gyration and M is the mass of a molecular cluster. On the basis of the percolation approach, the Rouse model, which assumes no hydrodynamic interaction between polymeric clusters, predicts $n = d/(d_f + 2)$ and with $d = 3$ (the space dimension) and $d_f = 2.5$ (percolation statistics) n assumes a value of 0.67. In the electrical analogy, a suggested isomorphism between the complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors yields a value of $n = 0.72$.

If we consider a situation where the strand length between cross-linking points of the incipient gel varies, one may anticipate that increasing strand length should enhance the excluded volume effect. In order to take this into account, Muthukumar¹⁵ suggested that if the excluded volume interaction is fully screened, the scaling exponent can be expressed as

$$n = d(d + 2 - 2d_f)/2(d + 2 - d_f) \quad (2.8)$$

Quite recently, the relation between the viscoelastic and structural properties of systems of cross-linking polymers near the gel point was considered in the framework of a mechanical ladder model, which predicts a scaling law for the complex shear modulus with an exponent $0 \leq n \leq 0.5$. It was shown that the parameter n is related to the spectral dimension $d_s \geq 1$ of the fractal through the relationship.

$$n = 1 - d_s/2 \quad (2.9)$$

2.4 Synthesis of TS-1 Zeolite

Since Taramasso et al¹⁶ discovered the TS-1 zeolite, there are many researchers tried to synthesize TS-1 with improving the Ti containing in the zeolite framework by different methods and materials because of the high efficiency and molecular selectivity in oxidation reactions employing H_2O_2 , such as the conversion of ammonia to hydroxylamine, secondary alcohols to ketones, secondary amines to dialkylhydroxylamines, or reactions, such as the hydroxylation, the olefin epoxidation, or the cyclohexanone ammoximation¹⁷.

The effect of organic amine to the formation of TS-1 zeolite was studied with various types of amine which are n-butylamine, TPAOH, TBAOH, 1,6-hexanediamine, ethylenediamine, diethylamine and triethanolamine. To decrease the cost, TPABr was used as a template instead of TPAOH. The $Ti(OC_4H_9)_4$ was used as the titanium source with the ratio of $Si/Ti = 33$. They found that the organic amine cannot act as a template in the presence of TPA^+ . It can only regulate the basicity of the gel. The order of the template effect of different templates is as follows: $TPA^+ > TBA^+ > TEA^+ >> \text{organic amine}^2$.

The synthesis of TS-1 in fluoride medium was prepared by two different methods, mixed alkoxide and wetness-impregnation. The preparation of a sol or a gel containing Si-O-Ti bonds prior to fluoride addition is the key step of the synthesis. The mixed alkoxide method used $TPAOH + HF$ and the wetness-impregnation used $TPABr + NH_4F$ and the mixture after addition of fluoride was transferred to Teflon-lined autoclave at $170^\circ C$ for 5 days. DR-UV result of mixed alkoxide method showed that the samples at the Si/Ti ratio of 42 showed only the band at 220 nm, indicating that all the

titanium is in the zeolite framework. For the wetness-impregnation method, the sample with the Si/Ti ratio of 90 exhibited only a strong band at 220 nm¹⁸.

Titanium silicate-1 (TS-1) was synthesized in the presence of small amount of TPAOH, as nonionic surfactant. The mixture was crystallized at 140°C for 18h under autogeneous pressure at the Si/Ti ratio of 33. The result from DR-UV showed a charge transfer band at 220 nm, which is a characteristic of isolated framework of Ti⁴⁺. The sample prepared without the use of surfactant, on the other hand, showed the band at 330 nm, which suggest the presence of extra framework of TiO₂¹⁹.

The crystallization kinetics of TS-1 zeolite using quaternary ammonium halides (TEACl+TBACl) as template was studied. TEOS and TBOT were used as sources of silica and titanium and the crystallization was carried out statically at 160°C for 6-10 days. From the kinetics study of crystallization, as increasing the temperature of crystallization the induction period decreased and the crystallization rate increased. With the increase of the Si/Ti ratio in the reaction mixture, the crystallization rate increased and the mean crystal size decreased gradually. The crystallization rate was also depended on the (TEA+TBA)/Si ratio. Increasing the (TEA+TBA)/Si ratio leads to the increase of crystallization rate, indicating that more template molecules are advantageous to the crystallization of TS-1. The dilution of the sol mixture with water decreased the rate of crystallization and increased the average crystal size. When increasing the NH₃/Si ratio, both the rate of crystallization and the crystallinity of the final product were increased²⁰.

Microwave-assisted synthesis of molecular sieves is a relatively new area of research. It offers many distinct advantages over conventional synthesis. They include rapid heating, resulting in homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels, and eventually a shorter crystallization time compared to those of conventional autoclave heating. Furthermore, it is energy-efficient and economical²¹. It has been postulated that the major mechanism of microwave heating is due to dipole orientation and ionic conduction. However, if one is pressed to explain the mechanism of microwave heating for a given compound, one cannot clearly explain it with the kind of motion of polar molecules and/or ions²².

Aluminophosphate molecular sieves (AlPO₄'s) were prepared by microwave heating without using organic template reagent. The microwave enhanced the

crystallization of aluminophosphate gels, and AlPO_4 were successfully obtained as single phase in a relatively short reaction time²³.

Agglomerated uniformly sized zeolite Y was prepared in a microwave oven in 10 min, whereas 10-15 h was required for the conventional heating technique, depending on the lattice Si/Al ratio. Relatively high Si/Al ratio, up to 5, could be obtained from hydrogels containing low aluminum contents without crystallization of undesired phases. ZSM-5 could also be synthesized in 30 min at 140°C by this technique²⁴.

Effect of the variation in alkoxide precursor ratio and templating agent concentration on the production of titanium silicate (TS-1) was investigated through analysis techniques. Across the range of compositions studied, x-ray diffraction indicated that all the samples have the MFI crystalline structure, and Raman demonstrated incorporation of titanium in the zeolite framework. Energy dispersive X-ray analysis showed that samples produced using an ultra-low alkali metal content templating agent generally resulted in a higher degree of titanium incorporation in the zeolite framework²⁵. IR spectra showed the characteristic of TS-1 at 960 cm^{-1} and DR-UV at 210 nm which is attributed to tetra-coordinated titanium².

2.5 Photocatalytic membrane reactor

The nanostructured mixed matrix membranes were synthesized using the method based on interfacial crosslinking or copolymerization. To prepare the capsules, an AB-type block copolymer surfactant, consisting of ten methylmethacrylate and eight methacrylic acid units ($\text{MMA}_{10}\text{MAA}_8$) was employed. At high pH, $\text{MMA}_{10}\text{MAA}_8$ is soluble in water and stabilizes w/o emulsions. Capsules were prepared by crosslinking the MAA group of neighbouring surfactants with hexanediamine. The membrane was formed using polymerization of capsules containing monomers of 70%MMA and 30%MAA combined with the interfacial crosslinking encapsulation method. The polymerization reaction was initiated by photo-initiator DMPA in combination with UV-light. The capsules containing films were prepared by dispersing the dry $\text{MMA}_{10}\text{MAA}_8$ capsules in the MMA/MAA mixture²⁶.

The accessible pore system of polymeric ultrafiltration membranes was modified by titanium dioxide and treated further with palladium acetate to yield catalytically

active, porous nanofiltration membrane. To overcome the drawback of low thermal stability of common polymeric membranes, the inorganic filler was added to the membrane casting solution. Polyacrylonitrile (PAN), polyetherimide (PEI) and polyamideimide (PAI) were chosen as polymer matrix. The pore system of membranes was modified by two-step procedure to produce catalytically active membranes for heterogeneous catalysis in gas or liquid phase. In the first step, the pore system was narrowed by creating an inorganic titanium oxide layer on the inner surface of the pores by dipping into a solution of 3.5 wt.% tetraethyl titanate in n-hexane. The second step produced an active layer of palladium on the top of these inorganic modified pores of the membrane. The introduction of the catalyst was performed by treating the titanium dioxide modified membrane with a solution of 3 wt.% palladium acetate in methyl ethyl ketone (MEK)²⁷.

Random copolymers of 2-hydroxyethyl acrylate (HEA) and methyl acrylate (MA) and homopolymer PHEA were prepared by free radical polymerization. The hydroxyl groups of PHEA were reacted with 3-(triethoxysilyl)propyl isocyanate to introduce triethoxysilyl (TREOS) groups. Co-hydrolysis and condensation of the TEOS groups with titanium tetrabutoxide yielded polymer/SiO₂/TiO₂ hybrid materials. At TiO₂ less than or equal to 7.4%, the hybrid membranes produced were transparent. Ti-specific imaging demonstrated that the TiO₂ phase was nano-sized and distributed uniformly inside the polymer matrix. Water vapor permeability across such hybrid membranes could be changed by varying the PHEA content and was very high for PHEA/SiO₂ membranes. The incorporation of MA into the hybrid allowed to reduce membrane swelling by water at no cost to membrane brittleness²⁸.

Mixed matrix membranes of 6FDA-6FpDA-DABA, a glassy polyimide and modified zeolites (ZSM-2) were fabricated. The ZSM-2 zeolites were functionalized with amine groups by reacting them with aminopropyltrimethoxysilane in toluene. The amine-ethered zeolites interacted through secondary forces with the carboxylic groups along the polymer backbone, as documented by FTIR. Band shifts associated with hydrogen bonding of the carbonyl and amine groups were observed in the spectra. These interactions promoted adhesion between the two components. The solubility coefficient for each gas (CO₂, O₂, N₂, He and CH₄) increased, except for N₂, which was largely unchanged. The changes in permeability for each gas correlated well with the

change in the diffusion coefficient. The permeabilities of He, CO₂ and CH₄ all decreased, while O₂ and N₂ increased²⁹.

The photocatalytic membrane reactors for degradation of organic pollutants in water were prepared by using 4-nitrophenol (4NP) as a probe polluting agent and titanium dioxide in suspension was used as catalyst. The commercial membranes were; NTR7410 and NTR7450 (Nitto enko), N30F and NF-PES-010 (Hoechst), MPCB0000R98 (SEPAREM). The measured permeate flux was in the range of 5-30 l/h m² at 4 bar and all membranes showed both a rejection and capacity to adsorb the pollutant with a transitory phase varying from 80 to 400 min at 4 bar. Three factors, viz. rejection, photocatalytic degradation and adsorption, were able to maintain 4NP concentration in the permeate at very low values³⁰.

The purification of bilge water by a combination of ultrafiltration and photocatalytic process was studied. The separation of oil from bilge water was performed on a laboratory-scale ultrafiltration pilot plant with tubular membranes made from poly(vinyl chloride) (PVC), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF). The examined membranes with MWCO 70 kD for PVC and PAN and 100 kD for PVDF produced a permeate with an oil content less than 15 ppm. The photocatalytic process was carried out using titanium dioxide based catalyst. The complete decomposition of oil was achieved after 2h for UV illumination using a K-TiO₂ photocatalyst with content amount of 0.8 g/dm³, and after 3h of UV illumination using 0.8g/dm³ of KOH/TiO₂ photocatalyst³¹.

The preparation of polycrystalline TiO₂ samples impregnated with a modified Cu(II)-phthalocyanine (TiO₂-CuPc) was reported along with an investigation on the photocatalytic behavior of this system compared with bare TiO₂ (both in the anatase and rutile forms) and with TiO₂ samples impregnated with not functionalized commercial phthalocyanine (TiO₂-CuPc) or with metal free phthalocyanine (TiO₂-Pc). The photocatalytic degradation of 4-nitrophenol was studied as a probe reaction. The presence of modified CuPc showed to be beneficial only for TiO₂ (anatase) while the commercial not functionalized CuPc also slightly showed for both TiO₂ (anatase) and TiO₂ (rutile). The metal free Pc did not show any beneficial influence on the photoactivity. A tentative explanation of the beneficial effect due to the presence of the Cu(II)-phthalocyanines both on the initial reaction rate and on the mineralization

process was provided by taking into account intrinsic electronic and physico-chemical properties³².

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CHAPTER III

OBJECTIVES

The objectives of this work are;

1. Study of a method for synthesizing and characterizing titanium glycolate and titanium triisopropanolamine precursors.
2. Study of the sol-gel process and viscoelastic property of titanium glycolate.
3. Study of the sol-gel process of mixed titanium glycolate and silatrane precursors.
4. Preparation of a mixed matrix membrane to study its photo-catalytic property, selectivity and permeability.

CHAPTER IV

OXIDE ONE POT SYNTHESIS OF A NOVEL TITANIUM GLYCOLATE AND ITS PYROLYSIS

Abstract

A much milder, simpler and more straightforward reaction to titanium glycolate product was successfully investigated by the reaction of titanium dioxide, ethylene glycol and triethylenetetramine using the oxide one pot synthesis (OOPS) process. FT-IR spectrum demonstrates the characteristics of titanium glycolate at 619 and 1080 cm^{-1} assigned to Ti-O stretching and C-O-Ti stretching vibration, respectively. ^{13}C -solid state NMR spectrum gives two peaks at 75.9 and 79.8 ppm due to the relaxation of the crystalline spiro titanate product. The percentage of carbon and hydrogen from elemental analysis are 28.6 and 4.8, respectively. Thermal analysis study from TGA exhibits one sharp transition at 340°C, corresponding to the decomposition transition of organic ligand, and giving a ceramic yield of 46.95% which is close to the theoretical yield of 47.5%. XRD patterns show the morphology change of its pyrolyzed product from anatase to rutile as increasing calcination temperatures from 500° to 1100°C while at 300°C the amorphous phase is formed.

Keywords: Titanium Dioxide, Titanium Glycolate, Oxide One Pot Synthesis, Pyrolysis, Phase Transformation

Introduction

Titania is a very useful material and has received a great attention in recent years for its humidity- and gas-sensitive behavior, excellent dielectric property, as well as catalysis applications.¹ The important factor to produce titania with good properties is the purity of titanium alkoxide precursor. However, the synthesis of titanium alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity and very expensive starting materials. In this work a great interest in titanium glycolate, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$, is owing to its difference from most crystalline titanium alkoxides, generally having low polymeric O-dimensional molecular. Nevertheless, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ is a novel crystalline complex with infinite one-dimensional chains, and exhibits outstanding high stability not only in alcohol, but also in water.²

The method required for the synthesis of alkoxy derivatives of an element generally depends on its electronegativity. In the case of comparatively less active metals, a catalyst is generally employed for successful synthesis of metal alkoxides. Wang *et al.*² synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ from very expensive starting material, tetraethyl orthotitanate to react with ethylene glycol using *n*-butylamine as a catalyst. The reaction took place under a very vigorous condition. It occurred in a Teflon-lined stainless steel autoclave at 160°-180 °C for 5 days. The alkalinity of the initial reaction mixture is a dominant factor of the product. The ethylene glycol served as both a solvent and a bidentate chelate occupying sites on titanium coordination sphere so as to bridge adjacent titanium atoms and formed the one-dimensional structure.

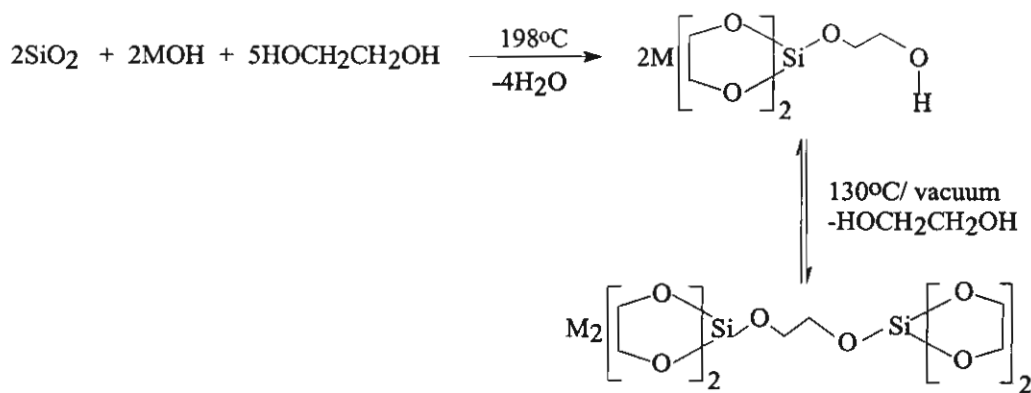
Gainsford *et al.*³⁻⁴ studied the synthesis and characterization of the soluble titanium glycolate complexes obtained from the reaction of titanium dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxides. The reaction of $\text{Ti}(\text{O-}i\text{-Pr})_4$ with 2 equivalent of sodium or potassium hydroxides provided tris(glycolate) salts, which were highly crystalline, hygroscopic materials, crystallized as salts and solvated with varying numbers of glycol molecules.

Suzuki *et al.*⁵ synthesized titanium tetraalkoxides from hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) and dialkyl carbonates in an autoclave at a heating rate of 90K h^{-1} . The effect of reaction temperature was studied. At temperature range of 495-533 K, practically completed conversion of hydrous titanium dioxide to $\text{Ti}(\text{OEt})_4$ could be attained. LiOH, NaOH, KOH, and CsOH were used as catalysts which NaOH gave the highest yield of $\text{Ti}(\text{OEt})_4$. The effect of the molar ratios of diethyl carbonate/hydrous

titanium dioxide was studied. As high molar ratio of 10 was required to obtain a high yield of $\text{Ti}(\text{OEt})_4$.

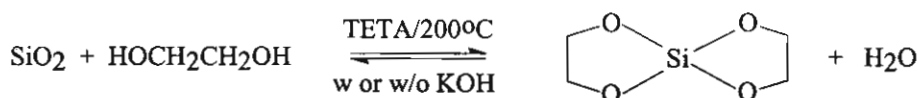
Related metalloglycolates formed from alkaline glycol were reported for aluminium and titanium⁶⁻¹¹. Potassium and sodium tris(glycotitanate) complexes were obtained from the reaction of titanium dioxide or titanium tetraisopropoxide with ethylene glycol in the presence of alkali metal hydroxides.³⁻⁴

Laine *et al.* investigated a straightforward, low-cost route to alkoxide precursors by direct reactions of a stoichiometric mixture of silica and group I metal hydroxide with ethylene glycol. This route, termed the 'oxide one pot synthesis' (OOPS) process, provides processable precursors, as shown in Scheme 1.¹²⁻¹⁴



Scheme 1

Recently, Jitchum *et al.* synthesized neutral alkoxysilanes, tetracoordinated spiro-silicates, directly from silica and ethylene glycol or ethylene glycol derivatives, using triethylenetetramine as catalyst, in the absence or presence of potassium hydroxide as co-catalyst (Scheme 2).¹⁵



Scheme 2

The OOPS method is simple, low-cost and can produce new chemicals in only one step. Thus, the objective of this work is to use the OOPS process to synthesize titanium glycolate. The phase transformation of its pyrolyzed product is studied, as well.

Experimental

Materials

UHP grade nitrogen; 99.99% purity, was obtained from Thai Industrial Gases Public Company Limited (TIG). Titanium dioxide was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG), purchased from Malinkrodt Baker, Inc. (USA) was purified by fractional distillation under nitrogen at atmospheric pressure, 200°C before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by standard distilling over calcium hydride powder.

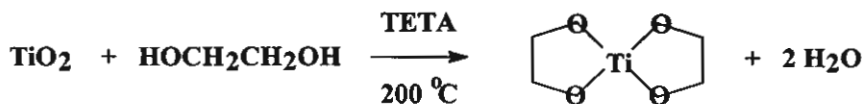
Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm⁻¹ using transparent KBr pellets containing 0.001 g of the sample was ground and mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10 °C/min over 30°-800°C temperature range. Mass spectrum using the positive fast atom bombardment mode (FAB⁺-MS) was measured on a Fison Instrument (VG Autospec-ultima 707E) with VG data system using glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. ¹³C- solid state NMR spectroscopy modeled Bruker AVANCE DPX-300 MAS-NMR was used to determine peak position of carbon containing in the product. Elemental analysis (EA) was carried out on a C/H/O Analyser (Perkin Elmer PE2400 series II). X-ray diffraction patterns were analyzed using a D/MAX-2200H Rigaku equipped with Cu X-ray generator.

Methodology

The titanium glycolate was synthesized by the OOPS method, see Scheme 3. A mixture of TiO₂ (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated at the boiling point of EG under N₂ atmosphere. After heating for 24 h the solution was centrifuged to separate the unreacted TiO₂ from the

solution part. The excess EG and TETA were removed by vacuum distillation to obtain crude precipitate product. The white solid product was washed with acetonitrile and dried in a vacuum desiccator.



Scheme 3

Results and Discussion

Synthesis

The reaction of titanium dioxide, triethylenetetramine catalyst and ethylene glycol used as both solvent and reactant was achieved by heating in a simple distillation apparatus. The glycol was slowly distilled off along with water generated during the condensation reaction to drive the reaction forward. The resulting product was isolated by distilling off glycol, followed by addition of acetonitrile to remove residual glycol and TETA. The final product, titanium glycolate, was moisture-stable.

Characterization

FT-IR spectrum of titanium glycolate is shown in Figure 1. As compared with the work done by Wang², the result clearly shows the characteristics of titanium alkoxide at 1080 and 619 cm^{-1} bands, corresponding to C-O-Ti and Ti-O stretching, respectively. Moreover, the band at 2927-2855 cm^{-1} is assigned to the C-H stretching of ethylene glycol ligand.

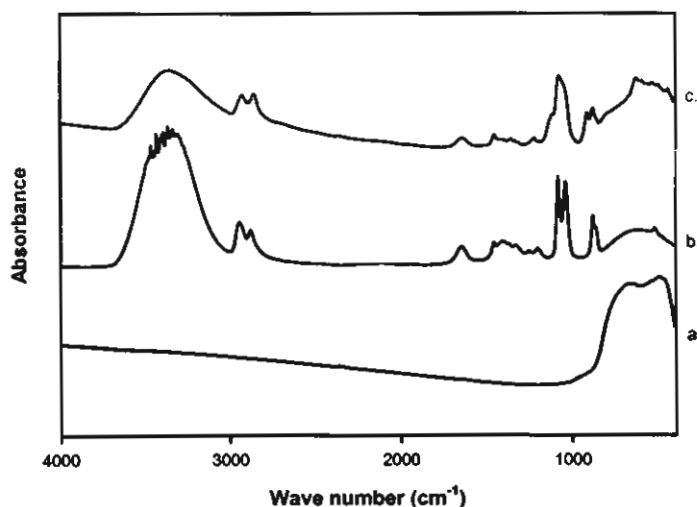


Figure 1 FT-IR spectra of a) TiO_2 , b) $\text{HOCH}_2\text{CH}_2\text{OH}$ and c) $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

Due to the insolubility of the product in organic solvent, ^{13}C -solid state NMR was employed. The obtained spectrum, see Figure 2, gives two peaks at 74.8 and 79.2 ppm. It is due to the crystalline phase of titanium glycolate, causing the peak to split during relaxation time of nuclei, as discussed by Wang.²

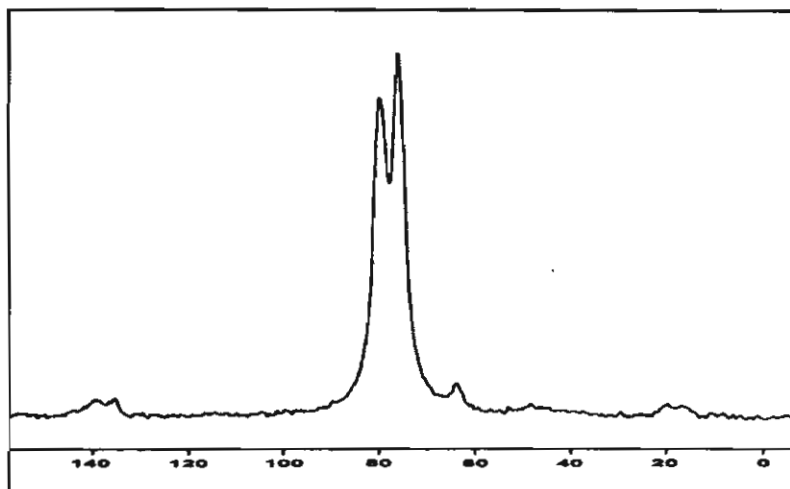


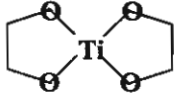
Figure 2 ^{13}C -Solid state NMR spectrum of the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

To confirm the structure of the desired product, both elemental analysis and mass spectroscopy techniques are carried out. The results are shown in Tables 1 and 2, respectively. The obtained C/H percentages are close to those calculated theoretically. The proposed fragmentation and structures presented in Table 2 also confirms the expected structure of the titanium glycolate product.

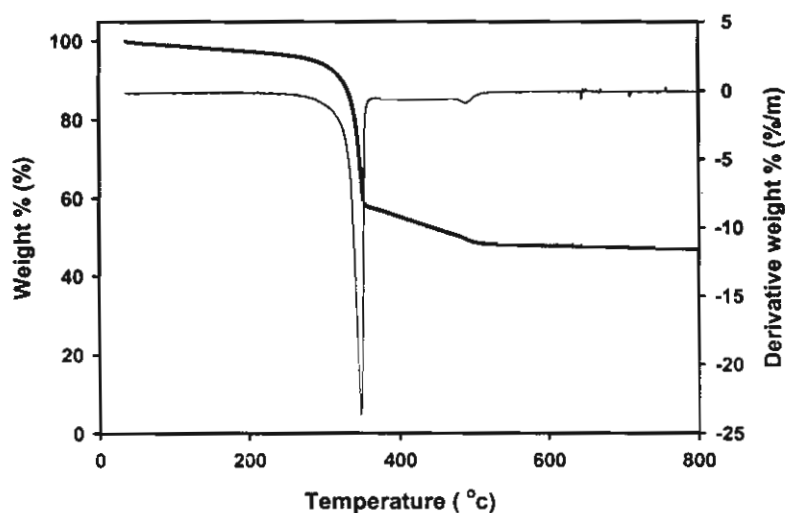
Table1 Percentages of C and H presented in the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

Element (%)	Theoretical	Experimental
C	27.9	28.6
H	5.6	4.8

Table 2 Proposed fragmentation and product structures of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

M/e	%intensity	Proposed structure
169	8.5	 + H^+
94	73.5	O-Ti-OCH_2
45	63.5	$\text{CH}_2\text{CH}_2\text{OH}$

As for its thermal stability, Figure 3 shows the same TGA thermogram as obtained by Wang². The result exhibits one sharp transition at 340°C , corresponding to the decomposition transition of the glycol ligand. The final ceramic yield obtained is 46.95% that is close to the theoretical yield of 47.5%.

Figure 3: TGA curve of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

Phase transformation

The TGA result indicates the oxidation of organic compound at 340°C , and the crystallization at 500°C . Study of the phase transformation was conducted at the calcinations temperature ranging from 300° to 1100°C . The crystalline titanium glycolate decomposed and changed to amorphous phase at 300°C (Figure 4). As

increasing the calcination temperature, the XRD pattern gives anatase phase at 500 °C to 900 °C and completely changes to rutile phase at 1100°C.

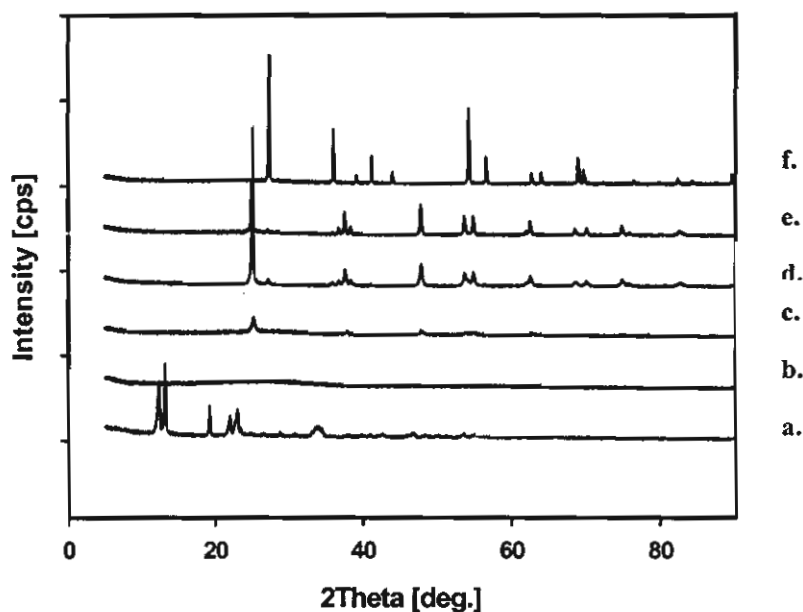


Figure 4 XRD patterns of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ at different temperatures: a) ambient, b) 300°, c) 500°, d) 700°, e) 900° and f) 1100°C.

Conclusions

Titanium glycolate is successfully synthesized using low cost starting materials, and a much simpler and milder reaction condition. The product shows good property in moisture stability. The results from spectroscopy, namely, FT-IR, EA, Solid state NMR, and TGA, confirm the product structure. The transformation from anatase to rutile phase indicates the anatase stability up to 900°C. The stability of the synthesized product remarkably provides researchers to make use in many applications.

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CHAPTER V

STRUCTURAL AND RHEOLOGICAL ASPECT OF MESOPOROUS NANOCRYSTALLINE TiO_2 SYNTHESIZED VIA SOL-GEL PROCESS

Abstract

Mesoporous nanocrystalline titanium dioxide was prepared via the sol-gel technique using titanium glycolate as precursor in 1M HCl solution at various HCl:H₂O ratios. XRD analysis indicates the anatase phase forms at calcination temperatures in the range 600°-800°C. From the average grain sizes, we deduce that the nucleation rate dominates the kinetics at lower temperature, and growth rate becomes the controlling factor at higher temperature for materials prepared at HCl:H₂O ratios of 0.28 and 0.33. At higher volume ratios, the growth rate appears to be the dominant factor at all temperatures. The highest specific surface area (BET) obtained was 125 m²/g at the HCl:H₂O ratio of 0.28. A small decrease of specific surface area was observed from low to high acid ratio and a substantial decrease from lower to higher temperature. The material calcined at 800°C was found to consist primarily of spherical particles with diameters smaller than 1 μ . Application of the Winter rheological criteria for the gel point indicates that the gelation time increases with increase of the HCl:H₂O volume ratio. The fractal dimension of the critical gel cluster decreases with acid ratio, whereas the gel strength increases with acid ratio. Thus increase of acidity leads to a less dense but stronger network structure.

Keywords: Titanium glycolate, Titania, Rheology, Sol-gel process and Viscoelastic properties

Introduction

Titanium dioxide or titania, TiO_2 , is widely used in the field of catalysis, as filters, adsorbents, and catalyst supports¹⁻². The porous anatase form, as compared to the rutile phase, is of greater importance and interest due to its better catalytic properties. Therefore, a key goal is to prepare anatase nanoparticles, with high surface area, uniform particle size and pore structure, and a high anatase-rutile transformation temperature³.

Sol-gel processing has become one of the most successful techniques for preparing nanocrystalline metallic oxide materials. In general, this method involves the hydrolysis and polycondensation of a metal alkoxide, to ultimately yield hydroxide or oxide under well-specified reaction conditions⁴. The key advantage of preparing metallic oxides by the sol-gel method is the possibility to control their microstructure and homogeneity. To obtain homogeneous nanoscale macromolecular oxide networks via sol-gel processing, control of hydrolysis is essential. The properties and nature of the product are controlled by the particular alkoxide used, the presence of acidic or basic additives, the solvent, and various other processing conditions (e.g. temperature). The calcination temperature is also a key factor, especially for titania preparation. Too low a temperature results in incomplete combustion and too high a temperature causes phase transformation.

Many studies have been directed to prepare titania powder with increased textural and structural stability. For example, Zhang *et al.*⁵ prepared and studied mesoporous nanocrystalline TiO_2 by a sol-gel technique using butanediol mixed with tetrapropylorthotitanate. A surface area of $97 \text{ m}^2/\text{g}$ was obtained after calcination at 400°C for 2h. Wei *et al.*⁶ prepared nanodisperse spherical TiO_2 particles by forced hydrolysis using boiling reflux $\text{Ti}(\text{SO}_4)_2$ solution in the presence of H_2SO_4 . The particle size distribution was in the range 70-100 nm. Sun *et al.*⁷ prepared nanosized anatase titania with average grain sizes ranging from 7.4 to 15.2 nm using MOCVD technology to pyrolyze titanium tetrabutoxide in an oxygen containing atmosphere. The smallest average grain size and the highest surface area were obtained at 700°C . Kim *et al.*⁸ synthesized ultrafine titania particles by hydrolysis of titanium tetraisopropoxide (TTIP) in the aqueous cores of water/NP-5/cyclohexane microemulsions with increasing calcination temperature from 300° to 700°C , the specific surface area of the TiO_2 particles decreased from 325.6 to $5.9 \text{ m}^2/\text{g}$, whereas the average pore radius increased

from 1.4 to 25.1 nm. Wu *et al.*⁹ synthesized nanocrystalline titanium dioxide using the sol-hydrothermal method with titanium *n*-butoxide (TNB) as precursor, in various acidic media (HCl, HNO₃, H₂SO₄, and CH₃COOH). Nanocrystals of pure rutile with size < 10 nm were obtained at higher HCl concentrations under mild conditions. The propensity of acidic medium for rutile formation is shown as follows: HCl > HNO₃ > H₂SO₄ > HAc.

Knowledge of the evolution in rheological properties during sol-gel processing is a useful guide to the manufacturer when formulating dispersions to optimize the physical properties required in the final product¹⁰. Thus, in this work, our aims are to synthesize high surface area anatase TiO₂ and to study the rheological properties of titanium glycolate synthesized directly from inexpensive and widely available TiO₂ and ethylene glycol via the Oxide One Pot Synthesis (OOPS) method¹¹. We also investigate the influence of the acid concentration used in acid-catalyzed hydrolysis, the effect of calcination temperature on morphology and phase transformation, and gain some insight into the gel mechanism.

Experimental

Materials

Titanium dioxide (surface area 12 m²/g) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinkrodt Baker, Inc. (USA) and purified by fractional distillation at 200°C under nitrogen at atmospheric pressure, before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder.

Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm⁻¹ using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over 30°-800°C temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) with VG data system, using

the positive fast atomic bombardment mode (FAB⁺-MS) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. ¹³C-solid state NMR spectroscopy was performed using a Bruker ADVANCE DPX-300 MAS-NMR. Elemental analysis (EA) was carried out on a C/H/N Analyser (Perkin Elmer PE2400 series II).

Preparation of titanium glycolate

The procedure adopted followed previous work¹¹. A mixture of TiO₂ (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR, ¹³C-solid state NMR, EA, FAB⁺-MS, and TGA.

FTIR: 2927-2855 cm⁻¹ (νC-H), 1080 cm⁻¹ (νC-O-Ti bond), and 619 cm⁻¹ (νTi-O bond). ¹³C-solid state NMR: two peaks at 74.8 and 79.2 ppm. EA: 28.6% C and 4.8% H. FAB⁺-MS: approximately 8.5% of the highest m/e at 169 of [Ti(OCH₂CH₂O)₂]⁺H⁺, 73% intensity at 94 of [OTiOCH₂] and 63.5% intensity at m/e 45 of [CH₂CH₂OH]. TGA: one sharp transition at 340°C and 46.95% ceramic yield corresponding to Ti(OCH₂CH₂O)₂.

Sol-gel processing of titanium glycolate

The hydrolysis of titanium glycolate (0.026 g) was carried out via addition of 160 μL of 1M HCl mixed with distilled water in volume ratios of HCl:H₂O 0.45, 0.39, 0.33, and 0.28. The mixtures were magnetically stirred and heated in a water bath at 50°C until a clear gel was obtained. The gels were calcined for 2 h at 600°, 700°, and 800°C.

Rheological study of titanium glycolate

Gelation occurs when aggregation of particles or molecules takes place in a liquid, under the action of Van der Waals forces or via the formation of covalent or noncovalent bonds¹². The process can be conveniently monitored using rheological measurement techniques¹³. The rheometric measurements were conducted using an ARES rheometer with parallel plate geometry, 25 mm in diameter. The storage (G') and loss (G'') moduli were determined using oscillatory shear at frequencies in the range 0.2-6.4 rad/s. The strain amplitude was small enough to ensure that all experiments

were conducted within the linear viscoelastic region, where G' and G'' are independent of the strain amplitude. Titanium glycolate 0.026 g was hydrolyzed at different HCl:H₂O volume ratios of 0.45, 0.39, 0.33 or 0.28. The hydrolysis temperature was selected to be 30°C. The mixtures were stirred until homogeneous before being transferred to the rheometer.

Characterization of calcined materials

Crystallinity and average grain sizes were characterized using a D/MAX-2200H Rigaku diffractometer with CuK α radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range between 5° to 90°. Specific surface area, nitrogen adsorption-desorption, and pore size distribution were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 cc/min. Nitrogen was used to calibrate the analyzer, and also as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2h at 150°C, prior to exposure to the adsorbent gas. Material morphology was observed using a JEOL 5200-2AE(MP 15152001) scanning electron microscope. Samples were prepared for SEM analysis by attachment to aluminum stubs, after pyrolysis at 800°C. Prior to analysis, the specimens were dried in a vacuum oven at 70°C for 5 h followed by coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at x10,000 magnification.

Results and discussion

The investigation of the hydrolysis reaction of titanium glycolate precursor using FTIR is illustrated in figure 1. The spectra show an increase in the peak intensity of Ti-O-Ti stretching at approximately 500-800 cm⁻¹ due to hydrolysis of the precursor. The peak at 1000-1100 cm⁻¹, corresponding to C-O stretching of ethylene glycol also increases, reflecting the production of ethylene glycol during the hydrolysis reaction. In the case of higher acid ratio (0.45), the degree of crosslinking is greater than those obtained from the hydrolysis in lower acid ratios. The acid can act as a catalyst to hydrolyze the alkoxide by protonating the ethoxy ligands during hydrolysis. Thus, the

elimination of the protonated ethoxy ligand leaving group is no longer the rate limiting step, and, as a result, the hydrolysis occurs more rapidly.

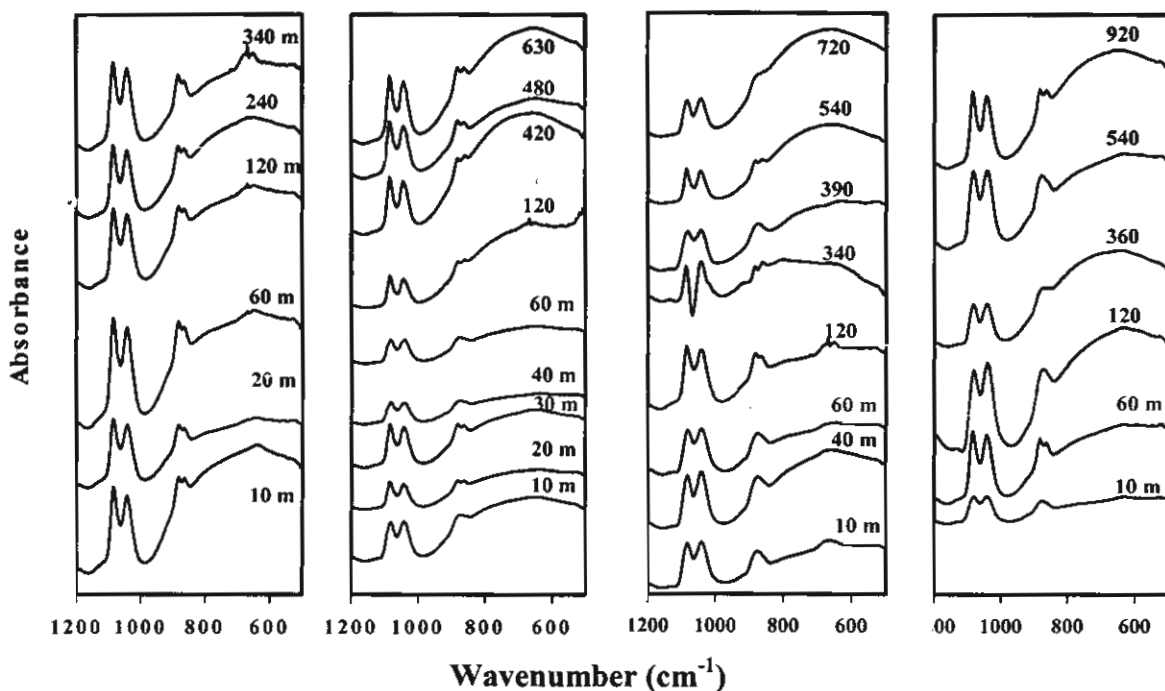


Figure 1 FT-IR spectra of titania gel at HCl:H₂O volume ratios of a) 0.28, b) 0.33, c) 0.39 and d) 0.45

Calcination is a treatment commonly used to improve the crystallinity of TiO₂ powder. When TiO₂ is calcined at higher temperature, a transformation to rutile phase usually occurs¹³ and comprises anatase, rutile, and brookite. XRD patterns (Fig. 2) show the phase transformations encountered when titanium glycolate precursor is calcined at temperatures in the range 300°-1100°C. Amorphous material is obtained at the lowest temperature (300°C) whereas at 500°C broader anatase peaks appear. As the calcination temperature increases, the intensity of anatase peaks becomes stronger and well resolved. However, if the calcination temperature is increased to 900°C, small rutile peaks are found, indicating the onset of the transformation to rutile.

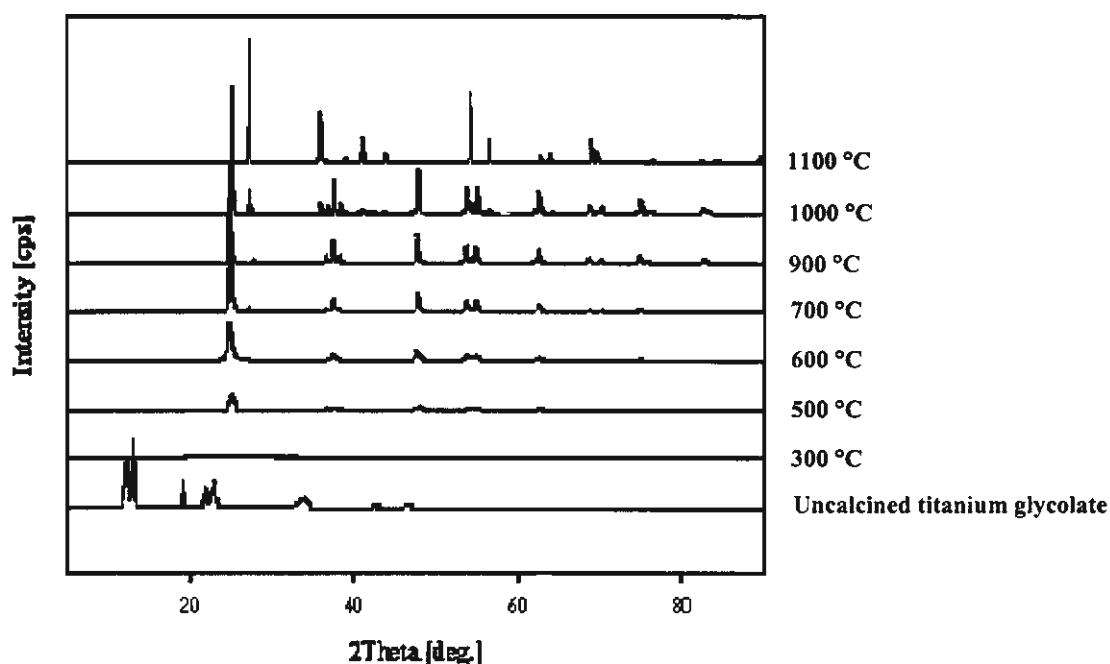


Figure 2 XRD patterns of uncalcined and calcined titanium glycolate precursor at different temperatures.

The synthesis procedure was changed to obtain porous anatase for better catalytic properties. Specimens obtained via the sol-gel process at different volume ratios of $\text{HCl}:\text{H}_2\text{O}$, viz. 0.45, 0.39, 0.33, and 0.28, were subjected to calcination at 600°, 700°, and 800°C, to obtain porous anatase titania³. Fig. 3 shows the XRD patterns of anatase formation in a specimen at the $\text{HCl}:\text{H}_2\text{O}$ volume ratio of 0.28. Our results indicate that the synthesized anatase is stable up to calcination temperatures of 800°C, which is a little higher than previous studies, which report the transformation of anatase to rutile in the range of 600°-700°C^{7, 13-14}.

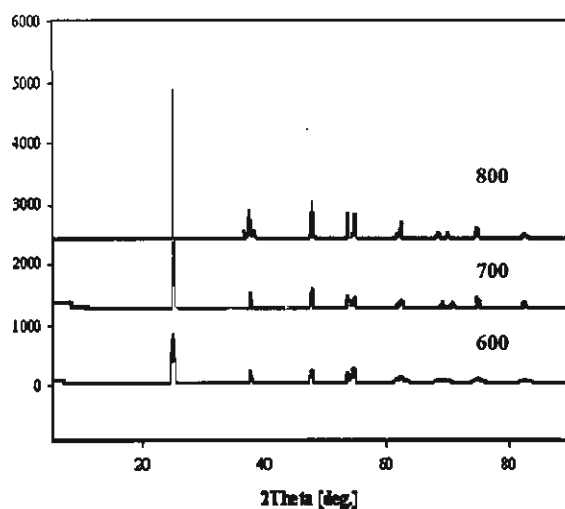


Figure 3 XRD patterns of titania gel using the $\text{HCl}:\text{H}_2\text{O}$ volume ratio of 0.28 and calcined at a) 600°, b) 700° and c) 800°C.

As can be seen in Fig. 4, at 0.28 and 0.33 ratios, the average grain size decreases significantly from 600°C (18.8 and 17.1 nm) to 700°C (13.9 and 14.2 nm) and then increases substantially again at 800°C (31.3 and 29.8 nm). These results are reminiscent of observations by Sun et al⁷ of the temperature dependence of grain sizes of anatase produced by the MOCVD method. The size variation was interpreted in terms of the rate of particle growth relative to the rate of particle nucleation. Use of elevated temperatures accelerates not only the nucleation rate but also the particle growth rate. For acid:water ratios of 0.28 and 0.33, at lower temperatures, the nucleation rate is dominant, whereas the growth rate becomes the controlling factor at higher temperature. Acid:water ratios of 0.39 and 0.45 ratios show a slightly different pattern, in which grain size increases mildly between 600° and 700°C, and then more dramatically at 800°C, suggest that the growth rate is dominant at all temperatures.

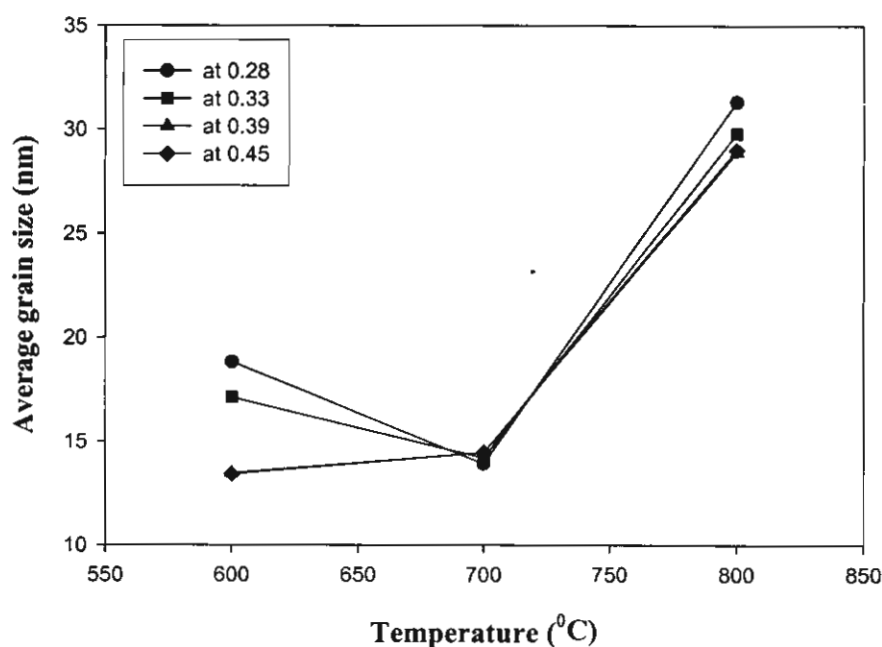


Figure 4 The average grain sizes of the particles prepared at different volume ratios of HCl:H₂O (0.28, 0.33, 0.39, 0.45, respectively) and different calcination temperatures (600°, 700° and 800°C).

Coincidentally, the nitrogen adsorption-desorption isotherm of the material obtained at 0.28 HCl:H₂O volume ratio and calcined at 600°C for 2h indicates a mesoporous structure, as seen in figure 5(a). The isotherm is of type IV, characteristic

of mesoporous material. The hysteresis loop exhibited by the specimen is mainly of type H2. The pore size distribution in figure 5(b) shows a major porosity in the range of 4-18 nm. To confirm an increase in crystallinity as temperature increases, specific surface area measurements were carried out and, as expected, we find that the higher the calcined temperature, the lower the specific surface area. The powders become dense and predominantly nonporous when the precursor is calcined at 800°C. It is known that a lower acid concentration results in a higher specific surface area due to an increasing in the cross-linking level³. This is consistent with our observation that the specific surface area decreases in the following order; 0.28 > 0.33 > 0.39 > 0.45 (Table 1). It can be concluded that sol-gel processing indeed provides a larger specific surface area which decreases with increasing calcinations temperature and acid concentration.

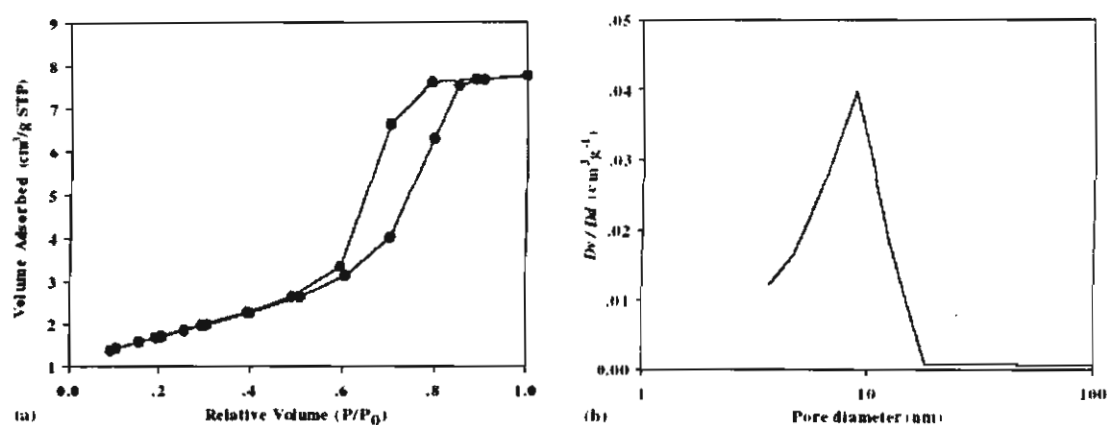


Figure 5 The nitrogen adsorption-desorption isotherm for mesoporous titania (a.) and Pore size distribution (b.) for the material obtained from 0.28 HCl:H₂O volume ratio and calcined at 600°C

Table 1 BET surface area (S_{BET} , m²/g) of titania at various HCl:H₂O volume ratios and calcinations temperatures.

Temperature (°C)	Surface area (m ² /g)/ HCl:H ₂ O			
	0.28	0.33	0.39	0.45
600	125	111	107	105
700	60	59	55	50
800	20	18	17	15

* Surface area of the starting material TiO₂ = 20 m²/g

The particle morphology of the samples obtained using a HCl:H₂O ratio of 0.33, when calcined at temperatures in the range 600°-800°C, is shown in Fig. 6. At the lowest two temperatures, Figs. 6(a) and 6(b), the material consists of particles of large size, whereas the micrograph (Fig. 6c) of the material calcined at 800°C shows a finely-divided morphology in the anatase form consisting of spherical particles approximately 1 μm in size.

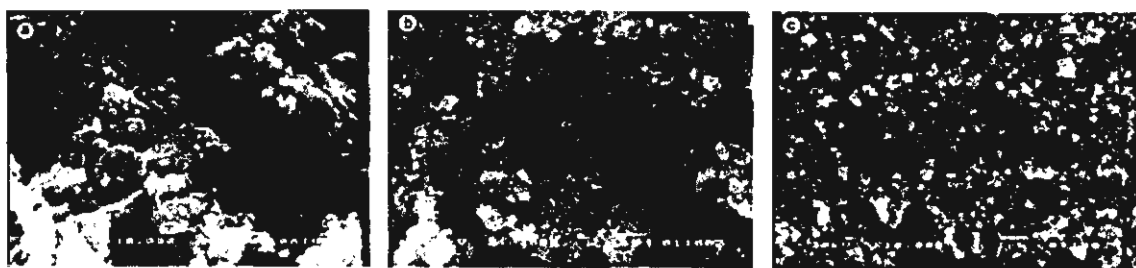


Figure 6 SEM micrographs of titania powder prepared at 0.33 volume ratio of HCl:H₂O and calcined at a.) 600°, b.) 700° and c.) 800°C

Viscoelastic studies of the four different gelling systems (volume ratios of 0.28, 0.33, 0.39, and 0.45 of HCl:H₂O, respectively) were carried out using the criteria proposed by Winter and Chambon¹⁵ to determine the gel point, as the gelation time where a frequency-independent value of $\tan\delta$ is observed. The variation in the frequency-dependence of $\tan\delta$ with gelation time is shown in fig. 7, and indeed indicates $\tan\delta$ become frequency independent at a particular gelation time. The shortest gelation time was observed for the system at 0.28 volume ratio (365 s) and the longest gelation time for the system of 0.45 volume ratio (870 s). An alternative method¹⁶ to determine the gel point is to plot the time evolution of the apparent viscoelastic exponents n' and n'' obtained from the frequency-dependence of the modulus ($G' \propto \omega^{n'}$, $G'' \propto \omega^{n''}$), as shown in fig. 8 for the system at 0.45 volume ratio. The gel point is identified as the time where a crossover $n'=n''=n$ is observed. The points of intersection (t_{gel}) are found to be the same as those deduced from the plot of $\tan\delta$ versus time.

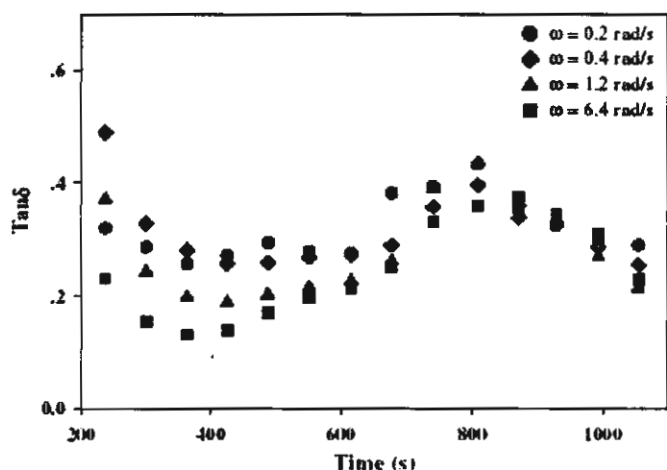
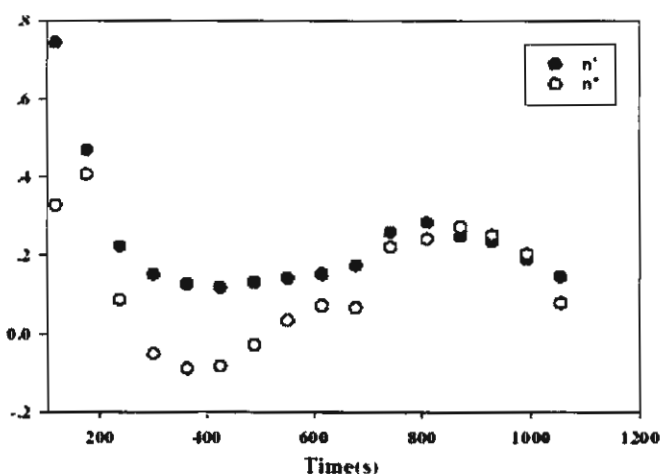


Figure 7 The plots of $\tan\delta$ with time(s) at HCl:H₂O volume ratio of 0.45

Figure 8 The plots of the apparent exponents, the storage moduli (n') and the loss moduli (n'') during the course of gelation for the 0.45 acid ratio.



It is important to note that these gelling systems are highly elastic even well before the gel point, as evidenced by the fact that $\tan\delta \ll 1$. Also, the system rheology evolves relatively slowly in the vicinity of the gel point, as seen by plotting the frequency dependence of G' (Pa), G'' (Pa) at pregel stage, gel point, and postgel stage, shown in fig. 9. The data are shifted horizontally by a factor B. A similar trend is observed for all systems in that G' is higher than G'' , i.e. elastic behavior predominates before as well as after the gel point. We attribute this behavior to the fact that we are dealing with a concentrated colloidal dispersion, which is converted to a gel by hydrolysis from the outer surfaces of the colloidal particles. Despite this heterogeneous structure, at the gel point, the systems fulfill the Winter criteria that $n' = n'' = n_{gel}$, and $\tan\delta = \tan(n_{gel}\pi/2)$ are superimposed¹⁵⁻¹⁹. The viscoelastic exponent n_{gel} of the system as shown in table 2 has its highest value at 0.45 volume acid ratio and the value decreases as the volume acid ratio decreases. Figure 10 shows the effect of HCl:H₂O volume ratio

on the gel strength parameter, S , evaluated from the relationship¹⁶⁻¹⁹ $G'(\omega) = \Gamma(1-n)\cos(n\pi/2)S\omega^n$ where $\Gamma(1-n)$ is the Legendre Γ function. It is evident that the gel strength increases with increasing acid ratio and reaches its highest value acid ratio = 0.39, then decreases slightly. Thus, at low acid ratio, the critical gel cluster is relatively weak, at high acid ratio it is stronger.

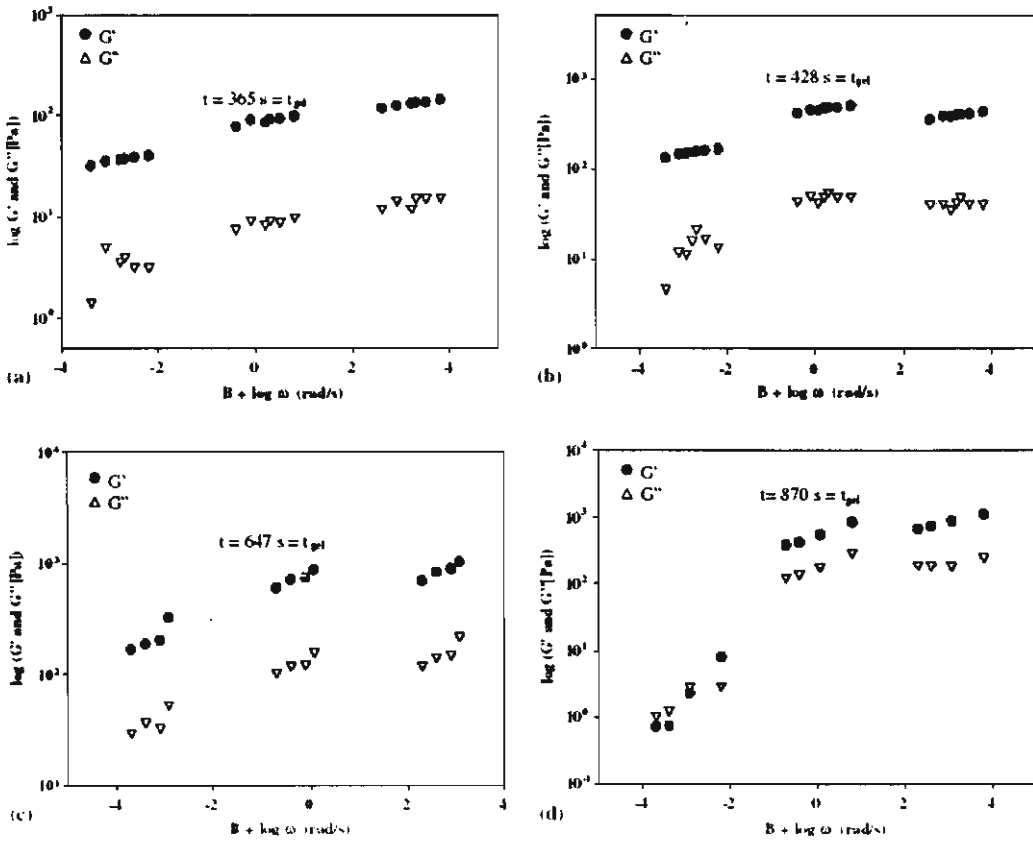
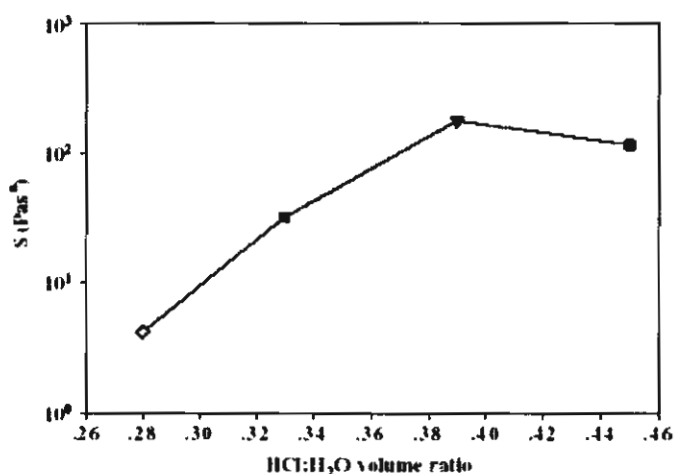


Figure 9 The frequency dependence curves of $G'(\omega)$ and $G''(\omega)$ at (●) pregel stage ($B = -3$), (■) gel point, and ($B = 0$), and (▲) postgel stage ($B = 3$) of a.) 0.28, b.) 0.33, c.) 0.39 and d.) 0.45 HCl:H₂O ratios.

Figure 10 The plot of gel strength parameter S at the gel point as a function of HCl:H₂O volume ratio: 0.28 (◆), 0.33 (■), 0.39 (▲) and 0.45 (●).



According to the model of Muthukumar²⁰ the fractal dimension of the critical gel cluster can be obtained from the viscoelastic exponent n as $n = d(d+2-2d_f)/2(d+2-d_f)$ where d = spatial dimension = 3. The effect of acid ratio on the fractal dimension of incipient gel is shown in fig. 11 and table 2. The fractal dimension decreases with increasing the acid ratio. A lower fractal dimension mean that the molecular weight grows slower with radius, i.e. $M \sim R^{d_f}$. Thus the critical gel at high acid ratio has a more open structure than at low acid ratio. This is somewhat surprising since we expect the cross-link density to be higher at higher acid ratio. Again we attribute this result to the heterogeneous character of the system at the gel point. The particles which comprise the gel network at low acid ratio are less hydrated and hence more dense than those at higher acid ratio.

Figure 11 The plot of fractal dimension of the critical gel cluster as a function of acid ratio

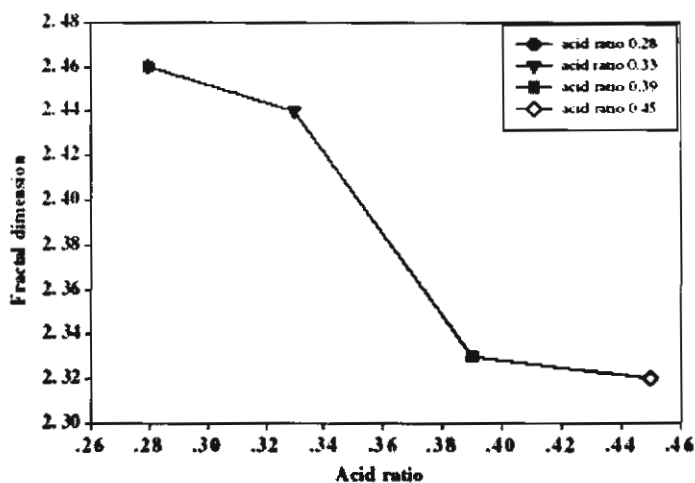


Table 2 Summary of viscoelastic exponent, fractal dimension, and gelation time(s) at various HCl:H₂O volume ratios.

Acid ratio	n	d _f	Gelation time (s)
0.28	0.05	2.46	365
0.33	0.07	2.44	428
0.39	0.19	2.33	647
0.45	0.20	2.32	870

Figure 12 shows the frequency dependence of the dynamic viscosity at pregel stage, gel point, and postgel stage. Consistent with the highly elastic behavior evident in figure 9, at all stages $\eta^*(\omega)$ exhibits power law frequency dependence with an exponent at the gel point of $n-1$. The time dependence of the complex viscosity at low frequency ($\omega = 0.4$ rad/s) is illustrated in fig. 13. The location of the gel point for each system as determined by the Winter criteria¹⁶⁻¹⁹ are indicated by arrows. At low acid ratio, the viscosity is initially high but approaches an asymptotic value which is relatively low. At high acid ratio, the viscosity is initially low but reaches a high asymptotic value. Thus, the gel strength and asymptotic complex viscosity are self-consistent and indicate that the gel becomes stronger under high acidity conditions. We interpret these results as indicating that at low acid, the precursor particles are poorly hydrated and form a more heterogeneous weak gel structure. At high acid, the particles are well solvated and form a less heterogeneous (more open) yet stronger network.

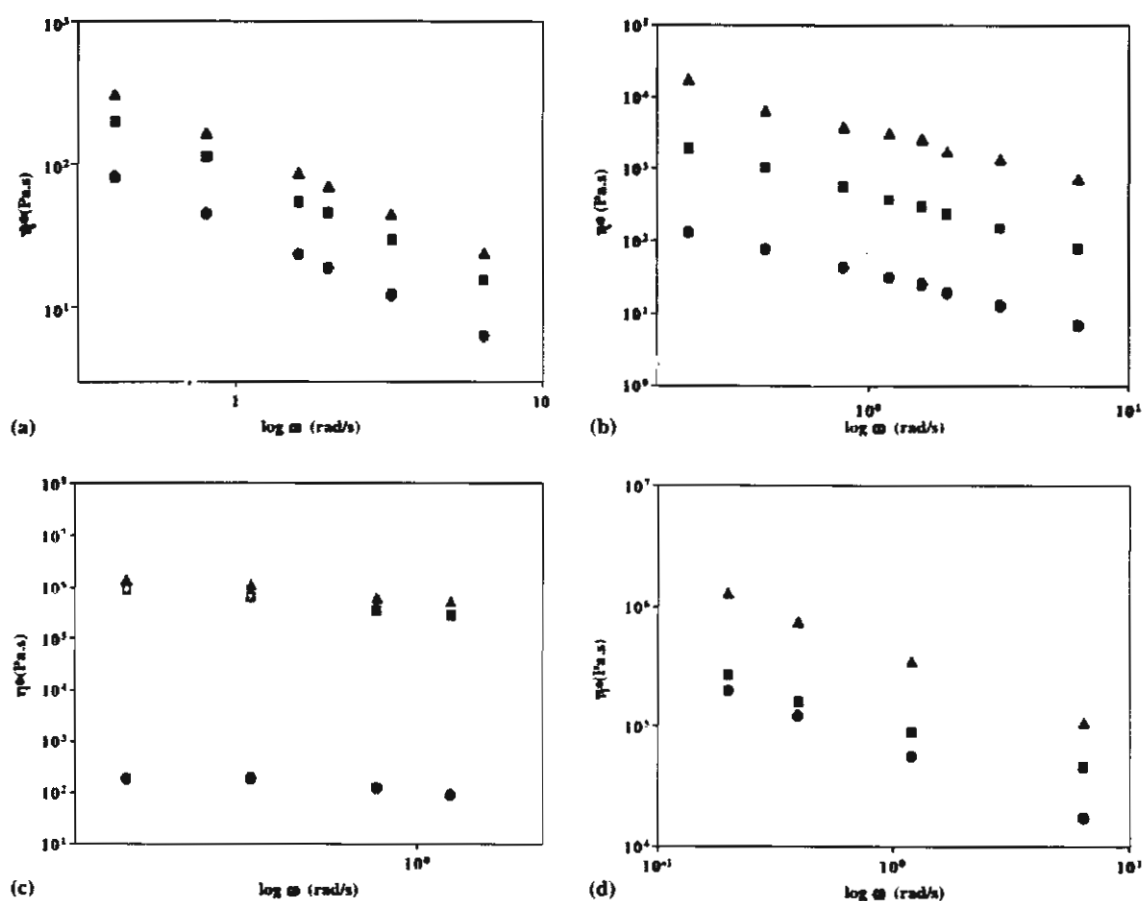


Figure 12 The effect of frequency on the complex viscosity at pregel stage, gel point, and postgel stage of a.) 0.28, b.) 0.33, c.) 0.39 and d.) 0.45 HCl:H₂O volume ratios

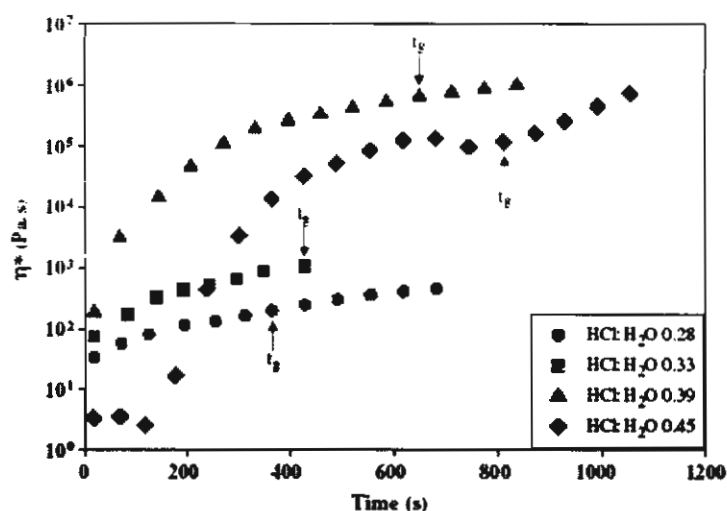


Figure 13 The time evolution of the complex viscosity (at fixed frequency of 0.4 rad/s) of a) 0.28, b) 0.33, c) 0.39 and d) 0.45 HCl:H₂O volume ratio

Conclusions

Anatase TiO₂ nanoparticles were successfully prepared by sol-gel technology, using inexpensive and moisture-stable titanium glycolate as precursor in 1M HCl solution. The calcination temperature and the HCl:H₂O volume ratio has a substantial influence on the surface area, phase transformation, and morphology of the products. Anatase titania is produced at calcination temperatures in the range 600° to 800°C, above which transformation to rutile occurs. Increase of temperature results in anatase of higher crystallinity but lower specific surface area, and induces a morphological change from large irregular agglomerates to more homogeneous particles of spherical shape. From XRD measurements of average grain sizes, we deduce that nucleation rate dominates the kinetics at low temperatures, and growth rate becomes the controlling factor at high temperature and low HCl:H₂O ratios. Increase of HCl:H₂O ratio results in a small but significant decrease in porosity. The highest specific surface area 125 m²/g is obtained at lowest HCl:H₂O ratio 0.28 and lowest calcination temperature (600°C). From rheological analysis, as evaluated by the Winter criteria, the gelation time increases with increase of HCl:H₂O volume ratio. The fractal dimension determined from the frequency scaling exponent of the modulus at the gel point indicates a denser critical gel structure at low acid ratio. However the complex viscosity and gel strength increase as a function of acid ratio. We interpret this behavior as indicative that, at low acidity, the gel is composed of poorly hydrated particles forming a dense but weak structure. Increased acidity increases hydration and cross-link density leading to a more open and stronger gel network.

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CHAPTER VI

STRUCTURAL AND CRYSTALLIZATION OF HIGH Ti LOADED TS-1 ZEOLITE

Abstract

The TS-1 with high Ti loading was successfully synthesized using low cost and moisture-stable precursors, titanium glycolate and silatrane. The microwave instrument was used as a heating source for synthesis. The effects of the compositions (TPA^+ , NaOH , H_2O) and conditions (aging time, reaction temperature, reaction time) were studied. The Si:Ti molar ratios were varied from 100.00-5.00 and the ability of Ti incorporated into the zeolite framework was studied. The XRD, FT-IR, SEM and DR-UV were used to characterize the TS-1 samples and all samples showed the characteristic of MFI type. The small amount of extra-framework titanium dioxide was also identified at 5.0 Si:Ti molar ratio. The photocatalytic decomposition of 4-NP was used to test the activity of TS-1 samples and the results of all samples showed high efficiency in photocatalytic decomposition (PCD).

Keywords: Photocatalytic decomposition, Silatrane, Titanium glycolate, TS-1 and Zeolite

Introduction

Titanium silicate-1 (TS-1), a Ti-containing zeolite with the MFI structure, is a highly selective and active crystalline microporous heterogeneous oxidation catalyst employing H_2O_2 under mild conditions. The titanium in TS-1 isomorphously replaces silicon in a tetrahedral site of the MFI silicate lattice. It combines the advantages of the high coordination ability of Ti^{4+} ions with the hydrophobicity of the silicate framework, while retaining the spatial selectivity and specific local geometry of the active sites of the molecular sieve structure¹. The catalytic properties of titanosilicate are unique with a variety of liquid-phase oxidation, such as phenol hydroxylation, olefin epoxidation, cyclohexanone ammoximation and the oxidation of saturated hydrocarbons and alcohol²⁻³. With H_2O_2 , solvolysis produces TiOOH and SiOH with the former giving rise to the active catalytic oxidation center.

After year 1983 which Taramasso *et al*⁴ reported the hydrothermal synthesis of TS-1 for the first time, there are many researches tried to increase the amount of Ti^{IV} in the zeolite framework. A major problem often encountered the synthesis of TS-1 molecular sieve is the precipitation of oxide of the titanium outside the lattice framework, leading to samples, inactivity for oxidation reactions⁵. The synthesis of materials containing isolated tetrahedral Ti is rather difficult, given its strong tendency to polymerize in aqueous systems which often resulting in the formation of separate titanium dioxide phase¹. Two methods to synthesize were described in the original patent using different Si sources, tetraethylorthosilicate (TEOS) and Ludox colloidal silica. TS-1 is usually synthesized using tetrapropylammonium hydroxide (TPAOH) solution, which acts as the structure directing agent and provides the alkalinity necessary for the crystallization of the zeolite⁶. From many previous works, maximum amount of Ti^{IV} that can incorporated in the zeolite framework is at Si:Ti less than 35^{1,3,6}.

Microwave-assisted-hydrothermal synthesis is the process has been used for the rapid synthesis of numerous ceramic oxides and porous materials. It offers many advantages over conventional synthesis, including the increase of temperature of the reactant to a desired range quickly in a few minutes, homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels and shorter crystallization time. The heat is supposedly induced by the friction of molecular rotation enhanced by microwave irradiation, thus, it is possible to heat the reactants selectively and homogeneously from inside. Furthermore, It is energy efficient and economical⁷⁻⁸.

In this work, we synthesized the TS-1 zeolite from moisture stable and low cost starting materials, silatrane and titanium glycolate, used for silica and titanium dioxide sources, and TPABr as a template. The hydrothermal treatment by microwave heating and various amounts of Ti incorporated in the zeolite framework were studied. The samples were characterized using XRD, SEM, FT-IR and DR-UV. The photocatalytic decomposition of 4-NP was used to test the activity of TS-1 samples.

Experimental

Materials

Titanium dioxide (surface area $12 \text{ m}^2/\text{g}$) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinckrodt Baker, Inc. (USA) and purified by fractional distillation at 200°C under nitrogen atmosphere, before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder. 4-Nitrophenol was purchased from Sigma-Aldrich Chemical Co. Inc. (USA).

Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over $30^\circ\text{--}800^\circ\text{C}$ temperature range.

Preparation of titanium glycolate

The procedure adopted followed previous work⁹. A mixture of TiO_2 (2 g , 0.025 mol) and TETA (3.65 g , 0.0074 mol) was stirred vigorously in excess EG (25 cm^3) and heated to 200°C for 24 h . The resulting solution was centrifuged to separate the unreacted TiO_2 . The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR and TGA.

FTIR: 2927-2855 cm^{-1} ($\nu\text{C-H}$), 1080 cm^{-1} ($\nu\text{C-O-Ti}$ bond), and 619 cm^{-1} ($\nu\text{Ti-O}$ bond). TGA: one sharp transition at 340°C with 46.95% ceramic yield corresponding to $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$.

Preparation of silatrane⁹

A mixture of $\text{Si}(\text{OH})_2$ (6g, 0.1 mol) and TEA (18.648g, 0.125 mol) was stirred vigorously in excess EG (100 cm^3) and heated to 200°C for 10 h. The resulting solution was vacuumed to remove EG to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR and TGA.

FT-IR : 3422 cm^{-1} ($\nu\text{ O-H}$), 2986-2861 cm^{-1} ($\nu\text{ C-H}$), 2697 cm^{-1} ($\nu\text{ N-Si}$), 1459-1445 cm^{-1} ($\delta\text{ C-H}$), 1351 cm^{-1} ($\delta\text{ C-N}$), 1082 cm^{-1} ($\delta\text{ Si-O-C}$), 579 cm^{-1} ($\nu\text{ N-Si}$). TGA: one sharp transition at 380°C with 21.6% ceramic yield corresponding to $\text{N}[\text{CH}_2\text{CH}_2\text{O}]_3\text{SiOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$.

Preparation of TS-1 zeolite

Hydrothermal syntheses were carried out using microwave irradiation. The TS-1 solution with the initial molar composition of gel is equal to $\text{SiO}_2:0.1\text{TiO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$. The effects of conditions were studied by varying the aging time (20, 60, 70, 90, 110, 130, 150, 170h), reaction time (5, 10, 15, 20h) and reaction temperature (120, 150, 180°C), amounts of TPA^+ , NaOH and H_2O . For the study of the Ti incorporated in the zeolite framework, the $\text{SiO}_2:x\text{TiO}_2:0.3\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$ ($x = 0.1, 0.3, 0.5, 0.7, 1.0, 1.3, 1.7, 2.0$) was used. The solution was then aged at room temperature for 110h. After aging, the solution was transferred into Teflon vessel and heated under microwave irradiation at 150°C for various reaction times. The obtained TS-1 zeolite was washed several times with distilled water, dried at 60°C overnight and calcined at 550°C for 2h (0.5°C/min).

Photocatalytic decomposition of 4-nitrophenol

Photocatalytic reactions were carried out in a 250 ml batch reactor with a gas inlet and outlet at the flow rate of O_2 gas 20 ml/min. The cooling water jacket was used to control the temperature at 30°C. The suspensions were illuminated by using a Hg Philip UV lamp. The concentration of 4-NP was 40 ppm and the solution was continuously magnetically stirred. The TS-1 zeolite prepared at Si/Ti molar ratios of 100.00, 14.29, 7.69 and 5.00 was added in the solution with 0.8 g/l of catalyst, 10

mmol/l H_2O_2 was then slowly dropped. The samples were taken out and analyzed the concentration of 4-NP using Shimadzu UV-240 spectrophotometer.

TS-1 characterization

TS-1 samples were characterized by various techniques. XRD patterns were characterized using a D/MAX-2200H Rigaku diffractometer with $\text{CuK}\alpha$ radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range between 5° to 50° . Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Samples were prepared for SEM analysis by attachment to aluminum stubs, after pyrolysis at 550°C . Prior to analysis, the specimens were dried in a vacuum oven at 70°C for 5 h followed by coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at $\times 7,500$ magnification. Diffuse reflectance ultraviolet-visible (DR-UV) spectra were analyzed

Results and Discussion

Synthesis of TS-1

TS-1 is successfully synthesized by microwave hydrothermal treatment using silatrane and titanium glycolate as precursors in the condition with NaOH and TPABr. The XRD pattern (figure 1) shows the characteristic of MFI structure as reported by many literatures^{1,3,10-11}. The single peaks at $2\theta = 24.4^\circ$ indicate a change from monoclinic symmetry (silicate) to orthorhombic symmetry (TS-1)^{1,12}. The FT-IR spectra of TS-1 in the framework Ti-O-Si bond stretching region shows an absorption band located at 960 cm^{-1} (figure 2). This band has been also observed in Ti-containing zeolites, being mainly assigned to the stretching mode of $[\text{SiO}_4]$ tetrahedral bond with Ti atoms¹³⁻¹⁴. However, such assignment has been interpreted in term of Si-OH groups with many defect structures¹⁵. The bands at 550 and 800 cm^{-1} are assigned to $\delta(\text{Si-O-Si})$ and $\nu(\text{Si-O-Si})$, respectively. The diffuse reflectance spectra as figure 3 shows only one absorption band with a maximum at 210 nm , attribute to tetra-coordinated titanium, and there is no peak at 330 nm which is the peak of titanium dioxide extra-framework.

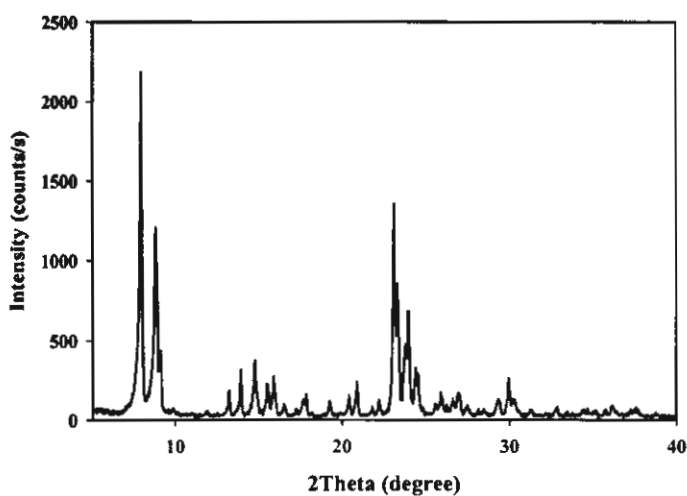


Figure 1 The XRD pattern of calcined TS-1 sample.

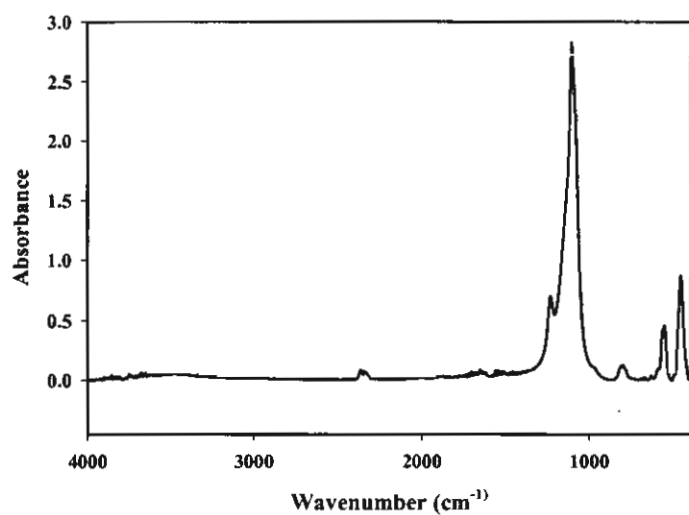


Figure 2 The FT-IR spectra of calcined TS-1 sample.

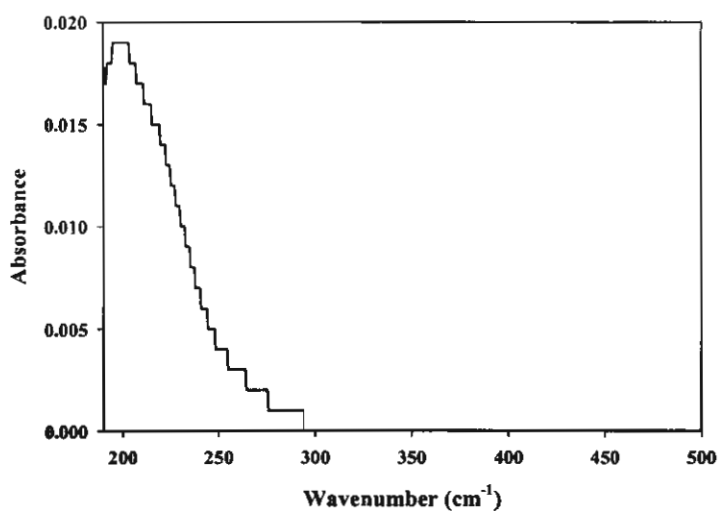


Figure 3 The DR-UV spectra of calcined TS-1 sample.

Effect of crystallization conditions and compositions of TS-1

1 Effect of reaction temperature

The effect of reaction temperature is studied by varying the temperature at 120°, 150° and 180°C. The synthesis formula is $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$. Figure 4 shows the XRD patterns of all samples, the intensity of peak increases as the reaction temperature. It means that when increasing the reaction temperature leads to a higher rate of crystallization. From the SEM micrograph of calcined samples, the crystal size increases with the reaction temperature. At 120°C (figure 5.1), the crystals have a round shape and are not uniform (0.5-2.5 μm). As increasing the temperature to 150°C (figure 5.2), the crystals are uniform with a cubic structure (1 μm). The largest crystal size (4 μm) is observed at 180°C (figure 5.3) and indicates larger growth in the c direction with a hexagonal shape. When rising the temperature to 180°C, the degradation of the organic template is occurred. From the result, the suitable reaction temperature for a smallest and uniformly crystal is at 150°C.

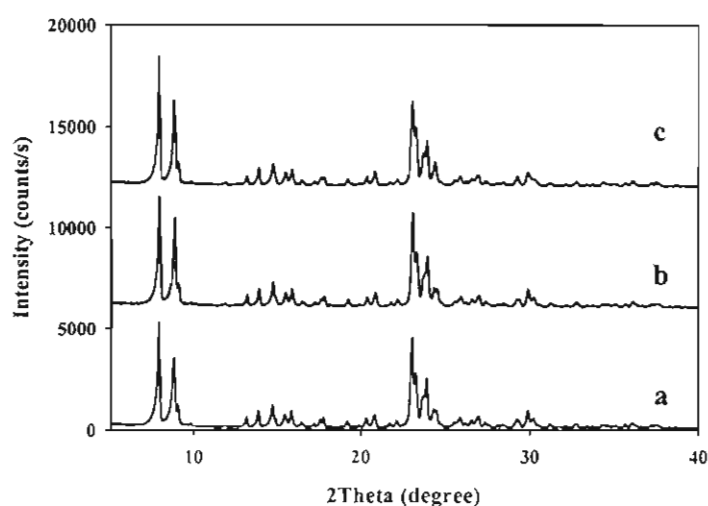


Figure 4 The XRD pattern of TS-1 samples at various reaction temperatures of a) 120°, b) 150° and c) 170°C.



Figure 5. The SEM micrograph of TS-1 sample at various reaction temperatures of a) 120°, b) 150° and c) 170°C.

The $\text{Si:0.1Ti:0.4NaOH:0.1TPA:114H}_2\text{O}$ formula is used to study the effect of reaction time to the crystallization of TS-1 zeolite. The reaction times are varies from 5, 10, 15 and 20 h at reaction temperature 150°C . The results show that at low reaction time the amorphous phase occurs and the conversion to TS-1 zeolite is lower than at higher time. It is mean that increasing the reaction time causes the increasing of the rate of crystallization. The SEM micrograph (figure 6) shows the large crystal size ($5\mu\text{m}$) at 5h and the size decreases dramatically to $1.3\mu\text{m}$ at 15h, the crystals have uniformly cubic shape. Increasing the reaction time to 20 h causes the larger crystal size and has a higher growth in b direction.

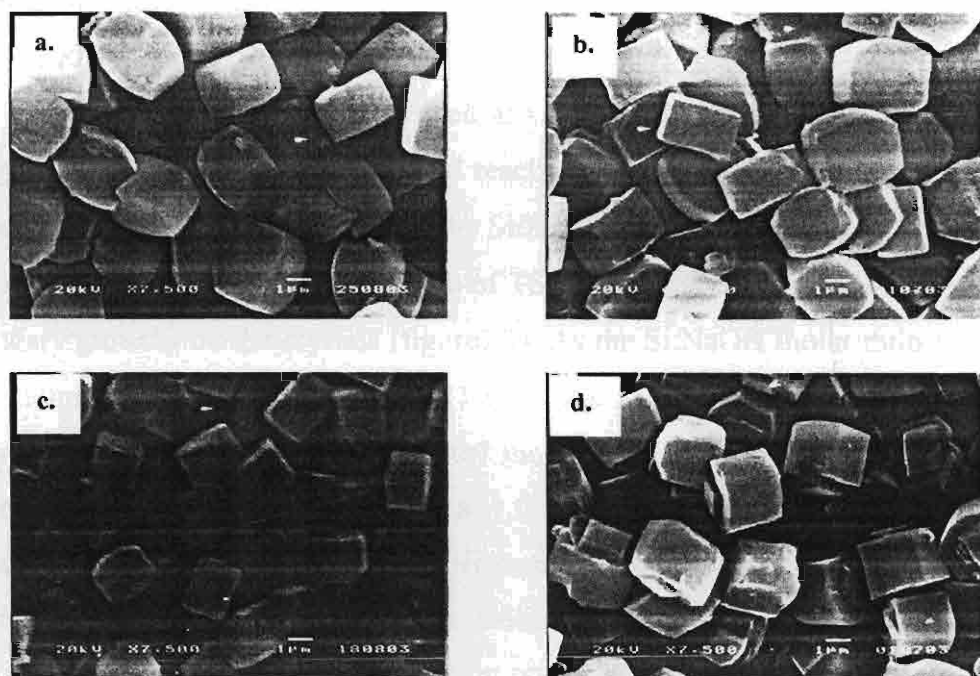


Figure 6. The SEM micrograph of TS-1 samples at various reaction times of a) 5, b) 10, c) 15 and d) 20h.

3 Effect of Aging time

The TS-1 samples at varies aging times (20, 60, 70, 90, 110, 130, 150 and 170h) are carried out at $\text{Si:0.1Ti:0.4NaOH:0.1TPA:114H}_2\text{O}$, reaction temperature 150°C and reaction time 15h. From the SEM micrographs in figure 7, at lower aging time, the large crystal sizes are formed with lower conversion to the TS-1 zeolite and present the large amount of amorphous phase. When the time increases, the crystal size becomes smaller until at aging time 130h the size increases again. The hydrolysis and condensation

reactions of silatrane and titanium precursors cause the polymerization to form the network and initially at low aging time the hydrolysis of precursor does not involve all the alkyl ligand, therefore, some organic ligands still present in the solution. The remaining organic ligand can participate with the organic template and form a primary unit, then the primary units are agglomerate and the nucleation occurs. At longer aging time, the large amount of primary particles occurs and results in the higher agglomeration and crystallization rate caused the smaller size with higher formation of zeolite after hydrothermal synthesis, which the growth rate is dominant. At longer aging time (130h), the limit of the primary unit formation occurs, therefore, the agglomeration occurs at the former nuclei.

4 Effect of NaOH:Si

The effect of NaOH:Si is studied at varying ratio from 0.1 to 1.0 mol ratio at aging time 110h, reaction time 15h and reaction temperature 150°C. At 0.1 mol ratio, the product is amorphous as shown in the SEM micrograph (figure 8). When increasing the ratio to 0.3, a very large crystal size of TS-1 zeolite is occurred (10µm) with many secondary growths on the crystals (figure 7.2). As the Si:NaOH molar ratio increases to 0.4, the uniform and smaller crystals (1.3µm) are formed (figure 7.3). Increasing the ratios to 0.5 causes the larger size and 0.7 molar ratio has many secondary growths on the crystals (figures 7.4 and 7.5). Until at 1.0 molar ratio (figure 7.6), the particles loss the cubic shape. The increasing of NaOH causes the increasing in the concentration of reactive species available in solution for zeolite nucleation which NaOH accelerates the hydrolysis rate, after that the condensation occurs and starts to form a zeolite network with greater numbers of nuclei are generated and smaller particle size products are formed (0.3 molar ratio). At large amount of NaOH, the hydrolysis increases and the large crystals with secondary growths are formed (0.5 and 0.7 molar ratios). When increasing to a very high amount of NaOH, the sodium will efficiently occupy the surface of the silica gel particles cause the retardation of the nucleation because the TPA-Silica interaction is greatly reduced. A large part of the silica is in the core of the gel bodies and not accessible for nucleation formation¹⁶.

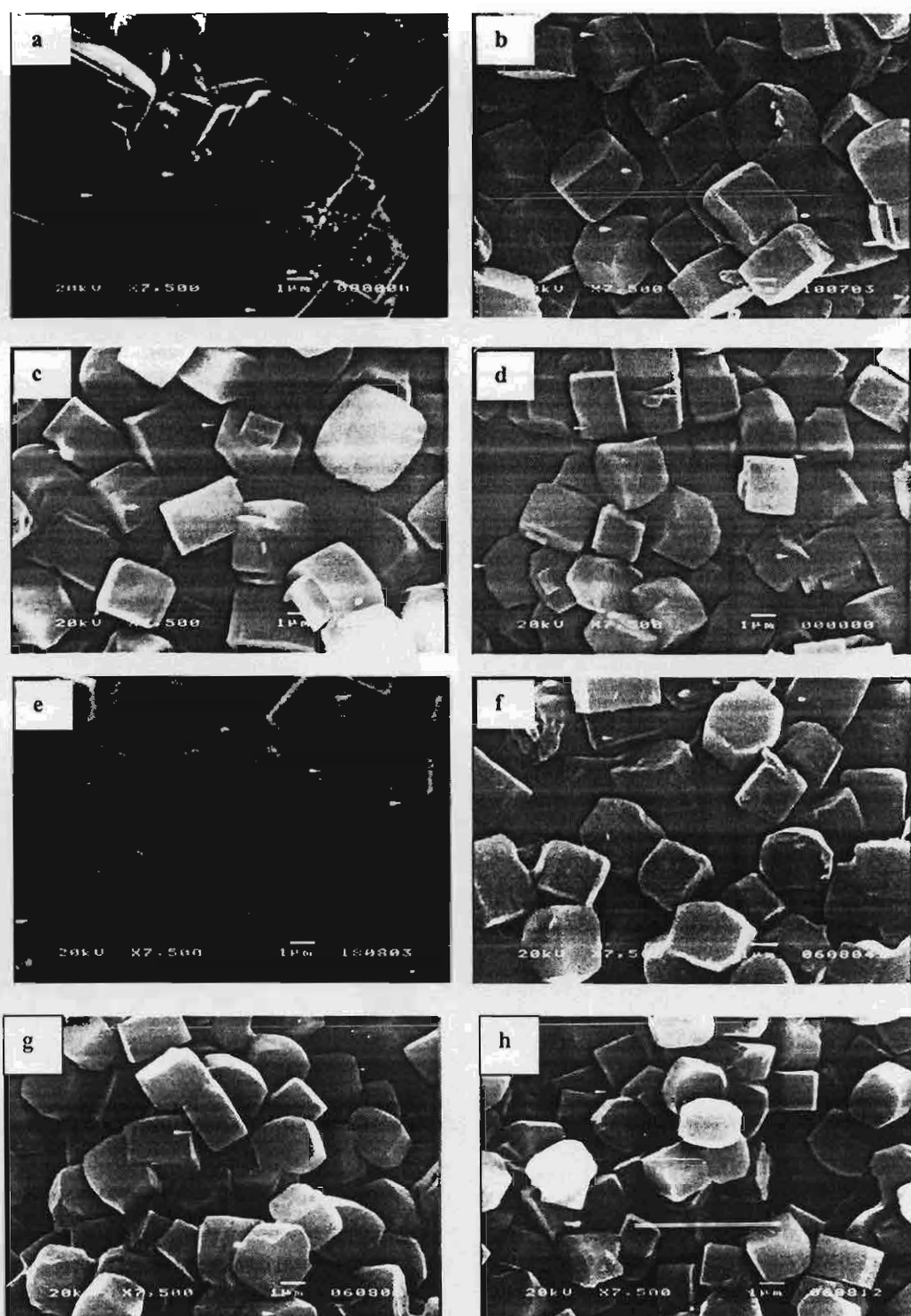


Figure 7. The SEM micrograph of TS-1 samples at various aging times of a) 20, b) 60, c) 70, d) 90, e) 110, f) 130, g) 150 and h) 170h.

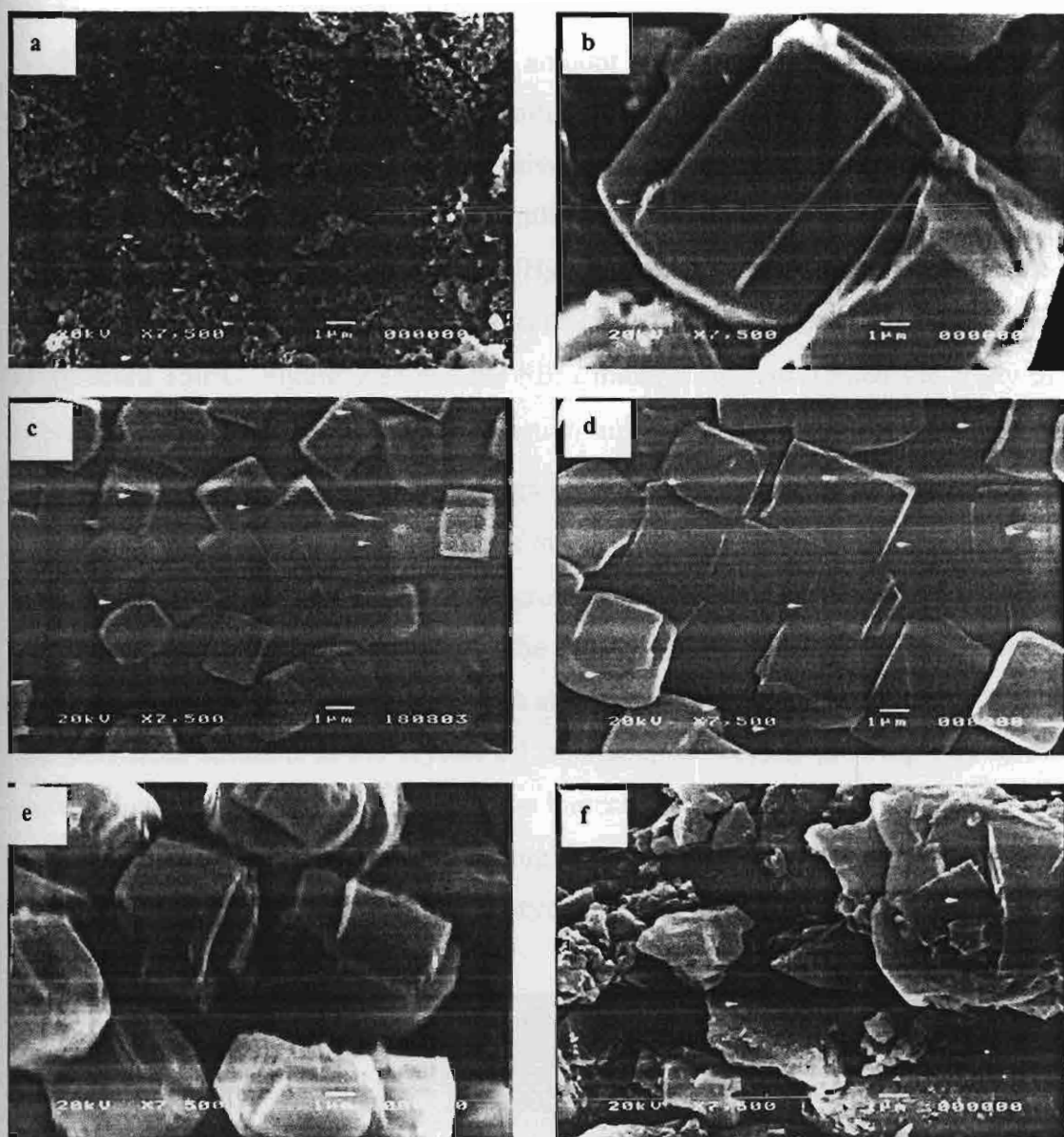


Figure 8. The SEM micrographs of TS-1 samples at various NaOH:Si molar ratios of a) 0.1, b) 0.3, c) 0.4, d) 0.5, e) 0.7 and f) 1.0.

5 Effect of TPA:Si

The steric stabilization of nuclear-sized entities, is also critically dependent on the cation balance. The TPA^+ cation is widely used in the synthesizing of zeolite, the bulky quaternary ammonium cations adsorbed on to particle surfaces provide steric stabilization, preventing aggregation upon collision¹⁶. There are many types of template use for synthesize the zeolite such as TPAOH, TBABr, 1,6-hexanediamine and TPABr. Wang et al.⁶ found that the synthesis by using TBABr will produce a favorable effect on

the formation of ZSM-11 and synthesize by 1,6-hexanediamine can use only for low titanium content which increasing the amount of titanium leads to a decrease of crystallinity. To decrease the cost of synthesis, TPAOH is replaced by TPABr. From many works TPABr showed a good selective oxidation reaction^{6,12}.

In our work, TPABr is used to synthesize TS-1 zeolite and the effect of TPA^+ is studied at $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:x\text{TPA}^+:114\text{H}_2\text{O}$ ($x = 0.05, 0.1, 0.2, 0.3, 0.4$ and 0.5). The crystallization conditions are at aging time 110 h, reaction time 15h and reaction temperature 150°C . Figure 9 shows the SEM micrograph represented the study of the effect of $\text{TPA}^+:\text{Si}$ at aging time 110h, reaction time 15h, 150°C and 0.4 Si:NaOH molar ratio. At low molar ratio (0.05), the large crystals are formed ($10\mu\text{m}$). Increasing the amount of TPA^+ causes the decreasing of the crystal size ($1.2\mu\text{m}$ at 0.3 molar ratio) but at large amount of TPA^+ , the secondary growths occur (0.4 and 0.5 molar ratios). From the explanation of the Koegler *et al.*¹⁷, the nucleation starts to occur on the surface of the large gel sphere; both TPA^+ and silica are abundance, into the gel sphere. TPA^+ will transport from solution to the crystal/gel interface, the crystal growing and formed a perfected cubic shape. Its mean that if we increase the amount of TPA^+ , it will lead to the higher nucleation as shown here. At higher TPA^+ , the dendritic growth occurs at the surface of zeolite. This is indicative of very high supersaturation.

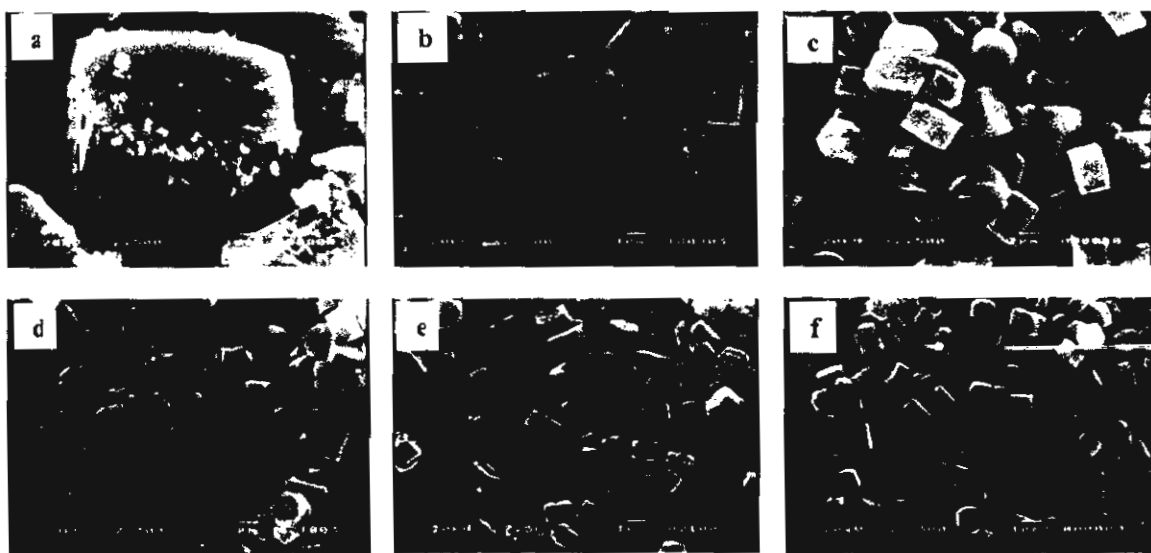


Figure 9. The SEM micrographs of TS-1 samples at various TPA:Si molar ratios of a) 0.05, b) 0.1, c) 0.2, d) 0.3, e) 0.4 and f) 0.5.

6 Effect of $H_2O:Si$ ratio

The dilution is studied at $Si:0.1Ti:0.4NaOH:0.3TPA:xH_2O$ ($x = 80, 114, 140, 170$ and 200). The reaction time is 15h, $150^\circ C$ and aging time 110h. From the SEM micrograph as figure 10, at lower $H_2O:Si$ shows a non-uniform crystal structure. As increasing the ratio to 114, the uniform and completely cubic structures are formed but when further increasing to higher ratio the crystal size are larger and have many defects.

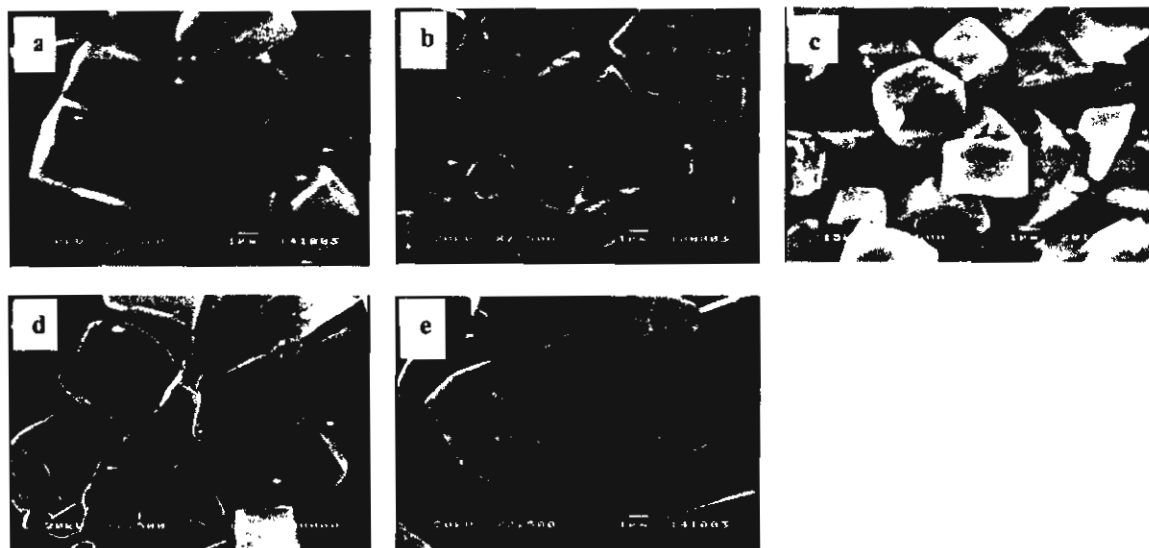


Figure 10. The SEM micrographs of TS-1 samples at various $H_2O:Si$ molar ratios of a) 80, b) 114, c) 140, d) 170 and e) 200.

7 Effect of $Si:Ti$ ratio

The effect of $Si:Ti$ on the crystallization of TS-1 is carried out at $Si:xTi:0.4NaOH:0.3TPA:114H_2O$ ($x = 100.00, 33.33, 20.00, 14.29, 10.00, 7.69, 5.88$ and 5.0). The reaction temperature is $150^\circ C$, aging time 110h and reaction times are varied from 15 to 35 h depending on the Ti loading (Table 1). We find that at high Ti loading, increasing the reaction time leads to the higher Ti incorporation. Figure 11 illustrates the FT-IR spectra of TS-1 samples A-H. The peak at 960 cm^{-1} attributes to a stretching mode of an $[SiO_4]$ unit bonded to a Ti^{4+} ion. $(O_3SiOTi)^{12}$ represents the incorporation of titanium in the MFI framework. A strong band at 550 cm^{-1} is the characteristic of MFI structure⁸. The DR-UV spectra of the samples A-H are shown in figure 12. The strong peak at 210 nm has been assigned to the tetra-coordinate of titanium in the zeolite framework. The broad band peak at 280 nm indicates the partially

polymerized hexa-coordinated Ti species, which contain Ti-O-Ti and belong to a silicon-rich amorphous phase¹⁹. The band at 330 nm, which assigns to the extra-framework anatase phase, is shown as a little peak in sample H. The peaks at both 210 and 280 nm are increase from sample A to H as higher titanium content and the band shift to higher wavelengths at sample with lower Si/Ti ratio because of the higher proportion of hexa-cooordinate species. The peak at 280 nm increases stronger than 210 nm at sample F that means the hexa-coordinated Ti species will form at higher titanium loaded. The SEM micrograph and XRD of TS-1 samples A-H are shown in figures 13 and 14, all of the samples show the characteristic of TS-1 zeolite with the MFI structure.

Table1 The TS-1 samples at varies Si:Ti molar ratios and reaction time (h).

Sample	Si/Ti molar ratio	Reaction time (h)
a	100.00	15
b	33.33	15
c	20.00	20
d	14.29	25
e	10.00	25
f	7.69	35
g	5.88	35
h	5.00	35

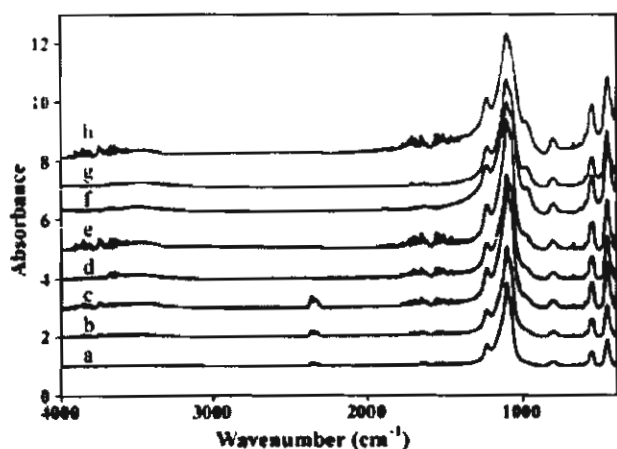


Figure 11 The FT-IR spectra of TS-1 sample at various Si:Ti molar ratios of a) 100.00, b) 33.33, c) 20.00, d) 14.29, e) 10.00, f) 7.69, g) 5.88 and h) 5.00.

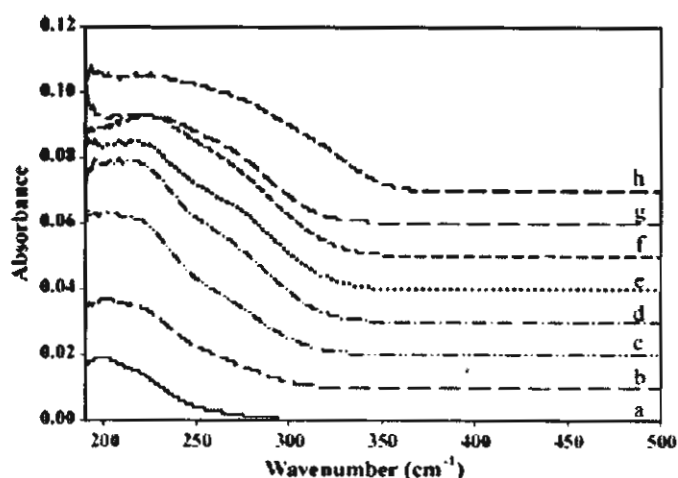


Figure 12 The DR-UV spectra of TS-1 sample at various Si:Ti molar ratios of a) 100.00, b) 33.33, c) 20.00, d) 14.29, e) 10.00, f) 7.69, g) 5.88 and h)

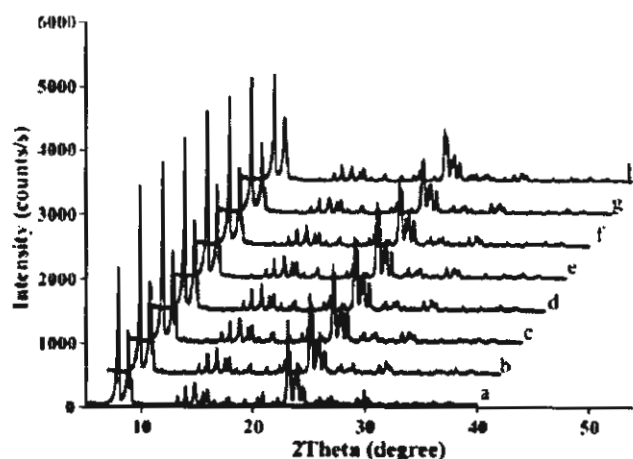


Figure 13 The XRD pattern of TS-1 sample at various Si:Ti molar ratios of a) 100.00, b) 33.33, c) 20.00, d) 14.29, e) 10.00, f) 7.69, g) 5.88 and h) 5.00.

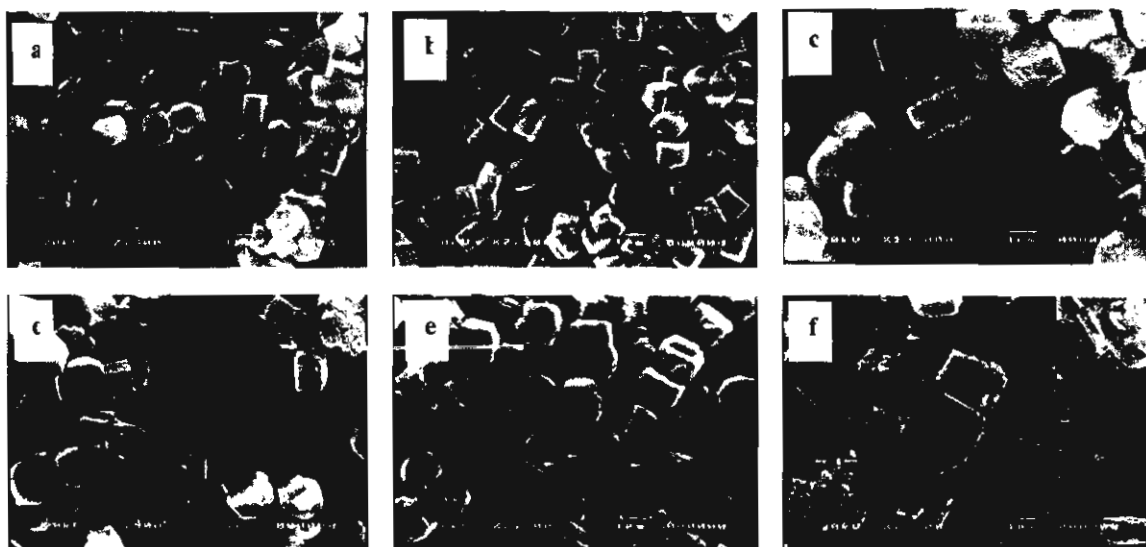


Figure 14 The SEM micrograph of TS-1 sample at various Si:Ti molar ratios of a) 100.00, b) 33.33, c) 20.00, d) 14.29, e) 10.00, f) 7.69, g) 5.88 and h) 5.00.

Photocatalytic decomposition of 4-nitrophenol

From the discussion of Lee *et al* and Lea *et al.*²⁰⁻²¹, the photocatalytic decomposition of 4-NP was completely in the presence of H₂O₂ and UV irradiation. The photodecomposition of 4-NP is governed by [•]OH radical reactions. The [•]OH can be easily formed from titanium-hydroperoxide species. Thus, in our work we carried out the PCD of 4-NP at 1.0 mmol/l of H₂O₂ under UV irradiation. Table 2 shows the results from PCD of 4-NP with TS-1 zeolite at various Si/Ti molar ratios. The PCD increases with the amount of titanium incorporated in the zeolite and the fastest complete decomposition is at 5.0 Si:Ti molar ratio.

Table2 Photocatalytic degradation of 4-nitrophenol

Si/Ti (molar ratio)	Time for completely photocatalytic decomposition of 4-NP (h)
100.00	4.00
14.29	2.00
7.69	1.30
5.00	1.00

Conclusions

The TS-1 with highly titanium incorporated in the zeolite framework was synthesized from low cost and moisture-stable precursors, silatrane and titanium glycolate, under microwave instrument. The effect of the compositions (TPA⁺, NaOH and H₂O) and conditions (aging time, reaction time and reaction temperature) were studied. The suitable condition for synthesizing TS-1 was Si:0.1Ti:0.4NaOH:0.3TPA:114H₂O at aging time 110h, reaction time 15h and reaction temperature 150°C. The Si:Ti molar ratio 100.00-5.00 was studied and the results from XRD, FT-IR, SEM and DR-UV indicated that from this route highly crystalline and the Ti atoms are occupying in the zeolite framework. The reaction times were varied at different Ti loaded, which at higher titanium loading the higher reaction time was an important factor. The photocatalytic decomposition of 4-NP was used to test the activity

of prepared TS-1 samples. The samples showed high efficiency in PCD of 4-NP and the PCD increased with amount of titanium loading.

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CHAPTER VII

PHOTOCATALYTIC MEMBRANE REACTOR OF A NOVEL HIGH SURFACE AREA TiO_2

Abstract

Photocatalytic membranes were successfully prepared using an efficient TiO_2 catalyst with high surface area, dispersed into different polymeric matrices, viz. cellulose acetate, polyacrylonitrile and polyvinyl acetate. The catalyst was directly synthesized using titanium triisopropanolamine as precursor. The membranes were characterized using FT-IR, SEM and their photocatalytic performance was tested, viz. stability, permeate flux and photocatalytic degradation of 4-nitrophenol (4-NP). We find that polyacrylonitrile provides the most effective matrix, showing the highest stability and the lowest permeate flux. The amount of TiO_2 loaded in the membrane was varied between 1, 3 and 5 wt% to explore the activity and stability of membranes in the photocatalytic reaction of 4-NP. As expected, the higher the loading of TiO_2 loaded, the higher the resulting catalytic activity.

Keywords: Mixed Matrix Membrane, Photocatalytic Reactor, 4-Nitrophenol
and Titanium Triisopropanolamine

Introduction

Purification of industrial wastewater has become an increasingly important issue, and many researchers are engaged in developing methodology to obtain efficient, low cost wastewater treatment to render harmless of all toxic species present without leaving hazardous residues. Many technologies developed for wastewater treatment, including air stripping, the use of granular activated carbon, biological degradation¹, chemical oxidation and heterogeneous photocatalysis²⁻³, have been demonstrated to be effective for complete mineralization of many toxic, bacteria and bio-resistant organic compounds in wastewater under mild experimental conditions⁴⁻⁷. The heterogeneous photocatalysis process harnesses radiant energy from natural or artificial light sources to degrade organic pollutants into their mineral components⁸. TiO_2 is a well-established catalyst for photocatalytic degradation due to its combination of high activity, chemical stability and non-toxic properties. Photocatalytic degradation generally occurs via production of $\text{OH}^\bullet$ radicals. When semiconductive TiO_2 is illuminated by radiation of appropriate energy, electrons and holes are generated within the TiO_2 structure. In the presence of O_2 , $\text{OH}^\bullet$ radicals are formed by reaction between the valence band holes and activated OH groups, e.g from adsorbed H_2O on the TiO_2 surface. To accelerate the oxidation reaction, efficient scavenging of e^- by O_2 is necessary. The organic pollutant is attacked by hydroxyl radicals and generates organic radicals or intermediates⁹⁻¹². The main drawback to practical implementation of the photocatalysis method arises from the need for an expensive liquid-solid separation process, due to the formation of milky dispersions upon mixing the catalyst powder with water¹³.

Currently, this drawback is solved by the use of a TiO_2 membrane, consisting of fine TiO_2 particles dispersed in a porous matrix. Such titania membranes have attracted a great deal of attention in recent years due to their unique characteristics, including high water flux, semiconducting properties, efficient photocatalysis and chemical resistance relative to other membrane materials, such as silica and γ -alumina¹⁴.

Many techniques have been explored for the fixation of titania powder, including sputtering on glass, silicon or alumina¹⁵, coating via sol-gel processing on porous stainless steel plate, $\alpha\text{-Al}_2\text{O}_3$ or zeolites¹⁶⁻¹⁹ were studied. However, the use of mixed matrix membranes (MMM), i.e. membranes containing microencapsulated TiO_2 , becomes of increasing interest because of their high selectivity combined with outstanding separation performance, processing capabilities, and low cost, when

polymers are used as the matrix. Many researchers²⁰⁻²⁷ have explored ways to develop and facilitate the separation process, using very thin microencapsulated membranes to allow for high fluxes. Such a membrane must have a high volume fraction of homogeneously distributed encapsulated particles in a defect- and void-free polymer matrix²⁸. Polymeric membranes are not appropriate for use in membrane reactor applications where high temperatures are needed for reaction. Thus, application of MMM for catalysis of low temperature reactions has become a main topic for many researchers, for examples, hydrogenation of propyne²⁹, photomineralization of n-alkanoic acids³⁰, wet air oxidation of dyeing wastewater, and photocatalytic oxidations³¹⁻³⁴.

To obtain a high photocatalytic activity, the surface area of catalyst is very important. Thus, in our work, thermally stable TiO₂ with high surface area is synthesized from moisture-stable titanium triisopropanolamine. The performance of this material as a component of an MMM was evaluated in a photocatalytic membrane reactor, using 4-nitrophenol as a model substrate, with regard to stability tests, effect of membrane type (PAN, PVac, CA), and TiO₂ loading. A comparison is made between as-prepared and commercial TiO₂.

Experimental

Materials

Titanium dioxide (surface area 12 m²/g) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinckrodt Baker, Inc. (USA) and purified by fractional distillation at 200°C under nitrogen atmosphere before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Triisopropanolamine (TIS) and 4-nitrophenol were purchased from Sigma-Aldrich Chemical Co. Inc. (USA).

Titanium tri-isopropanolamine precursor preparation

A mixture of TiO₂ (2g, 0.025 mol), TIS (9.55g, 0.05 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA were removed by vacuum distillation at 150°C to obtain a crude precipitate.

The product was characterized using FTIR, FAB⁺-MS and TGA. Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm⁻¹. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over 30°-800°C temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) using the positive fast atomic bombardment mode (FAB⁺-MS) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration.

High surface area TiO₂ preparation

After removal of any excess solvent from titanium triisopropanolamine precursor, the precursor was transferred to a crucible and calcined at 600°C for 2h at heating rate of 0.25°C/min. The white powder was ground and stored in a desiccator for further use.

Membrane preparation

Polyacrylonitrile membrane

A 10 wt% mixture of polyacrylonitrile powder in dimethyl formamide (DMF) was vigorously stirred at 50°C until homogeneous. A specified amount of TiO₂ was added to the stirred polymer solution. Partial vacuum was applied for a brief duration to ensure the removal of air bubbles. The mixture was then coated on a clean glass plate using a casting knife. The resulting membrane was allowed to set for 2 min before being dried in a vacuum oven at 40°C overnight following by 60°C for 2h and 80°C for 2h. The prepared membrane was cut into a circular shape with a diameter of 6 cm and thickness of 15 µm.

Cellulose acetate membrane

The membrane preparation was followed Kunprathippanja's method³². To a suspension of TiO₂, cellulose acetate was added. A partial vacuum was applied for a brief duration to ensure the removal of air bubbles, while the suspension was stirred to obtain a homogeneous suspension. The solution was then coated on the surface of a clean glass plate. The membrane was allowed to set for 2 min, followed by submersion in an ice water bath for 2 min. The membrane was then soaked in a hot water bath at 90°C for 1h before being dried. The obtained membrane was cut into a circular shape with a diameter of 6 cm and thickness of 15 µm.

Polyvinyl acetate membrane

The polymer was dissolved at 50°C in tetrahydrofuran (THF) and stirred until all the polymer had dissolved in the solvent. TiO₂ was then added to the stirring polymer solution, followed by degassing to remove air bubbles. The mixture was transferred to a teflon flat sheet and cast to the desired thickness. The prepared membrane was left overnight at room temperature to slowly evaporate solvent and then dried in a vacuum oven at 40°C for 2h. The membrane was cut into a circular shape with a diameter of 6 cm and thickness of 15 µm.

Stability test of prepared membranes

The prepared polymeric membranes (PAN, CA and PVAc) were placed in the membrane reactor and irradiated under UV irradiation for 15 h. The concentration of 4-NP used was 140 ppm. The samples were withdrawn and analyzed for total organic carbon (TOC) to verify that the organic components were released from the prepared membrane. SEM was used to investigate the presence of defects in membranes before and after the stability test.

Photocatalytic decomposition of 4-nitrophenol

The photocatalytic reactions were carried out in a 500 ml continuous batch glass reactor, figure 1, with a gas inlet and outlet at an O₂ flow rate of 20 ml/min. A cooling water jacket was used to maintain the temperature at 30°C. The suspensions and membrane were illuminated using a 100 Watt Hg Philip UV lamp. The concentration of 4-NP used was 140 ppm and the solution was continuously stirred. The obtained permeate was removed at 1h intervals and analyzed to determine the concentration of 4-NP using a Shimadzu UV-240 spectrophotometer.

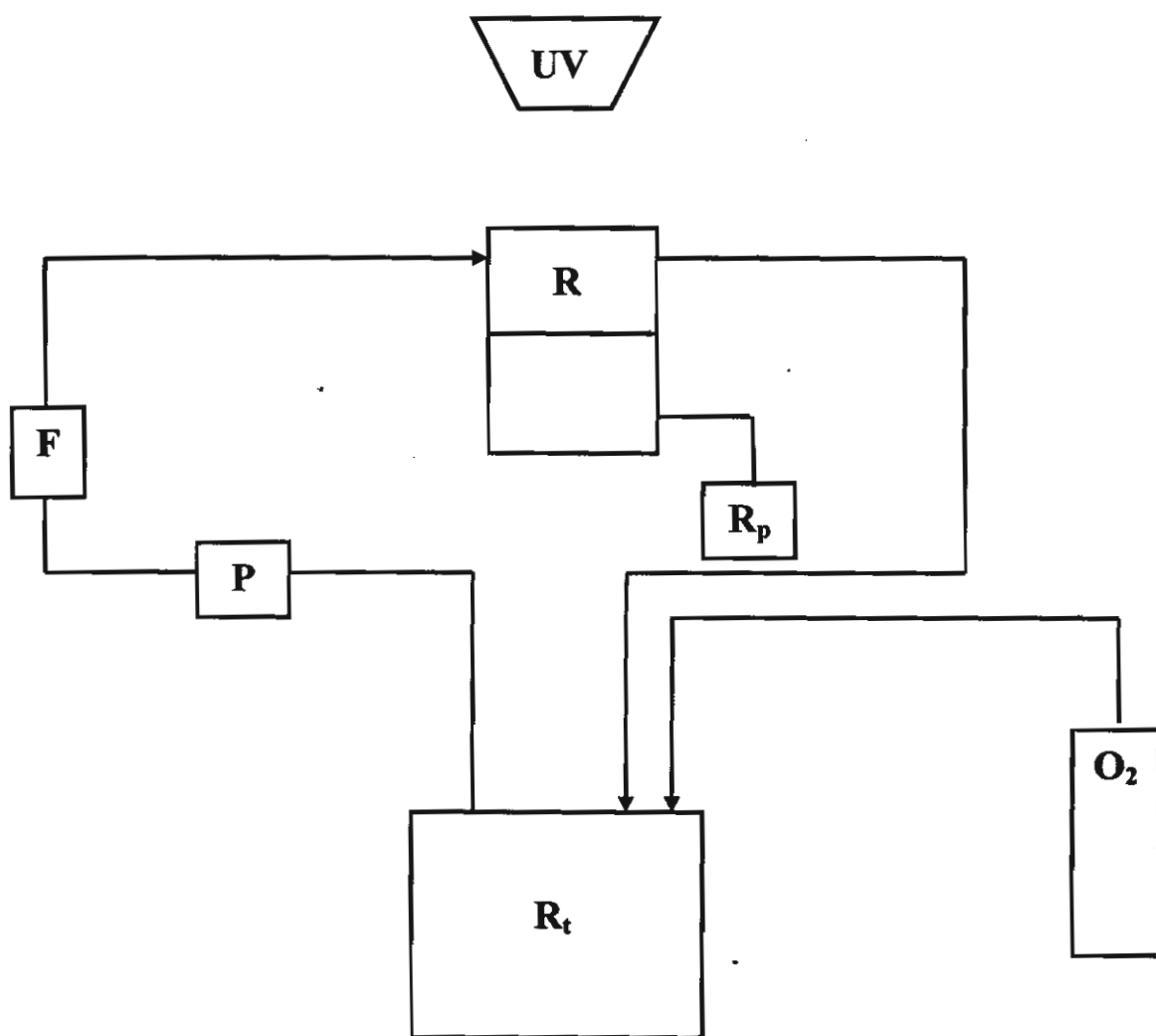


Figure 1 The schematic diagram of photocatalytic membrane reactor (F, flowmeter; R, reactor; R_p , permeate reservoir; R_t , recirculating tank and P, peristaltic pump).

Titanium triisopropanolamine and TiO_2 catalyst characterization

High surface area TiO_2 was characterized by various techniques. The XRD pattern was obtained using a D/MAX-2200H Rigaku diffractometer with $CuK\alpha$ radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range of 5° to 90° . Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} . Samples pyrolyzed at 600°C were analyzed using SEM by attachment onto aluminum stubs after coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at

x7,500 magnification. Specific surface area and nitrogen adsorption-desorption were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 cc/min. Nitrogen was used to calibrate the analyzer, and also as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2h at 150°C, prior to exposure to the adsorbent gas.

Membrane characterization

Three different types of membranes made from PAN, CA and PVAc were characterized using SEM, FT-IR and DR-UV. The morphology of membranes was analyzed by attachment onto aluminum stubs and coated with gold via vapor deposition. The membranes were frozen in liquid nitrogen and fractured to examine the cross-sectional areas. The samples were characterized on a JEOL 5200-2AE(MP 15152001) scanning electron microscope. Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. The samples were also analyzed to determine the amount of TiO_2 using a Shimadzu UV-240 spectrophotometer.

Results and discussion

Titanium triisopropanolamine precursor characterization

The synthesized titanium triisopropanolamine was characterized using FT-IR, TGA, MS and SEM. The IR spectrum (fig 2.) of the product shows bands at 3400 cm^{-1} (OH group), 2927-2855 cm^{-1} (C-H stretching), 1460 cm^{-1} (C-H bending of CH_2 group), 1379 cm^{-1} (C-H bending of CH_3 group), 1085 cm^{-1} (C-O-Ti stretching), 1020 cm^{-1} (C-N bending) and 554 cm^{-1} (Ti-O stretching). The TGA thermogram, as seen in figure 3, shows two transitions, at 280° and 365°C, corresponding to the decomposition of unreacted triisopropanolamine and the triisopropanolamine ligand, respectively, reflecting the use of excess triisopropanolamine in the reaction and no purification of the obtained product. The final ceramic yield of the product was calculated from the starting point of the second decomposition transition, and was found to be 16.60%, close to the theoretical ceramic yield of 18.65%. The results of mass spectral analysis, summarized in table1, confirm the prepared sample has the desired structure.

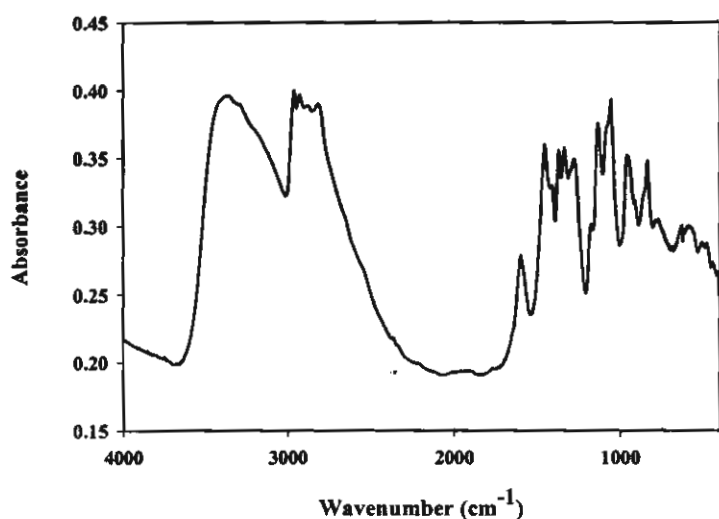


Figure 2 FT-IR spectrum of titanium triisopropanolamine.

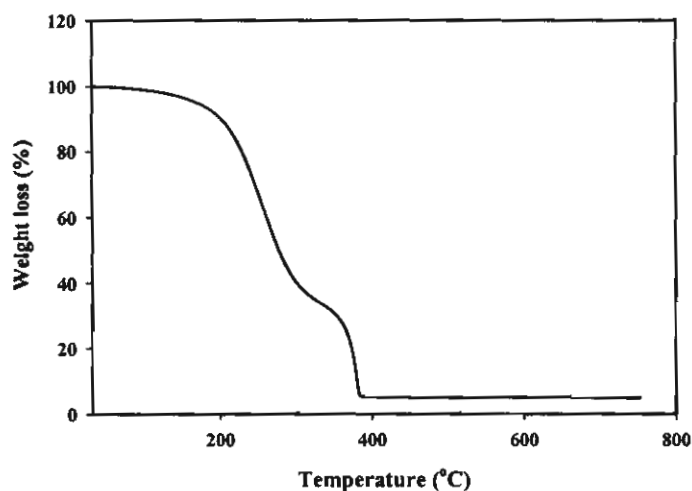


Figure 3 TGA thermogram of titanium triisopropanolamine.

Table 1 The proposed structure and fragments of the synthesized titanium triisopropanolamine.

M/e	%intensity	Proposed structure
428	10	$\text{H}^+[\text{HOCH}_3\text{CHCH}_2]\text{N}[\text{CH}_2\text{CH}_3\text{CHO}]_2\text{Ti}[\text{OCHCH}_3\text{CH}_2]_2\text{N}[\text{CH}_2\text{CHCH}_3\text{OH}]\text{H}^+$
410	5	$[\text{CH}_3\text{CH}_2\text{CH}_2]\text{N}[\text{CH}_2\text{CHCH}_3\text{O}]_2\text{Ti}[\text{OCHCH}_3\text{CH}_2]_2\text{N}[\text{CH}_2\text{CHCH}_3\text{OH}]$
214	58	$[\text{H}_2\text{NCHCH}_3\text{CH}_2\text{O}]_2\text{Ti}[\text{OH}]$
192	100	$\text{H}+\text{N}[\text{CH}_2\text{CHCH}_3\text{OH}]_3$

TiO₂ catalyst characterization

The calcined product was characterized using XRD, BET surface area and SEM to confirm the presence of the active anatase phase of TiO₂. The XRD pattern shown in fig. 4, exhibits diffraction peaks at $2\theta = 25.28, 37.66, 47.90, 54.64, 62.58, 69.76, 75.26$ and 82.72 , and the particle morphology (fig. 5) shows irregularly-shaped particles, characteristic of the anatase phase of TiO₂, as previously reported³⁵. The surface area measurement of a sample calcined at 600°C for 2h shows a high surface area of 163 m²/g. Also, the nitrogen adsorption-desorption isotherm of this material exhibits type IV character (fig. 6.) indicative of a mesoporous structure.

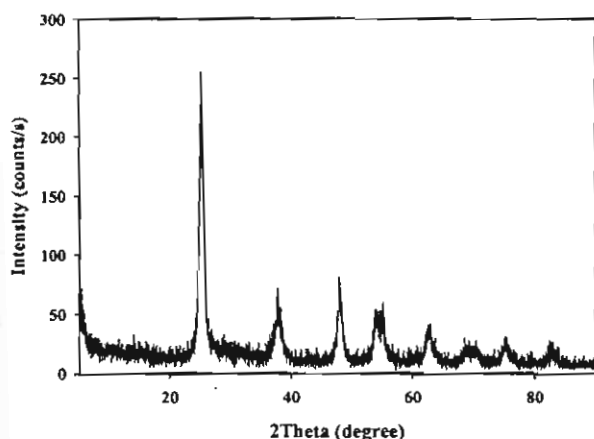


Figure 4 XRD pattern of the anatase phase of the prepared TiO₂ catalyst calcined at 600°C for 2h.

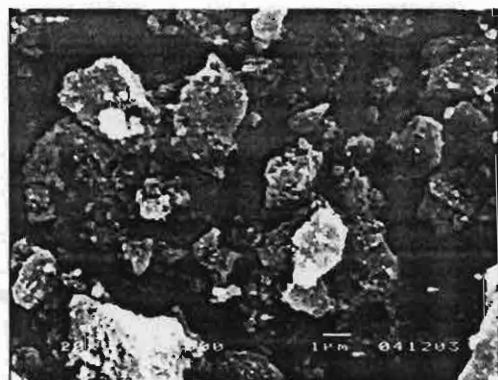


Figure 5 SEM micrograph of the anatase phase of the prepared TiO₂ catalyst calcined at 600°C for 2h.

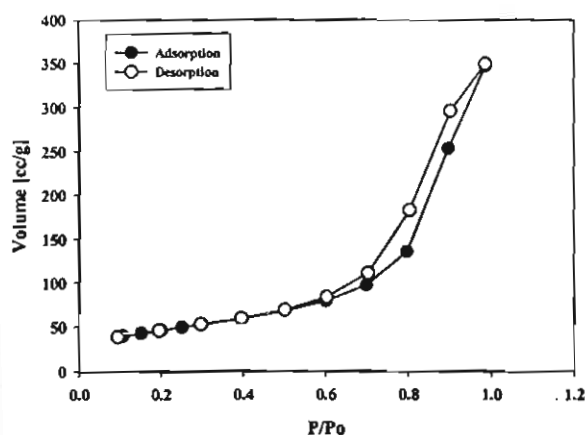


Figure 6 Nitrogen adsorption-desorption isotherm for the prepared mesoporous titania calcined at 600°C

Membranes characterization

The prepared mixed matrix membranes were characterized with respect to their functional groups using FT-IR, their morphology using scanning electron microscopy (SEM) and the amount of TiO_2 loaded in the membrane using diffuse reflectance UV. The membrane stability test was also carried out to demonstrate that the obtained material is suitable for use as a membrane.

The FT-IR spectrum of CA (fig. 7a) shows the characteristic absorption bands of C=O, C-O-C and C-C bonds at 1780, 1174 and 1020 cm^{-1} , respectively. The peak in the region of 800-500 cm^{-1} is associated with the vibration of the Ti-O bond²⁵. For the PAN membrane (fig 7b), the band at 2260 cm^{-1} is characteristic of the CN bond while the spectrum of PVAc in fig. 7c shows bands at 1780 and 1200 cm^{-1} representing the C=O and C-C bonds, respectively.

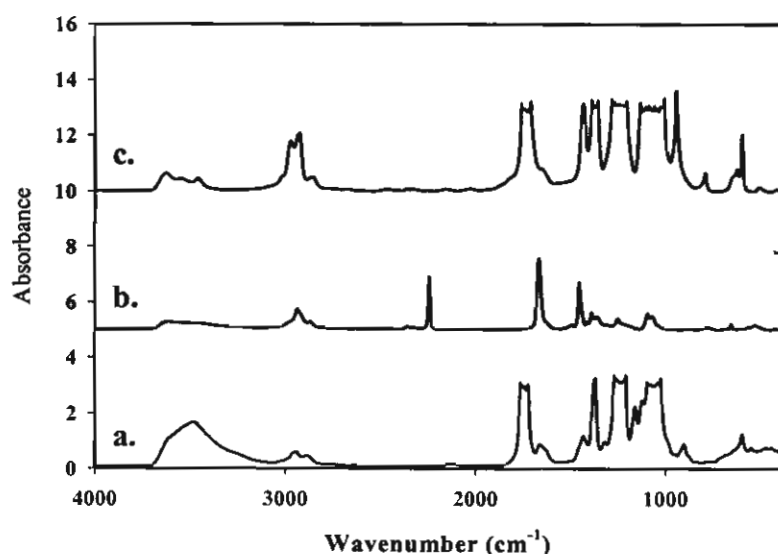


Figure 7 FT-IR spectra of the prepared membranes using 1 wt% TiO_2 mixed in a). cellulose acetate, b). polyacrylonitrile and c). polyvinyl acetate.

SEM micrographs of the fracture surfaces of all three types of membranes are shown in figure 8. The CA membrane (fig. 8a.) presents a porous surface distinctly different from the surfaces of PAN and PVAc (fig.8b. and 8c.). The TiO_2 particles are immobilized within the polymeric matrix. No significant loss of particles was observed during the membrane formation process on the glass plate. The micrographs reveal no

evidence for the presence of voids between the polymer and TiO_2 . TiO_2 particles are well distributed across the surface and do not agglomerate.

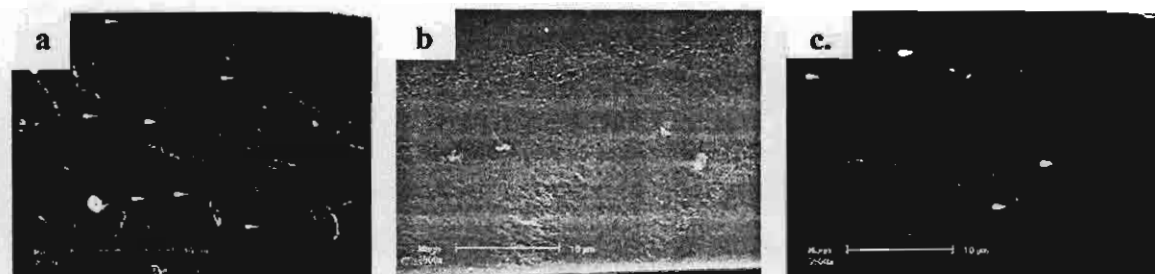


Figure 8 SEM micrographs of mixed matrix membranes using a.) cellulose acetate, b.) polyacrylonitrile and c.) polyvinyl acetate.

The PAN membrane type was selected to study the effect of TiO_2 loading, varying the percentage of TiO_2 between 1, 3 and 5 wt%. Figure 9 shows the DR-UV spectra of the prepared membranes. As expected, the absorbance at 320 nm, which is characteristic of TiO_2 , increases with the amount of TiO_2 . Morphological analysis by SEM, shown in fig. 10, indicates that TiO_2 particles are well dispersed throughout the PAN matrix at all loadings.

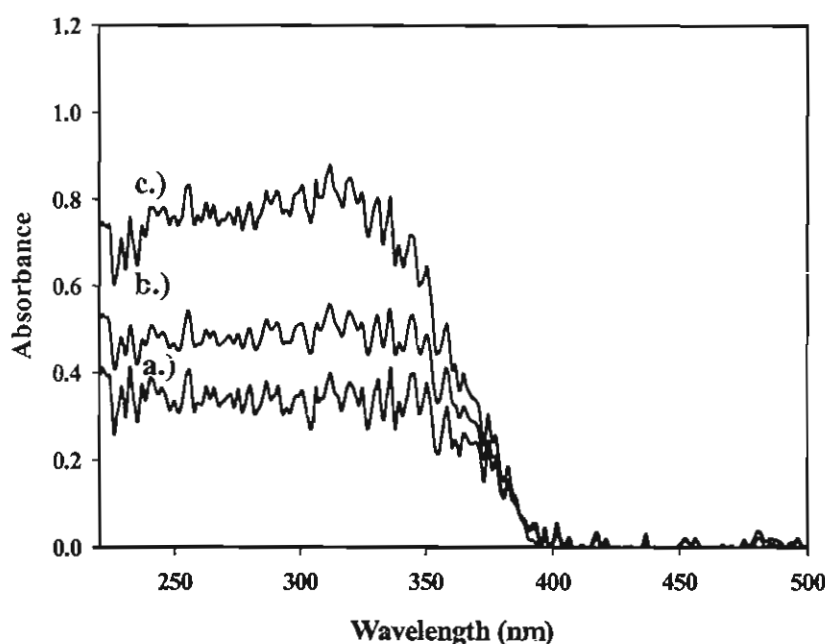


Figure 9 DR-UV spectra of polyacrylonitrile membranes at various percentages of TiO_2 ; a) 1, b) 3 and c) 5wt%.



Figure 10 SEM micrographs of polyacrylonitrile membranes at various percentages of TiO_2 ; a) 1, b) 3 and c) 5wt%

The stability of the prepared membranes was tested using UV illumination and exposure to 4-NP for 15h, and evaluation by TOC, as summarized in table 2. The PAN and CA membranes were stable under these conditions, as indicated by essentially no change in TOC values. However, the PVAc membrane showed a higher TOC value, indicative that the PVAc membrane was not stable and undergoes decomposition.

Table 2 The stability tests of the prepared membranes.

Membrane type	TOC (at initial)	TOC (after 15h)
PAN	22.39	22.68
CA	22.63	22.57
PVAc	22.35	32.22

Photocatalytic degradation of 4-nitrophenol

The photocatalytic activities of the three membrane types were assessed using the photoreactor shown in fig. 1, employing 1 wt% immobilized photocatalyst TiO_2 , oxygen flow rate of 20 ml/min, 4-NP flow rate of 30 ml/min and 4-NP concentration of 140 ppm. The permeation flux data (fig. 11) shows that CA and PAN membranes have constant low permeate flux levels, 12.38 and 5.31 l/h m^2 , respectively, whereas the PVAc membrane shows a steep increase in permeate flux from 10.62 to 120 l/h m^2 as reaction time increases from 1 to 2h. The higher permeate flux of CA membrane than PAN is consistent with the SEM observation in fig. 8, that the CA membrane is more porous than the PAN membrane. The dramatic increase in permeate flux of the PVAc membrane occurs because of the decomposition of this membrane, which generates

defects during the reaction, as confirmed by the SEM micrograph in figure 12. The holes generated in the polymer matrix cause an increase in the flux and a decrease in the photodegradation activity. The efficiencies of the PAN and CA membranes for photocatalytic degradation of 4-NP are illustrated in fig. 13, which indicates, at 1 wt% Ti loading, no substantive differences in the rate of degradation of 4-NP between the PAN and CA membranes. During the first hour of UV illumination, the concentration of 4-NP permeating through the PAN membrane is higher than through the CA membrane. This is unexpected and may reflect experimental uncertainty, since, in view of the higher permeate flux of the CA membrane, more 4-NP molecules should penetrate through the CA membrane. However, after 7hr of illumination, each membrane shows similar activity, as expected at such low TiO_2 loadings. For the PVAc membrane, the reaction could not be monitored through 7hr because the defects produced by degradation causing an extremely high flux, as discussed above.

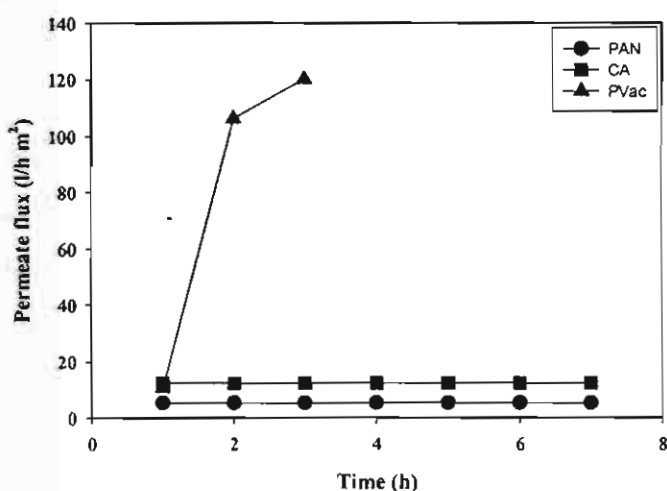


Figure 11 The permeate flux versus reaction time of all three types of the prepared membranes.

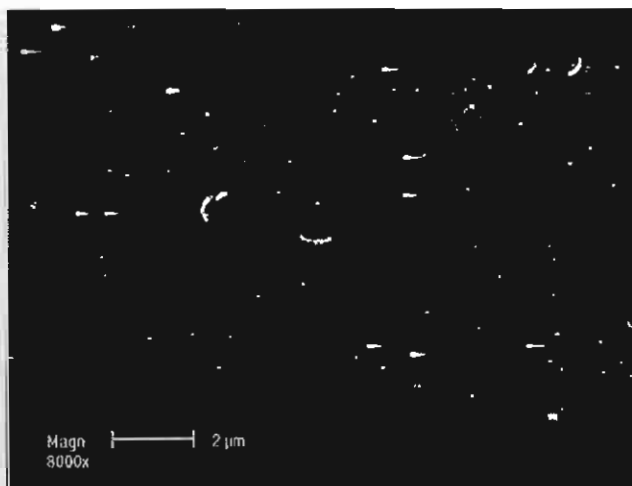


Figure 12 SEM micrograph showing the defect of polyvinyl acetate membrane after the reaction.

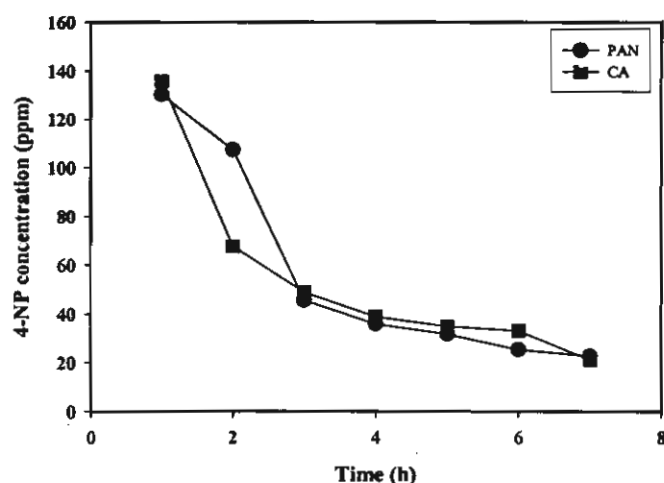


Figure 13 The degradation of 4-NP with the reaction time of polyacrylonitrile and cellulose acetate membranes.

Effect of various amounts of TiO_2 in PAN membrane on the photocatalytic degradation of 4-nitrophenol

The PAN membrane was selected to investigate the effect of TiO_2 loading on the efficiency of photocatalytic degradation because of its stability and the fact that it exhibits the lowest permeant flux. Figure 14 shows the permeant flux of PAN membranes at the three loading levels, 1, 3 and 5 wt% of TiO_2 . We find that the flux is constant for all three samples, and increases with the amount of TiO_2 from 5.31, to 8.13 to 12.73 l/h m^2 , respectively. In fig. 15, the efficiency of degradation of 4-NP at the three loading levels of TiO_2 is reported. Initially, the decrease of 4-NP at 3 and 5% loadings appears to be faster than at 1%. As for Fig. 13, however, this may be experimental error. At long times, there appears to be no significant differences in the concentrations of 4-NP measured. The reason may be that the percentage of TiO_2 is too low to see any differences in the degree of degradation of 4-NP. However, when compared with literature results³⁴, performed at much higher loading levels of TiO_2 , it appears that these membranes show a higher level of catalytic activity.

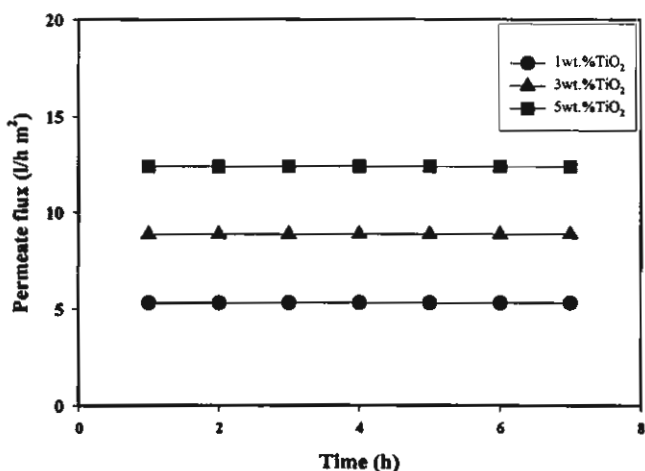


Figure 14 The permeate flux versus reaction time of polyacrylonitrile membranes at various percentages of TiO_2 .

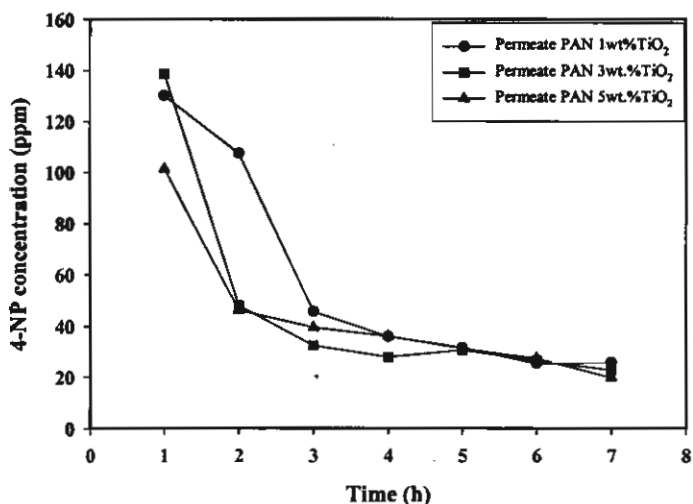


Figure 15 The degradation of 4-NP with the reaction time of polyacrylonitrile membranes at various percentages of TiO₂.

Commercial TiO₂ (Degussa P25) is also studied to compare with our TiO₂ at loading level of 3wt%. The result, see fig. 16, indicates no permeation of 4-NP through membrane prepared using commercial TiO₂ and the efficiency of degradation of 4-NP measured from the retentate of two membranes shows that the degradation of 4-NP in the membrane prepared using our TiO₂ is distinguishably lower.

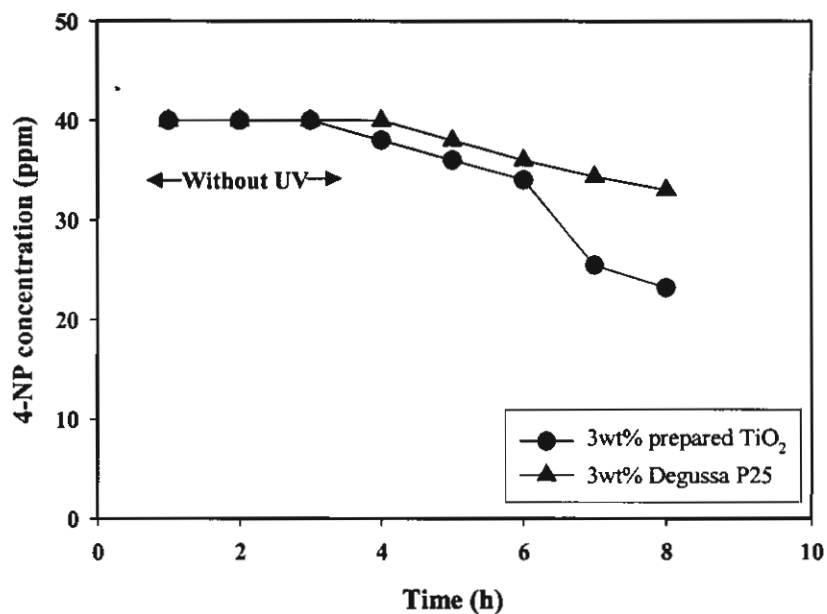


Figure 16 Effect of TiO₂ type mixed in the polyacrylonitrile membrane on the degradation of 4-NP.

Conclusions

The titanium triisopropanolamine precursor can be prepared by a very simple method (the oxide one pot synthesis) from low cost starting materials, and yields a TiO_2 catalyst with high surface area was obtained after calcinations of the precursor at 600°C for 2h. Polymeric membranes loaded with the as-prepared TiO_2 catalyst show an impressively high efficiency for the photocatalytic degradation of 4-NP. Examination of the properties of three different types of membrane (PAN, CA and PVAc) indicates that the highest stability and lowest permeate flux is observed with the PAN membrane and the poor stability occurs with the PVAc membrane. The photocatalytic degradation of 4-NP increases with increased percentage of TiO_2 loaded in the PAN membrane.

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CHAPTER VIII

CONCLUSIONS

Titanium glycolate and titanium triisopropanolamine are successfully synthesized using low cost starting materials, and a much simpler and milder reaction condition. The products show good property in moisture stability. The results from spectroscopy, namely, FT-IR, EA, Solid state NMR, and TGA, confirm the product structure. The transformation from anatase to rutile phases of calcined titanium glycolate indicates the anatase stability up to 900°C. The stability of the synthesized product remarkably provides researchers to make use in many applications. Anatase TiO₂ nanoparticles were successfully prepared by the sol-gel technology, using moisture-stable titanium glycolate as precursor in 1M HCl solution. The calcination temperature and the HCl:H₂O volume ratio have a substantial influence on the surface area, phase transformation and morphology of the products. Anatase titania is produced at calcination temperatures in the range of 600° to 800°C, above which transformation to rutile occurs. Increase of temperature results in anatase of higher crystallinity but lower specific surface area, and induces a morphological change from large irregular agglomerates to more homogeneous particles of spherical shape. From XRD measurements of average grain sizes, we deduce that nucleation rate dominates the kinetics at low temperatures, and growth rate becomes the controlling factor at high temperature and low HCl:H₂O ratios. Increase of HCl:H₂O ratio results in a small but significant decrease in porosity. The highest specific surface area 125 m²/g is obtained at the lowest HCl:H₂O ratio of 0.28 and the lowest calcination temperature (600°C). From rheological analysis, as evaluated by the Winter criteria, the gelation time increases with increase of HCl:H₂O volume ratio. The fractal dimension determined from the frequency scaling exponent of the modulus at the gel point indicates a denser critical gel structure at low acid ratio. However, the complex viscosity and gel strength increase as a function of acid ratio. We interpret this behavior as indicative that, at low acidity, the gel is composed of poorly hydrated particles forming a dense but weak structure. Increase in acidity increases hydration and cross-link density leading to a more open and stronger gel network. From the rheological study of different ceria gelling system using HCl:alkoxide molar ratio of 0.8, 0.9, 1.0 and 1.1, as evaluated by

Winter et al., the gelation time increases as increasing HCl:alkoxide molar ratio. The gel strength increases as a function of acid ratio and the fractal dimension determined from the frequency scaling exponent of the modulus at the gel point indicate a tight structure at low acid ratio. The TS-1 with highly titanium incorporated in the zeolite framework was synthesized from moisture-stable precursors, silatrane and titanium glycolate, under microwave treatment. The effects of the compositions (TPA^+ , NaOH and H_2O) and conditions (aging time, reaction time and reaction temperature) showed that the suitable condition for synthesizing TS-1 was Si:0.1Ti:0.4NaOH:0.3TPA:114 H_2O at aging time 110h, 15h reaction time and reaction temperature of 150°C. As for the Si:Ti molar ratio, from XRD, FT-IR, SEM and DR-UV results, it is indicated that high crystallinity and the Ti atoms are occupying in the zeolite framework. Moreover, at higher titanium loading the higher reaction time was an important factor. It is also important to the photocatalytic decomposition of 4-NP. The samples showed high efficiency in PCD of 4-NP and the PCD increased with amount of titanium loading.

The titanium triisopropanolamine precursor was successfully prepared using the same method, and yields a TiO_2 catalyst with high surface area after calcinations of the crude precursor at 600°C for 2h. Polymeric membranes loaded with the as-prepared TiO_2 catalyst show an impressively high efficiency for the photocatalytic degradation of 4-NP. Examination of the properties of three different types of membrane (PAN, CA and PVAc) indicates that the highest stability and the lowest permeate flux are observed with the PAN membrane and the poor stability occurs with the PVAc membrane. The photocatalytic degradation of 4-NP increases with increasing percentage of TiO_2 loaded in the PAN membrane.

APPENDIX: Project Outputs

A. National Patent

สำเนา

แบบ สป/สพ/อสป/001-ก

หน้า 1 ของจำนวน 3 หน้า

 คำขอรับสิทธิบัตร/อนุสิทธิบัตร ☒ การประดิษฐ์ ☐ การออกแบบผลิตภัณฑ์ ☐ อนุสิทธิบัตร ข้าพเจ้าผู้ลงนามชื่อในคำขอรับสิทธิบัตร/อนุสิทธิบัตรมี ขอรับสิทธิบัตร/อนุสิทธิบัตร ตามพระราชบัญญัติสิทธิบัตร พ.ศ. 2522 แก้ไขเพิ่มเติมโดยพระราชบัญญัติสิทธิบัตร (ฉบับที่ 2) พ.ศ. 2535 และ พระราชบัญญัติสิทธิบัตร (ฉบับที่ 3) พ.ศ. 2542	สำหรับเจ้าหน้าที่	
	วันรับคำขอ 19 ต.ค.	เลขที่คำขอ
	วันยื่นคำขอ	103423
	สัญลักษณ์งานนอกการประดิษฐ์ระหว่างประเทศ	
	ใช้กับแบบผลิตภัณฑ์ ประเภทผลิตภัณฑ์	
วันประกาศโฆษณา	เลขที่ประกาศโฆษณา	
วันออกสิทธิบัตร/อนุสิทธิบัตร	เลขที่สิทธิบัตร/อนุสิทธิบัตร	
ลงมือชื่อเจ้าหน้าที่		
1. ชื่อที่แสดงถึงการประดิษฐ์/การออกแบบผลิตภัณฑ์ เขียนสำหรับย่อถลาถสารพันและเรือโรคควมตง		
2. คำขอรับสิทธิบัตรการออกแบบผลิตภัณฑ์นี้เป็นคำขอสำหรับแบบผลิตภัณฑ์อย่างเดียวกันและเป็นคำขอลำดับที่ ในจำนวน คำขอ ที่อื่นในคราวเดียวกัน		
3. ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร และที่อยู่ (เลขที่ ถนน ประเทศ) ดูที่หน้า 3	3.1 สัญชาติ	
	3.2 โทรศัพท์	
	3.3 โทรสาร	
	3.4 อีเมล	
4. สิทธิในการขอรับสิทธิบัตร/อนุสิทธิบัตร ☐ ผู้ประดิษฐ์/ผู้ออกแบบ ☒ ผู้รับโอน ☐ ผู้ขอรับสิทธิโดยเหตุอื่น		
5. คำนวน(ด้ามี)ที่อยู่ (เลขที่ ถนน จังหวัด รหัสไปรษณีย์) นางมณฑล แก้วมหา สถาบันทรัพย์สินทางปัญญาแห่งจุฬาลงกรณ์มหาวิทยาลัย ชั้น 9 ห้อง 904 อาคารเทพทวาราวดี คณะนิติศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ถนนพญาไท แขวงวังใหม่ เขตปทุมวัน กรุงเทพฯ 10330	5.1 คำนวนเลขที่ 1453	
	5.2 โทรศัพท์ 0-2218-2895-6	
	5.3 โทรสาร 0-2215-0115	
	5.4 อีเมล	
6. ผู้ประดิษฐ์/ผู้ออกแบบผลิตภัณฑ์ และที่อยู่ (เลขที่ ถนน ประเทศ) รองศาสตราจารย์ ดร.สุจิตรา วงศ์เกษมจิตต์ และ นางสาวนพพรพร พชรธรรมชัย วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย แขวงวังใหม่ เขตปทุมวัน กรุงเทพฯ 10330		
7. คำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้แยกจากหรือเกี่ยวข้องกับคำขอเดิม ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอให้อธิบายได้อื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ ในวันเดียวกับคำขอรับสิทธิบัตร เลขที่ วันอื่น เพราะคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้แยกจากหรือเกี่ยวข้องกับคำขอเดิมเพราะ ☐ คำขอเดิมมีการประดิษฐ์หลายอย่าง ☐ ถูกคัดค้านเนื่องจากผู้ขอไม่มีสิทธิ ☐ ขอเปลี่ยนแปลงประเภทของสิทธิ		

หมายเหตุ ใบกรณีที่ไม่อาจจะประมวลผลได้ครบถ้วน ให้จัดทำเป็นเอกสารแนบท้ายแบบฉบับนี้โดยระบุรายละเอียดคำกับข้อและหัวข้อที่แสดงรายละเอียด
เพิ่มเติมดังกล่าวด้วย

แบบ สป/สพ/อสป/001-ก

หน้า 2 ของจำนวน 3 หน้า

8.การยื่นคำขออนุญาตราชอาณาจักร				
วันยื่นคำขอ	เลขที่คำขอ	ประเทศ	สัญลักษณ์จำนวนการ ประดิษฐ์ระหว่างประเทศ	สถานะคำขอ
8.1				
8.2				
8.3				
8.4 ☐ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอสิทธิให้ถือว่าได้ยื่นคำขอนี้ในวันที่ได้ยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรในต่างประเทศเป็นครั้งแรกโดย ☐ ได้ยื่นเอกสารหลักฐานพร้อมคำขอนี้ ☐ ขอยื่นเอกสารหลักฐานหลังจากวันยื่นคำขอนี้				
9.การแสดงผลการประดิษฐ์ หรือการออกแบบผลิตภัณฑ์ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรได้แสดงผลการประดิษฐ์ที่หน่วยงานของรัฐเป็นผู้จัด วันแสดง วันเปิดงานแสดง ผู้จัด				
10.การประดิษฐ์เกี่ยวกับจุลชีพ				
10.1 เลขทะเบียนฝากเก็บ		10.2 วันที่ฝากเก็บ		10.3 สถาบันฝากเก็บประเทศ
11.ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอยื่นเอกสารภาษาต่างประเทศก่อนในวันยื่นคำขอนี้ และจะจัดยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ที่จัดทำ เป็นภาษาไทยภายใน 90 วัน นับจากวันยื่นคำขอนี้ โดยขอเป็นภาษา ☐ อังกฤษ ☐ ฝรั่งเศส ☐ เยอรมัน ☐ ญี่ปุ่น ☐ อื่นๆ				
12.ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอให้อธิบดีประกาศโฆษณาคำขอรับสิทธิบัตร หรือรับจดทะเบียน และประกาศโฆษณาอนุสิทธิบัตรนี้ หลังจากวันที่ เดือน พ.ศ. ☐ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอให้ใช้รูปเขียนหมายเลข ในการประกาศโฆษณา				
13.คำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ประกอบด้วย			14.เอกสารประกอบคำขอ	
ก. แบบพิมพ์คำขอ 2 หน้า			☒ เอกสารแสดงสิทธิในการขอรับสิทธิบัตร/อนุสิทธิบัตร	
ข. รายละเอียดการประดิษฐ์ หรือคำพรรณนาแบบผลิตภัณฑ์ 6 หน้า			☐ หนังสือรับรองการแสดงผลการประดิษฐ์/การออกแบบ ผลิตภัณฑ์	
ค. ข้ออธิบาย 2 หน้า			☒ หนังสือมอบอำนาจ	
ง. รูปเขียน รูป หน้า			☐ เอกสารรายละเอียดเกี่ยวกับจุลชีพ	
จ. ภาพแสดงแบบผลิตภัณฑ์			☐ เอกสารการขอนับวันยื่นคำขอในต่างประเทศเป็นวันยื่น คำขอในประเทศไทย	
☐ รูปเขียน รูป หน้า			☐ เอกสารขอเปลี่ยนแปลงประเภทของสิทธิ	
☐ ภาพถ่าย รูป หน้า			☒ เอกสารอื่น ๆ	
ฉ. บทสรุปการประดิษฐ์ 1 หน้า				
15. ข้าพเจ้าขอรับรองว่า ☒ การประดิษฐ์นี้ไม่เคยยื่นขอรับสิทธิบัตร/อนุสิทธิบัตรมาก่อน ☐ การประดิษฐ์นี้ได้พัฒนาปรับปรุงมาจาก.....				
16.ลายมือชื่อ (☐ ผู้ขอรับสิทธิบัตร / อนุสิทธิบัตร; ☒ ตัวแทน) นายมงคล แก้วมหา นกนก เกตุพันธ์				

หมายเหตุ บุคคลอื่นขอรับสิทธิบัตรการประดิษฐ์หรือการออกแบบผลิตภัณฑ์ หรืออนุสิทธิบัตร โดยการแสดงความยินยอมเป็นเพียงแก่พนักงานเจ้าหน้าที่ เพื่อให้
ได้ไปแจ้งสิทธิบัตรหรืออนุสิทธิบัตร ต่อกระทรวงพาณิชย์ตามกฎหมาย หรือปรับไม่เกินห้าพันบาท หรือทั้งจำทั้งปรับ

แบบ สป/ตม/อสป/ก01-ก
หน้า 3 ของจำนวน 3 หน้า

3.ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร และที่อยู่ (เลขที่ ถนน ประเทศ)

จุฬาลงกรณ์มหาวิทยาลัย

อยู่ที่ จุฬาลงกรณ์มหาวิทยาลัย ถนนพญาไท แขวงวังใหม่ เขตปทุมวัน กรุงเทพฯ 10330

3.1 สัญชาติ ไทย 3.2 โทรศัพท์ 0-2218-2895-6 3.3 โทรสาร 0-2215-0115

สำนักงานกองทุนสนับสนุนการวิจัย

อยู่ที่ ชั้น 14 อาคาร เอส เอ็ม ทาวเวอร์ 979/17-21 ถนนพหลโยธิน แขวงสามเสนใน เขตพญาไท กรุงเทพฯ 10400

3.1 สัญชาติ ไทย 3.2 โทรศัพท์ 0-2298-0455 3.3 โทรสาร 0-2298-0476

หน้าที่ 1 ของจำนวน 6 หน้า

รายละเอียดการประดิษฐ์

ชื่อที่แสดงถึงการประดิษฐ์

เยื่อแผ่นสำหรับย่อยสลายสารพิษและเชื้อโรคด้วยแสง

5

ลักษณะและความมุ่งหมายของการประดิษฐ์

การประดิษฐ์นี้เกี่ยวข้องกับเยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง (Polymeric Membranes for Photocatalytic Degradation) ซึ่งประกอบด้วย โพลีอะคลิไธโนไทรล์, โดเมซิลฟอรัมามายด์ และ โททาเนียมไดออกไซด์

10

ในอีกรูปแบบหนึ่งของการประดิษฐ์ เยื่อแผ่น ซึ่งประกอบด้วย โพลีไวนิลอะซิเตด, เตตระไฮโดรฟูแรน และ โททาเนียมไดออกไซด์

ในอีกรูปแบบหนึ่งของการประดิษฐ์ เยื่อแผ่น ซึ่งประกอบด้วย เซลลูโลสอะซิเตด, อะซิโตน และ โททาเนียมไดออกไซด์

15

ความมุ่งหมายของการประดิษฐ์นี้ เพื่อนำไปใช้สลายสารอินทรีย์จำพวกเบนซีนและอนุพันธ์ของเบนซีน ซึ่งเป็นสารก่อโรคมะเร็งภายในร่างกายมนุษย์ และยังใช้ย่อยสลายเชื้อโรคและแบคทีเรีย เยื่อเลือกผ่านนี้มีคุณสมบัติของสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงสำหรับกระบวนการสลายสารอินทรีย์ด้วยแสง

สาขาวิทยาการที่เกี่ยวข้องกับการประดิษฐ์

20

การประดิษฐ์นี้เกี่ยวข้องกับวิทยาการต่างๆ ได้แก่ การกำจัดน้ำเสียจากอุตสาหกรรมปิโตรเคมี โดยใช้กระบวนการแตกสลายสารอินทรีย์ด้วยแสง (Photocatalysis) กระบวนการเพิ่มไฮโดรเจนอะตอมแก่โมเลกุลของสารโพรไพน์ (Hydrogenation of propyne) กระบวนการเพิ่มออกซิเจนอะตอมแก่สารอินทรีย์ (Oxidation of organic compound) กระบวนการแยกแก๊ส (Gas separation) และกระบวนการกำจัดแบคทีเรียด้วยแสง (Bactericidal activity of photocatalyst)

25

ภูมิหลังของศิลปะหรือวิทยาการที่เกี่ยวข้อง

กระบวนการย่อยสลายสารอินทรีย์และสารอนินทรีย์ที่เป็นองค์ประกอบในน้ำทิ้งจากโรงงานอุตสาหกรรมจัดว่าเป็นประเด็นสำคัญมากในปัจจุบัน ดังนั้น จึงได้รับความสนใจจากนักวิทยาศาสตร์มากมายในการศึกษาและวิจัย เพื่อจุดมุ่งหมายในการเพิ่มประสิทธิภาพของการกำจัดน้ำเสีย รวมถึงการกำจัดน้ำเสียด้วยกระบวนการที่ใช้ต้นทุนต่ำ และย่อยสลายสารโดยไม่เหลือสารพิษตกค้างในน้ำ นอกจากนี้ ในปัจจุบันมลภาวะจากสิ่งแวดล้อมเป็นปัญหาที่ต้องแก้ไข

30

หน้า 2 ของจำนวน 6 หน้า

โดยเร็ว ซึ่งมลภาวะเหล่านี้ ได้แก่ อนุภาคสิ่งมีชีวิตขนาดเล็กที่พบในน้ำ และอากาศ การกำจัดเชื้อโรคต่างๆ ในน้ำนั้นมีประโยชน์โดยตรงต่อการอุปโภค บริโภคของมนุษย์ อีกทั้งยังมีส่วนต่อการผลิตผลิตภัณฑ์ต่างๆ ที่ใช้ในคน และสัตว์ กระบวนการกำจัดเชื้อโรคในอากาศนั้นมีความสำคัญมากในทางการแพทย์ ซึ่งต้องการความระมัดระวังเป็นอย่างสูงในเรื่องการปนเปื้อนของสารทางชีวภาพต่างๆ เนื่องจากในกระบวนการทดลองเกี่ยวกับสัตว์ พืช และคนนั้นมีโอกาสที่จะติดเชื้อได้ง่าย กระบวนการกำจัดที่ใช้กันอย่างแพร่หลายในประเทศพัฒนาแล้วคือ วิธีการเพิ่มคลอรีน (Chlorination) การเติมโอโซน (Ozonation) และกระบวนการย่อยสลายด้วยแสง (Photocatalytic degradation) ซึ่งเป็นวิธีที่มีประสิทธิภาพและใช้ในระดับใหญ่

กระบวนการย่อยสลายสารด้วยแสงเป็นกระบวนการที่มีประสิทธิภาพสูงซึ่งใช้พลังงานแสงจากธรรมชาติและแสงที่ประดิษฐ์ขึ้นเป็นแหล่งพลังงานที่ใช้ในกระบวนการย่อยสลายสารโดยใช้สารไททาเนียมไดออกไซด์เป็นตัวเร่งปฏิกิริยา ซึ่งสารไททาเนียมไดออกไซด์นี้มีประสิทธิภาพสูงและใช้กันอย่างแพร่หลาย นอกจากนั้น ยังมีความเสถียรต่อสารเคมีสูง และที่สำคัญมากกว่านั้น คือ เป็นสารที่ไม่เป็นพิษต่อสิ่งแวดล้อมอีกด้วย ในปัจจุบันกระบวนการย่อยสลายด้วยแสงที่มีสารไททาเนียมไดออกไซด์เป็นองค์ประกอบนั้นเป็นที่ยอมรับและใช้กันอย่างแพร่หลายรวมทั้งมีการศึกษาวิจัยและพัฒนาเพื่อใช้กับการใช้งานในรูปแบบใหม่ๆ เช่น หน้ากากกำจัดแบคทีเรีย (Environmental safety mask and respirator) ระบบกรองอากาศด้วยกระบวนการย่อยสลายสารด้วยแสง (Photocatalytic air filtration system) ระบบการกำจัดเชื้อรา จุลินทรีย์ เชื้อไวรัส และแบคทีเรียในน้ำ (Deactivation of fungi, microorganisms, viruses and bacteria in water) นอกจากนี้ยังมีการใช้ปฏิกิริยาการย่อยสลายด้วยแสงที่มีสารไททาเนียมไดออกไซด์เป็นองค์ประกอบในการสลายเซลล์มะเร็ง และเนื้องอก อีกทั้งยังใช้ในทางทันตกรรม คือ เป็นวัสดุอุดฟัน เพื่อป้องกันการเจริญเติบโตของแบคทีเรียในช่องปาก และใช้เป็นองค์ประกอบในแปรงสีฟันที่มีการกระตุ้นด้วยแสง (Light activated tooth brush)

ข้อเสียของกระบวนการย่อยสลายสารด้วยแสงในน้ำเกิดขึ้น เนื่องจากต้องใช้กระบวนการแยกของเหลวออกจากของแข็งที่เกิดจากการกระจายตัวของสารไททาเนียมไดออกไซด์ในน้ำ หลังจากเสร็จสิ้นกระบวนการย่อยสลายซึ่งกระบวนการนี้มีราคาแพง และใช้เวลานาน ในปัจจุบันได้มีการแก้ไขข้อเสียดังกล่าวโดยการใช้เยื่อแผ่นที่มีสารไททาเนียมไดออกไซด์กระจายตัวฝังอยู่ในเยื่อแผ่น ดังนั้น เยื่อแผ่นที่ประกอบด้วยสารไททาเนียมไดออกไซด์จึงเป็นที่สนใจและใช้กันอย่างแพร่หลายเนื่องจากเยื่อแผ่นนี้มีลักษณะเฉพาะคือ มีปริมาณการไหลผ่านของน้ำสูง มีคุณสมบัติในการเป็นสารกึ่งตัวนำ มีประสิทธิภาพในการย่อยสลายสารอินทรีย์ และมีความเสถียรต่อสารเคมีสูง อีกทั้งยังลดกระบวนการในการแยกสารไททาเนียมไดออกไซด์ออกจากสารผสมอีกด้วย

หน้า 3 ของจำนวน 6 หน้า

กระบวนการแยกอนุภาคของสารโททาเนียมไดออกไซด์ลงบนวัสดุรองรับนั้นสามารถทำได้หลายวิธี เช่น การพ่นอนุภาคโททาเนียมไดออกไซด์ลงบนแก้ว ซิลิกอน หรืออะลูมินา การเคลือบลงบนผิวของสารซีโอไลต์ หรือแผ่นสแตนเลสที่มีรูพรุนด้วยกระบวนการโรล-เจต แต่อย่างไรก็ตาม การใช้เยื่อแผ่นที่มีการเชื่อมกันระหว่างของผสม (Mixed Matrix Membrane) ซึ่งเป็นเยื่อแผ่นที่มีสารโททาเนียมไดออกไซด์เป็นองค์ประกอบนั้นกำลังเป็นที่สนใจในปัจจุบัน เนื่องจากมีความโดดเด่นคือ

5 ความสามารถในการเลือกผ่านโมเลกุลสาร มีราคาถูก และมีวิธีการเตรียมที่ไม่ซับซ้อน

การเปิดเผยการประดิษฐ์โดยสมบูรณ์

การประดิษฐ์นี้เกี่ยวข้องกับเยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง (Polymeric Membranes for Photocatalytic Degradation) ซึ่งประกอบด้วย โพลีอะคลิไนด์ไทรล์ 1-2 กรัม ไดมethylฟอร์มามายด์ 8-10 กรัม และ โททาเนียมไดออกไซด์ 0.1-0.2 กรัม

10

วิธีการเตรียมประกอบด้วย การผสมสารโพลีอะคลิไนด์ไทรคิโนสารไดเมธิลฟอร์มามายด์ คนสารผสมอย่างต่อเนื่องรวมทั้งให้ความร้อนแก่สารผสมที่อุณหภูมิ 50 องศาเซลเซียส จนกระทั่งโพลีอะคลิไนด์ไทรคิโนสารละลายในไดเมธิลฟอร์มามายด์อย่างสมบูรณ์ ตั้งสารทิ้งไว้จนเย็น จากนั้นจึง

15 ผสมสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงลงไป คนสารผสมอย่างต่อเนื่องจนกระทั่งสารโททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอในสารละลายของโพลีอะคลิไนด์ไทรคิโนสาร จากนั้นจึงเทสารผสมลงบนกระดาษเรียบและใช้มีดสำหรับหล่อแบบปาดสารผสมให้เป็นแผ่น ตั้งสารไว้ที่อุณหภูมิห้อง เป็นเวลา 30-60 นาที เพื่อให้เยื่อแผ่นคงรูป นำเยื่อแผ่นไปอบในตู้อบแบบสุญญากาศ โดยปรับอุณหภูมิของตู้อบเป็น 40 องศาเซลเซียส เป็นเวลา 15-20 ชั่วโมง ต่อจากนั้นปรับอุณหภูมิ

20 เป็น 60 องศาเซลเซียส เป็นเวลา 2-3 ชั่วโมง ตามด้วยการเพิ่มอุณหภูมิเป็น 80 องศาเซลเซียส เป็นเวลา 2-3 ชั่วโมง

ในอีกรูปแบบหนึ่งของการประดิษฐ์ เยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง (Polymeric Membranes for Photocatalytic Degradation) ซึ่งประกอบด้วย โพลีไวนิลอะซิเตด 1-2 กรัม เติตระไฮโดรฟูแรน 8-10 กรัม และ โททาเนียมไดออกไซด์ 0.1-0.2 กรัม

25

วิธีการเตรียมประกอบด้วย การผสมสารโพลีไวนิลอะซิเตดในตัวทำละลายเติตระไฮโดรฟูแรน คนสารผสมอย่างต่อเนื่องรวมทั้งให้ความร้อนแก่สารผสมที่อุณหภูมิ 50 องศาเซลเซียส จนกระทั่งสารทั้งสองละลายเข้าด้วยกันอย่างสมบูรณ์ ตั้งสารทิ้งไว้รอจนเย็น จากนั้นจึงผสมสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงลงไป คนสารผสมอย่างต่อเนื่องจนกระทั่งสารโททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอในสารละลายของโพลีไวนิลอะซิเตด เทสารผสมลงบนแผ่น

30 เทฟลอนผิวเรียบและใช้มีดสำหรับหล่อแบบปาดสารผสมให้เป็นแผ่น ตั้งเยื่อแผ่นไว้ที่อุณหภูมิห้อง

หน้าที่ 4 ของจำนวน 6 หน้า

เป็นเวลา 15-20 ชั่วโมง นำเยื่อแผ่นไปอบในตู้อบแบบสุญญากาศโดยปรับอุณหภูมิของตู้อบเป็น 40-50 องศาเซลเซียส เป็นเวลา 2-3 ชั่วโมง

- 5 ในอีกรูปแบบหนึ่งของการประดิษฐ์ เยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง (Polymeric Membranes for Photocatalytic Degradation) ซึ่งประกอบด้วย เรลลูโลสอะซิเตด 1-2 กรัม อะซิโตน 8-10 กรัม และ โททาเนียมไดออกไซด์ 0.1-0.2 กรัม

- 10 วิธีการเตรียมประกอบด้วย การละลายเรลลูโลสอะซิเตดในตัวทำละลายอะซิโตน คนสารผสมอย่างต่อเนื่องจนกระทั่งสารทั้งสองละลายเข้าด้วยกันอย่างสมบูรณ์ ผสมสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงลงในสารละลายดังกล่าวพร้อมทั้งคนสารผสมอย่างต่อเนื่องจนกระทั่งสารโททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอในสารละลายของเรลลูโลสอะซิเตด เทสารผสมลงบนกระดาษผิวเรียบและใช้มีดสำหรับหล่อแบบปาดสารผสมให้เป็นแผ่น ตั้งสารไว้ที่อุณหภูมิห้องเป็นเวลา 2-5 นาที เพื่อให้เยื่อแผ่นคงรูป นำเยื่อแผ่นไปแช่ในน้ำเย็นเป็นเวลา 2-5 นาที จากนั้นจึงนำเยื่อแผ่นแช่ในน้ำร้อน 90 องศาเซลเซียสเป็นเวลา 1-2 ชั่วโมง

- 15 สารโททาเนียมไดออกไซด์ เป็นสารซึ่งสังเคราะห์จากสารตั้งต้นโททาเนียมไดไฮดรอกไซด์ในลามีน

- 20 สารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงเตรียมได้จากสารโททาเนียมไดไฮดรอกไซด์ในลามีน ซึ่งประกอบด้วยขั้นตอนของการเผาสารละลายชั้นหนืดของโททาเนียมไดไฮดรอกไซด์ในลามีนด้วยเตาเผาที่อุณหภูมิ 600 องศาเซลเซียส เป็นเวลา 2 ชั่วโมงด้วยอัตราเร็วของการเพิ่มอุณหภูมิ 0.1-0.5 องศาเซลเซียสต่อนาที นำสารที่ได้มาบด

- 25 สารโททาเนียมไดไฮดรอกไซด์ในลามีนได้จากการสังเคราะห์สารโททาเนียมไดออกไซด์และไดไฮดรอกไซด์ในลามีน ซึ่งประกอบด้วยขั้นตอนของการผสมสารประกอบโททาเนียมไดออกไซด์ 2-2.5 กรัม ไดไฮดรอกไซด์ในลามีน 9-10 กรัม ไตรเอทิลอะซิเตต 3-4 กรัม และเอทิลไกลคอล 20-25 มิลลิลิตร คนสารละลายผสมพร้อมทั้งให้ความร้อน กลั่นสารละลายที่อุณหภูมิประมาณ 200 องศาเซลเซียส เป็นเวลา 1 วัน จากนั้นจึงทำการกลั่นเพื่อกำจัดเอทิลไกลคอล และไตรเอทิลอะซิเตตที่มีมากเกินไปที่อุณหภูมิ 150 องศาเซลเซียส

สมบัติในการทนต่อสาร 4-ไนโตรฟีนอล และรังสียูวีของเยื่อแผ่นทั้งสามชนิด สรุปไว้ในตารางดังต่อไปนี้

หน้า 5 ของจำนวน 6 หน้า

* ปริมาณสารอินทรีย์ทั้งหมด (Total Organic Carbon)
** 4-ไนโตรฟีนอล (4-nitrophenol)

ชนิดของเยื่อแผ่น และสภาวะในการทดสอบ	ค่า TOC* เริ่มต้น (มิลลิกรัมต่อลิตร)	ค่า TOC หลังจากทดสอบเป็นเวลา 6 ชั่วโมง (มิลลิกรัมต่อลิตร)
โพลีอะคลิไนด์ในไตรล์+น้ำ+รังสียูวี	0	0
เรลกูโดลอะซิเตด+น้ำ+รังสียูวี	0	0
โพลีไวนิลอะซิเตด+น้ำ+รังสียูวี	0	11.79
โพลีอะคลิไนด์ในไตรล์+4-NP**+รังสียูวี	22.35	22.34
เรลกูโดลอะซิเตด+4-NP+รังสียูวี	22.35	22.35
โพลีไวนิลอะซิเตด+4-NP+รังสียูวี	22.35	32.22
โพลีอะคลิไนด์ในไตรล์+4-NP	22.35	22.36
เรลกูโดลอะซิเตด+4-NP	22.35	22.35
โพลีไวนิลอะซิเตด+4-NP	22.35	36.44

5 ตัวอย่าง

ตัวอย่างที่จะกล่าวถึงต่อไปนี้มีวัตถุประสงค์เพื่อที่จะให้เกิดความเข้าใจในการประดิษฐ์ให้มากขึ้น ตัวอย่างถูกตั้งใจที่จะให้เป็นแบบแสดงให้เห็นเพื่ออธิบายเท่านั้น และไม่สามารถถือเป็นการจำกัดขอบเขตการประดิษฐ์

ตัวอย่างที่ 1 การเตรียมเยื่อแผ่นจากสารผสมสูตร I รวมถึงการทดสอบการทนต่อสาร 4-ไนโตรฟีนอล และรังสียูวี

ขั้นแรก:1.การสังเคราะห์สารโททาเนียมไดออกไซด์โพลฟานอลามีนจากโททาเนียมไดออกไซด์ และไตรโอโรโพลฟานอลามีน

ผสมสารประกอบโททาเนียมไดออกไซด์ 2-2.5 กรัม ไตรโอโรโพลฟานอลามีน 9-10 กรัม ไตรเอธิลีนแคดเตรมีน 3-4 กรัม และเอธิลีนไกลคอล 20-25 มิลลิลิตร คนสารละลายผสมพร้อมทั้งให้ความร้อน กลั่นสารละลายที่อุณหภูมิประมาณ 200 องศาเซลเซียสเป็นเวลา 1 วัน จากนั้นจึงทำ

หน้าที่ 6 ของจำนวน 6 หน้า

การกลั่นเพื่อกำจัดเฮกซามีนไฮดรอกไซด์ และไตรเฮกซามีนไฮดรอกไซด์ที่มีมากเกินไปที่อุณหภูมิ 150 องศาเซลเซียส

ตรวจสอบสารละลายชั้นหนึ่งที่มีองค์ประกอบของสารผลิตภัณฑ์รวมกับสารไตรไฮโดรฟอสฟอไรนที่มากเกินไป ด้วยเครื่อง FT-IR, TGA และ FAB-MS

5 2. การเตรียมสารโททาเนียมที่มีพื้นที่ผิวสูงจากสารโททาเนียมไดไฮโดรฟอสฟอไรน

ผสมสารละลายชั้นหนึ่งของโททาเนียมไดไฮโดรฟอสฟอไรนด้วยเตาเผาที่อุณหภูมิ 600 องศาเซลเซียสเป็นเวลา 2 ชั่วโมงด้วยอัตราเร็วของการเพิ่มอุณหภูมิ 0.1-0.5 องศาเซลเซียสต่ออนาที นำสารที่ได้มาทดสอบด้วยเครื่อง XRD, SEM และ TGA

ขั้นที่สอง: การเตรียมเยื่อแผ่นโพลีอะคลิไนด์ไนไตรด์

10 ผสมสารโพลีอะคลิไนด์ไนไตรด์ (1-2 กรัม) ในสารไดเมทิลฟอร์มาไมด์ (8-10 กรัม) คนสารผสมอย่างต่อเนื่องรวมทั้งให้ความร้อนแก่สารผสมที่อุณหภูมิ 50 องศาเซลเซียสจนกระทั่งโพลีอะคลิไนด์ไนไตรด์ละลายในไดเมทิลฟอร์มาไมด์อย่างสมบูรณ์ ตั้งสารทิ้งไว้จนเย็นจากนั้นจึงผสมสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงประมาณ 0.1-0.2 กรัม ลงไป คนสารผสมอย่างต่อเนื่องจนกระทั่งสารโททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอในสารละลายของโพลีอะคลิไนด์ไนไตรด์

15 จากนั้นจึงเทสารผสมลงบนกระดาษเรียบและใช้มีดสำหรับหล่อแบบปาดสารผสมให้เป็นแผ่น ตั้งสารไว้ที่อุณหภูมิห้องเป็นเวลา 30-60 นาทีเพื่อให้เยื่อแผ่นคงรูป นำเยื่อแผ่นไปอบในตู้อบแบบสุญญากาศโดยปรับอุณหภูมิของตู้อบเป็น 40 องศาเซลเซียสเป็นเวลา 15-20 ชั่วโมง ต่อจากนั้นปรับอุณหภูมิเป็น 60 องศาเซลเซียสเป็นเวลา 2-3 ชั่วโมง ตามด้วยการเพิ่มอุณหภูมิเป็น 80 องศาเซลเซียสเป็นเวลา 2-3 ชั่วโมง

20 ขั้นที่สาม: การทดสอบความทนต่อสาร 4-ไนโตรฟีนอล และรังสียูวี

แช่เยื่อแผ่นโพลีอะคลิไนด์ไนไตรด์ลงในสารละลาย 4-ไนโตรฟีนอลที่มีความเข้มข้น 40-60 มิลลิกรัมต่อลิตร หรือน้ำกลั่น เปรียบเทียบระหว่างผลที่เกิดจากการฉายและไม่ฉายรังสียูวี ดูสารออกมาทดสอบการเปลี่ยนแปลงค่า TOC หลังจากทำการทดลองเป็นเวลา 3-6 ชั่วโมงเพื่อตรวจสอบปริมาณสารอินทรีย์ที่หลุดออกมาจากเยื่อแผ่นโพลีอะคลิไนด์ไนไตรด์

25 วิธีการในการประดิษฐ์ที่ดีที่สุด

เหมือนกับที่ได้กล่าวไว้แล้วในหัวข้อการเปิดเผยการประดิษฐ์โดยสมบูรณ์

หน้าที่ 1 ของจำนวน 2 หน้า

ข้อปฏิบัติ

1. เยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง ซึ่งประกอบด้วย โพลีอะคลิไนด์ไทรด์ 1-2 กรัม ไดเมธิลฟอร์มาไมด์ 8-10 กรัม และ ไททาเนียมไดออกไซด์ 0.1-0.2 กรัม

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2. วิธีการเตรียมเยื่อแผ่นตามข้อปฏิบัติ 1 ซึ่งประกอบด้วย การผสมสารโพลีอะคลิไนด์ไทรด์ในสารไดเมธิลฟอร์มาไมด์ คนสารผสมอย่างต่อเนื่องรวมทั้งให้ความร้อนแก่สารผสมที่อุณหภูมิ 50 องศาเซลเซียส จนกระทั่งโพลีอะคลิไนด์ไทรด์ละลายในไดเมธิลฟอร์มาไมด์อย่างสมบูรณ์ ตั้งสารทิ้งไว้จนเย็น จากนั้นจึงผสมสารไททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงลงไป คนสารผสมอย่างต่อเนื่องจนกระทั่งสารไททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอในสารละลายของโพลีอะคลิไนด์ไทรด์ จากนั้นจึงเทสารผสมลงบนกระจกผิวเรียบและใช้มีดสำหรับหล่อแบบปาดสารผสมให้เป็นแผ่น ตั้งสารไว้ที่อุณหภูมิห้อง เป็นเวลา 30-60 นาที เพื่อให้เยื่อแผ่นคงรูป นำเยื่อแผ่นไปอบในตู้อบแบบสุญญากาศโดยปรับอุณหภูมิของตู้อบเป็น 40 องศาเซลเซียส เป็นเวลา 15-20 ชั่วโมง ต่อจากนั้นปรับอุณหภูมิเป็น 60 องศาเซลเซียส เป็นเวลา 2-3 ชั่วโมง ตามด้วยการเพิ่มอุณหภูมิเป็น 80 องศาเซลเซียส เป็นเวลา 2-3 ชั่วโมง

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3. เยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง ซึ่งประกอบด้วย โพลีไวนิลอะซิเตด 1-2 กรัม เดตระไฮโดรฟูแรน 8-10 กรัม และ ไททาเนียมไดออกไซด์ 0.1-0.2 กรัม

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4. วิธีการเตรียมเยื่อแผ่นตามข้อปฏิบัติ 3 ซึ่งประกอบด้วย การผสมสารโพลีไวนิลอะซิเตดในตัวทำละลายเดตระไฮโดรฟูแรน คนสารผสมอย่างต่อเนื่องรวมทั้งให้ความร้อนแก่สารผสมที่อุณหภูมิ 50 องศาเซลเซียสจนกระทั่งสารทั้งสองละลายเข้าด้วยกันอย่างสมบูรณ์ ตั้งสารทิ้งไว้รอจนเย็น จากนั้นจึงผสมสารไททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงลงไป คนสารผสมอย่างต่อเนื่องจนกระทั่งสารไททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอในสารละลายของโพลีไวนิลอะซิเตด เทสารผสมลงบนแผ่นเทฟลอนผิวเรียบและใช้มีดสำหรับหล่อแบบปาดสารผสมให้เป็นแผ่น ตั้งเยื่อแผ่นไว้ที่อุณหภูมิห้องเป็นเวลา 15-20 ชั่วโมง นำเยื่อแผ่นไปอบในตู้อบแบบสุญญากาศโดยปรับอุณหภูมิของตู้อบเป็น 40-50 องศาเซลเซียส เป็นเวลา 2-3 ชั่วโมง

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หน้าที่ 2 ของจำนวน 2 หน้า

5. เยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสง ซึ่งประกอบด้วย
เซลลูโลสอะซิเตด 1-2 กรัม อะซิโตน 8-10 กรัม และ โททาเนียมไดออกไซด์ 0.1-0.2 กรัม
- 5 6. วิธีการเตรียมเยื่อแผ่นตามข้อถ้อยสิทธิ 5 ซึ่งประกอบด้วย การละลายเซลลูโลสอะซิเตดในตัว
ทำละลายอะซิโตน คนสารผสมอย่างต่อเนื่องจนกระทั่งสารทั้งสองละลายเข้าด้วยกันอย่าง
สมบูรณ์ ผสมสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงลงในสารละลายดังกล่าวพร้อมทั้งคน
สารผสมอย่างต่อเนื่องจนกระทั่งสารโททาเนียมไดออกไซด์กระจายตัวอย่างสม่ำเสมอใน
สารละลายของเซลลูโลสอะซิเตด เทสารผสมลงบนกระจกผิวเรียบและใช้มีดสำหรับหล่อ
แบบปาดสารผสมให้เป็นแผ่น ตั้งสารไว้ที่อุณหภูมิห้องเป็นเวลา 2-5 นาที เพื่อให้เยื่อแผ่นคง
10 รูป นำเยื่อแผ่นไปแช่ในน้ำเย็นเป็นเวลา 2-5 นาที จากนั้นจึงนำเยื่อแผ่นแช่ในน้ำร้อน 90
องศาเซลเซียสเป็นเวลา 1-2 ชั่วโมง
7. เยื่อแผ่นตามข้อถ้อยสิทธิ 1 หรือ 3 หรือ 5 ที่ซึ่งโททาเนียมไดออกไซด์เป็นสารซึ่งสังเคราะห์
จากสารตั้งต้นโททาเนียมไดไฮโดรโพลฟอสฟอโนลามีน
- 15 8. วิธีการตามข้อถ้อยสิทธิ 2 หรือ 4 หรือ 6 ที่ซึ่งสารโททาเนียมไดออกไซด์ที่มีพื้นที่ผิวสูงเตรียมได้
จากสารโททาเนียมไดไฮโดรโพลฟอสฟอโนลามีน ซึ่งประกอบด้วยขั้นตอนของการเผาสารละลาย
ชั้นหนืดของโททาเนียมไดไฮโดรโพลฟอสฟอโนลามีนด้วยเตาเผาที่อุณหภูมิ 600 องศาเซลเซียส
เป็นเวลา 2 ชั่วโมงด้วยอัตราเร็วของการเพิ่มอุณหภูมิ 0.1-0.5 องศาเซลเซียสต่อนาที นำสาร
20 ที่ได้ออกมา
9. วิธีการตามข้อถ้อยสิทธิ 7 ที่ซึ่งสารโททาเนียมไดไฮโดรโพลฟอสฟอโนลามีนได้จากการสังเคราะห์
สารโททาเนียมไดออกไซด์ และไดไฮโดรโพลฟอสฟอโนลามีน ซึ่งประกอบด้วยขั้นตอนของการ
ผสมสารประกอบโททาเนียมไดออกไซด์ 2-2.5 กรัม ไดไฮโดรโพลฟอสฟอโนลามีน 9-10 กรัม ไตร
25 เอธิลีนเตตระมีน 3-4 กรัม และเอธิลีนไกลคอล 20-25 มิลลิลิตร คนสารละลายผสมพร้อมทั้ง
ให้ความร้อน กลั่นสารละลายที่อุณหภูมิประมาณ 200 องศาเซลเซียส เป็นเวลา 1 วัน
จากนั้นจึงทำการกลั่นเพื่อกำจัดเอธิลีนไกลคอล และไตรเอธิลีนเตตระมีนที่มีมากเกินไปพอที่
อุณหภูมิ 150 องศาเซลเซียส

หน้าที่ 1 ของจำนวน 1 หน้า

บทสรุปการประดิษฐ์

การประดิษฐ์นี้เกี่ยวข้องกับเยื่อแผ่นสำหรับกระบวนการย่อยสลายสารพิษและเชื้อโรคด้วยแสงที่ไรโทพลาเนียมไดออกไซด์เป็นตัวเร่งปฏิกิริยา

**B. Photocatalytic Membrane of a Novel High Surface Area TiO_2
Synthesized from Titanium Triisopropanolamine Precursor**

Photocatalytic membrane of a novel high surface area TiO₂ synthesized from titanium triisopropanolamine precursor

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Received 4 October 2005; Revised 25 October 2005; Accepted 10 April 2006

Photocatalytic membrane was successfully prepared using an efficiently high surface area TiO₂ catalyst, dispersed into polyacrylonitrile matrix. The catalyst was directly synthesized using titanium triisopropanolamine as a precursor. The membranes were characterized using FT-IR, TGA, SEM and their photocatalytic performance tested, viz. stability, permeate flux and photocatalytic degradation of 4-NP. We find that polyacrylonitrile is an effective matrix, showing high stability and low permeate flux. The amount of TiO₂ loaded in the membrane was varied between 1, 3 and 5 wt% to explore the activity and stability of membranes in the photocatalytic reaction of 4-NP. As expected, the higher the loading of TiO₂ loaded, the higher the resulting catalytic activity. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: mixed matrix membrane; photocatalysis; 4-nitrophenol; titanium triisopropanolamine

1 INTRODUCTION

The use of mixed matrix membranes (MMM), i.e. membranes containing microencapsulated TiO₂, is of increasing interest because of their high selectivity combined with outstanding separation performance, processing capabilities and low cost, when polymers are used as the matrix. Many researchers^{1–4} have explored ways to develop and facilitate the separation process, using very thin microencapsulated membranes to allow for high fluxes. Such a membrane must have a high volume fraction of homogeneously distributed encapsulated particles in a defect- and void-free polymer matrix.⁵ Polymeric membranes are not appropriate for use in membrane reactor applications where high temperatures are needed for reaction. Thus, application of MMM for catalysis of low temperature reactions has become a main topic for many researchers, examples being hydrogenation

of propyne,⁶ photomineralization of *n*-alkanoic acids,⁷ wet air oxidation of dyeing wastewater, and photocatalytic oxidations.^{8–11}

The heterogeneous photocatalysis process harnesses radiant energy from natural or artificial light sources to degrade organic pollutants into their mineral components.¹² TiO₂ is a well-established catalyst for photocatalytic degradation due to its combination of high activity, chemical stability and non-toxic properties. Photocatalytic degradation generally occurs via production of OH[•] radicals. The organic pollutant is attacked by hydroxyl radicals and generates organic radicals or intermediates.^{13–16} The main drawback to practical implementation of the photocatalysis method arises from the need for an expensive liquid–solid separation process due to the formation of milky dispersions upon mixing the catalyst powder with water.¹⁷

Currently, this drawback is solved by the use of a TiO₂ membrane, consisting of fine TiO₂ particles dispersed in a porous matrix. Such titania membranes have attracted a great deal of attention in recent years due to their unique characteristics, including high water flux, semiconducting properties, efficient photocatalysis and chemical resistance relative to other membrane materials, such as silica and γ -alumina.¹⁸

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Contract/grant sponsor: Postgraduate Education and Research Program in Petroleum and Petrochemical Technology Fund.

Contract/grant sponsor: Ratchadaphisakra Sompote Fund.

Contract/grant sponsor: Chulalongkorn University.

Contract/grant sponsor: Thailand Research Fund.

To obtain a high photocatalytic activity, the surface area of catalyst is very important. Thus, in our work, thermally stable TiO_2 with high surface area is synthesized from moisture-stable titanium triisopropanolamine. The performance of this material as a component of an MMM was evaluated in a photocatalytic membrane reactor, using 4-nitrophenol as a model substrate, with regard to stability tests and TiO_2 loading.

EXPERIMENTAL

Materials

Titanium dioxide (surface area $12 \text{ m}^2/\text{g}$) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinkrodt Baker Inc. (USA) and purified by fractional distillation at 200°C under nitrogen atmosphere before use. Triethylenetetramine (TETA) was purchased from Facal Polytech. Co. Ltd (Bangkok, Thailand) and distilled under vacuum (0.1 mmHg) at 130°C prior to use. Triisopropanolamine (TIS) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA). 4-Nitrophenol was purchased from Sigma-Aldrich Chemical Co. Inc. (USA).

Titanium tri-isopropanolamine precursor preparation and characterization

A mixture of TiO_2 (2 g, 0.025 mol), triisopropanolamine (9.55 g, 0.05 mol) and triethylenetetramine (3.65 g, 0.0074 mol) was stirred vigorously in excess ethylene glycol (25 cm^3) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO_2 . The excess EG and TETA were removed by vacuum distillation at 150°C to obtain a crude precipitate. The product was characterized using FTIR, FAB⁺-MS and TGA. Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 Bruker spectrometer with a spectral resolution of $4/\text{cm}$. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over a $30\text{--}800^\circ\text{C}$ temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) using the positive fast atomic bombardment mode (FAB⁺-MS) with glycerol as the matrix, cesium gun as initiator and cesium iodide (CsI) as a standard for peak calibration. FT-IR: 3400 ($\nu\text{-OH}$), $2927\text{--}2855$ ($\nu\text{-C-H}$), 1460 ($\delta\text{-C-H}$ of CH_2 group), 1379 ($\delta\text{-C-H}$ of CH_3 group), 1085 ($\nu\text{-C-O-Ti}$), 1020 ($\delta\text{-C-N}$) and $554/\text{cm}$ ($\nu\text{-Ti-O}$); TGA: decomposition transition at 365°C with 16.60% ceramic yield (theoretical ceramic yield of 18.65%); FAB⁺-MS: $\text{Ti}(\text{OCHCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CHCH}_2\text{OH})_2\text{H}^+$ at m/e 428.

High surface area TiO_2 preparation and characterization

After removal of any excess solvent from titanium triisopropanolamine precursor, the precursor was transferred to a crucible and calcined at 600°C for 2 h at heating rate of

$0.25^\circ\text{C}/\text{min}$. TiO_2 was characterized by various techniques. The XRD pattern was obtained using a D/MAX-2200H Rigaku diffractometer with $\text{CuK}\alpha$ radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range of 5° to 90° . Thermal stability was characterized on a Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over $30\text{--}800^\circ\text{C}$ temperature range. Samples pyrolyzed at 600°C were analyzed using SEM by attachment onto aluminum stubs after coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at $\times 7500$ magnification. Specific surface area and nitrogen adsorption-desorption were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of $30 \text{ cm}^3/\text{min}$. Nitrogen was used to calibrate the analyzer and also used as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2 h at 150°C , prior to exposure to the adsorbent gas.

Membrane preparation and characterization

A 10 wt% mixture of polyacrylonitrile powder in dimethyl formamide (DMF) was vigorously stirred at 50°C until homogeneous. A specified amount of TiO_2 was added to the stirred polymer solution. Partial vacuum was applied for a brief duration to ensure the removal of air bubbles. The mixture was then coated on a clean glass plate using a casting knife. The resulting membrane was allowed to set for 2 min before being dried in a vacuum oven at 40°C overnight following by 60°C for 2 h and 80°C for 2 h. The prepared membrane with thickness of $15 \mu\text{m}$ was cut into a circular shape with a diameter of 6 cm.

The membrane made was characterized using SEM and TGA. The morphology of membranes was analyzed by attachment onto aluminum stubs and coated with gold via vapor deposition. The membranes were frozen in liquid nitrogen and fractured to examine the cross-sectional areas. The samples were characterized on a Jeol 5200-2AE (MP 15152001) scanning electron microscope. The samples were also analyzed using Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over $30\text{--}500^\circ\text{C}$ temperature range to determine the organic residue in the prepared membranes.

Stability tests of prepared membranes

The experiment was carried out to check the stability of prepared polymeric membrane (PAN) by placing the prepared membranes in a Petri dish containing either distilled water or 40 ppm 4-NP solution with and without irradiation for 6 h. The solutions were then withdrawn and analyzed for total organic carbon (TOC) to verify the organic components released from the membrane.

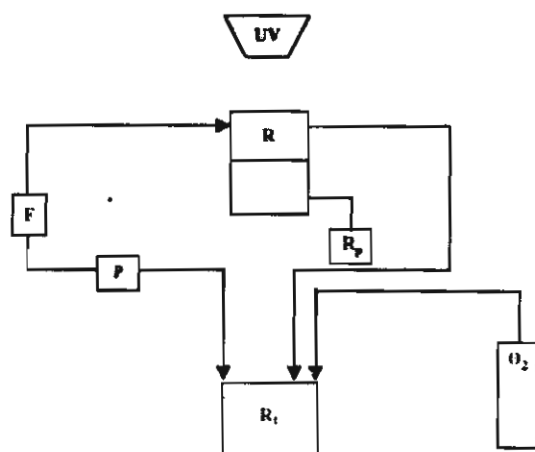


Figure 1. Schematic diagram of photocatalytic membrane reactor (F, flowmeter; R, reactor; R_p , permeate reservoir; R_t , recirculating tank; and P, peristaltic pump).

Photocatalytic decomposition of 4-nitrophenol

The photocatalytic reactions were carried out in a 1000 ml continuous batch glass reactor, Fig. 1, with gas inlet and outlet at an O_2 flow rate of 20 ml/min. A cooling water jacket was used to maintain the temperature at 30 °C. The suspensions and membrane were illuminated using a 100 W Hg Philip UV lamp. The concentration of 4-NP used was 40 ppm and the solution was continuously stirred. The obtained permeate was removed at 1 h intervals and analyzed to determine the concentration of 4-NP using a Shimadzu UV-240 spectrophotometer. For different pH value, H_2SO_4 was used to adjust the pH value measured using an Ecscan pH meter.

RESULTS AND DISCUSSION

TiO_2 catalyst preparation

High surface area TiO_2 catalyst was characterized using XRD, TGA, BET and SEM to confirm the presence of the active anatase phase of TiO_2 . The TGA thermogram (not given) illustrates absence of organic species, meaning the formation of pure TiO_2 , while the XRD pattern shown in Fig. 2, exhibits diffraction peaks at $2\theta = 25.28, 37.94, 47.98, 54.64, 62.58, 69.76, 75.26$ and 82.72 . The average grain size of calcined TiO_2 calculated from Scherrer equation, is 12.42 nm. The SEM micrograph (not shown) presents similar particle morphology of the prepared anatase phase of TiO_2 to those in the literature.^{19–21} The surface area measurement shows a high surface area of $163 \text{ m}^2/\text{g}$; also, the nitrogen adsorption–desorption isotherm of this material exhibits type IV character (Fig. 3), indicative of a mesoporous structure.

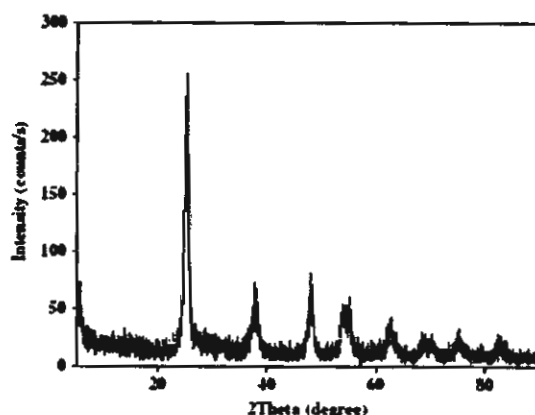


Figure 2. XRD pattern of the anatase phase of the prepared TiO_2 catalyst after calcinations of the precursor at 600 °C for 2 h.

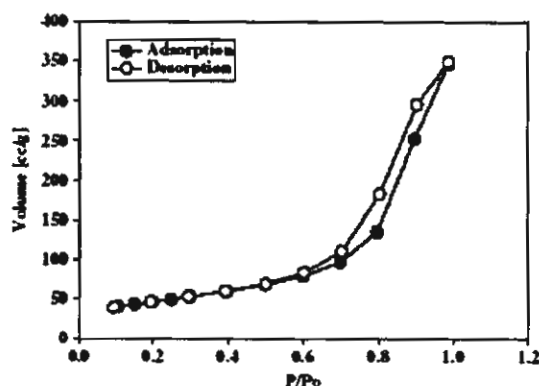


Figure 3. Nitrogen adsorption–desorption isotherm for the prepared mesoporous titania calcined at 600 °C.

Membranes preparation

The prepared mixed matrix membranes were characterized with respect to their purity using TGA thermogram and their morphology using scanning electron microscopy (SEM). The TGA thermogram (not given) gives only one transition at around 300 °C, referring to the degradation of PAN membrane,^{22,23} respectively. An SEM micrograph of the surface of the prepared membrane is shown in Fig. 4(a). When the TiO_2 particles are immobilized within the polymeric matrix, the micrographs reveal no evidence for the presence of voids between the polymer and TiO_2 , implying that the membranes are dense. TiO_2 particles are well distributed across the surface. As varying the percentage of TiO_2 between 1, 3 and 5 wt%, morphological analysis by SEM, as shown in

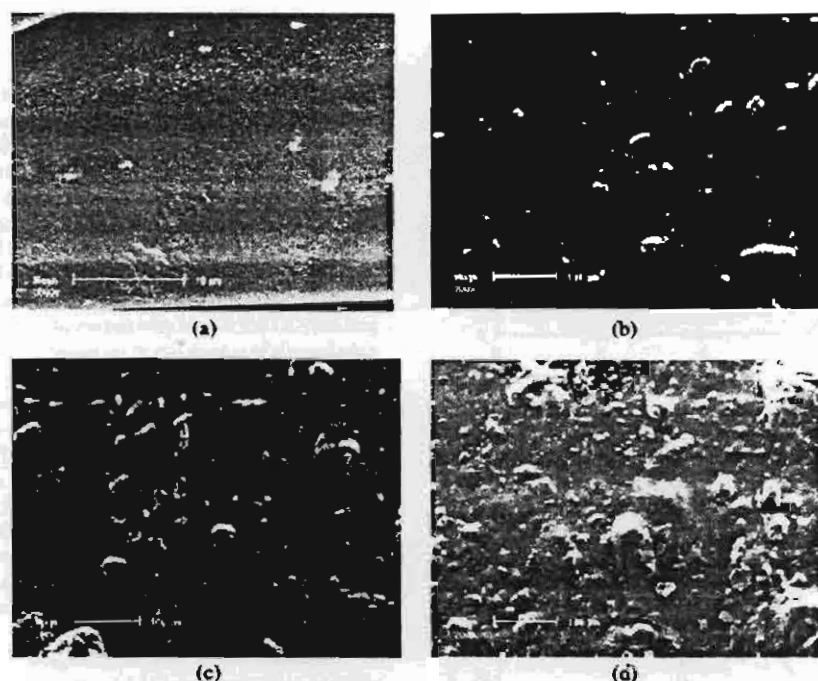


Figure 4. SEM micrographs of mixed matrix membranes using (a) polyacrylonitrile (PAN), (b) PAN + 1 wt% TiO_2 , (c) PAN + 3 wt% TiO_2 and (d) PAN + 5 wt% TiO_2 .

Fig. 4(b–d), indicates, TiO_2 particles are dispersed throughout the PAN matrix at all loadings.

Stability tests of prepared membranes

The stability of the prepared PAN membranes is summarized in Table 1, presenting the TOC results of the tested membrane. It was found that the PAN membrane is undoubtedly stable even under irradiation conditions.

The photocatalytic degradation of 4-nitrophenol

The photocatalytic activity of the PAN membrane was assessed using the photoreactor, employing 1 wt% immobilized photocatalyst TiO_2 , oxygen flow rate of 20 ml/min, 4-NP flow rate of 30 ml/min and 4-NP concentration of 40 ppm at pH 3.^{9,10,24} The permeate flux data (not shown) indicate that the prepared PAN membrane has constant low

Table 1. The stability tests of the prepared membranes

Membrane type and condition	TOC value at initial (ppm)	TOC value after 6 h (ppm)
PAN + H_2O + UV	0	0
PAN + 4-NP + UV	22.35	22.34
PAN + 4-NP	22.35	22.36

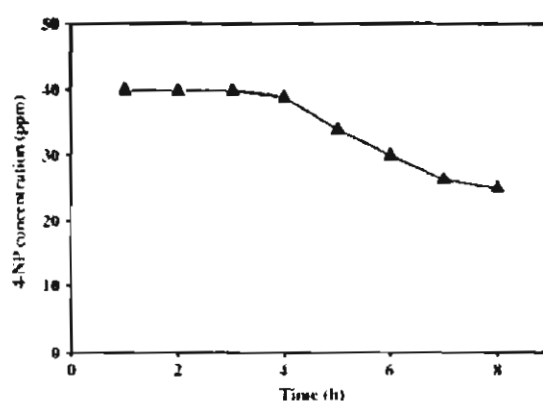


Figure 5. The degradation of 4-NP with the reaction time of the PAN membranes performed at pH 3.

permeate flux level, 5.31 l/h m^2 . The efficiency of the PAN membrane for photocatalytic degradation of 4-NP is illustrated in Fig. 5, which indicates that, at 1 wt% Ti loading in PAN membrane, the degradation of 4-NP occurs faster after 4 h irradiation.

Effect of various amounts of TiO_2 in PAN membrane on the photocatalytic degradation of 4-nitrophenol

4-NP auto-photolysis was first carried out without the mixed matrix membrane and showed no degradation. The experiment was thus performed to study the permeate flux of PAN membranes at the three loading levels, 1, 3 and 5 wt% of TiO_2 (Fig. 6). We found that the flux is constant for all three samples, and increases with the amount of TiO_2 from 5.3, to 8.1 to 12.7 l/h m^2 , respectively. In Fig. 7, the efficiency of degradation of 4-NP at the three loading levels of TiO_2 is reported. The decrease of 4-NP at 3 and 5% loadings appears to be faster than at 1%. The reason may be that the TiO_2 loading is too low to see any differences in the degree of degradation of 4-NP. However, when compared with literature results,¹¹ performed at much higher loadings of TiO_2 , it appears that these membranes show a higher level of catalytic activity.

Commercial TiO_2 (Degussa P25) was also studied for comparison with our TiO_2 at loading level of 3 wt%. The result, see Fig. 8, indicates no permeation of 4-NP through a membrane prepared using commercial TiO_2 and the efficiency of degradation of 4-NP measured from the retentate of two membranes shows that the degradation of 4-NP in the membrane prepared using our TiO_2 is distinguishably lower.

Effect of pH on degradation of 4-nitrophenol

From the literature, the rate of 4-NP decomposition at lower pH is faster and shows the highest activity at pH 3.^{9,10,24} Therefore, we compare the experiment of 4-NP solution at pH = 3 (adjust pH value of 4-NP solution by H_2SO_4) with pH = 7 (without the pH adjustment of 4-NP solution). It was found that the results indeed are the same after irradiation, see Fig. 9. The 4-NP concentration at pH = 3 declines sharply when applied the UV irradiation and reaches to the complete degradation after 8 h reaction time. Only 25% degradation occurs in the solution having pH = 7. Figure 10

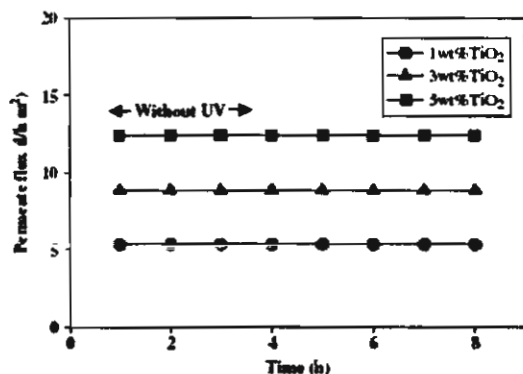


Figure 6. The permeate flux vs reaction time of polyacrylonitrile membranes at various percentages of TiO_2 and pH 3.

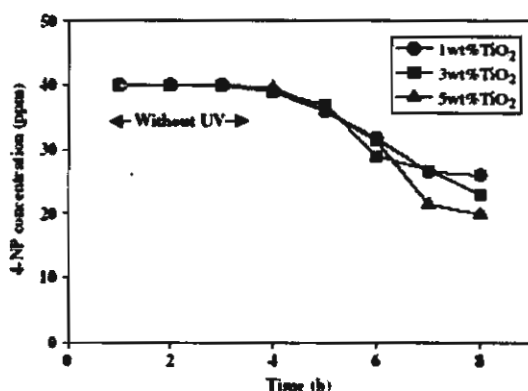


Figure 7. The degradation of 4-NP with the reaction time of polyacrylonitrile membranes at various percentages of TiO_2 and pH 3.

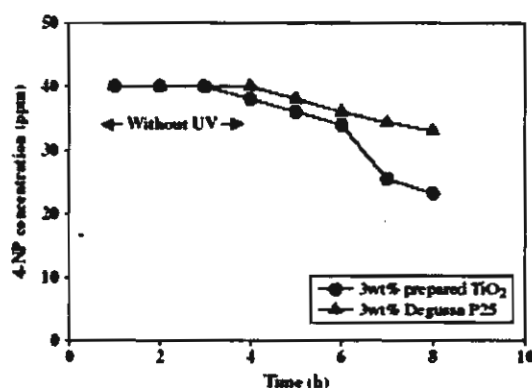


Figure 8. Effect of TiO_2 type mixed in the polyacrylonitrile membrane on the degradation of 4-NP.

shows the UV spectra of 4-NP concentration at pH = 3 in which the 4-NP is completely degraded. The surface of TiO_2 is positively charged in acidic media, therefore, the higher H^+ concentration leads to the higher OH radicals for the photodegradation of 4-NP.²⁵

CONCLUSIONS

The titanium triisopropanolamine precursor can be prepared by a very simple method (the oxide one pot synthesis) from low cost starting materials, and yields a TiO_2 catalyst with high surface area obtained after calcinations of the precursor at 600 °C for 2 h. Polymeric membranes loaded with the as-prepared TiO_2 catalyst show an impressively

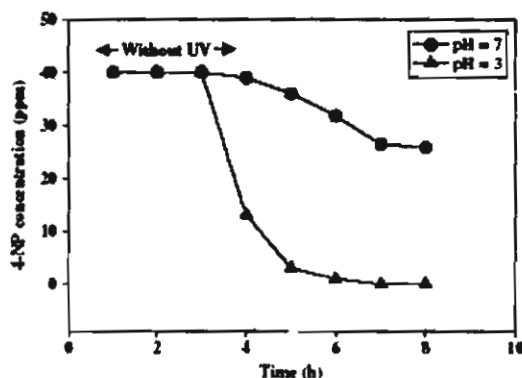


Figure 9. Effect of pH on the degradation of 4-NP using 3 wt% TiO_2 loaded in the polyacrylonitrile membrane.

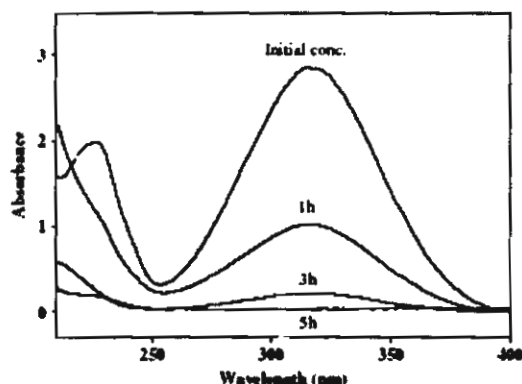


Figure 10. The UV spectra of 4-NP solution analyzed at different reaction time and pH = 3 using 1 wt% TiO_2 loaded in the polyacrylonitrile membrane.

efficiency of photocatalytic degradation of 4-NP is illustrated at lower pH value.

Acknowledgements

This research work was supported by the Postgraduate Education and Research Program in Petroleum and Petrochemical Technology (ADB) Fund, Ratchadapaisake Sompote Fund, Chulalongkorn University and the Thailand Research Fund (TRF).

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C. Crystallization and catalytic activity of high titanium loaded TS-1 zeolite



Crystallization and catalytic activity of high titanium loaded TS-1 zeolite

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Received 19 August 2004; received in revised form 15 August 2005; accepted 23 August 2005

Abstract

TS-1 zeolite with high Ti loading was successfully synthesized from low-cost and moisture-stable precursors, titanium glycolate and silatrane, using microwave heating. The effect of composition, viz. tetrapropylammonium ion (TPA⁺), NaOH, H₂O, and reaction conditions, viz. aging time, reaction temperature, and reaction time, was studied. The Si:Ti mole ratios were varied from 100.00 to 5.00 and the extent to which Ti is incorporated into the zeolite framework was evaluated. The TS-1 samples were characterized by XRD, FT-IR, S.E.M. and DR-UV, and confirmed the fingerprint of MFI type zeolite. A small amount of extra-framework titanium dioxide was also identified at a Si:Ti mole ratio of 5.0. Photocatalytic decomposition of 4-nitrophenol (4-NP) was used to test the catalytic activity of the TS-1 samples. All samples showed high catalytic efficiency, which increased with Ti loading.

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Keywords: Photocatalytic decomposition; Silatrane; Titanium glycolate; TS-1 zeolite

1. Introduction

Titanium silicate-1 (TS-1), a Ti-containing zeolite with the MFI structure, is a microporous crystalline material, used as a highly-selective heterogeneous oxidative catalyst, employing H₂O₂ under mild conditions. The titanium isomorphously replaces silicon in a tetrahedral site of the MFI silicate lattice. TS-1 combines the advantages of having the high coordination ability of Ti⁴⁺ ions with the hydrophobicity of the silicate framework, while retaining the spatial selectivity and specific local geometry of the active sites of the molecular sieve structure [1]. The catalytic properties of titanosilicate are unique, encompassing a variety of liquid-phase oxidations, such as phenol hydroxylation, olefin epoxidation, cyclohexanone ammoximation and the oxidation of saturated hydrocarbons and alcohols [2,3]. With H₂O₂, solvolysis produces TiOOH and SiOH, the former giving rise to the active catalytic oxidation center.

Since 1983, when Taramasso et al. [4] reported the hydrothermal synthesis of TS-1 for the first time, many attempts have been made to increase the amount of Ti(IV) in the zeolite framework.

A major problem often encountered in the synthesis of TS-1 molecular sieves is the precipitation of titanium oxide outside the lattice framework, leading to materials which are inactive for oxidative catalysis [5]. The synthesis of materials containing isolated tetrahedral Ti is challenging due to the strong tendency of Ti to polymerize under aqueous conditions, often forming a separate titanium dioxide phase [1]. Two methods to synthesize TS-1 were described in the original patent using different Si sources, tetraethylorthosilicate (TEOS) and Ludox colloidal silica, and typically employing tetrapropylammonium hydroxide (TPAOH) as the structure directing agent and to provide the alkalinity necessary for the crystallization of the zeolite [6]. From previous work, the maximum amount of Ti(IV) incorporated in the zeolite framework corresponds to a Si:Ti ratio of approximately 33–35 [1,3,6]. Furthermore, attempts to achieve a higher degree of substitution (Si/Ti = 10, 15 and 30) have not been successful with Ti fully incorporated into the lattice framework.

Microwave-assisted-hydrothermal synthesis is a process which has been used for the rapid synthesis of numerous ceramic oxides and porous materials [7–9]. It offers many advantages over conventional synthesis including quick and homogeneous heating in a few minutes, homogeneous nucleation, fast super-saturation through rapid dissolution of precipitated gels and shorter crystallization times. Heating is induced via the friction of molecular motion enhanced by microwave irradiation, thus it

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is possible to heat the reactants selectively and homogeneously throughout the material. Furthermore, microwave heating is energy efficient and economical [10,11].

In this work, we synthesized TS-1 zeolite from moisture-stable, low-cost starting materials, silatrane and titanium glycolate, as sources of silica and titanium dioxide, respectively, and using tetrapropylammonium bromide (TPABr) as a template and microwave heating. Various amounts of Ti were incorporated in the zeolite framework. The samples were characterized using XRD, S.E.M., FT-IR and DR-UV. Photocatalytic decomposition of 4-NP was carried out to test the activity of the TS-1 samples.

2. Experimental

2.1. Materials

Titanium dioxide (surface area $12 \text{ m}^2 \text{ g}^{-1}$) was purchased from Sigma-Aldrich Chemical Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Mallinckrodt Baker Inc. (USA) and purified by fractional distillation at 200°C under nitrogen at atmospheric pressure before use. Triethylenetetramine (TETA) was purchased from Facai Polytech Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mmHg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder. 4-Nitrophenol was purchased from Sigma-Aldrich Chemical Co. Inc. (USA).

2.2. Instrumental

Fourier transform-infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer thermal analysis system with a heating rate of $10^\circ\text{C min}^{-1}$ over $30\text{--}800^\circ\text{C}$ temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec Ultima 707E) with VG data system, using the positive fast atomic bombardment mode (FAB⁺-MS) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. ^{13}C -solid-state NMR spectroscopy was performed using a Bruker AVANCE DPX-300 MAS-NMR. Elemental analysis (EA) was carried out on a C/H/N Analyzer (Perkin-Elmer PE2400 series II).

2.3. Preparation of titanium glycolate

The procedure adopted followed previous work [12]. A mixture of TiO_2 (2 g , 0.025 mol) and TETA (3.65 g , 0.0074 mol) was stirred vigorously in excess EG (25 cm^3) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO_2 . The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FT-IR, ^{13}C -solid-state NMR, EA, FAB⁺-MS, and TGA.

FT-IR: $2927\text{--}2855 \text{ cm}^{-1}$ ($\nu\text{C-H}$), 1080 cm^{-1} ($\nu\text{C-O-Ti}$ bond), and 619 cm^{-1} ($\nu\text{Ti-O}$ bond). ^{13}C -solid-state NMR: two peaks at 74.8 and 79.2 ppm . EA: $28.6\% \text{ C}$ and $4.8\% \text{ H}$. FAB⁺-MS: approximately 8.5% of the highest *m/e* at 169 of $[\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2]\text{H}^+$, 73% intensity at 94 of $[\text{TiOCH}_2]\text{H}^+$ and 63.5% intensity at *m/e* 45 of $[\text{CH}_2\text{CH}_2\text{OH}]^+$. TGA: a single sharp transition at 340°C and 46.95% ceramic yield corresponding to $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$.

2.4. Preparation of silatrane

The procedure adopted followed Wongkarnkij's work [13]. A mixture of $\text{Si}(\text{OH})_4$ (6 g , 0.1 mol) and TEA (18.648 g , 0.125 mol) was stirred vigorously in excess EG (100 cm^3) and heated to 200°C for 10 h. The resulting solution was placed under vacuum to remove EG and obtain a crude precipitate. The white

solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FT-IR, FAB⁺-MS, and TGA.

FT-IR: 3422 cm^{-1} ($\nu\text{O-H}$), $2986\text{--}2861 \text{ cm}^{-1}$ ($\nu\text{C-H}$), 2697 cm^{-1} ($\nu\text{N-Si}$), $1459\text{--}1445 \text{ cm}^{-1}$ ($\delta\text{C-H}$), 1351 cm^{-1} ($\delta\text{C-N}$), 1082 cm^{-1} ($\delta\text{Si-O-C}$), 579 cm^{-1} ($\nu\text{N-Si}$). FAB⁺-MS: approximately 100% of the *m/e* at 174 of $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}]^+$, 11.3% intensity at 236 of $[\text{H}^+\text{OCH}_2\text{CH}_2\text{OSi}(\text{OCH}_2\text{CH}_2)_3\text{N}]$, 2.6% intensity at 323 of $[\text{H}^+\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OSi}(\text{OCH}_2\text{CH}_2)_3\text{N}]$ and 0.04% intensity at *m/e* 409 of $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}^+\text{SiOCH}_2\text{CH}_2\text{OSi}(\text{OCH}_2\text{CH}_2)_3\text{N}]$. TGA: a single mass loss transition at 390°C with 18.5% ceramic yield corresponding to $\text{Si}((\text{OCH}_2\text{CH}_2)_3\text{N})_2\text{H}_2$.

2.5. Preparation of TS-1 zeolite

The hydrothermal syntheses were carried out using microwave irradiation and a sample mixture with initial molar composition equal to $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$. The effect of reaction conditions was studied by varying the aging time ($20, 60, 70, 90, 110, 130, 150$ and 170 h), reaction time ($5, 10, 15$ and 20 h) and reaction temperature ($120, 150$ and 180°C). The effect of composition was studied by varying the concentration of TPA^+ , NaOH and H_2O . To investigate the Ti amount incorporated into the zeolite framework, compositions with the formula $\text{SiO}_2:x\text{TiO}_2:0.3\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$ ($x=0.01, 0.03, 0.05, 0.07, 0.1, 0.13, 0.17$ and 0.2) were used. The solutions were aged at room temperature for 110 h and heated in a microwave at 150°C for various reaction times. The TS-1 zeolite product was washed several times with distilled water, dried at 60°C overnight and calcined at 550°C for 2 h at a heating rate of $0.5^\circ\text{C min}^{-1}$.

2.6. Photocatalytic decomposition of 4-nitrophenol

The photocatalytic reactions were carried out in a 250 ml batch reactor with a gas inlet and outlet at an O_2 flow rate of 20 ml min^{-1} . A cooling water jacket was used to control the temperature at 30°C . The suspensions were illuminated using a 100 W Hg Philips UV lamp. The concentration of 4-NP used was 40 ppm and the solution was continuously, magnetically stirred. The TS-1 zeolite at Si/Ti molar ratios of $100.00, 14.3, 7.7$ and 5.0 was added into the solution. The concentration of catalyst was fixed at 0.8 g l^{-1} . Ten millimoles per liter H_2O_2 was then dropped into the mixture. The samples were taken out and analyzed to determine the concentration of 4-NP using a Shimadzu UV-240 spectrophotometer.

2.7. TS-1 characterization

The TS-1 samples were characterized by various techniques. XRD patterns were characterized using a D/MAX-2200H Rigaku diffractometer with

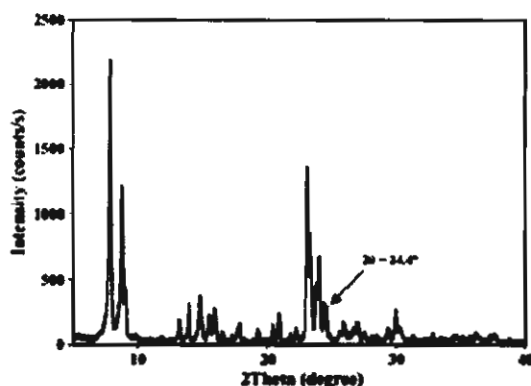


Fig. 1. The XRD pattern of a calcined TS-1 sample prepared from a reaction mixture of composition $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$; arrow indicates location of peak at $2\theta = 24.4^\circ$.

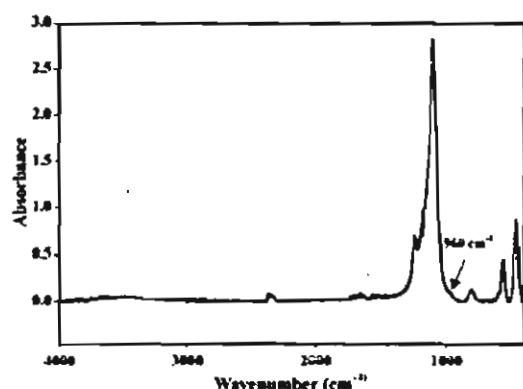


Fig. 2. The FT-IR spectra of a calcined TS-1 sample prepared from a reaction mixture of composition $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^*:0.4\text{NaOH}:114\text{H}_2\text{O}$; arrow indicates location of shoulder at 960cm^{-1} .

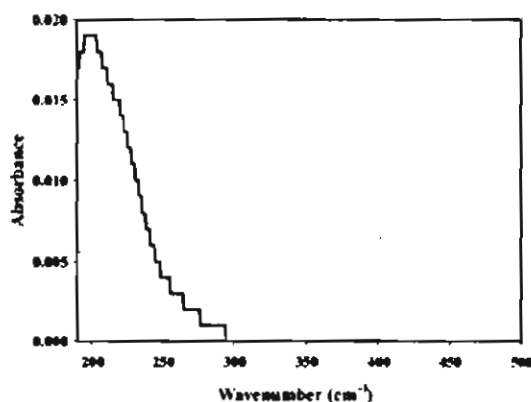


Fig. 3. DR-UV spectra of a calcined TS-1 sample prepared from a reaction mixture of composition $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^*:0.4\text{NaOH}:114\text{H}_2\text{O}$.

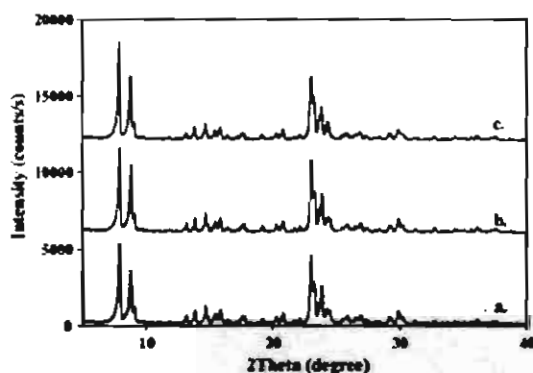


Fig. 4. XRD patterns of TS-1 samples prepared from reaction mixtures of composition $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^*:0.4\text{NaOH}:114\text{H}_2\text{O}$ at reaction temperatures of (a) 120°C , (b) 150°C and (c) 170°C .

Ca K α radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range between 5° and 50° . Fourier transform-infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. The morphology of samples attached to aluminum stubs was analyzed using S.E.M., after pyrolysis at 550°C . Prior to analysis, the specimens were dried in a vacuum oven at 70°C for 5 h followed by coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at $7,500\times$ magnification. Diffuse reflectance ultraviolet-visible (DR-UV) spectra were analyzed using Shimadzu UV-240 spectrophotometer.

3. Results and discussion

3.1. Synthesis of TS-1

Our results indicate that TS-1 is successfully synthesized by microwave hydrothermal treatment using silatrane and titanium

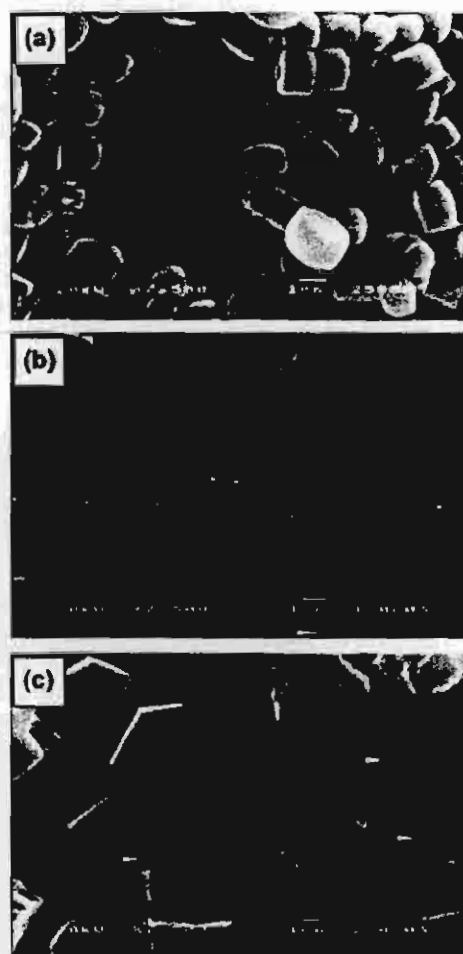


Fig. 5. S.E.M. micrographs of TS-1 samples prepared from reaction mixtures of composition $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^*:0.4\text{NaOH}:114\text{H}_2\text{O}$ at the reaction temperature of (a) 120°C , (b) 150°C and (c) 170°C .

glycolate as precursors, NaOH as a catalyst and TPABr as a template. The XRD pattern (Fig. 1) shows the characteristics of the MFI structure as widely reported in the literature [1,3,14,15]. The single peak at $2\theta = 24.4^\circ$ indicates a change from monoclinic symmetry (silicate) to orthorhombic symmetry (TS-1) [1,16]. The FT-IR spectrum of TS-1 in the Ti–O–Si stretching region shows an absorption band at 960 cm^{-1} (Fig. 2), which is observed in Ti-containing zeolites, and is typically assigned to the stretching mode of the $[\text{SiO}_4]$ tetrahedral bond with Ti atoms [17,18]. However, such assignment has also been interpreted in term of Si–OH groups with many defect structures [19]. The bands at 550 and 800 cm^{-1} are assigned to $\delta(\text{Si–O–Si})$ and $\nu(\text{Si–O–Si})$, respectively. The diffuse reflectance spectrum in Fig. 3 shows one weak absorption band with a maximum at 210 nm , attributed to tetra-coordinated titanium. No peak is observed at 330 nm , which is characteristic of extra-framework titanium dioxide.

3.2. Effect of crystallization conditions and compositions of TS-1

3.2.1. Effect of reaction temperature

The effect of reaction temperature was studied by varying the temperature at 120 , 150 and 180°C . The composition used was $\text{Si}:0.01\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$. Fig. 4 shows the XRD patterns of all samples investigated. The peak intensities slightly increase with temperature, implying that increase of temperature leads to a higher rate of crystallization. From the S.E.M. micrographs of the calcined samples (Fig. 5), the crystal size increases with reaction temperature. At 120°C (Fig. 5a), the crystals have rounded shapes and are not uniform in size

(0.5 – $2.5\text{ }\mu\text{m}$). On increasing the temperature to 150°C (Fig. 5b), the crystals become larger and more uniform, and have a cubic shape (1 – $2\text{ }\mu\text{m}$). The largest crystal sizes ($\sim 4\text{ }\mu\text{m}$) are observed at 180°C (Fig. 5c), and the shape becomes hexagonal, indicating increased growth in the c -direction. Additionally, at 180°C , degradation of the organic template also occurs. Thus, the most suitable reaction temperature to obtain the smallest and most uniform crystals is at 150°C .

3.2.2. Effect of reaction time

A composition of $\text{Si}:0.01\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$ was used to investigate the effect of reaction time on the crystallization of TS-1 zeolite. The reaction times were varied from 5 , 10 , 15 to 20 h at a reaction temperature of 150°C . The results show that, at reaction times shorter than 5 h , amorphous phase occurs and the conversion to TS-1 zeolite is low. It was found that the longer the reaction time, the higher is the crystallization rate. The S.E.M. micrographs (Fig. 6) show a large crystal size ($5\text{ }\mu\text{m}$) after 5 h reaction time, and the size decreases dramatically to $1.3\text{ }\mu\text{m}$ after 15 h . These crystals have a uniform cubic shape. Further increase of the reaction time to 20 h results in a larger crystal size and more extensive growth in the b -direction. Thus, 15 h reaction time is optimum to obtain uniform crystals for the specified composition.

3.2.3. Effect of aging time

TS-1 samples at various aging times (20 , 60 , 70 , 90 , 110 , 130 , 150 and 170 h) were prepared with composition $\text{Si}:0.01\text{Ti}:0.4\text{NaOH}:0.1\text{TPA}:114\text{H}_2\text{O}$ formula at a reaction temperature of 150°C and reaction time of 15 h . From the S.E.M. micrographs in Fig. 7, at the shortest aging time, large crys-

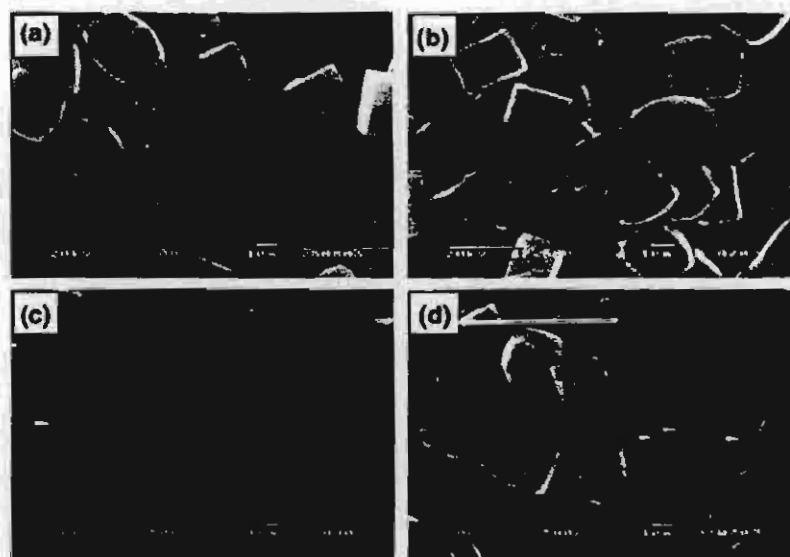


Fig. 6. S.E.M. micrographs of TS-1 samples prepared from reaction mixtures of composition $\text{SiO}_2:0.01\text{TiO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$ at reaction times of (a) 5 h , (b) 10 h , (c) 15 h and (d) 20 h .

tals of TS-1 are observed, which coexist with a large amount of amorphous phase (not shown). On increasing the aging time, the crystal size becomes smaller. However, at an aging time of 130 h the size increases again. During the aging process, the hydrolysis and condensation reactions of silatrane and titanium precursors induce polymerization to form a network. Initially, only partial hydrolysis of the precursors occurs. Therefore, some organic ligand remains and interacts with the organic template to form a primary unit. The primary units then agglomerate and

nucleation occurs [20]. At longer aging times, large numbers of primary particles are created, resulting in higher agglomeration and crystallization rates, which, in turn, results in formation of larger amounts of zeolite but with crystals of smaller size. During hydrothermal synthesis, using microwave heating, the crystal growth rate becomes dominant. At the longest aging time of 130 h, a limit is reached in the formation of primary units, and therefore further agglomeration occurs at the existing nuclei, leading to more rounded crystals.

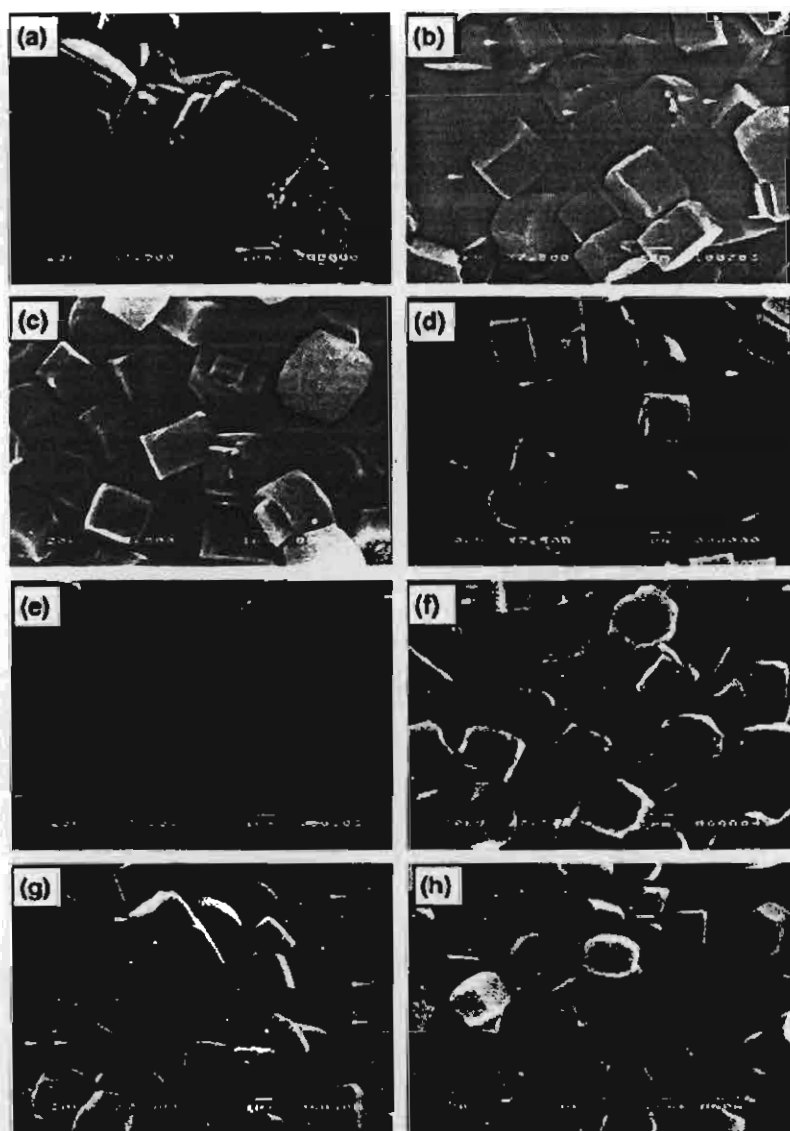


Fig. 7. S.E.M. micrographs of TS-1 samples prepared from reaction mixtures of composition $\text{SiO}_2:0.01\text{TlO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$ at aging times of (a) 20 h, (b) 60 h, (c) 70 h, (d) 90 h, (e) 110 h, (f) 130 h, (g) 150 h and (h) 170 h.

3.2.4. Effect of the NaOH:Si ratio

The NaOH:Si ratio was varied from 0.1 to 1.0 mole ratio at 110 h aging time, 15 h reaction time and 150 °C reaction temperature. At 0.1 mole ratio, the product is clearly amorphous, as evident in the S.E.M. micrograph (Fig. 8a). On increasing the ratio to 0.3, very large crystals (10 μm) of TS-1 zeolite were formed, with many secondary growths on the crystals (Fig. 8b). When the NaOH:Si ratio increases to 0.4, more uniform and smaller crystals (1–2 μm) are formed (Fig. 8c). Further increase in the ratio to 0.5 produces crystals of larger size and at a ratio of 0.7, many secondary growths occur on the crystals (Fig. 8d and e, respectively). At the highest NaOH:Si ratio, 1.0 (Fig. 8f), the cubic shape of the particles is damaged. Higher concentrations of NaOH accelerate the hydrolysis rate, resulting in an increase in reactive species for zeolite nucleation. This leads to the formation of smaller crystals on initially increasing the NaOH:Si ratio to 0.3 mole ratio. However, at too high a NaOH concentration, the hydrolysis and condensation reaction rates become too rapid which generates larger crystals with secondary growths (at 0.5 and 0.7 mole ratios). At the highest concentration of NaOH (1.0 mole ratio) it appears sufficient sodium ions are present to saturate the surface of the silica particles, causing retarda-

tion of nucleation due to a reduction in the TPA-Si interaction [21].

3.2.5. Effect of the TPA:Si ratio

The steric stabilization of nuclear-sized entities is also critically dependent on the cation balance. The TPA⁺ cation widely used in the synthesis of zeolite contains bulky quaternary ammonium cations, which adsorb to particle surfaces, and provide steric stabilization, preventing aggregation upon collision [20]. Many types of templates have been used to synthesize TS-1 zeolites, including TPAOH, TPABr, TBABr and 1,6-hexanediamine. However, Wang and Guo [6] found that use of TBABr increase formation of unwanted ZSM-11, and that use of 1,6-hexanediamine led to a decrease in crystallinity when the amount of Ti was increased. To reduce the cost of the synthesis, TPAOH may be replaced by TPABr. In fact, much previous work indicates use of TPABr as template for TS-1 generates product with high selective catalytic efficiency [6,15].

In our work, TPABr was used to synthesize TS-1 zeolite and the effect of TPA⁺ concentration was studied by investigating the behavior of systems with the composition

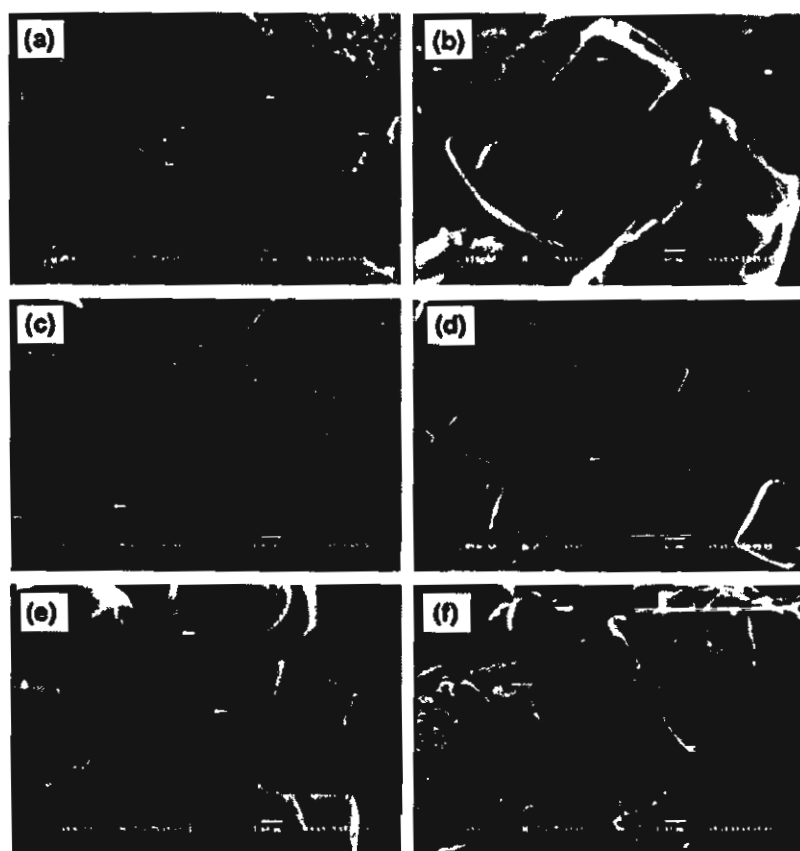


Fig. 8. S.E.M. micrographs of TS-1 samples at NaOH:Si mole ratios of (a) 0.1, (b) 0.3, (c) 0.4, (d) 0.5, (e) 0.7 and (f) 1.0.

$\text{Si}:0.01\text{Ti}:0.4\text{NaOH}:x\text{TPA}^+:114\text{H}_2\text{O}$ ($x=0.05, 0.1, 0.2, 0.3, 0.4$ and 0.5). The crystallization conditions were set at 110 h aging time, 15 h reaction time and the 150°C reaction temperature. Fig. 9 shows S.E.M. micrographs describing the effect of $\text{TPA}^+:\text{Si}$ ratio with a $\text{Si}:\text{NaOH}$ mole ratio of 0.4. At low $\text{TPA}^+:\text{Si}$ ratio (0.05), large crystals are formed ($10\text{ }\mu\text{m}$), and with increasing level of TPA^+ the crystal size decreases ($1\text{--}2\text{ }\mu\text{m}$ at 0.3 mole ratio). However, at too high a concentration of TPA^+ (0.4 and 0.5 mole ratios), secondary growths occur. Following the interpretation of Koepler et al. [21], when both TPA^+ and silica are abundant, nucleation occurs at the surfaces of the gel particles created by hydrolysis and condensation reaction. TPA^+ diffuses from solution to the crystal/gel interface, resulting in new crystal growth, as seen here.

3.2.6. Effect of the $\text{H}_2\text{O}:\text{Si}$ ratio

The effect of dilution was studied using systems with the composition $\text{Si}:0.1\text{Ti}:0.4\text{NaOH}:0.3\text{TPA}:x\text{H}_2\text{O}$ ($x=80, 114, 140, 170$ and 200). The reaction time and temperature were set at 15 h, 150°C , respectively, and the aging time at 110 h. From the S.E.M. micrographs in Fig. 10, the lowest $\text{H}_2\text{O}:\text{Si}$ ratio shows a non-uniform crystal structure. On increasing the ratio to 114, more uniform and completely cubic structures are

Table 1

The TS-1 samples at various Si:Ti molar ratios and reaction times (h)

Samples	Si/Ti molar ratio	Reaction time (h)
A	100.0	15
B	33.3	15
C	20.0	20
D	14.3	25
E	10.0	25
F	7.7	35
G	5.9	35
H	5.0	35

obtained, but further increase generates larger crystals with many defects.

3.2.7. Effect of the Si:Ti ratio

The effect of the Si:Ti ratio on the crystallization of TS-1 was carried out by investigating systems with the composition $\text{Si}:x\text{Ti}:0.4\text{NaOH}:0.3\text{TPA}:114\text{H}_2\text{O}$ formula ($x=0.01, 0.03, 0.05, 0.07, 0.1, 0.13, 0.17$ and 0.2). The reaction temperature and the aging time were fixed at 150°C and 110 h, respectively. The reaction times were varied from 15 to 35 h depending on the Ti loading (samples labeled A–H in Table 1). Longer reaction

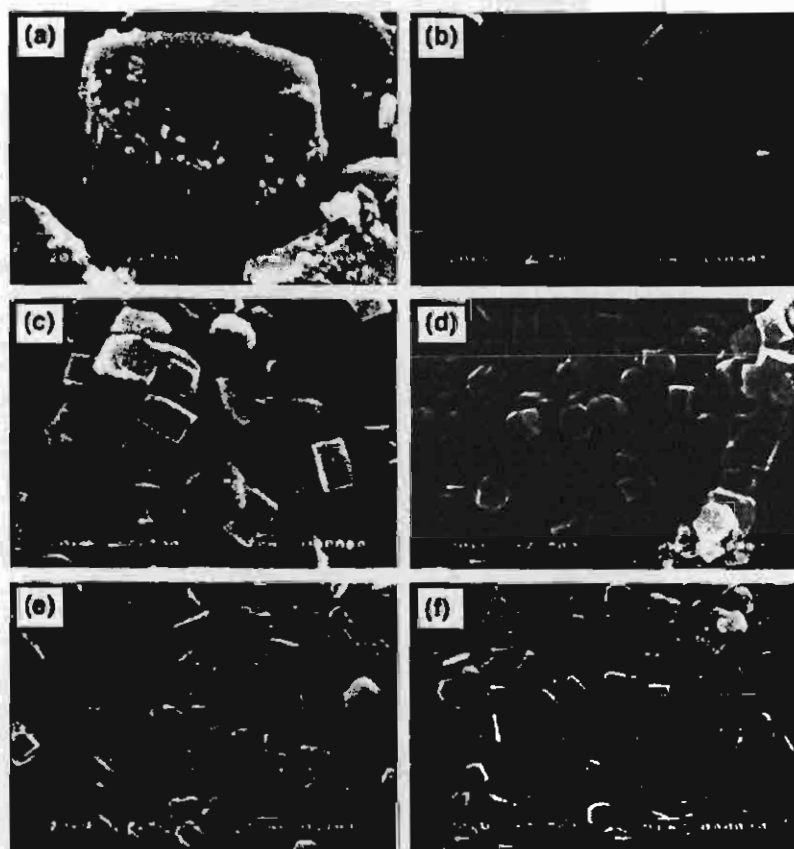


Fig. 9. S.E.M. micrographs of TS-1 samples at $\text{TPA}:\text{Si}$ mole ratios of (a) 0.05, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4 and (f) 0.5.

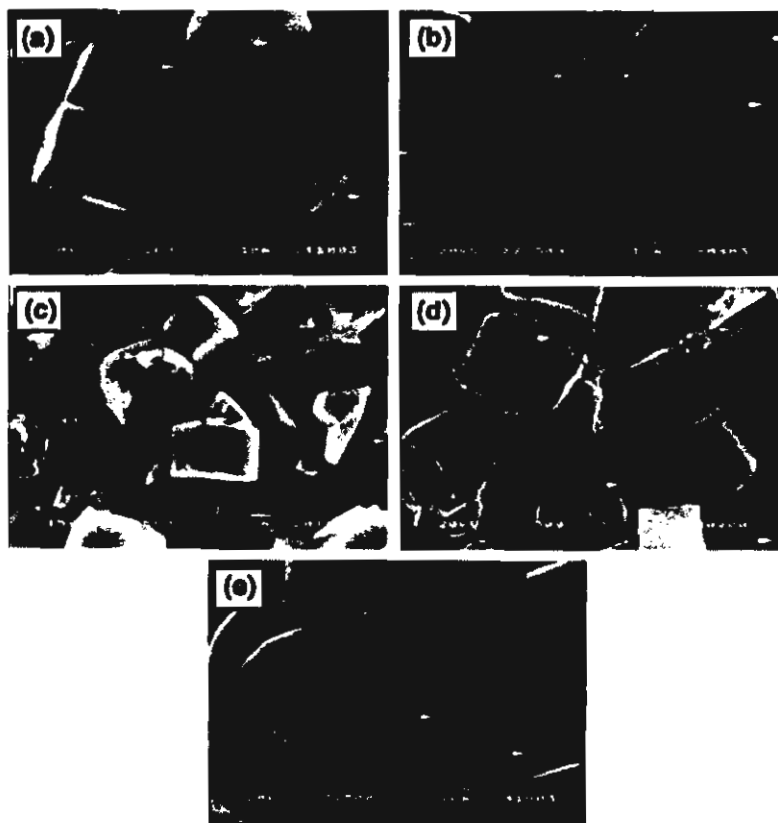


Fig. 10. S.E.M. micrographs of TS-1 samples at $\text{H}_2\text{O}:\text{Si}$ mole ratios of (a) 80, (b) 114, (c) 140, (d) 170 and (e) 200.

times were found to be necessary at higher Ti loadings to ensure complete incorporation of Ti in the zeolite framework. Fig. 11 exhibits the corresponding FT-IR spectra of TS-1 samples. The peak at 960 cm^{-1} is attributed to the stretching mode of $[\text{SiO}_4]$ units bonded to a Ti^{4+} ion (O_3SiOTi) [15] and indicates increasing incorporation of titanium in the MFI framework. A strong

band at 550 cm^{-1} is characteristic of the MFI structure [22]. The DR-UV spectra of these samples are shown in Fig. 12. The strong peak at 210 nm is assigned to tetra-coordinated titanium in the zeolite framework. A broad shoulder at 280 nm indicates partially polymerized hexa-coordinated Ti species, containing

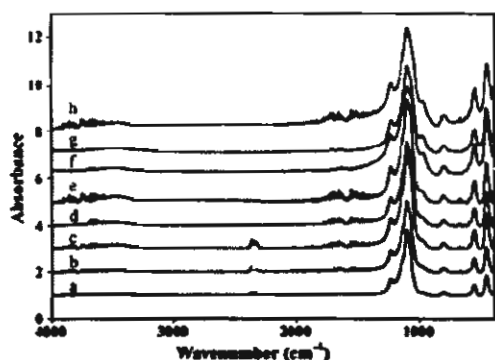


Fig. 11. FT-IR spectra of TS-1 samples at Si:Ti mole ratios of (a) 100.0, (b) 33.3, (c) 20.0, (d) 14.3, (e) 10.0, (f) 7.7, (g) 5.9 and (h) 5.0.

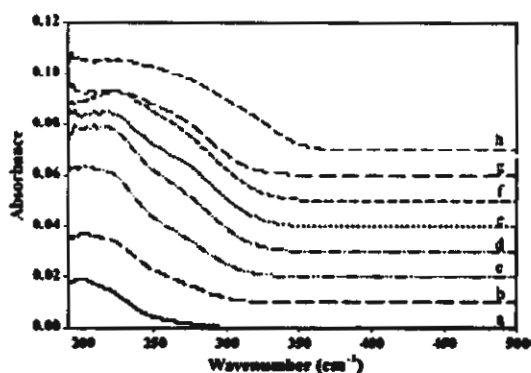


Fig. 12. DR-UV spectra of TS-1 samples at Si:Ti mole ratios of (a) 100.0, (b) 33.3, (c) 20.0, (d) 14.3, (e) 10.0, (f) 7.7, (g) 5.9 and (h) 5.0.

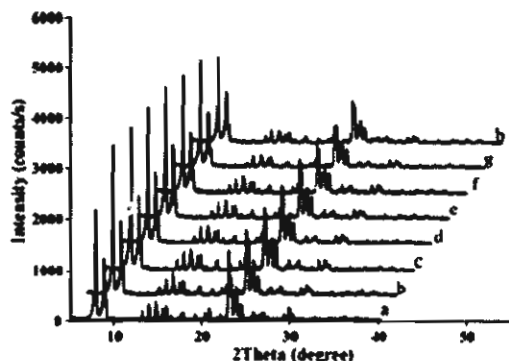


Fig. 13. XRD patterns of TS-1 samples at Si/Ti mole ratios of (a) 100.0, (b) 33.3, (c) 20.0, (d) 14.3, (e) 10.0, (f) 7.7, (g) 5.9 and (h) 5.0.

Ti–O–Ti. We deduce that these species are present in the zeolite framework rather than a silicon-rich amorphous phase [23], on the basis of XRD and S.E.M. results, which show no evidence of an amorphous phase. Moreover, absorbance at 330 nm is assigned to the extra-framework anatase phase, and is observed as a small contribution only in sample H. Peaks at 210 and 280 nm increase from sample A to H reflecting increasing titanium content and there is an apparent shift of the 210 nm band to higher wavelength because of the increased proportion of hexa-coordinate species. The intensity of the 280 nm peak of samples F–H increases more strongly than that at 210 nm, indicating that hexa-coordinated Ti species are preferentially formed at higher titanium loadings. The S.E.M. micrographs and XRD patterns of TS-1 samples A–H are shown in Figs. 13 and 14. All samples show the characteristics of TS-1 zeolite with the MFI structure.

3.3. Photocatalytic decomposition of 4-nitrophenol

From the reports of Lee et al. [24] and Lea and Adesina [25], the photocatalytic decomposition (PCD) of 4-NP goes to completion in the presence of H_2O_2 under UV irradiation. The photodecomposition of 4-NP is initiated by $^{\bullet}OH$ radicals, which are easily formed via formation of titanium-hydroperoxide complexes. Thus, we investigated the catalytic activity of our Ti-containing TS-1 zeolites on the PCD of 4-NP in the presence of 1.0 mmol l^{-1} of H_2O_2 under UV irradiation. Table 2 summarizes the results as a function of Si/Ti mole ratio. The rate of PCD increases uniformly with the amount of titanium incorporated in the zeolite, the fastest complete decomposition occurring with the 5.0 Si/Ti molar ratio.

Table 2
The photocatalytic degradation of 4-nitrophenol

Si/Ti molar ratio	Time for completely photocatalytic decomposition of 4-NP (h)
100.0	4.0
14.3	2.0
7.7	1.3
5.0	1.0

4. Conclusions

TS-1 zeolites with high titanium content incorporated in the zeolite framework were synthesized using low cost and moisture-stable precursors, silatrane and titanium glycolate, under microwave heating. The effect of the reactant composition (TPA^+ , $NaOH$ and H_2O) and conditions (aging time, reaction time and reaction temperature) were studied and we found that the optimum condition for synthesizing TS-1 is at a composition of $Si:0.01Ti:0.4NaOH:0.3TPA:114H_2O$, with 110 h aging time, 15 h reaction time and at $150^\circ C$ reaction temperature. Si/Ti molar ratios in the range 100.0–5.0 were studied and the results from XRD, FT-IR, S.E.M. and DR-UV indicate that via this novel route highly crystalline materials, having high content of Ti atoms incorporated in the zeolite framework are obtained. The reaction times were varied at different Ti loadings, and show that at higher titanium loadings, longer reaction times are necessary. Photocatalytic decomposition of 4-NP was used as an assay for the catalytic activity of the prepared TS-1 samples, and demonstrated increased efficiency with increasing level of titanium loading.

Acknowledgements

This research work was supported by the Postgraduate Education and Research Program in Petroleum and Petrochemical Technology (ADB) Fund, Ratchadapisek Sompote Fund, Chulalongkorn University and the Thailand Research Fund (TRF).

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**D. Structural and Rheological Aspect of Mesoporous Nanocrystalline TiO_2
via Sol-Gel Process and Its Rheological Study**

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Structural and rheological aspect of mesoporous nanocrystalline TiO_2 synthesized via sol–gel process

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Received 4 April 2003; received in revised form 30 July 2003; accepted 20 September 2003

Abstract

Mesoporous nanocrystalline titanium dioxide was prepared via the sol–gel technique using titanium glycolate as precursor in 1 M HCl solution at various $\text{HCl}:\text{H}_2\text{O}$ ratios. XRD analysis indicates the anatase phase forms at calcination temperatures in the range 600–800 °C. From the average grain sizes, we deduce that the nucleation rate dominates the kinetics at lower temperature, and growth rate becomes the controlling factor at higher temperature for materials prepared at $\text{HCl}:\text{H}_2\text{O}$ ratios of 0.28 and 0.33. At higher volume ratios, the growth rate appears to be the dominant factor at all temperatures. The highest specific surface area (BET) obtained was 125 m^2/g at the $\text{HCl}:\text{H}_2\text{O}$ ratio of 0.28. A small decrease of specific surface area was observed from low to high acid ratio and a substantial decrease from lower to higher temperature. The material calcined at 800 °C was found to consist primarily of spherical particles with diameters smaller than 1 μm . Application of the Winter rheological criteria for the gel point indicates that the gelation time increases with increase of the $\text{HCl}:\text{H}_2\text{O}$ volume ratio. The fractal dimension of the critical gel cluster decreases with acid ratio, whereas the gel strength increases with acid ratio. Thus, increase of acidity leads to a less dense but stronger network structure.

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Keywords: Titanium glycolate; Titania; Rheology; Sol–gel process and viscoelastic properties

1. Introduction

Titanium dioxide or titania, TiO_2 , is widely used in the field of catalysis, as filters, adsorbents, and catalyst supports [1,2]. The porous anatase

form, as compared to the rutile phase, is of greater importance and interest due to its better catalytic properties. Therefore, a key goal is to prepare anatase nanoparticles, with high surface area, uniform particle size and pore structure, and a high anatase–rutile transformation temperature [3].

Sol–gel processing has become one of the most successful techniques for preparing nanocrystalline metallic oxide materials. In general, this method

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involves the hydrolysis and polycondensation of a metal alkoxide, to ultimately yield hydroxide or oxide under well specified reaction conditions [4]. The key advantage of preparing metallic oxides by the sol-gel method is the possibility to control their microstructure and homogeneity. To obtain homogeneous nanoscale macromolecular oxide networks via sol-gel processing, control of hydrolysis is essential. The properties and nature of the product are controlled by the particular alkoxide used, the presence of acidic or basic additives, the solvent, and various other processing conditions (e.g. temperature). The calcination temperature is also a key factor, especially for titania preparation. Too low a temperature result in incomplete combustion and too high a temperature causes phase transformation.

Many studies have been directed to prepare titania powder with increased textural and structural stability. For example, Zhang et al. [5] prepared and studied mesoporous nanocrystalline TiO_2 by a sol-gel technique using butanediol mixed with tetrapropylorthotitanate. A surface area of $97 \text{ m}^2/\text{g}$ was obtained after calcination at 400°C for 2 h. Wei et al. [6] prepared nanodisperse spherical TiO_2 particles by forced hydrolysis using boiling reflux $\text{Ti}(\text{SO}_4)_2$ solution in the presence of H_2SO_4 . The particle size distribution was in the range 70–100 nm. Sun et al. [7] prepared nanosized anatase titania with average grain sizes ranging from 7.4 to 15.2 nm using MOCVD technology to pyrolyze titanium tetrabutoxide in an oxygen containing atmosphere. The smallest average grain size and the highest surface area were obtained at 700°C . Kim et al. [8] synthesized ultrafine titania particles by hydrolysis of titanium tetraisopropoxide (TTIP) in the aqueous cores of water/NP-5/cyclohexane microemulsions. With increasing calcination temperature from 300 to 700°C , the specific surface area of the TiO_2 particles decreased from 325.6 to $5.9 \text{ m}^2/\text{g}$, whereas the average pore radius increased from 1.4 to 25.1 nm. Wu et al. [9] synthesized nanocrystalline titanium dioxide using the sol-hydrothermal method with titanium *n*-butoxide (TNB) as precursor, in various acidic media (HCl, HNO_3 , H_2SO_4 and CH_3COOH). Nanocrystals of pure rutile with size $<10 \text{ nm}$ were obtained at higher HCl concentrations under mild conditions.

The propensity of acidic medium for rutile formation is shown as follows: $\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HAc}$. Ding and Liu [14] synthesized nanocrystalline titania powders via sol-gel processing of tetrabutyltitanate in anhydrous ethanol, and showed that HCl-catalyzed hydrolysis favors the formation of the anatase crystal phase.

Knowledge of the evolution in rheological properties during sol-gel processing is a useful guide to the manufacturer when formulating dispersions to optimize the physical properties required in the final product [10]. Thus, in this work, our aims are to synthesize high surface area anatase TiO_2 and to study the rheological properties of titanium glycolate synthesized directly from inexpensive and widely available TiO_2 and ethylene glycol via the oxide one pot synthesis (OOPS) method [11]. We also investigate the influence of the acid concentration used in acid-catalyzed hydrolysis, the effect of calcination temperature on morphology and phase transformation, and gain some insight into the gel mechanism.

2. Experimental

2.1. Materials

Titanium dioxide (surface area $12 \text{ m}^2/\text{g}$) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinkrodt Baker, Inc. (USA) and purified by fractional distillation at 200°C under nitrogen at atmospheric pressure, before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder.

2.2. Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Thermal gravi-

metric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10 °C/min over 30–800 °C temperature range. The mass spectrum was obtained on a Fison instrument (VG Autospec-ultima 707E) with VG data system, using the positive fast atomic bombardment mode (FAB⁺-MS) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. ¹³C-solid state NMR spectroscopy was performed using a Bruker AVANCE DPX-300 MAS-NMR. Elemental analysis (EA) was carried out on a C/H/N analyser (Perkin Elmer PE2400 series II).

2.3. Preparation of titanium glycolate

The procedure adopted followed previous work [11]. A mixture of TiO₂ (2 g, 0.025 mol) and TETA (3.65 g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated to 200 °C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FT-IR, ¹³C-solid state NMR, EA, FAB⁺-MS, and TGA.

FT-IR: 2927–2855 cm⁻¹ (νC–H), 1080 cm⁻¹ (νC–O–Ti bond), and 619 cm⁻¹ (νTi–O bond). ¹³C-solid state NMR: two peaks at 74.8 and 79.2 ppm. EA: 28.6% C and 4.8% H. FAB⁺-MS: approximately 8.5% of the highest *m/e* at 169 of [Ti(OCH₂CH₂O)₂]⁺, 73% intensity at 94 of [OTiOCH₂] and 63.5% intensity at *m/e* 45 of [CH₂CH₂OH]. TGA: one sharp transition at 340 °C and 46.95% ceramic yield corresponding to Ti(OCH₂CH₂O)₂.

2.4. Sol-gel processing of titanium glycolate

The hydrolysis of titanium glycolate (0.026 g) was carried out via addition of 160 μL of 1 M HCl mixed with distilled water in volume ratios of HCl:H₂O 0.45, 0.39, 0.33 and 0.28. The mixtures were magnetically stirred and heated in a water bath at 50 °C until a clear gel was obtained. The gels were calcined for 2 h at 600, 700 and 800 °C.

2.5. Rheological study of titanium glycolate

Gelation occurs when aggregation of particles or molecules takes place in a liquid, under the action of Van der Waals forces or via the formation of covalent or noncovalent bonds. The process can be conveniently monitored using rheological measurement technique [5]. The rheometric measurements were conducted using an ARES rheometer with parallel plate geometry, 25 mm in diameter. The storage (*G'*) and loss (*G''*) moduli were determined using oscillatory shear at frequencies in the range 0.2–6.4 rad/s. The strain amplitude was small enough to ensure that all experiments were conducted within the linear viscoelastic region, where *G'* and *G''* are independent of the strain amplitude. Titanium glycolate 0.026 g was hydrolyzed at different HCl:H₂O volume ratios of 0.45, 0.39, 0.33 or 0.28. The hydrolysis temperature was selected to be 30 °C. The mixtures were stirred until homogeneous before being transferred to the rheometer.

2.6. Characterization of calcined materials

Crystallinity and average grain sizes were characterized using a D/MAX-2200H Rigaku diffractometer with CuKα radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range between 5° and 90°. Specific surface area, nitrogen adsorption-desorption, and pore size distribution were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer–Emmett–Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 cc/min. Nitrogen was used to calibrate the analyzer, and also as the adsorbate at liquid nitrogen temperature. The samples were thoroughly out-gassed for 2 h at 150 °C, prior to exposure to the adsorbent gas. Material morphology was observed using a JEOL 5200-2AE(MP 15152001) scanning electron microscope. Samples were prepared for SEM analysis by attachment to aluminum stubs, after pyrolysis at 800 °C. Prior to analysis, the

specimens were dried in a vacuum oven at 70 °C for 5 h followed by coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at 10,000× magnification.

3. Results and discussion

The investigation of the hydrolysis reaction of titanium glycolate precursor using FT-IR is illustrated in Fig. 1. The spectra show an increase in the peak intensity of Ti–O–Ti stretching at approximately 500–800 cm^{-1} due to hydrolysis of the precursor. The peak at 1000–1100 cm^{-1} , corresponding to C–O stretching of ethylene glycol also increases, reflecting the production of ethylene glycol during the hydrolysis reaction. In the case of higher acid ratio (0.45), the degree of cross-linking is greater than those obtained from the hydrolysis in lower acid ratios. The acid can act as a catalyst to hydrolyze the alkoxide by protonating the ethoxy ligands during hydrolysis. Thus, the elimination of the protonated ethoxy ligand leaving group is no longer the rate limiting step, and, as a result, the hydrolysis occurs more rapidly.

Calcination is a treatment commonly used to improve the crystallinity of TiO_2 powder. When TiO_2 is calcined at higher temperature, a transformation to rutile phase usually occurs [13] and comprises anatase, rutile, and brookite. XRD patterns (Fig. 2) show the phase transformations encountered when titanium glycolate precursor is calcined at temperatures in the range 300–1100 °C. Amorphous material is obtained at the lowest temperature (300 °C) whereas at 500 °C broader anatase peaks appear. As the calcination temperature increases, the intensity of anatase peaks becomes stronger and well resolved. However, if the calcination temperature is increased to 900 °C, small rutile peaks are found, indicating the onset of the transformation to rutile.

The synthesis procedure was changed to obtain porous anatase for better catalytic properties. Specimens obtained via the sol-gel process at different volume ratios of $\text{HCl}:\text{H}_2\text{O}$, viz. 0.45, 0.39, 0.33 and 0.28, were subjected to calcination at 600, 700 and 800 °C, to obtain porous anatase titania [3]. Fig. 3 shows the XRD patterns of anatase formation in a specimen at the $\text{HCl}:\text{H}_2\text{O}$ volume ratio of 0.28. Our results indicate that the synthesized anatase is stable up to calcination tem-

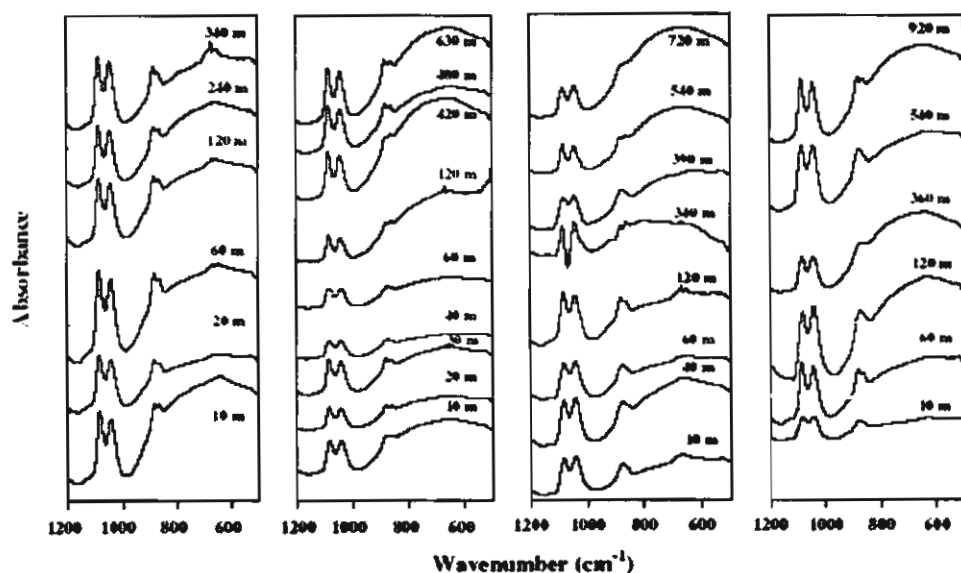


Fig. 1. The FT-IR spectra of titania gel at $\text{HCl}:\text{H}_2\text{O}$ volume ratio of (a) 0.28, (b) 0.33, (c) 0.39 and (d) 0.45.

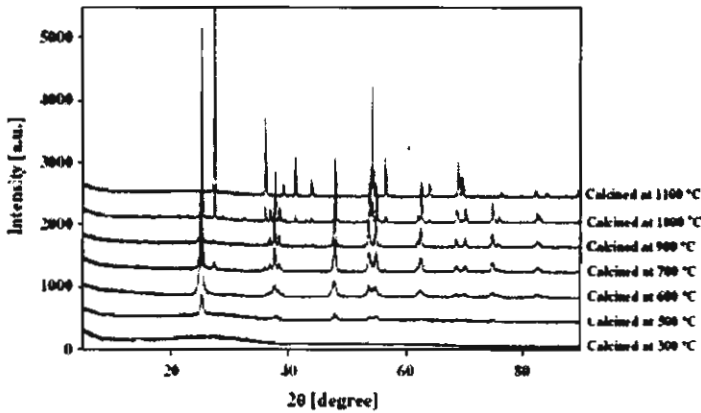


Fig. 2. XRD patterns of uncalcined and calcined titanium glycolate precursor at different temperatures.

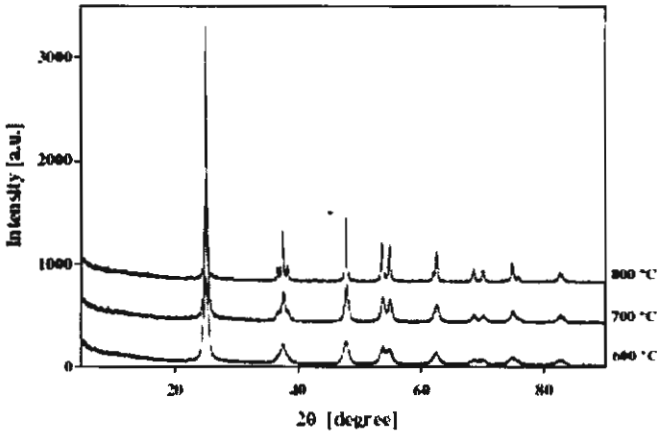


Fig. 3. XRD pattern of titania gel using the HCl:H₂O volume ratio of 0.28 calcined at (a) 600 °C, (b) 700 °C and (c) 800 °C.

peratures of 800 °C, which is a little higher than previous studies, which report the transformation of anatase to rutile in the range of 600–700 °C [5,7,12,13].

As can be seen in Fig. 4, at 0.28 and 0.33 ratios, the average grain size decreases significantly from 600 °C (18.8 and 17.1 nm) to 700 °C (13.9 and 14.2 nm) and then increases substantially again at 800 °C (31.3 and 29.8 nm). These results are reminiscent of observations by Sun et al. [7] of the temperature dependence of grain sizes of anatase produced by the MOCVD method. The size variation was interpreted in

terms of the rate of particle growth relative to the rate of particle nucleation. Use of elevated temperatures accelerates not only the nucleation rate but also the particle growth rate. For acid:water ratios of 0.28 and 0.33, at lower temperatures, the nucleation rate is dominant, whereas the growth rate becomes the controlling factor at higher temperature. Acid:water ratios of 0.39 and 0.45 show a slightly different pattern, in which grain size increases mildly between 600 and 700 °C, and then more dramatically at 800 °C, suggesting that the growth rate is dominant at all temperatures.

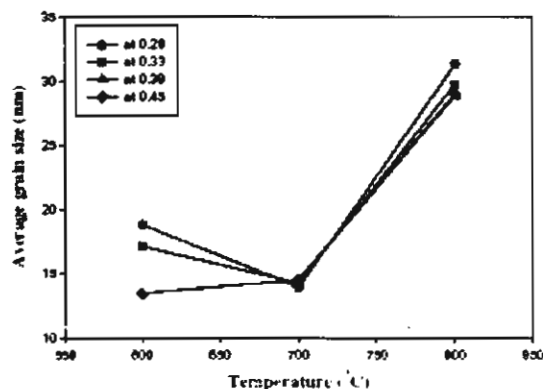


Fig. 4. The average grain sizes of the particles prepared at different volume ratios of $\text{HCl}:\text{H}_2\text{O}$ (0.28, 0.33, 0.39, 0.45, respectively) and different calcination temperatures (600, 700 and 800 °C).

Coincidentally, the nitrogen adsorption-desorption isotherm of the material obtained at 0.28 $\text{HCl}:\text{H}_2\text{O}$ volume ratio and calcined at 600 °C for 2 h indicates a mesoporous structure, as seen in Fig. 5(a). The isotherm is of type IV, characteristic of mesoporous material. The hysteresis loop exhibited by the specimen is mainly of type H2. The pore size distribution in Fig. 5(b) shows a major porosity in the range of 4–18 nm. To confirm an increase in crystallinity as temperature increases, specific surface area measurements were carried out and, as expected, we find that the higher the calcination temperature, the lower the specific surface area. The powders become dense and predominantly nonporous when the precursor is calcined at 800 °C. It is known [3] that a lower acid concentration results in a higher specific surface area due to an increase in the cross-linking level. This is consistent with our observation that the specific surface area decreases in the following order; $0.28 > 0.33 > 0.39 > 0.45$ (Table 1). It can be concluded that sol-gel processing indeed provides a larger specific surface area which decreases with increasing calcination temperature and acid concentration.

The particle morphology of the samples obtained using a $\text{HCl}:\text{H}_2\text{O}$ ratio of 0.33, when calcined at temperatures in the range 600–800 °C, is shown in Fig. 6. At the two lowest temperatures,

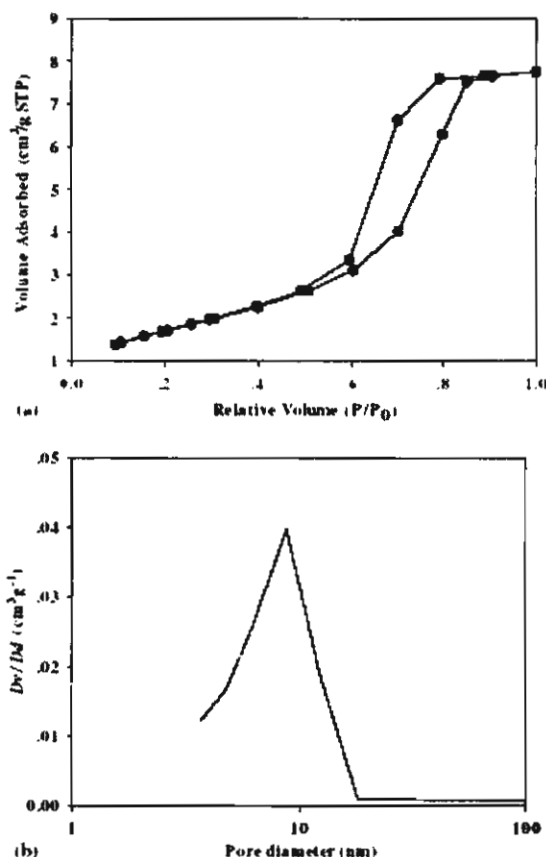


Fig. 5. The nitrogen adsorption-desorption isotherm for mesoporous titania (a) and pore size distribution (b) for the material obtained from 0.28 $\text{HCl}:\text{H}_2\text{O}$ volume ratio and calcined at 600 °C.

Table 1
BET surface area (S_{BET} , m^2/g) of titania at various $\text{HCl}:\text{H}_2\text{O}$ volume ratios and calcination temperature

Temperature (°C)	Surface area (m^2/g)			
	0.28	0.33	0.39	0.45
600	125	111	107	105
700	60	59	55	50
800	20	18	17	15

Surface area of the starting material $\text{TiO}_2 = 20 \text{ m}^2/\text{g}$.

Fig. 6(a) and (b), the material consists of particles of large size, whereas the micrograph (Fig. 6(c)) of the material calcined at 800 °C shows a finely-

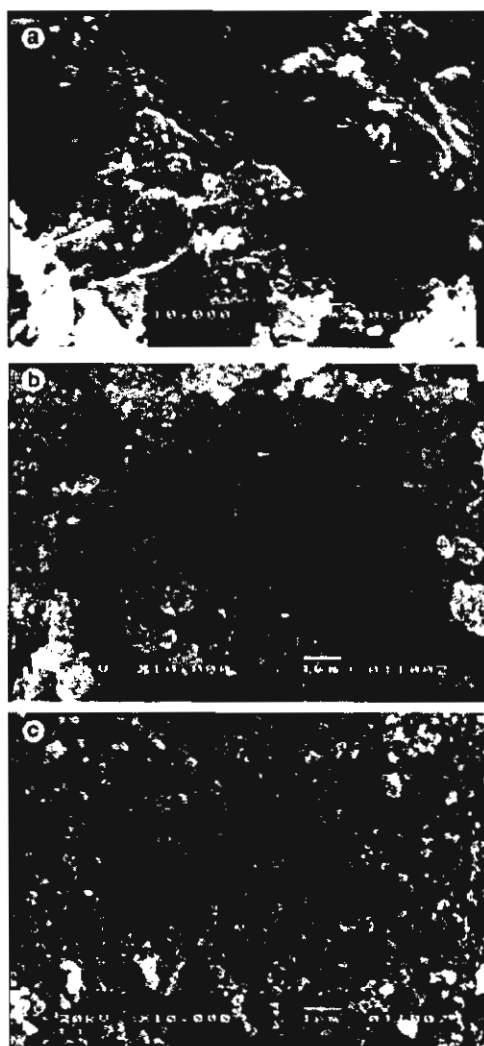


Fig. 6. SEM micrograph for titania powder at volume ratio 0.33 of HCl:H₂O calcined at (a) 600 °C, (b) 700 °C and (c) 800 °C.

divided morphology in the anatase form consisting of spherical particles approximately 1 μm in size.

Viscoelastic studies of the four different gelling systems (volume ratio 0.28, 0.33, 0.39 and 0.45 of HCl:H₂O, respectively) were carried out using the criteria proposed by Winter and Chambon [14] to determine the gel point, as the gelation time where a frequency independent value of $\tan \delta$ is observed. The variation in the frequency dependence

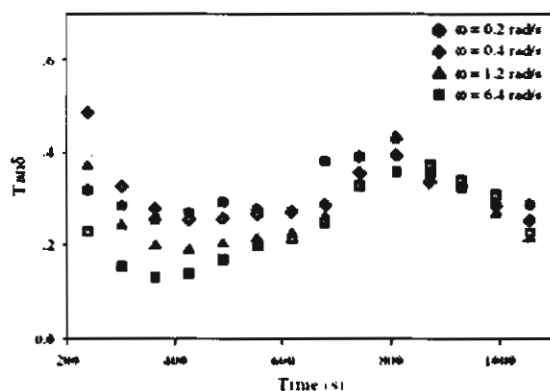


Fig. 7. The plots of $\tan \delta$ with time(s) at HCl:H₂O volume ratio of 0.45.

of $\tan \delta$ with gelation time is shown in Fig. 7, and indeed indicates that $\tan \delta$ becomes frequency independent at a particular gelation time. The shortest gelation time was observed for the system at 0.28 volume ratio (365 s) and the longest gelation time for the system of 0.45 volume ratio (870 s). An alternative method [15] to determine the gel point is to plot the time evolution of the apparent viscoelastic exponents n' and n'' obtained from the frequency dependence of the modulus ($G' \propto \omega^{n'}$, $G'' \propto \omega^{n''}$), as shown in Fig. 8 for the system at 0.45 volume ratio. The gel point is identified as the time where a cross-over $n' = n'' = n$ is observed. The

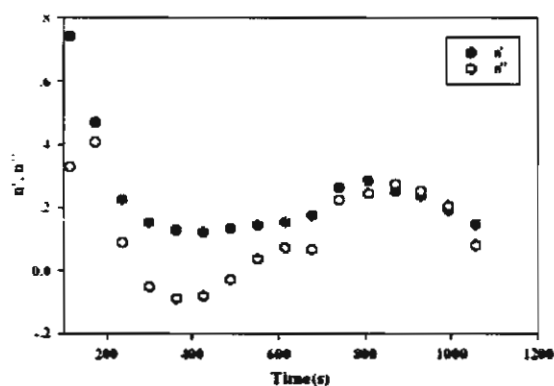


Fig. 8. The plot of the apparent exponents, the storage moduli (n') and the loss moduli (n'') during the course of gelation for the 0.45 acid ratio.

points of intersection (t_{gel}) are found to be the same as those deduced from the plot of $\tan \delta$ versus time.

It is important to note that these gelling systems are highly elastic even well before the gel point, as evidenced by the fact that $\tan \delta \ll 1$. Also, the system rheology evolves relatively slowly in the vicinity of the gel point, as seen by plotting the frequency dependence of G' (Pa), G'' (Pa) at pregel stage, gel point, and postgel stage, shown in Fig. 9. The data are shifted horizontally by a factor B . A similar trend is observed for all systems in that G' is higher than G'' , i.e. elastic behavior predominates before as well as after the gel point. We attribute this behavior to the fact that we are dealing with a concentrated colloidal dispersion, which is

converted to a gel by hydrolysis from the outer surfaces of the colloidal particles. Despite this heterogeneous structure, at the gel point, the systems fulfil the Winter criteria that $n' = n'' = n_{gel}$, and $\tan \delta = \tan(n_{gel}\pi/2)$ are superimposed [14–18]. The viscoelastic exponent n_{gel} of the system, as shown in Table 2, has its highest value at 0.45

Table 2

Summary of viscoelastic exponent, fractal dimension, and gelation time(s) at various HCl:H₂O volume ratios

Acid ratio	n	d_f	Gelation time (s)
0.28	0.05	2.46	365
0.33	0.07	2.44	428
0.39	0.19	2.33	647
0.45	0.20	2.32	870

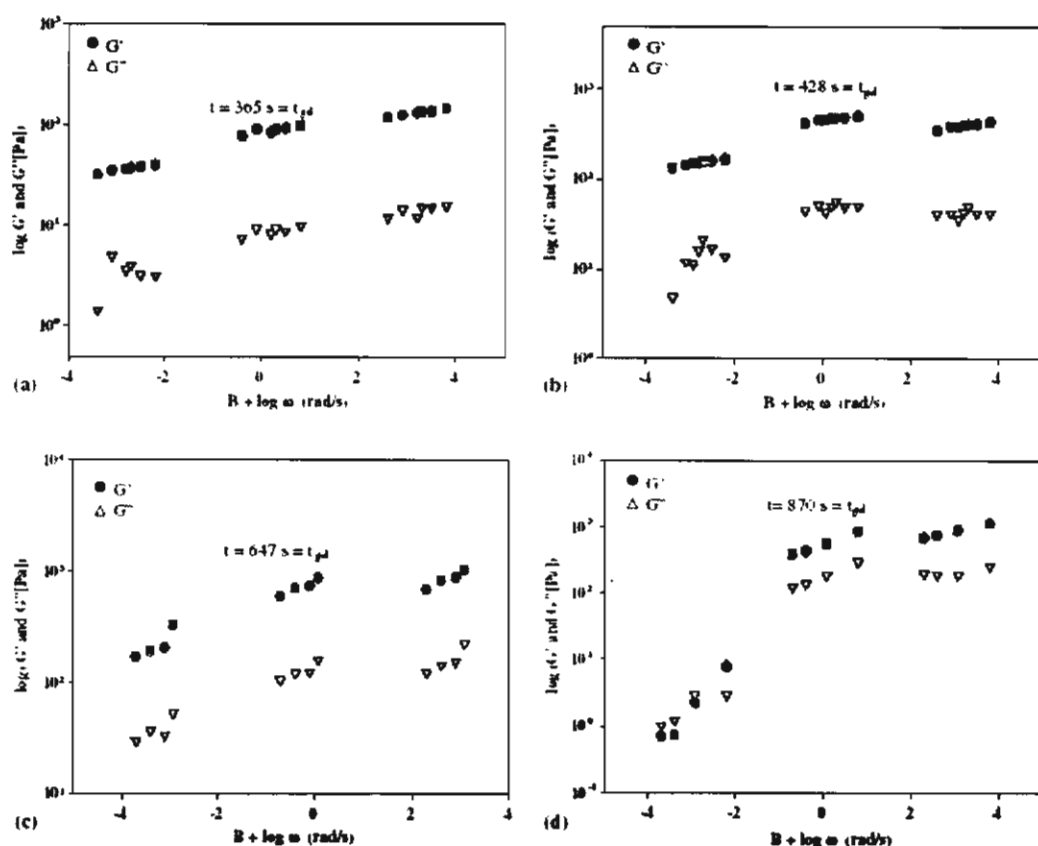


Fig. 9. The frequency dependence curves of $G'(\omega)$ and $G''(\omega)$ at (●) pregel stage ($B = -3$), (■) gel point ($B = 0$), and (Δ) postgel stage ($B = 3$) of (a) 0.28, (b) 0.33, (c) 0.39 and (d) 0.45 HCl:H₂O ratio.

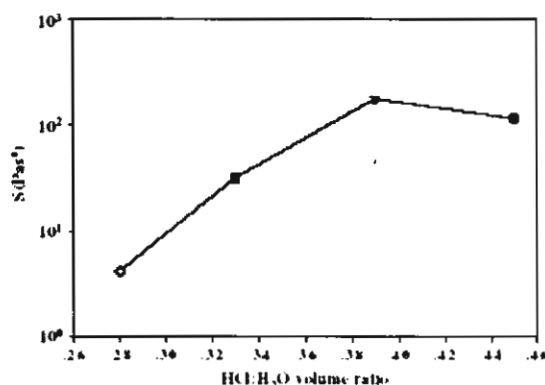


Fig. 10. The plot of gel strength parameter S at the gel point as a function of HCl:H₂O volume ratio: 0.28 (◇), 0.33 (□), 0.39 (▲) and 0.45 (●).

volume acid ratio and the value decreases as the volume acid ratio decreases. Fig. 10 shows the effect of HCl:H₂O volume ratio on the gel strength parameter, S , evaluated from the relationship [15–18] $G'(\omega) = \Gamma(1-n) \cos(n\pi/2) S \omega^n$ where $\Gamma(1-n)$ is the Legendre Γ function. It is evident that the gel strength increases with increasing acid ratio and reaches its highest value acid ratio = 0.39, then decreases slightly. Thus at low acid ratio, the critical gel cluster is relatively weak, at high acid ratio it is stronger.

According to the model of Muthukumar [19] the fractal dimension of the critical gel cluster can be obtained from the viscoelastic exponent n as $n = d/(d+2-2d_f)/2(d+2-d_f)$ where d = spatial dimension = 3. The effect of acid ratio on the fractal dimension of incipient gel is shown in Fig. 11 and Table 2. The fractal dimension decreases with increasing the acid ratio. A lower fractal dimension means that the molecular weight grows slower with radius, i.e. $M \sim R^d$. Thus the critical gel at high acid ratio has a more open structure than at low acid ratio. This is somewhat surprising since we expect the cross-link density to be higher at higher acid ratio. Again we attribute this result to the heterogeneous character of the system at the gel point. The particles which comprise the gel network at low acid ratio are less hydrated and hence more dense than those at higher acid ratio.

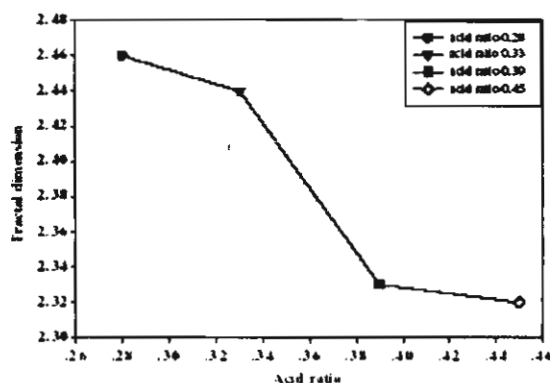


Fig. 11. The plot of fractal dimension of the critical gel cluster as a function of acid ratio.

Fig. 12 shows the frequency dependence of the dynamic viscosity at pregel stage, gel point and postgel stage. Consistent with the highly elastic behavior evident in Fig. 9, at all stages $\eta^*(\omega)$ exhibits power law frequency dependence with an exponent at the gel point of $n-1$. The time dependence of the complex viscosity at low frequency ($\omega = 0.4$ rad/s) is illustrated in Fig. 13. The location of the gel point for each system as determined by the Winter criteria (16–19) are indicated by arrows. At low acid ratio, the viscosity is initially high but approaches an asymptotic value which is relatively low. At high acid ratio, the viscosity is initially low but reaches a high asymptotic value. Thus, the gel strength and asymptotic complex viscosity are self-consistent and indicate that the gel becomes stronger under high acidity conditions. We interpret these results as indicating that at low acid, the precursor particles are poorly hydrated and form a more heterogeneous weak gel structure. At high acid, the particles are well solvated and form a less heterogeneous (more open) yet stronger network.

4. Conclusions

Anatase TiO₂ nanoparticles were successfully prepared by sol-gel technology, using inexpensive

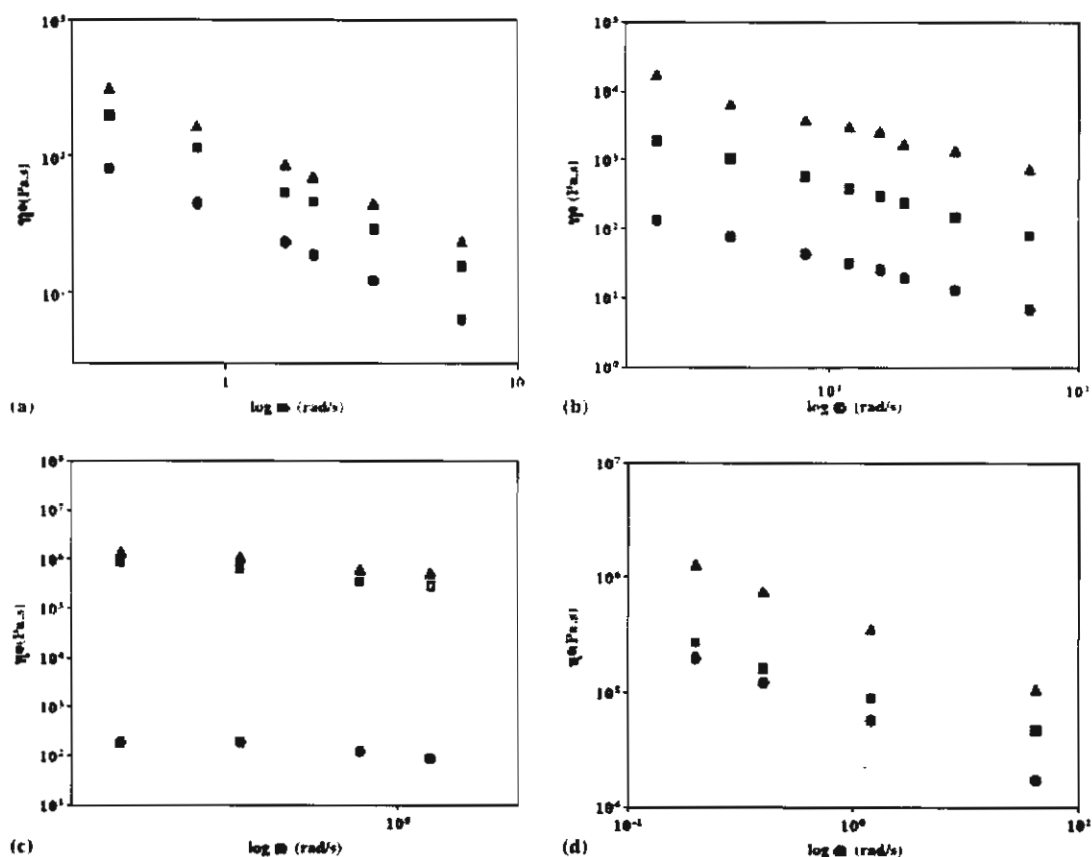


Fig. 12. The effect of frequency on the complex viscosity at pre-gel stage, gel point, and postgel stage of (a) 0.28, (b) 0.33, (c) 0.39 and (d) 0.45 HCl:H₂O volume ratio.

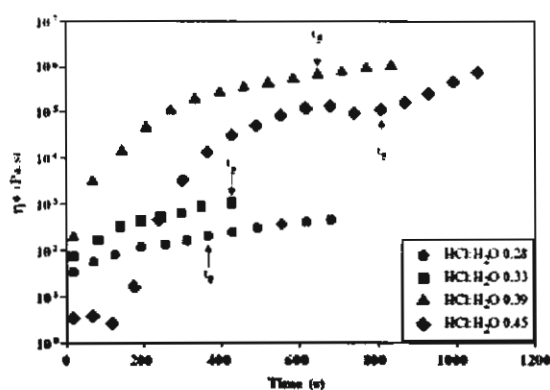


Fig. 13. The time evolution of the complex viscosity (at fixed frequency of 0.4 rad/s) of (a) 0.28, (b) 0.33, (c) 0.39 and (d) 0.45 HCl:H₂O volume ratio.

and moisture-stable titanium glycolate as precursor in 1 M HCl solution. The calcination temperature and the HCl:H₂O volume ratio has a substantial influence on the surface area, phase transformation, and morphology of the products. Anatase titania is produced at calcination temperatures in the range 600–800 °C, above which transformation to rutile occurs. Increase of temperature results in anatase of higher crystallinity but lower specific surface area, and induces a morphological change from large irregular agglomerates to more homogeneous particles of spherical shape. From XRD measurements of average grain sizes, we deduce that nucleation rate dominates the kinetics at low temperatures, and growth rate becomes the controlling factor at high temperature and low

HCl:H₂O ratios. Increase of HCl:H₂O ratio results in a small but significant decrease in porosity. The highest specific surface area 125 m²/g is obtained at the lowest HCl:H₂O ratio 0.28 and the lowest calcination temperature (600 °C). From rheological analysis, as evaluated by the Winter criteria, the gelation time increases with increase of HCl:H₂O volume ratio. The fractal dimension is determined from the frequency scaling exponent of the modulus at the gel point indicates a dense critical gel structure at low acid ratio. However, the complex viscosity and gel strength increase as a function of acid ratio. We interpret this behavior as indicative that, at low acidity, the gel is composed of poorly hydrated particles forming a dense but weak structure. Increased acidity increases hydration and cross-link density leading to a more open and stronger gel network.

Acknowledgements

This research work is supported by the Postgraduate Education and Research Program in Petroleum and Petrochemical Technology (ADB) Fund, Ratchadapisek Sompot Fund, Chulalongkorn University and the Thailand Research Fund (TRF).

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E. Oxide One Pot Synthesis of a Novel Titanium Glycolate and Its Pyrolysis

Oxide One Pot Synthesis of a Novel Titanium Glycolate and Its Pyrolysis

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Abstract

A much milder, simpler and more straightforward reaction gave a titanium glycolate product was successfully investigated by the reaction of titanium dioxide, ethylene glycol and triethylenetetramine using the oxide one pot synthesis (OOPS) process. The FT-IR spectrum demonstrates the characteristics of titanium glycolate at 619 and 1080 cm⁻¹ assigned to Ti-O stretching and C-O-Ti stretching vibrations, respectively. (Blohowiak, *et al.* 1992) C-solid state NMR spectrum gives two peaks at 75.9 and 79.8 ppm due to the relaxation of the crystalline spiro titanate product. The percentage of carbon and hydrogen from elemental analysis are 28.6 and 4.8, respectively. The thermal analysis study from TGA exhibits only one sharp transition at 340°C, corresponding to the decomposition transition of an organic ligand, and giving a ceramic yield, titanium glycolate, of 46.95% which is close to the theoretical yield of 47.50%. XRD patterns show the morphology change of its pyrolyzed product from anatase to rutile as increasing calcining temperatures from 500°C to 1100°C while at 300°C the amorphous phase is formed.

Keywords: Titanium Dioxide, Titanium Glycolate, Oxide One Pot Synthesis, Pyrolysis,
Phase Transformation

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Introduction

Titania is a very useful material and has received great attention in recent years for its humidity- and gas-sensitive behavior, excellent dielectric properties, as well as catalysis applications. (Ding and Liu, 1997). The most important factor to consider when producing titania with good properties is the purity of the titanium alkoxide precursor. However, the synthesis of titanium alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity and very expensive starting materials. In this work the great interest in titanium glycolate, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$, is owing to its difference from most crystalline titanium alkoxides, generally having low polymeric O-dimensional molecules. Nevertheless, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ is a novel crystalline complex with infinite one-dimensional chains, and exhibits outstanding high stability not only in alcohol but also in water (Wang, *et al.* 1999).

The method required for the synthesis of alkoxy derivatives of an element generally depends on its electronegativity. In the case of comparatively less active metals, a catalyst is generally employed for successful synthesis of metal alkoxides. Wang, *et al.* (1999) synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ from very expensive starting materials, tetraethyl orthotitanate to react with ethylene glycol using *n*-butylamine as a catalyst. The reaction took place under very vigorous conditions. It occurred in a Teflon-lined stainless steel autoclave at 160°-180°C for 5 days. The alkalinity of the initial reaction mixture is a dominant factor of the product. The ethylene glycol served as both a solvent and a bidentate chelate occupying sites on titanium coordination spheres so as to bridge adjacent titanium atoms and form a one-dimensional structure.

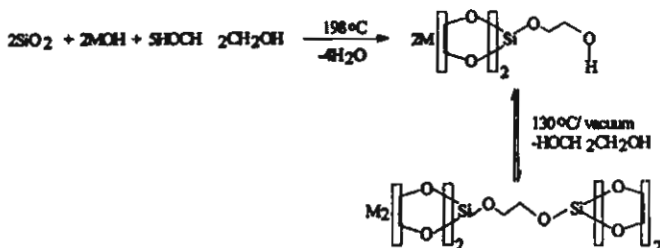
Gainsford, *et al.* (1995); and Gainsford, *et al.* (1995) studied the synthesis and characterization of the soluble titanium glycolate complexes obtained from the reaction of titanium

dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxides. The reaction of $\text{Ti}(\text{O-}i\text{-Pr})_4$ with 2 equivalent amounts of sodium or potassium hydroxides provided tris(glycolate) salts, which were highly crystalline, hygroscopic materials, crystallized as salts and solvated with varying numbers of glycol molecules.

Suzuki, *et al.* (1997) synthesized titanium tetraalkoxides from hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) and dialkyl carbonates in an autoclave at a heating rate of 90K h^{-1} . The effect of reaction temperature was studied. At a temperature range of 495-533 K, a practically complete conversion of hydrous titanium dioxide to $\text{Ti}(\text{OEt})_4$ could be attained. LiOH, NaOH, KOH, and CsOH were used as catalysts of which NaOH gave the highest yield of $\text{Ti}(\text{OEt})_4$. The effect of the molar ratios of diethyl carbonate/hydrous titanium dioxide was studied. A high molar ratio of 10 was required to obtain a high yield of $\text{Ti}(\text{OEt})_4$.

Related metalloglycolates formed from alkaline glycol were reported for aluminium and titanium. (Bickmore, *et al.* 1998; Yang, *et al.* 2001; Laine, *et al.* 1992; Laine, *et al.* 1993; Day, *et al.* 1996; and Duan, *et al.* 1997). Potassium and sodium tris(glycotitanate) complexes were obtained from the reaction of titanium dioxide or titanium tetraisopropoxide with ethylene glycol in the presence of alkali metal hydroxides. (Gainsford, *et al.* 1995; and Gainsford, *et al.* 1995)

Laine, *et al.* (1991) investigated a straightforward, low-cost route to alkoxide precursors by direct reactions of a stoichiometric mixture of silica and group I metal hydroxide with ethylene glycol. This route, termed the 'oxide one pot synthesis' (OOPS) process, provides processable precursors, as shown in Scheme 1. (Laine, *et al.* 1991; Blohowiak, *et al.* 1992; and Bickmore, *et al.* 1992).



Scheme 1.

Oxide One Pot Synthesis of a Novel Titanium Glycolate and Its Pyrolysis

Recently Jitchum, *et al.* (2001) synthesized neutral alkoxysilanes, tetracoordinated spiro-silicates, directly from silica and ethylene glycol or ethylene glycol

derivatives, using triethylenetetramine as a catalyst, in the absence or presence of potassium hydroxide as a co-catalyst (Scheme 2). (Jitchum, *et al.* 2001)



Scheme 2.

The OOPS method is simple, low-cost and can produce new chemicals in only one step. Thus, the objective of this work is to use the OOPS process to synthesize titanium glycolate. The phase transformation of its pyrolyzed product will be studied, as well.

Experimental

Materials

UHP grade nitrogen; 99.99% purity was obtained from the Thai Industrial Gases Public Company Limited (TIG). Titanium dioxide was purchased from the Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG), was purchased from Malinkrodt Baker, Inc. (USA), and purified by fractional distillation under nitrogen at atmospheric pressure, 200°C before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from the Lab-Scan Company Co. Ltd.

Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm⁻¹ using transparent KBr pellets, 0.001 g of the sample was ground and mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over

a 30°-800°C temperature range. Mass spectrum using the positive fast atom bombardment mode (FAB⁺-MS) was measured on a Fison Instrument (VG Autospec-ultima 707E) with a VG data system using glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. (Blohowiak, *et al.* 1992) C- solid state NMR spectroscopy modeled Bruker AVANCE DPX-300 MAS-NMR was used to determine the peak position of carbon contained in the product. Elemental analysis (EA) was carried out on a C/H/O Analyser (Perkin Elmer PE2400 series II). X-ray diffraction patterns were analyzed using a D/MAX-2200H Rigaku equipped with Cu X-ray generator. The Carbolite model CSF 12/7 electrical muffle furnace is employed to calcine titanium glycolate with a heating rate of 10.0°C/min for 120 minutes at various temperatures of 600, 700, 800°C.

Methodology

The titanium glycolate was synthesized by the OOPS method, see Scheme 3. A mixture of TiO₂ (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated at the boiling point of EG under N₂ atmosphere. After heating for 24 h the solution was centrifuged to separate the unreacted TiO₂ from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile and dried in a vacuum desiccator.



Scheme 3.

Results and Discussion

Synthesis

The reaction of titanium dioxide, triethylenetetramine catalyst and ethylene glycol used as both a solvent and a reactant was achieved by heating in a simple distillation apparatus. The glycol was slowly distilled off along with water generated during the condensation reaction to drive the reaction forward. The resulting product was isolated by distilling off glycol, followed by addition of acetonitrile to remove residual glycol and TETA. The final product, titanium glycolate, was moisture-stable.

Characterization

The FT-IR spectrum of titanium glycolate is shown in Figure 1. As compared with the work done by Wang, *et al.* (1999) the result clearly shows the characteristics of titanium alkoxide at the 1080 and 619 cm^{-1} bands, corresponding to C-O-Ti and Ti-O stretching, respectively. Moreover, the band at 2927-2855 cm^{-1} is assigned to the C-H stretching of an ethylene glycol ligand.

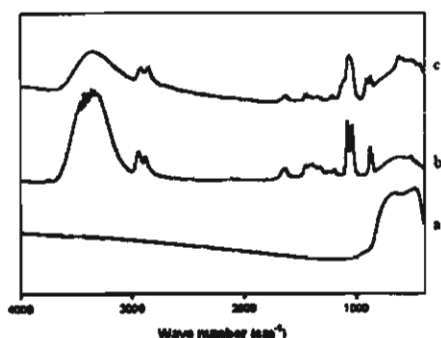


Figure 1 FT-IR spectra of (a). TiO_2 ; (b). $\text{HOCH}_2\text{CH}_2\text{OH}$ and (c). $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

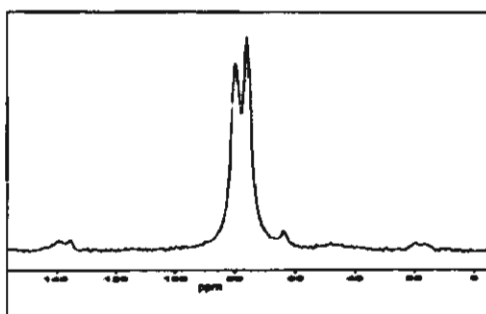


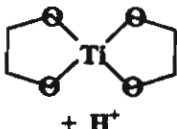
Figure 2 C-Solid state NMR spectrum of the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

Due to the insolubility of the product in an organic solvent, (Blohowiak, *et al.* 1992) C-solid state NMR was employed. The obtained spectrum, see Figure 2, gives two peaks at 74.8 and 79.2 ppm. It is due to the crystalline phase of titanium glycolate, causing the peak to split during the relaxation time of the nuclei, as discussed by Wang, *et al.* (1999).

Table1 Percentages of C and H present in the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

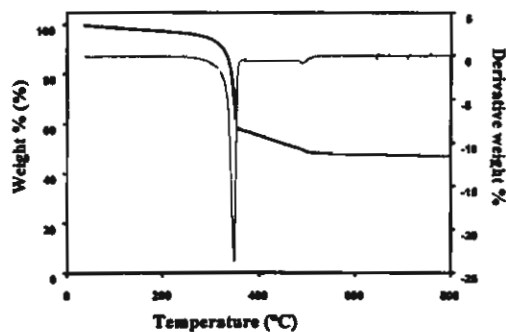
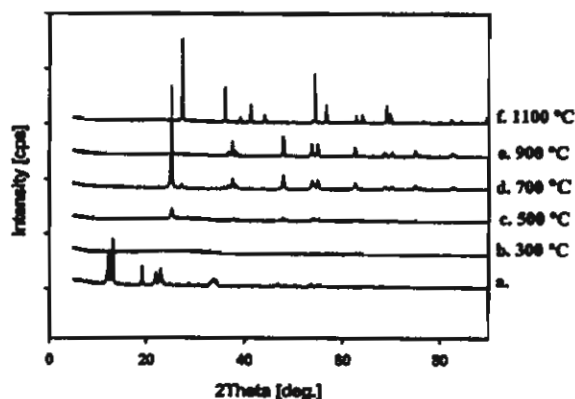
Element (%)	Theoretical	Experimental
C	27.9	28.6
H	5.6	4.8

Table 2 The Proposed fragmentation and product structures of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

M/e	%Intensity	Proposed structure
169	8.5	 + H^+
93	100	$\text{Ti-OCH}_2\text{CH}_2+\text{H}^+$
45	13	$\text{CH}_2\text{CH}_2\text{OH}$

To confirm the structure of the desired product, both elemental analysis and mass spectroscopy techniques are carried out. The results are shown in Tables 1 and 2, respectively. The obtained C/H percentages are close to those calculated theoretically. The proposed fragmentation and structures present in Table 2 also confirms the expected structure of the titanium glycolate.

As for its thermal stability, Figure 3 shows the same TGA thermogram as obtained by Wang, *et al.* (1999). The result exhibits one sharp transition at 340°C , corresponding to the decomposition transition of the glycol ligand. The final ceramic yield, titanium glycolate, obtained is 46.95% that is close to the theoretical yield, 47.5%.

**Figure 3** TGA curve of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ **Figure 4** XRD patterns of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ at different temperatures:

- a.) titanium glycolate without calcination
 b.) 300°C , amorphous; c.) 500°C , anatase;
 d.) 700°C , anatase; e.) 900°C , anatase;
 f.) 1100°C , rutile.

Phase transformation

The TGA result indicated the oxidation of organic compounds takes place at 340°C and the crystallisation at about 500°C . The crystalline titanium glycolate decomposed and changed to an amorphous phase at 300°C (Figure 4). As the calcination temperature is increased the XRD pattern gives an anatase phase at 500°C to 900°C and completely changes to a rutile phase at 1100°C .

Conclusions

Titanium glycolate is successfully synthesized using low cost starting materials, with much simpler and milder reaction conditions. The product shows the property of good moisture stability. The results from spectroscopy, namely, FT-IR, Solid state NMR, EA, and TGA, confirm the product structure. The transformation from the anatase to the rutile phase indicates anatase stability up to 900°C. The stability of the synthesized product remarkably enables researchers to make use of it in many applications.

Acknowledgement

This research work is supported by the Thailand Research Fund (TRF).

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**F. “High Surface Area and Thermally Stable TiO₂
Synthesized Directly from Titanium Triisopropanolamine Precursor”**

MICRO-AND MESOPOROUS MINERAL PHASES

Accademia Nazionale dei Lincei, Rome, December 6-7, 2004

HIGH SURFACE AREA AND THERMALLY STABLE TiO₂ SYNTHESIZED DIRECTLY FROM TITANIUM TRIISOPROPANOLAMINE PRECURSOR

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Introduction

Titanium dioxide, TiO₂, is widely used as humidity and gas sensors, dielectric ceramics, catalyst supporter, solar cell and catalyst, especially, photocatalyst.¹⁻⁶ Generally, most catalysts are used at high temperature, thus must present high thermal stability. Therefore, preparation of anatase nanoparticles with high surface area, uniform particle size, uniform pore structure and high anatase-rutile transformation temperature is truly desirable.

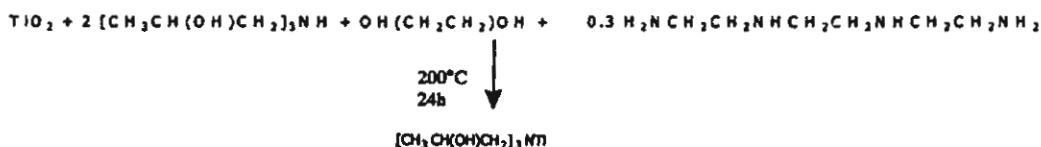
High surface area TiO₂ can be prepared by several methods, such as pyrolysis of titanium tetrabutoxide in oxygen containing atmosphere via the MOCVD method,⁷ hydrothermal treatment,⁸⁻⁹ or the most famous method, the so called sol-gel process.¹⁰⁻¹² Although these processes are widely used, they still present two major drawbacks, viz. expensive and sensitive starting materials. The important factor to produce titania with good properties is the purity of titanium alkoxide precursor. The titanium dioxide has most often been prepared using the titanium alkoxide, however, the synthesis of metal alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity because they contain an unsaturated Ti^{IV} center which is highly reactive to air and moisture, therefore, the reaction must be carried out under inert gas. Another reason is that those titanium alkoxides are synthesized from very expensive starting materials.

On the basis of our previous work, moisture stable titanium glycolate precursor was successfully synthesized from low cost starting material, TiO₂, using the Oxide One Pot Synthesis method (OOPS)¹³ and used as precursor to produce nanocrystalline mesoporous high surface area titanium dioxide by the sol-gel process.¹⁴ In this work, we demonstrate that moderately high surface area and thermally stable anatase TiO₂ can be obtained directly from the crude product, titanium triisopropanolamine precursor, synthesized by the reaction of TiO₂ and triisopropanolamine.

Results and Discussion

Titanium Triisopropanolamine Precursor Characterization

Titaniumtriisopropanolamine was synthesized by the direct reaction of titanium dioxide with triisopropanolamine in the presence of ethylene glycol and triethylenetetramine (reaction 1).



Reaction 1.

The crude titanium triisopropanolamine was characterized using FT-IR, TGA and FAB⁺-MS. The IR spectrum (figure1) shows the expected bands at 3400 cm⁻¹ (OH group), 2927-2855 cm⁻¹ (C-H stretching), 1460 cm⁻¹ (C-H bending of CH₂ group), 1379 cm⁻¹ (C-H bending of CH₃ group), 1085 cm⁻¹ (C-O-Ti stretching), 1020 cm⁻¹ (C-N bending) and 554 cm⁻¹ (Ti-O stretching). The result from TGA analysis, as can be seen in figure 2a, shows two transitions at 280° and 365°C corresponding to the decomposition of the unreacted triisopropanolamine and the triisopropanolamine ligand, respectively. The final ash yield, 16.6%, calculated from the starting point of the second decomposition transition is close to the theoretical ceramic yield of [HOCH₂CHCH₂]₃N[CH₂CH₂CHO]₂Ti[OCHCH₂CH₂]₂N[CH₂CHCH₂OH]₃, 18.7%. The mass spectrum result (Table1) confirms the desired structure of the as-synthesized product.

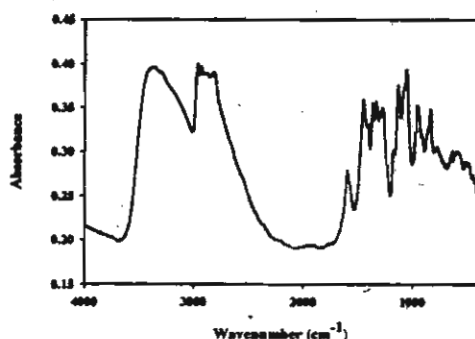


Figure 1. The FT-IR spectra of titaniumtriisopropanolamine

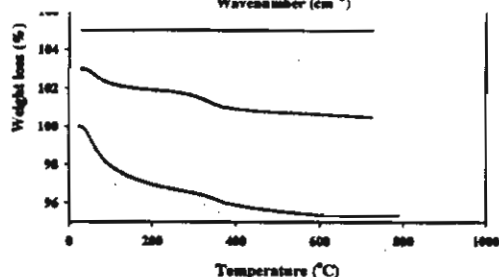


Figure 2. The TGA thermograms of a.) titanium triisopropanolamine, TiO₂ calcined at 600°C and holding time of b.) 1 h, c.) 2 h, and d.) TiO₂ calcined at 500°C for 2 h

Table 1. The proposed structure of the synthesized titanium triisopropanolamine.

M/e	% Intensity	Proposed structure
428	10	$H^+[HOCH_2CHCH_2]N[CH_2CH_2CHO]_2Ti[OCHCH_2CH_2]_2N[CH_2CHCH_2OH]H^+$
410	5	$[CH_2CH_2CH_2]N[CH_2CHCH_2O]_2Ti[OCHCH_2CH_2]_2N[CH_2CHCH_2OH]$
214	58	$[H_2NCHCH_2CH_2O]_2Ti[OH]$
192	100	$H+N[CH_2CHCH_2OH]_3$

TiO₂ catalyst characterization

Effect of calcination rate

The effect of calcination rate on the surface area is studied at 0.25, 0.5 and 1.0°C/min at calcination temperature of 600°C for 2h. The results of specific surface area summarized in table 2 show that at the lowest calcination rate (0.25°C/min) the highest surface area is observed. This is probably due to having more time for TiO₂ units to orderly arrange themselves.

Table 2. The specific surface area of calcined TiO₂ at various calcinations temperature rates.

Calcination rate (°C/min)	Specific surface area (m ² /g)
0.25	163.6
0.5	86.6
1.0	67.0

Effect of holding time

Holding time at 600°C calcination temperature also affects to the surface area. In this study, 1, 2 and 4h holding times show that using calcination rate of 0.25°C/min, the highest specific surface area, 163.6 m²/g (table 3), was found at 2h holding time while at 1h holding time the final powder was gray in color, meaning that some organic residues remained in the sample. The TGA thermograph in figure 2b confirms that indeed there was still some organic residue, as indicated at the decomposition transition at 365°C. The TGA thermograph in figure 2c presents pure TiO₂ without any organic residue. As the holding time increased to 4h, the specific surface area came down to 74 m²/g.

Table 3. The specific surface area of calcined TiO₂ at various holding times.

Holding time (h)	Specific surface area (m ² /g)
1	65.08
2	163.64
4	74.04

From the variations of calcination rate and holding temperature, the sample with calcination rate of 0.25°C/min and holding time of 2h was selected to study the effect of calcination temperature to determine the phase transformation of TiO₂. The calcined product is characterized using XRD, BET and SEM to confirm the active and thermally stable anatase phase of TiO₂. The XRD patterns in figure 3 and the particle morphology in figure 4 clearly illustrate the anatase phase of TiO₂, as previously studied [2]. Coincidentally, the nitrogen adsorption-desorption isotherm (figure 5) of the material calcined at 600°C for 2h indicates a mesoporous structure, having the isotherm of type IV.

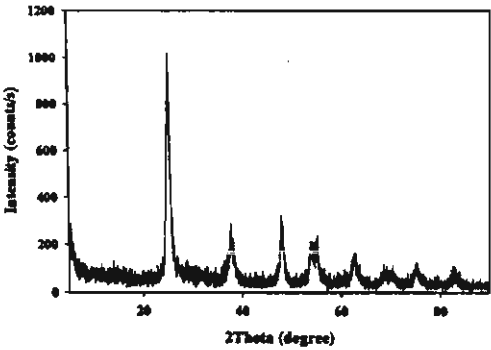


Figure 3. XRD pattern of TiO₂ at the 0.25°C/min calcinations rate, 2h holding time and 600°C calcination temperature.

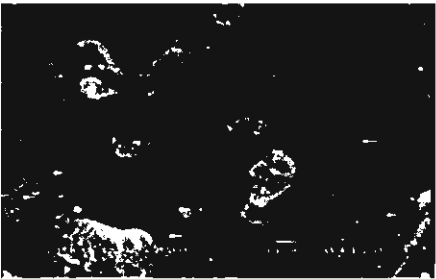


Figure 4. The SEM micrograph of TiO₂ at the 0.25°C/min calcinations rate, 2h holding time and 600°C calcination temperature.

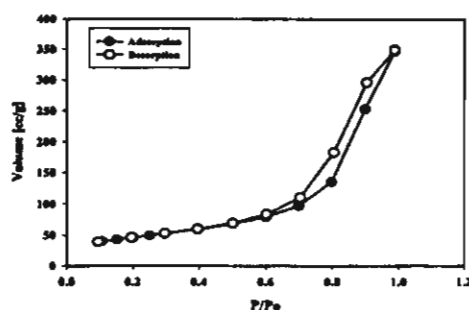


Figure 5. The nitrogen adsorption-desorption isotherm of the obtained mesoporous TiO_2 at $0.25^\circ\text{C}/\text{min}$ calcinations rate, 2h holding time and 600°C calcination temperature.

Effect of calcination temperature

The phase transformation of TiO_2 is studied at different calcination temperature, viz. 300° , 500° , 600° , 700° , 800° and 900°C using $0.25^\circ\text{C}/\text{min}$ calcination rate and 2h holding time. The sample at 300°C calcination temperature has black color, indicating incomplete removal of organic compounds. The XRD pattern (figure 6a.) and SEM micrograph (figure 7a.) show the amorphous phase of sample. By increasing the temperature to 500°C , most of the sample has white color and little in gray. This is in agreement with the result of TGA (figure 2d.) showing moisture and organic residue decomposition transitions. The XRD pattern (figure 6b.) and SEM (figure 7b.) present the anatase phase of TiO_2 .^{2,10} At higher calcination temperatures (600° - 800°C), the anatase phase is continuously formed, see the XRD patterns in figure 6c-e, and the intensity of the peaks increases with the calcination temperature, meaning that higher crystallinity occurs as the temperature increases. The SEM micrographs of the anatase phase showed in figure 7c-e can confirm the crystalline morphology. As the temperature was increased to 900°C the XRD pattern (figure 6f) and SEM micrograph (figure 7f) indicated the rutile phase of TiO_2 .²¹⁻²² The specific surface areas of TiO_2 at different calcinations temperatures are shown in table 4 in which the highest specific surface area ($163.64 \text{ m}^2/\text{g}$) is at calcinations temperature of 600°C .

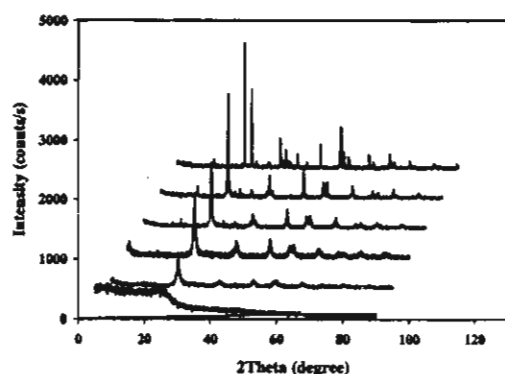


Figure 6. XRD patterns of TiO_2 at the temperature of a.) 300° , b.) 500° , c.) 600° , d.) 700° , e.) 800° and f.) 900°C .

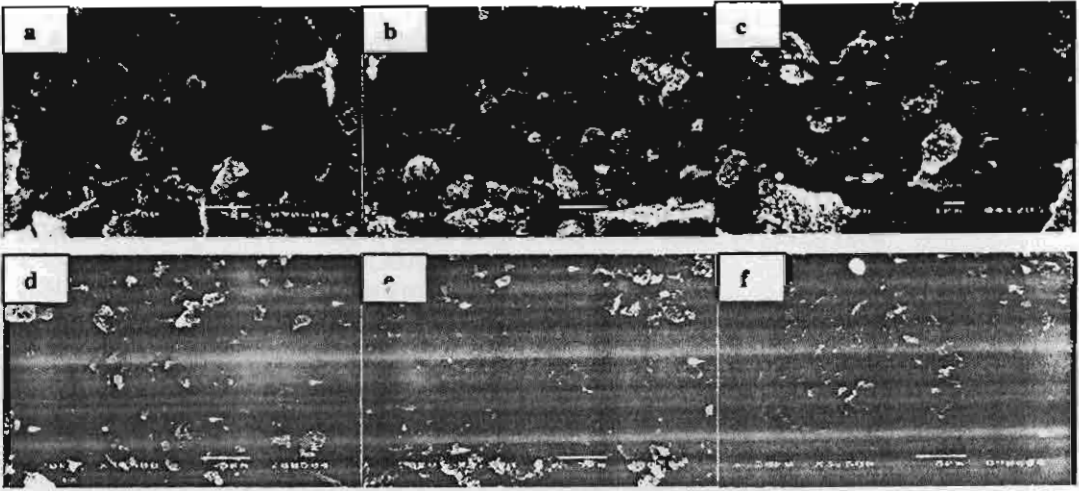


Figure 7. The SEM micrographs of TiO_2 at the temperature of:
a.) 300°, b.) 500°, c.) 600°, d.) 700°, e.) 800° and f.) 900°C.

Table 4. The specific surface area of calcined TiO_2 at various calcinations temperatures.

Calcinations temperature (°C)	Specific surface area (m^2/g)
500	122.69
600	163.64
700	54.94
800	24.30
900	3.86

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