



รายงานวิจัยฉบับสมบูรณ์

โครงการ

"การศึกษาวิธีการสังเคราะห์ และการประยุกต์สารไทเทเนียมไดออกไซด์-ซิลิกอนไดออกไซด์เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

โดย นางสุจิตรา วงศ์เกษมจิตต์และคณะ

สัญญาเลขที่ BRG4680013

รายงานวิจัยฉบับสมบูรณ์



โครงการ

"การศึกษาวิธีการสังเคราะห์ และการประยุกต์สารไทเทเนียมไดออกไซด์-ซิลิกอนไดออกไซด์
เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

คณะผู้วิจัย

1. นางสาวจิตรา วงศ์เกษมจิตต์
2. นางสาวนพวรรณ พรธรรมชัย
3. นางสาวเมธิรา กฤษณะเศรษฐ์

สังกัด

- วิทยาลัยปิโตรเลียมและปิโตรเคมี
วิทยาลัยปิโตรเลียมและปิโตรเคมี
วิทยาลัยปิโตรเลียมและปิโตรเคมี

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย
(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกวาไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณสำนักงานกองทุนสนับสนุนการวิจัย ที่ได้ให้การสนับสนุนโครงการวิจัยนี้
ด้วยดีตลอดทั้งโครงการ

บทคัดย่อ

รหัสโครงการ : BRG4680013

ชื่อโครงการ : "การศึกษาวิธีการสังเคราะห์ และการประยุกต์สารไททาเนียมไดออกไซด์-ซิลิกอนไดออกไซด์เพื่อใช้เป็นเมมเบรนที่มีสมบัติพิเศษในการแยกสาร"

ชื่อนักวิจัย : นางสาวจิตรา วงศ์เกษมจิตต์

วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย

E-mail Address : c.sujitra@chula.ac.th

ระยะเวลาโครงการ : 3 ปี

งานวิจัยนี้ได้มีการสังเคราะห์สารประกอบโลหะอัลคอกไซด์คือ สารไททาเนียมไกลโคเลตและสารไททาเนียมไตรไอโซโพรพานอลามีนจากวัตถุดิบที่หาง่ายและราคาถูก ด้วยกระบวนการสังเคราะห์สารประกอบออกไซด์ขั้นตอนเดียวที่เรียกกันว่า Oxide One Pot Synthesis (OOPS) โดยสารที่สังเคราะห์ได้มีสมบัติที่เป็นเอกลักษณ์ที่มีความสำคัญมากในกระบวนการโซล-เจล จากการวิเคราะห์สารตัวอย่างด้วยเครื่อง XRD พบว่า สารที่ผ่านการเผาด้วยอุณหภูมิสูงจะมีการเปลี่ยนแปลงของโครงสร้างผลึกจากชนิดอนาเทส (anatase) เป็นรูไทต์ (rutile) ที่อุณหภูมิสูง ขณะที่อุณหภูมิ 300 องศาเซลเซียส สารไม่ก่อตัวเป็นโครงสร้างผลึก ในกระบวนการผลิตสารไททาเนียมที่มีผลึกระดับนาโนและมีรูพรุนขนาดกลางโดยกระบวนการโซล-เจlnั้น สารตั้งต้นที่ใช้เป็นไททาเนียมไกลโคเลตในสภาวะที่มีองค์ประกอบเป็นน้ำและกรด ผลการวิเคราะห์จากเครื่อง XRD พบโครงสร้างผลึกชนิดอนาเทสที่อุณหภูมิการเผาสารในช่วง 600-800 องศาเซลเซียส และมีพื้นที่ผิวสูงถึง 125 ตารางเมตรต่อกรัม ที่อัตราส่วนโดยปริมาตรระหว่างกรดไฮโดรคลอริกและน้ำเท่ากับ 0.28 ถ้าสารไททาเนียมที่เผาที่อุณหภูมิ 800 องศาเซลเซียส ผลึกไททาเนียมไดออกไซด์จะมีลักษณะเป็นทรงกลมที่มีขนาดเล็กประมาณ 1 ไมครอน จากการศึกษาทางด้านรีโอโลยีของสารไททาเนียมไกลโคเลตโดยวิธีการของวินเทอร์พบว่าเวลาในการเกิดเจlnั้น ขึ้นอยู่กับอัตราส่วนของกรดไฮโดรคลอริกและน้ำ ความแข็งแรงของเจlnั้นเพิ่มขึ้นเมื่ออัตราส่วนของกรดและน้ำสูงขึ้น ดังนั้น สามารถกล่าวได้ว่า การเพิ่มความเข้มข้นกรดจะส่งผลให้ความแข็งแรงของโครงสร้างเพิ่มขึ้นและไม่ก่อให้เกิดการยุบตัว จากการศึกษารีโอโลยีของไททาเนียมไกลโคเลตเจlnี้อัตราส่วนโดยโมลของกรดไฮโดรคลอริกและสารอัลคอกไซด์เท่ากับ 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

E-mail Address : dsujitra@chula.ac.th

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

Table Content

	Page
Title page	ii
Acknowledgement	iii
Abstract (Thai)	iv
Abstract (English)	vi
Executive Summary	viii
Table Content	x
CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	4
2.1 Synthesis of Metal Alkoxides	4
2.2 Sol-gel Process of Metal Alkoxides	6
2.3 Rheological Study of Metal Alkoxides	8
2.4 Synthesis of TS-1 Zeolite	10
2.5 Photocatalytic Membrane Reactor	12
References	15
III OBJECTIVES	18
IV OXIDE ONE POT SYNTHESIS OF A NOVEL TITANIUM GLYCOLATE AND ITS PYROLYSIS	19
Abstract	19
Introduction	20
Experimental	22
Results and Discussion	23
Conclusions	26
References	26
V STRUCTURAL AND RHEOLOGICAL ASPECT OF MESOPOROUS NANOCRYSTALLINE TiO ₂ SYNTHESIZED VIA SOL-GEL PROCESS	27
Abstract	27

Introduction	28
Experimental	29
Results and discussion	31
Conclusions	42
References	42
VI STRUCTURAL AND CRYSTALLIZATION OF HIGH Ti- LOADED TS-1 ZEOLITE	44
Abstract	44
Introduction	45
Experimental	46
Results and Discussion	48
Conclusions	59
References	60
VII PHOTOCATALYTIC MEMBRANE REACTOR OF A NOVEL	62
Abstract	62
Introduction	63
Experimental	64
Results and discussion	68
Conclusions	77
References	77
VIII CONCLUSIONS	80
APPENDIX PROJECT OUTPUTS	82
A. National Patent: สุจิตรา วงศ์เกษมจิตต์ และนพวรรณ พรรณชัย เรื่อง "เยื่อแผ่นสำหรับย่อยสลายสารพิษและเชื้อโรคด้วยแสง" เลขที่คำขอ 103423 เมื่อวันที่ 19 สิงหาคม พ.ศ. 2548	83
B. 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	95

- C. 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).102
- 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.

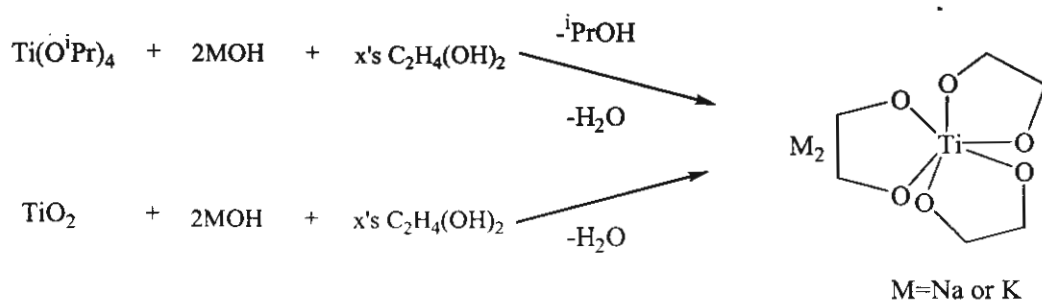
In this work titanium glycolate ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$) and titanium triisopropanol amine ($\text{Ti}(\text{OCHCH}_3\text{CH}_2)_2\text{N}(\text{CH}_2\text{CHCH}_3\text{OH})_2$) were synthesized using the Oxide One Pot Synthesis (OOPS) method and low cost starting materials. $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ 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

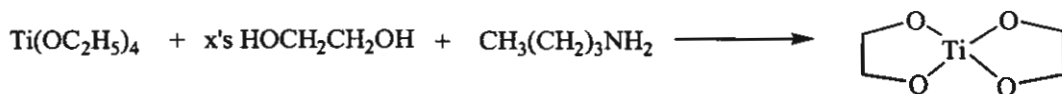
2.1 Synthesis of Metal Alkoxides

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



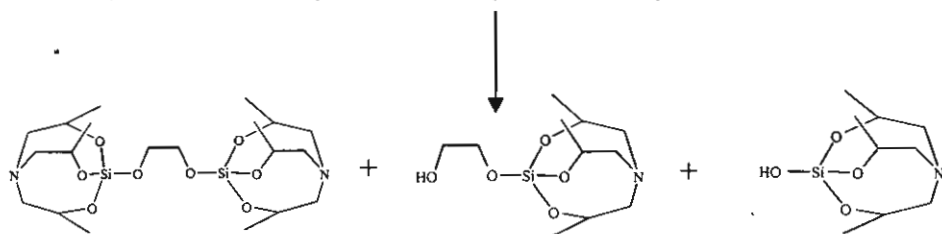
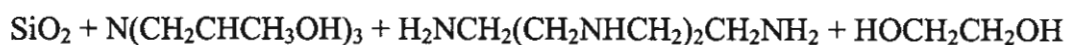
Scheme 2.1 The preparation of synthesized anionic titanium tris(glycolate) complex.

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.



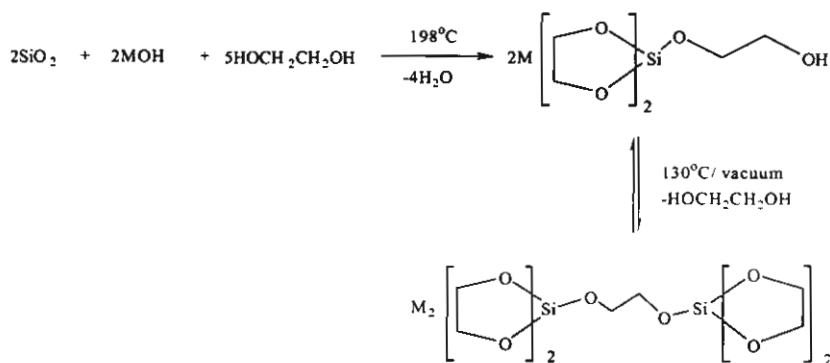
Scheme 2.2 The preparation of titanium glycolate complex by reacting titanium tetraethoxide with glycol.

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, TEAOH, 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 (TEOS) 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.

References

1. a). Gainsford, G.J., Kemmitt, T., Lensink, C., and Milestone, N.B. *Inorg. Chem.* 1995, 34, 746-748; b). Gainsford, J.G., Kemmitt, T., and Milestone, B.N. *Inorg. Chem.* 1995, 34, 5244-5251.
2. Wang, D., Yu, R., Kumada N. (1999) Hydrothermal synthesis and characterization of a novel one-dimensional titanium glycolate complex single crystal: $(\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2)$, *Chemistry of Materials*, 11, 2008-2012.
3. P. Piboonchaisit, S. Wongkasemjit and R. Laine, "A Novel Route to Tris(silatranyloxy-i-propyl)amine Directly from Silica and Triisopropanolamine", *Sci. Asia*, 25, 113-119 (1999).
4. a). Bickmore, C.R., Waldner, K.F., Baranwal, R., Hinklin, T., Freadwell, D.R., Laine R.M. (1998) Ultrafine titania by flame spray pyrolysis of a titanatrane complex. *European Polymer Journal*, 18, 287-297; b). Laine, R.M., Youngdahl, K.A., Nardi, P. Washington Research Foundation, U.S. Pat. No. 5,099,052, 1992; c). Laine, R.M., Youngdahl, K.A. Washington Research Foundation, U.S. Pat. No. 5,216,155, 1993.
5. Suzuki, E., Kusano, S., Hatayama, H., Okamoto, M., and Ono, Y. *J.Mater.Chem* 1997, 7(10), 2049-2051.
6. Yi, G., Sayer, M., *Ceram. Bulletin.*, 1991, 70, 1173.
7. Zhang, Y., Weidenkaff, A., Reller A. (2002) Mesoporous structure and phase transition of nanocrystalline TiO_2 . *Materials Letters*, 54, 375-381.
8. Wei, Y., Wu, R., Zhang Y. (1999) Preparation of monodispersed spherical TiO_2 powder by forced hydrolysis of $\text{Ti}(\text{SO}_4)_2$ solution. *Materials Letter*, 41, 101-103.
9. Sun, Y., Li, A., Qi, M., Zhang, L., Yao, X. (2001) High surface area anatase titania nanoparticles prepared by MOCVD. *Material Science and Engineering: B*, 86, 185-188.
10. Kim, E.J., Hahn, S.H. (2001) Microstructural changes of microemulsion-mediated TiO_2 particles during calcinations. *Materials Letters*, 49, 244-249.

11. Wu, M., Lin, G., Chen, D., Wang, G., He, D., Feng, S., Xu R. (2002) Sol-hydrothermal synthesis and hydrothermally structure evolution of nanocrystal titanium dioxide. *Chemistry of Material*, 14, 1974-1980.
12. Khalil, K.M.S and Zaki, M.I. (2001) Preparation and characterization of sol-gel derived mesoporous titania spheroids. *Powder Technology*, 120, 256-263.
13. Kominami, H., Kohno, M., Takada, Y., Inoue, M., Inui, T., Kera, Y. (1999) Hydrolysis of titanium alkoxide in organic solvent at high temperatures: A new synthetic method for nanosized, thermally stable titanium (IV) oxide. *Industrial and Engineering Chemistry Research*, 38, 3925-3931.
14. Winter, H.H., Chambon, F. (1986) Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. *Journal of Rheology*, 30, 367-382.
15. Muthukumar M, (1989) Screening effect on viscoelasticity near the gel point. *Macromolecules*, 22, 4656-4658.
16. M. Taramasso, G. Perego, B. Notari, US Patent 4410501 (1983).
17. Marra, G.L., Artioli, G., Fitch, A.N., Milanesio, M., Lamberti, C. (2000) Orthorhombic to monoclinic phase transition in high-Ti-loaded TS-1: an attempt to locate Ti in the MFI framework by low temperature XRD. *Microporous and mesoporous Materials*, 40, 85-94.
18. Grieneisen, J.L., Kessler, H., Fache, E., Le Govic, A.M. (2000) Synthesis of TS-1 in fluoride medium. A new way to a cheap and efficient catalyst for phenol hydroxylation. *Microporous and Mesoporous Materials*, 37, 379-386.
19. Khomane, R.B., Kulkarni, B.D., Paraskar, A., Sainkar, S.R. (2002) Synthesis, characterization and catalytic performance of titanium silicate-1 prepared in micellar media. *Materials Chemistry and Physics*, 76, 99-103.
20. Xia, Q.H. and Gao, Z. (1997) Crystallization kinetics of pure TS-1 zeolite using quaternary ammonium halides as templates. *Materials Chemistry and Physics*, 47, 225-230.
21. Newalkar, B.L., Olanrewaju, J., Komarneni, S. (2001) Direct synthesis of titanium substituted mesoporous SBA-15 molecular sieve under microwave-hydrothermal conditions. *Chemistry of Materials*, 13, 552-557.
22. Ohgushi, T., Komarneni, S., Bhalla, A.S. (2001) Mechanism of microwave heating of zeolite A. *Journal of Porous Materials*, 8, 23-35.

23. Kunii, K., Narahara, K., Yamanaka, S. (2002) Template-free synthesis of $\text{AlPO}_4\text{-H1}$, -H2, and -H3 by microwave heating. *Microporous and Mesoporous Materials*, 52, 159-167.
24. Arafat, A., Jansen, J.C., Ebaid, A.R., Bekkum, H.V. (1993) Microwave preparation of zeolite Y and ZSM-5. *Zeolites*, 13, 162-165.
25. Li, Y.G., Lee, Y.M., Porter, J.F. (2002) The synthesis and characterization of titanium silicate-1. *Journal of Materials Science*, 37, 1959-1965.
26. Figoli, A., Sager, W., Wessling, M. (2002) Synthesis of novel nanostructured mixed matrix membranes. *Desalination*, 148, 401-405.
27. Ziegler, S., Theis, J., Fritsch, D. (2001) Palladium modified porous polymeric membranes and their performance in selective hydrogenation of propyne. *Journal of Membrane Science*, 187, 71-84.
28. Lu, Z., Liu, G., Duncan, S. (2003) Poly(2-hydroxyethyl acrylate-co-methyl acrylate)/ $\text{SiO}_2/\text{TiO}_2$ hybrid membranes. *Journal of Membrane Science*, 221, 113-122.
29. Pechar, T.W., Tsapatsis, M., Marand, E., Davis, R. (2002) Preparation and characterization of a glassy fluorinated polyimide zeolite-mixed matrix membrane. *Desalination*, 146, 3-9.
30. Molinari, R., Palmisano, L., Drioli, E., Schiavello, M. (2002) Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. *Journal of Membrane Science*, 206, 399-415.
31. Karakulski, K., Morawski, W.A., Grzechulska, J. (1998) Purification of bilge water by hybrid ultrafiltration and photocatalytic processes. *Separation and Purification Technology*, 14, 163-173.
32. Mele, G., Ciccarella, G., Vasapollo, G., Garcia-Lopez, E., Palmisano, L., Schiavello, M. (2002) Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO_2 samples impregnated with Cu(II) -phthalocyanine. *Applied Catalysis B: Environmental*, 38, 309-319.

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.

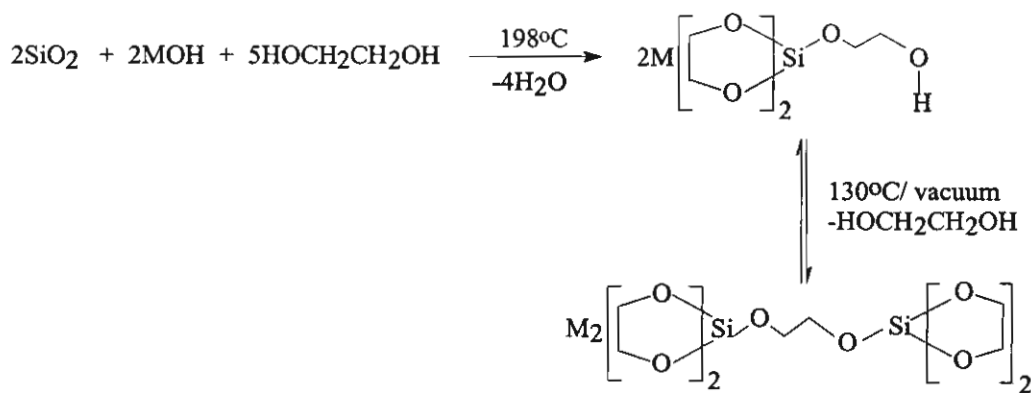
Gainsford *et al.*³⁻⁴ studied the synthesis and characterization of the soluble titanium glycolate complexes obtained from the reaction of titanium dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxides. The reaction of $\text{Ti}(\text{O-}i\text{-Pr})_4$ with 2 equivalent 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 $\text{Ti}(\text{OEt})_4$.

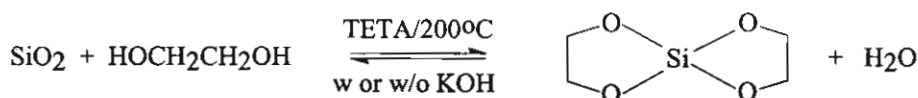
Related metalloglycolates formed from alkaline glycol were reported for aluminium and titanium⁶⁻¹¹. Potassium and sodium tris(glycotitanate) complexes were obtained from the reaction of titanium dioxide or titanium tetraisopropoxide with ethylene glycol in the presence of alkali metal hydroxides.³⁻⁴

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.

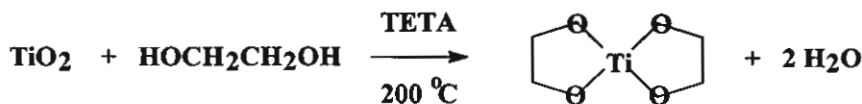
Instrumental

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.

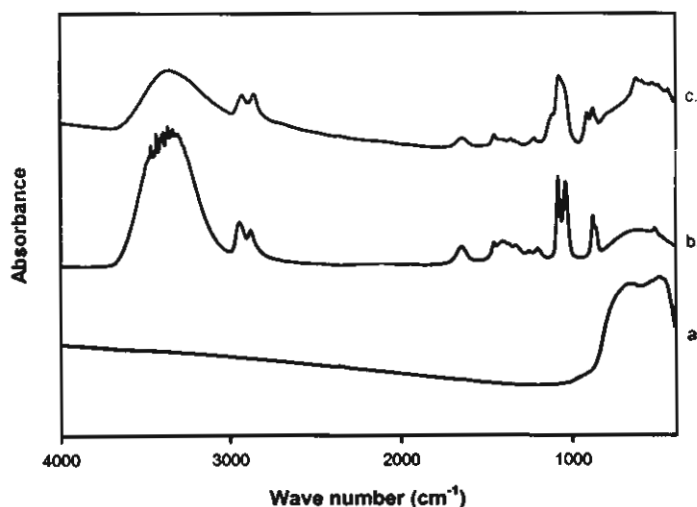


Figure 1 FT-IR spectra of a) TiO_2 , b) $\text{HOCH}_2\text{CH}_2\text{OH}$ and c) $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

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

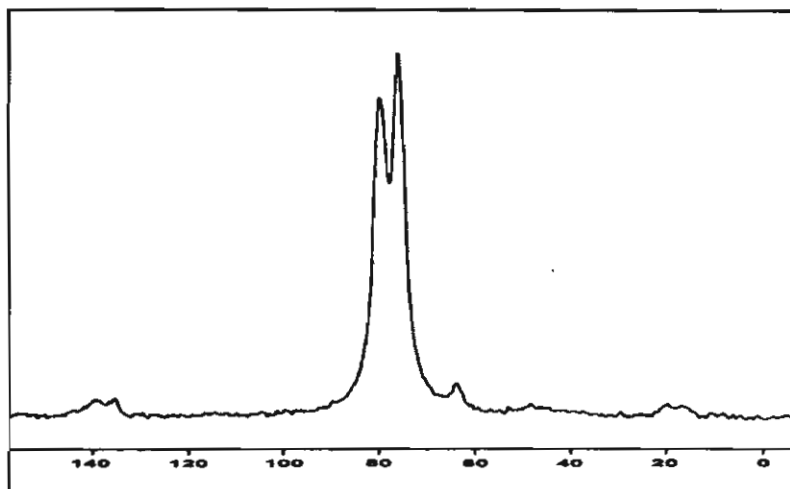


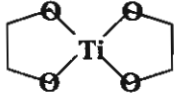
Figure 2 ^{13}C -Solid state NMR spectrum of the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

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.

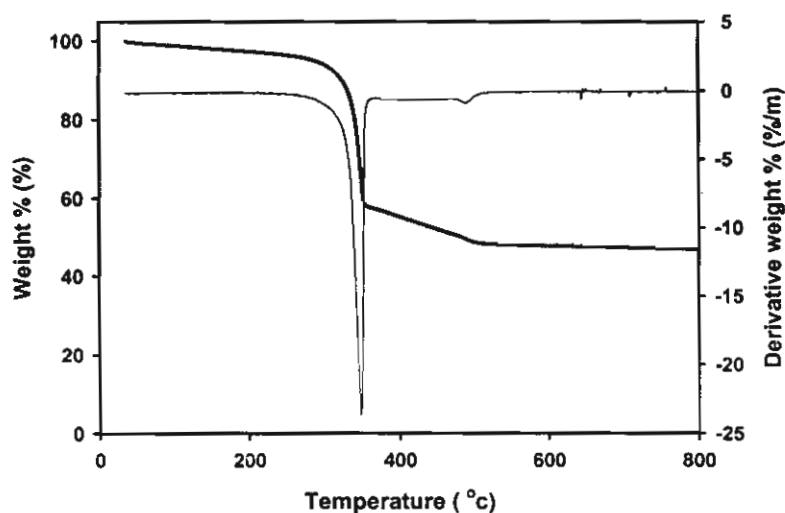
Table1 Percentages of C and H presented in the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

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.

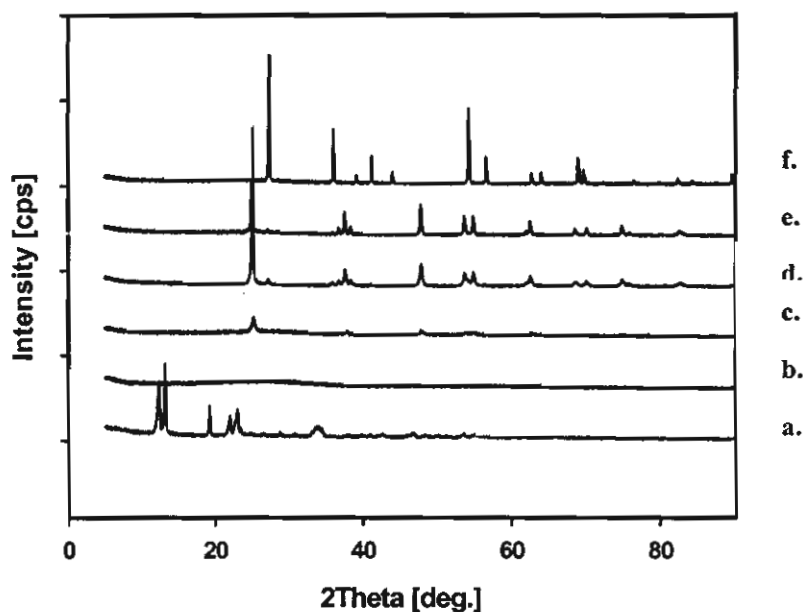


Figure 4 XRD patterns of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ at different temperatures: a) ambient, b) 300°, c) 500°, d) 700°, e) 900° and f) 1100°C.

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.

References

1. Ding, X.Z., and Liu, X.H. *Materials Science and Engineering A224*. 1997, 210-215
2. Wang, D., Yu, R., Kumada, N. *Chem. Mater.* 1999, 11, 2008-2012.
3. Gainsford, G.J., Kemmitt, T., Lensink, C., and Milestone, N.B. *Inorg. Chem.* 1995, 34, 746-748.

4. Gainsford, J.G., Kemmitt, T., and Milestone, B.N. *Inorg. Chem.* 1995, 34, 5244-5251.
5. Suzuki, E., Kusano, S., Hatayama, H., Okamoto, M., and Ono, Y. *J.Mater.Chem* 1997, 7(10), 2049-2051.
6. Bickmore, C.R., Waldner, K.F., Baranwal, R., Hinklin, T., Freadwell, D.R., and Laine, R.M. *Journal of the European ceramic Society.* 1998, 18, 287-297.
7. Yang, J., MEI, S., and Ferreira, J.M.F. *Materials Science and Engineering C* 2001, 15, 183-185.
8. Laine, R.M.; Youngdahl, K.A.; Nardi, P. Washington Research Foundation, U.S. Pat. No. 5,099,052, 1992.
9. Laine, R.M.; Youngdahl, K.A. Washington Research Foundation, U.S. Pat. No. 5,216,155, 1993.
10. Day, V.W., Eberspacher, .A., Frey, M.H., Klemperer, W.G., Liang, S. and Payne, D.A. *Chem Mater* 1996, 8, 330-332.
11. Duan, Z., Thomas, L.M., and Verkade, J.G. *Polyhedron* 1997, 16, 635-641.
12. Laine, R.M.; Blohowiak, K.Y.; Robinson, T.R.; Hoppe, M.L.; Nardi, P.; Kampf, J.: *Uhm, J. Nature* **1991**, 353, 642.
13. Blohowiak, K.Y.; Laine, R.M.; Robinson, T.R.; Hope, M,L.; Kampf, J.I. *Inorganic and Organometallic Polymers with Special Properites; ACS: Netherland*, 1992.
14. Bickmore, C.;Hoppe, M.L.; Laine, R.M. *Mat.Res.Soc.Symp.Proc.* 1992, 249, 81.
15. Jitchum, V.; Chivin, S.; Wongkasemjit S.; Ishida, H. *Tetrahedron* 2001, 57, 3997.

CHAPTER V

STRUCTURAL AND RHEOLOGICAL ASPECT OF MESOPOROUS NANOCRYSTALLINE TiO₂ 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.

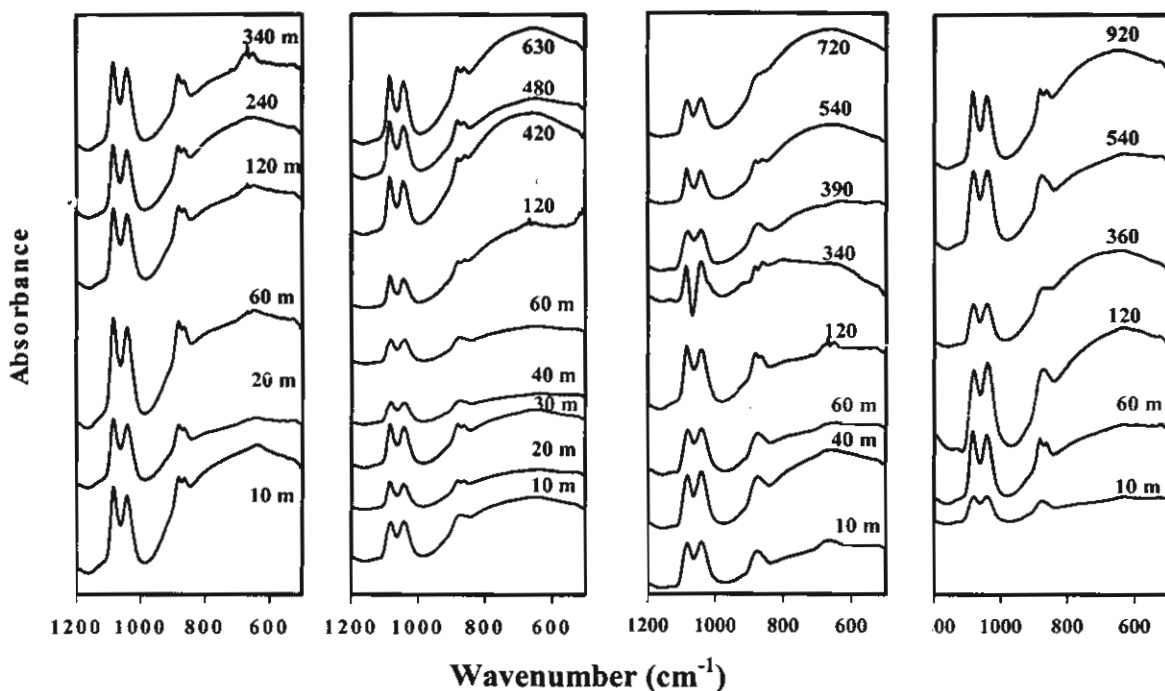


Figure 1 FT-IR spectra of titania gel at HCl:H₂O volume ratios of a) 0.28, b) 0.33, c) 0.39 and d) 0.45

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.

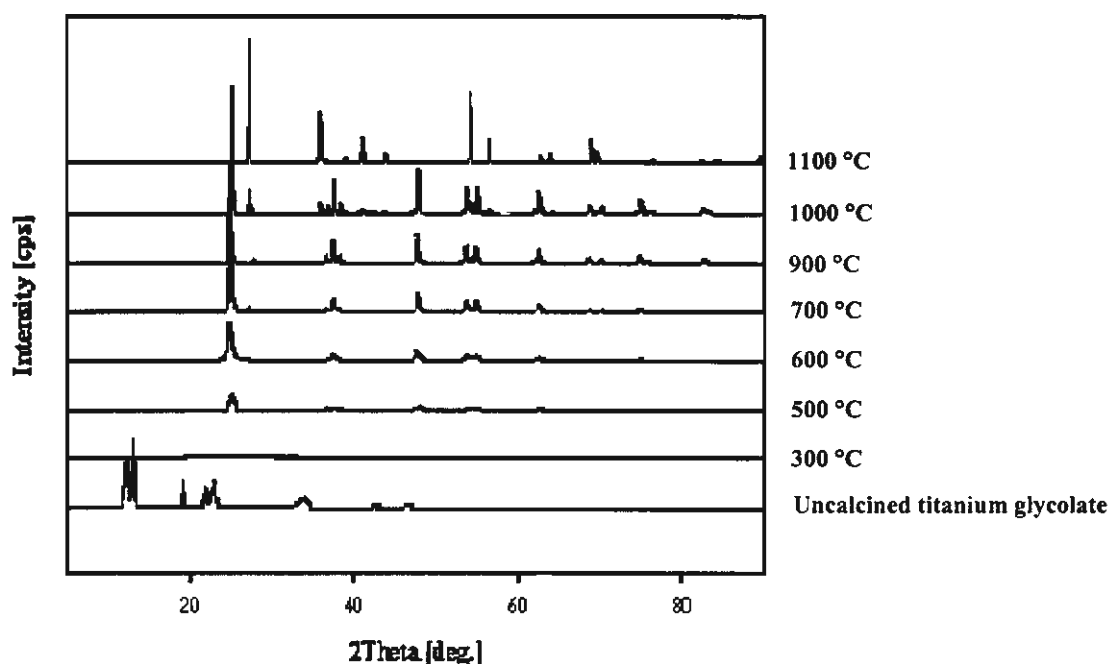


Figure 2 XRD patterns of uncalcined and calcined titanium glycolate precursor at different temperatures.

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}.

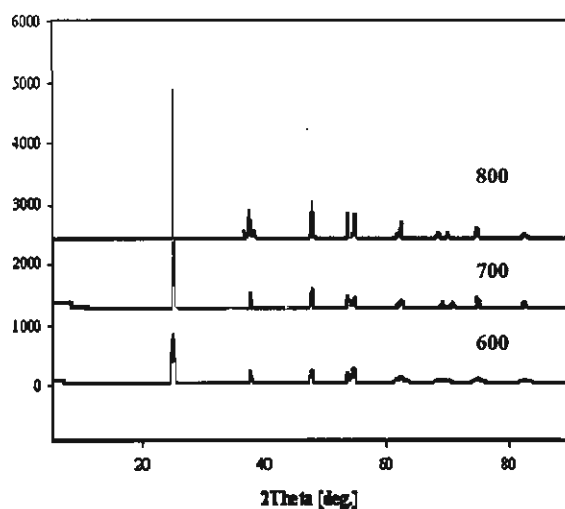


Figure 3 XRD patterns of titania gel using the $\text{HCl}:\text{H}_2\text{O}$ volume ratio of 0.28 and calcined at a) 600°, b) 700° and c) 800°C.

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.

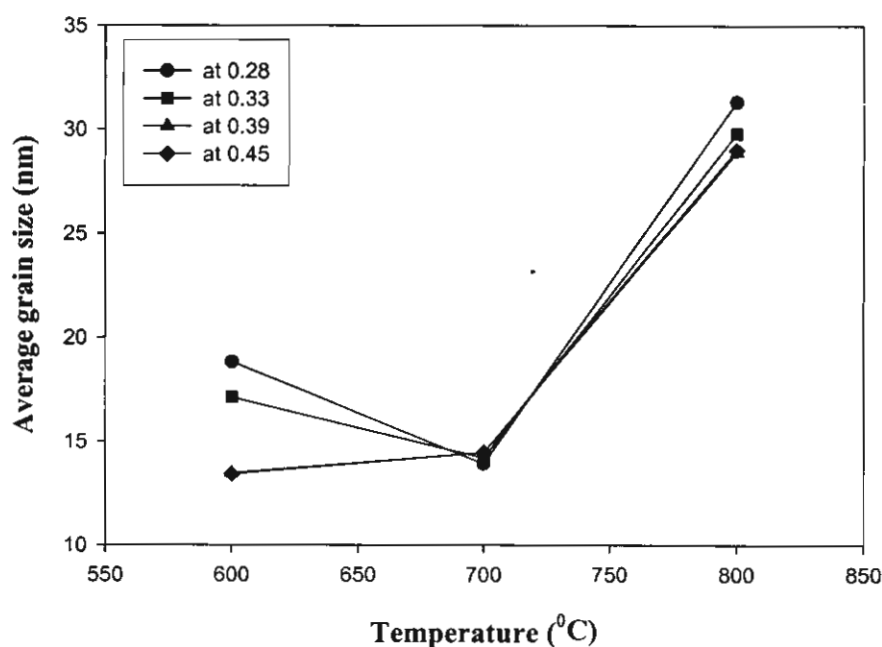


Figure 4 The average grain sizes of the particles prepared at different volume ratios of HCl:H₂O (0.28, 0.33, 0.39, 0.45, respectively) and different calcination temperatures (600°, 700° and 800°C).

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.

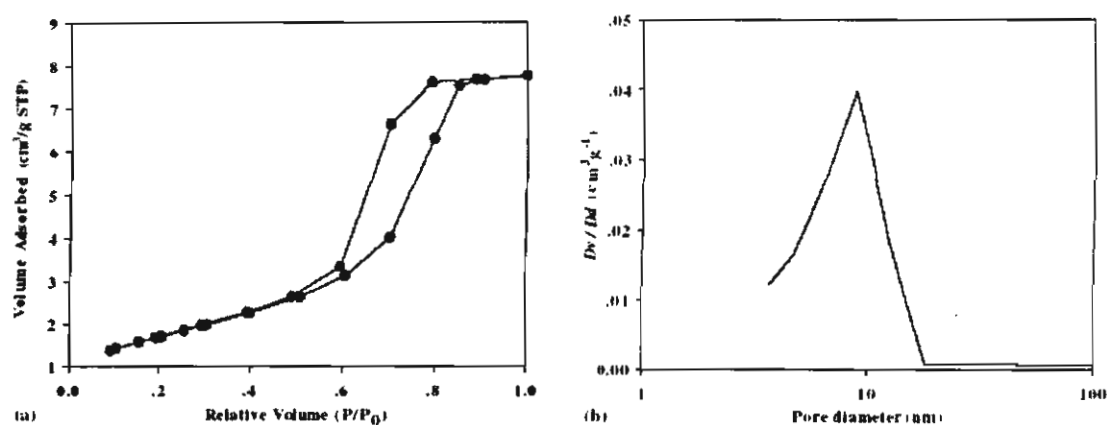


Figure 5 The nitrogen adsorption-desorption isotherm for mesoporous titania (a.) and Pore size distribution (b.) for the material obtained from 0.28 HCl:H₂O volume ratio and calcined at 600°C

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.

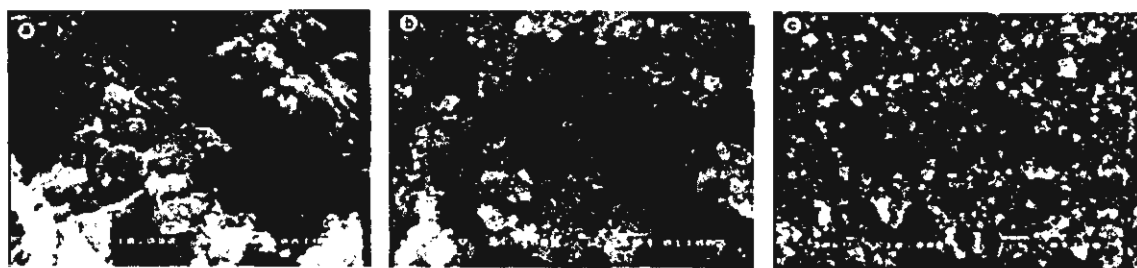


Figure 6 SEM micrographs of titania powder prepared at 0.33 volume ratio of HCl:H₂O and calcined at a.) 600°, b.) 700° and c.) 800°C

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.

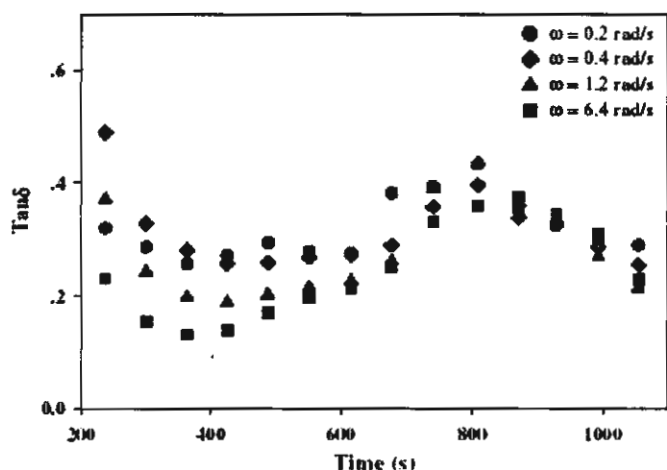
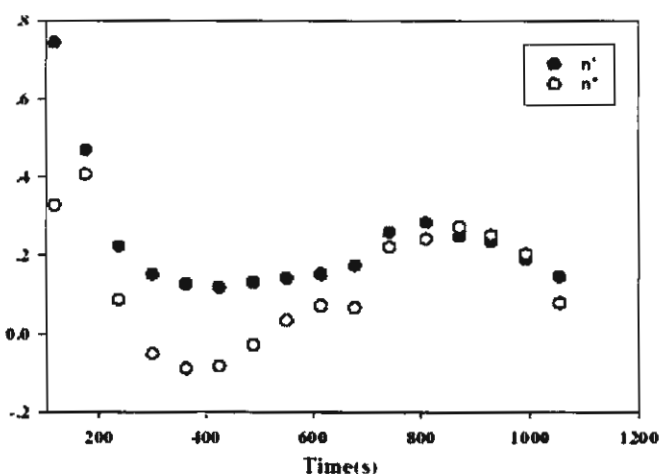


Figure 7 The plots of $\tan\delta$ with time(s) at HCl:H₂O volume ratio of 0.45

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