Synthesis of Mesoporous Titanium Dioxide

By

Muhammad Zaquan Bin Mohd Fauzan

Dissertation submitted in partial fulfilment of
the requirements for the
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(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Assoc. Prof. Dr Anita Bt Ramli)
DR ANITA RAMLI
Associate Professor
Fundamental & Applied Sciences Department
Universiti Teknologi PETRONAS, PERAK

UNIVERSITI TEKNOLOGI PETRONAS
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ABSTRACT

The objective of this research is to synthesize mesoporous Titanium Dioxide using sol-gel method while investigating the effect of pH and calcinations temperature to the characteristic of the synthesized mesoporous Titanium Dioxide. Mesoporous Titanium Dioxide have been tested previously to have photocatalytic activity in sunlight and promote widespread use in solar technology. A simple sol-gel method has been conducted to synthesize the mesoporous Titanium Dioxide using apparatus available in the Reaction Engineering Lab inside UTP campus. The sample is then analyzed to identify it's characteristics.

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Abbreviation

Titanium Dioxide	TiO_2
Iron Titanium Oxide	$FeTiO_3$
Titanium in its composition (sphene)	$CaTiSiO_5$
Titanium Tetrachloride	$TiCl_4$
X-ray Difractometer	XRD
Scanning Electron Microscopy	SEM
Brunauer-Emmet-Teller	BET
Fourier Transform InfraRed spectroscopy	FT-IR
Solid Oxide Fuel Cells	SOFC
UltraViolet	UV

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Titanium was discovered in 1791 by the Reverend William Gregor, an English pastor. Pure titanium was first produced by Matthew A. Hunter, an American metallurgist, in 1910. Titanium is the ninth most abundant element in the earth's crust and is primarily found in the minerals rutile (TiO_2), ilmenite ($FeTiO_3$) and sphene ($CaTiSiO_5$). Titanium makes up about 0.57% of the earth's crust.

Titanium is a strong, light metal. It is as strong as steel and twice as strong as aluminum, but is 45% lighter than steel and only 60% heavier than aluminum. Titanium is not easily corroded by sea water and is used in propeller shafts, rigging and other parts of boats that are exposed to sea water. Titanium and titanium alloys are used in airplanes, missiles and rockets where strength, low weight and resistance to high temperatures are important. Since titanium does not react within the human body, it is used to create artificial hips, pins for setting bones and for other biological implants. Unfortunately, the high cost of titanium has limited its widespread use.

Titanium oxide (TiO_2) is used as a pigment to create white paint and accounts for the largest use of the element. Pure titanium oxide is relatively clear and is used to create titania, an artificial gemstone. Titanium tetrachloride ($TiCl_4$), another titanium compound, has been used to make smoke screens.

Mesoporous materials are defined as natural or synthetic materials having a pore diameter of 2-50 nm, halfway between the pore sizes that define micro and macroporous materials. They have a large surface area and are particularly useful for applications in catalysis, separation, and absorption. Over the past 10 years, the concentration appears to have been on synthesis and structures of mesoporous materials. Methods of synthesis covered in the top 20 papers from this time period include block copolymer templating, oligomeric surfactant synthesis, and triblock copolymer synthesis, among others. Structures of particular interest include mesoporous materials with hybrid organic/inorganic frameworks and crystalline or semi-crystalline frameworks.

1.2 Problem Statement

Titanium Dioxide's chemical and biological inertness, easy and economically feasible production and photocatalytic activity in sunlight makes titania an ecofriendly material and promote widespread use. Research needs to be conducted to gain more benefit from this material for a better future. We need to find out the best condition during synthesizing to produce a high quality mesoporous Titanium Dioxide.

1.3 Problem Identification

The current research is not including on the effect of pH and temperature during calcinations.

1.4 Significant of the Project

The ability of TiO_2 as catalyst and other applications is among the significancy of the project development. It also opens the possibility to synthesize TiO_2 with large surface area.

1.5 Objective

1. To synthesize mesoporous Titanium Dioxide using sol-gel method

2. To investigate the effects of temperature range and duration to the characteristics of the product.

3. To analyze the characteristics of produced Titanium Dioxide.

1.6 Scope of study

1. Study about the methods to synthesize mesoporous titanium dioxide
2. Study on 11crystallization of the synthesized product using X-ray Diffraction method (XRD)
3. Study on the morphology of the synthesized product using Scanning electron Microscopy (SEM) equipment
4. Study on the surface area of the product using Brunauer-Emmet-Teller (BET) method
5. Study on the quality and consistency of the product using Fourier Transform InfraRed spectroscopy (FT-IR)

1.7 Relevancy of the project

This subject is relevant for me to study as a chemical engineering student. The various applications of mesoporous TiO_2 is also a relevancy to study this topic because we can increase the quality of current TiO_2. Although there are many methods to synthesize mesoporous metal oxides, sol-gel process is the relevant one due to limitations of the research.

On the recent years, there have been many researches in synthesizing mesoporous metal oxides. The current aim is to increase its thermal stability and surface area. As a proven catalyst, we need to study on the way to make a perfect mesoporous titanium dioxide for a certain purpose. Various manipulations on synthesizing titanium dioxide is a method to achieve this. In this research we chose to study the effect of pH and calcinations temperature to the characteristics of mesoporous titanium dioxide.

1.8 Feasibility

The project research is divided into 2 semesters. For the first semester, the related literature research study is completed and the literature review is wrapped up to brief on the scope of the project. Then, from the study research, the right methodology is developed to ensure all equipments are available for the work execution as well as to obtain the feasible time frame for research.

The second semester is followed by completion of the developed experimental work. The work execution is done based on the developed methodology to ensure the good work flow. The complete report of the work is attached with the result analysis and related documents are attached.

CHAPTER 2 : LITERATURE REVIEW

Titanium containing zeolites and related mesoporous titanosilicates are important heterogeneous catalysts for the opoxidation of alkenes and hydroxylation of arenes. The optimum catalytic efficiency of these solids is related to the presence of isolated framework Ti atoms. Because of this, it is important to develop simple experimental techniques that can report on the different Ti environments presence in the solid. This information would be extremely valuable in elucidating the relationship between structure and activity, and it would help in the attainment of titanosilicates with the higher catalytic performance. In this case, Ti containing mesoporous materials, it is well establish that the preparation procedure and Ti content play a significant role in the activity. It is believed that changes in activity are due to variations in the populations of Ti atoms among different sites exhibiting distinctive catalytic activity.

The earliest synthesis of the hexagonal mesoporous silica material was reported in US patent 3,556,725 by Chiola, Ritsko and Vanderpool. This patent claimed that high-purity silica can be prepared by conducting the ammoniacal hydrolysis of tetraalkyl orthosilicates (TEOS) in the presence of a cationic surfactant. TEOS as silica resource and cetyltrimethylammonium chloride (CTAC) as surfactant were used in the process. They managed to recover fine, pure silica from the aqueous hydrolysis of ethyl silicate with ammonia. The product bulk density was about $0.1 g/cm^3$. In 1997, Di-Renzo repeated the synthesis and found the product to be highly ordered hexagonal mesoporous silica material.

There are also another mesopore material sinthesized using sol-gel method which is Cerium Dioxide. Since the discovery of the ordered mesoporous silica

M41S series by Mobil oil researchers in 1992, many different mesoporous inorganic materials have been synthesized using various types of organic template. Applications of mesoporous materials now have extended to catalyst, control-release, sensors, capacitors, and so on. The different kinds of mesoporous metal oxide materials have been developed for the wide range of potential applications. However, the conventional amorphous pore wall of most mesoporous materials using organic template, limit their application in many field because of their poor thermal and mechanical stability. Recently, there has been some interest in the synthesis of non-silica as hard template, and the synthesis of numerous novel ordered nanostructure or nanoarray mesoporous materials, such as carbon, metal, transition metal oxides, sulphides, and polymer has been reported. The mesoporous transition metal oxides synthesized by this method are highly crystallized and hierarchical ordered structure on meso-scale as well as on atom scale.

The high activity of cerium dioxide in the redox reaction is attributed to the cerium dioxide reducibility and its high oxygen storage capacity, and facility of creating defects such as oxygen vacancies. The catalytic activity of the ceria is greatly dependent on three main factors which are particle size, structure distortion and chemical non-stoichiometry. Reducing the particle size to nanoscale will provide a large number of more reactive sides.

Cerium Dioxide is one of the most reactive rare earth metal oxides, which has been studied an employed in many applications such as ion conductors, oxygen storage capacitors, catalysts, UV blockers, polishing materials, and electrolytes for solid oxide fuel cells (SOFC). CeO_2 has also been found to be very important in environmental protection. In particular, supported CeO_2 and CeO_2-based mixed oxides are effective catalysts for oxidation of different hydrocarbons and for the removal of organics from polluted water from different sources.mCerium dioxide is interesting because of its catalytic activity and the ability to store and release oxygen depending on the redox environment. It is widely used as a promoter in three-way catalysts for the elimination of toxic auto-exhaust gases.

A method that has been used to synthesize oxide ceramics such as CeO_2 and TiO2 is sol-gel process. It has been studied to produce multicomponent oxides (glasses and ceramics). Based on cohydrolysis of molecular precursors such as metal alkoxides, the reaction rates which are highly dependent on the nature of metals, especially when silicon and transition metals are included in the composition, is the main problem. The difference in reactivity has been minimized by controlled prehydrolysis of the less reactive precursor or by chemical modification precursors to achieve homogeneous oxides with predetermined composition.

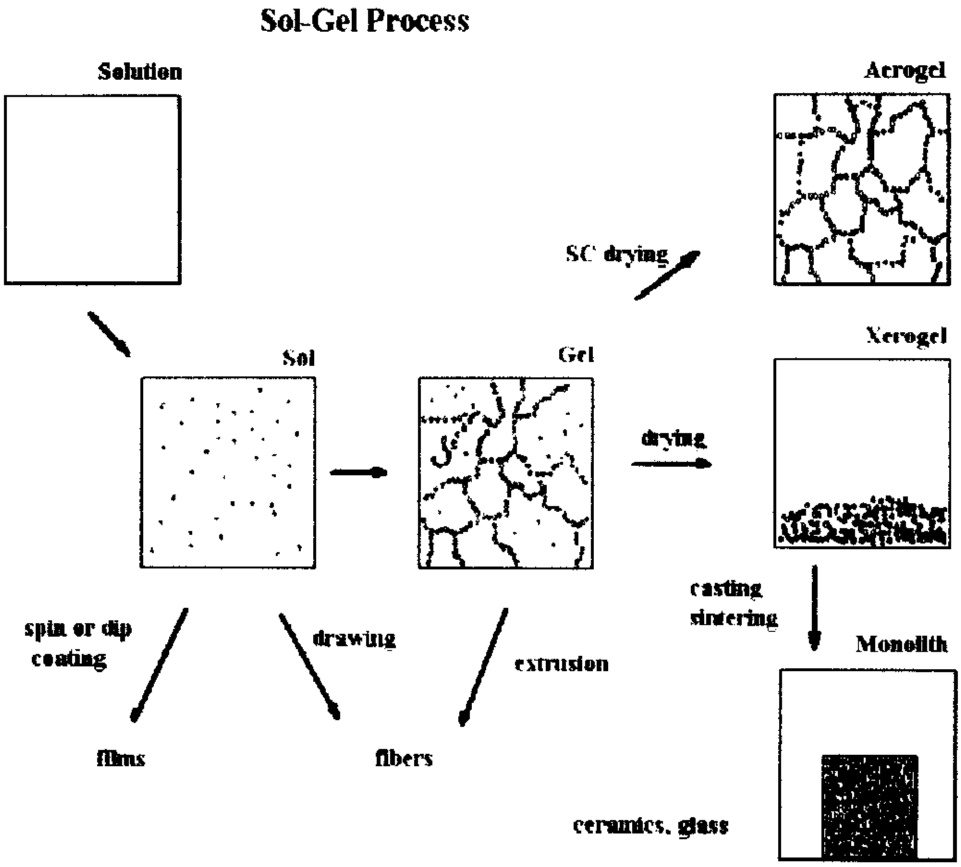

Figure 2.1 Sol-gel process

There is another method to synthesize mesoporous material which is called Sonochemistry. For this method, the surfactant is dissolved in a minimum amount of methanol in a sonication flask. Then the precursor is added followed with distilled water. The pH is maintained using ammonium hydroxide and the gel is sonicated for 3 hours. The surfactant was removed by calcinations.

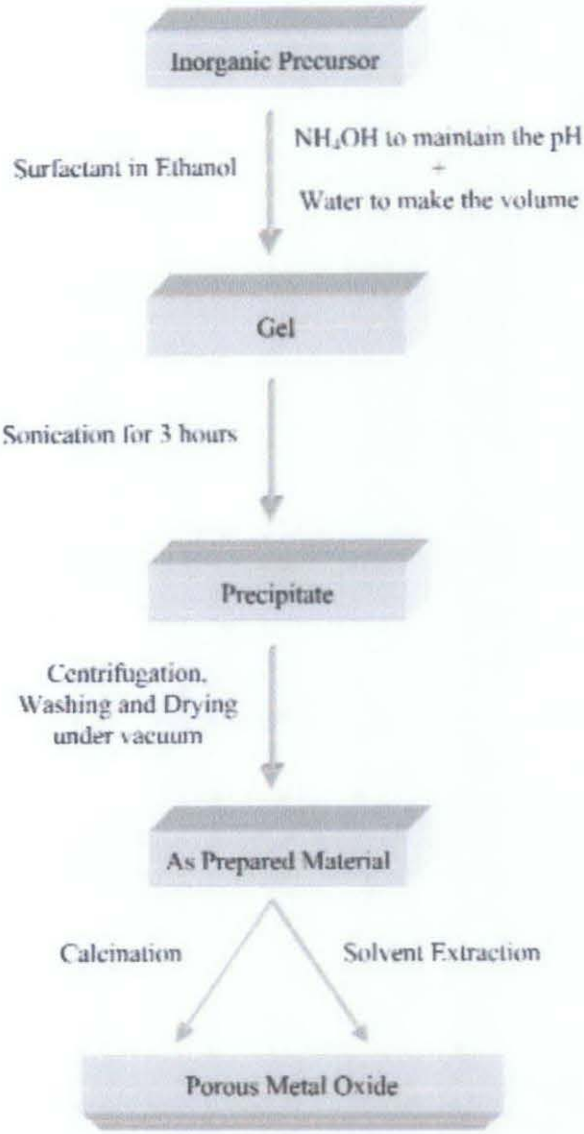

Figure 2.2 Schematic presentation of the method of preparation of porous metal oxide by sonochemistry technique

Currently, mesoporous titanium dioxide with high surface area has been prepared by different template-assisted methods. Such materials by virtue of their large surface are exhibit greater catalytic ability. With preparation in 1991 of mesoporous silica allowed the exploitation of high surface are materials. The use of surfactants as liquid-crystal templating agents so as to create a regular three-dimensional micellar array about which an inorganic precursor could form a framework gives a reliable method to produce mesoporous solids.

Pure ceria is poorly thermostable and undergoes rapid sintering under high-temperature conditions, therefore losing oxygen buffer capacity. Several attempts has been made to solve this problem. Substitution of another metal or metal oxide into ceria lattice is one of it. It will facilitate the formation of mixed oxides. Modifications can be made by replacing cerium ions by cations of different size or charge modifies ion mobility inside the modified lattice, resulting in the formation of a defective fluorite-structured solid solution. New properties such as better resistance to sintering at high temperatures and high catalytic ability will confer to the catalyst. The mixing of two different oxides could result in the formation of new stable compounds that may lead to totally different physic-chemical properties and catalytic behaviour.

There are some recent research that uses sol-gel method to synthesize mesoporous ceria using hydrothermal method. In a research by Institute of Applied Chemistry, Nanchang university, they synthesize mesoporous ceria using hydrothermal method. In that experiment, they dissolve glucose, acrylamide and ceric ammonium into deionized water one by one with magnetic stirring. 25 wt% of ammonia solution was added by adding it drop by drop into the solution until the pH value is about 10. After stirring, they place the mixture in a Teflon-line autoclave and was kept at 120°C-180°C in an oven. Finally the sample was calcined at 400°C for 4 hours. Using this method, the primary particle and mesopore ceria are both a few nanometers in size. They also proven that using ceric ion instead of ceious ion will result a larger surface area.

CHAPTER 3 : METHODOLOGY

3.1 Research Methodology

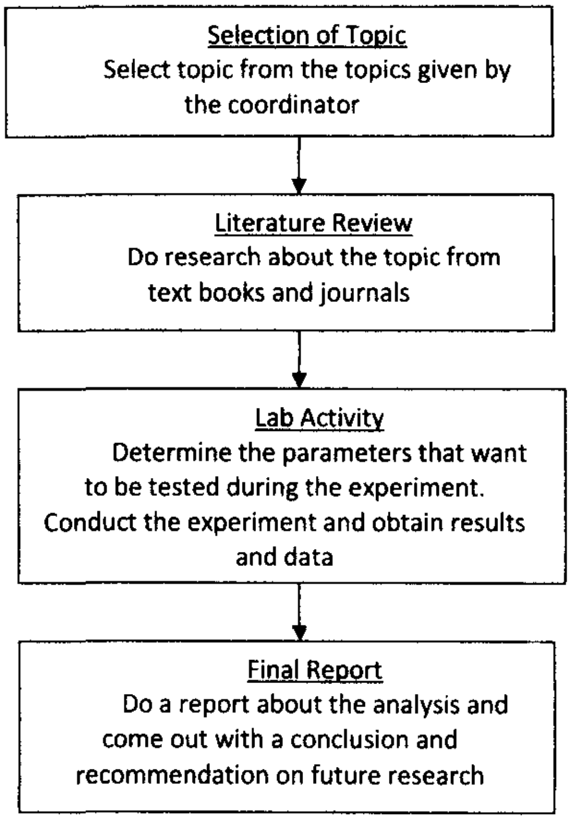

Figure 3.1 Research activity

There were many methods to synthesize Titanium Dioxide and some of them require costly material such as Pluronic acid. Therefore we chose the sol-gel process. In the beginning, the topic of this project is supposed to be about synthesizing mesoporous Titanium Dioxide. However, because of insufficient materials, the topic is changed to Titanium and replacing the method by materials available.

The materials used are:

1. Titanium chloride

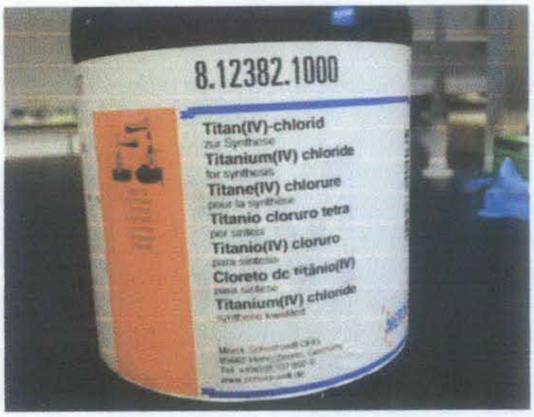

Figure 3.2 Titanium (IV) Chloride

2. Sodium Hydroxide

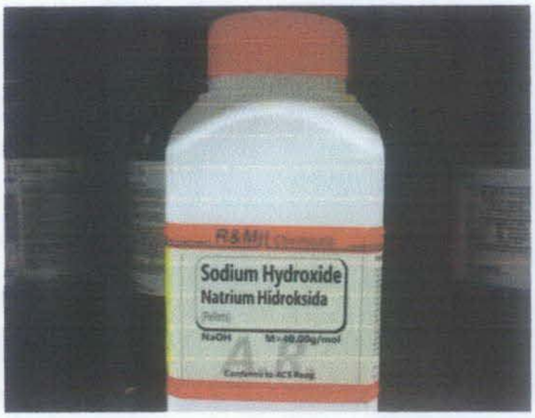

Figure 3.3 Sodium hydroxide

3. Hydrochloric acid

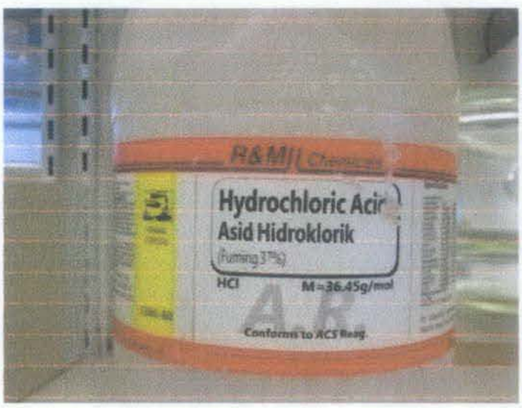

Figure 3.4 Hydrochloric Acid

3.2 Preparation of NaOH

The sodium hydroxide is prepared by diluting pellets into solvent. A value of 5.0M of NaOH is required for the experiment. By taking into account the dormula of molarity which are:

$$Molarity = \frac{Number\ of\ Moles\ x\ 1000}{Volume(ml)}$$

$$Number\ of\ moles = \frac{Mass}{Molecular\ Weight}$$

The mass required to achieve 5.0M is 100g og NaOH. The NaOH pellets are diluted in a 500ml volumetric flask.

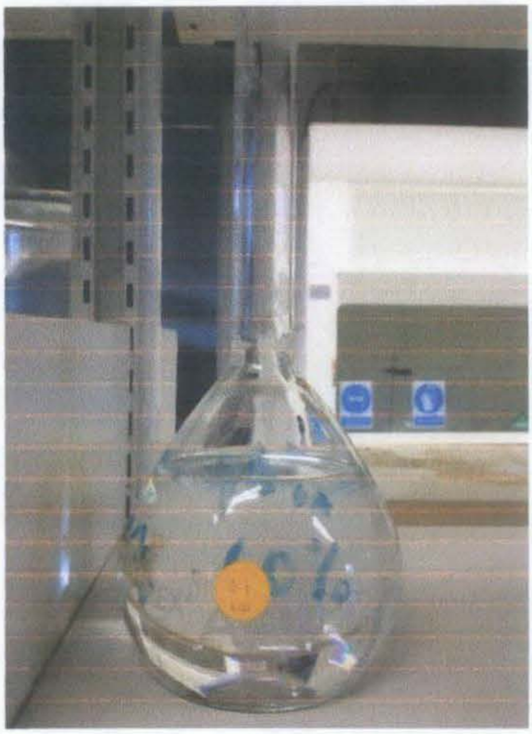

Figure 3.5 Diluted NaOH in a 500ml volumetric flask

3.3 Preparation of TiO_2

TiO_2 is synthesized by using sol-gel method by using titanium chloride as a precursor, while hydrochloric acid and deionized water as solvents. A fixed amount of HCl and deionized water are added dropwise to the $TiCl_4$ to give a concentration of HCl : $TiCl_4$: H_2O at the ratio of 1 : 2 :12 at 70°C under continous stirring using the magnetic hotplate. A required amount of sodium hydroxide is added to the aqueous solution to restrain the hydrolysis process and consequently to control the grain growth while maintaining the pH at pH1, pH2, pH3, pH4 and pH5. The solution is stirred vigorously until a gel was form. The gel-like form was then transferred into a Teflon lined stainless steel autoclave and heated at 150°C for several days. The gel is then collected by filtration and dried at 110°C for for 3 hours. After drying, the sample is divided into 3 portions which is A, B and C. Portion A, B and C are calcinated at 450°C, 500°C and 550°C respectively for 3 hours in N_2 environment.

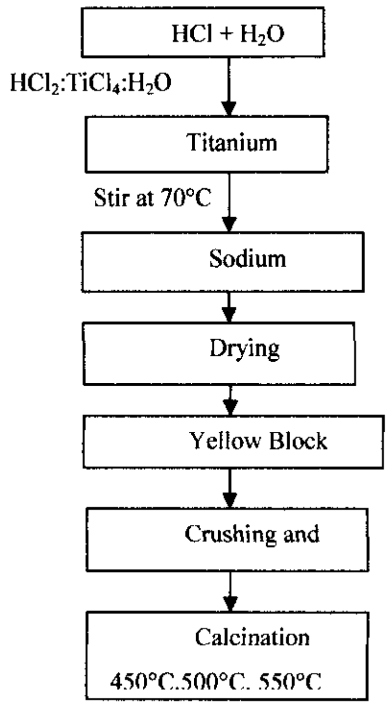

Figure 3.6 TiO_2 synthesis without presence of surfactant

Due to unavailable of autoclave, we alter the experiment to stirring for several days at room temperature. The result will be shown in the result and discussion part.

In this project, several lab sessions will be held to synthesize and analyze cerium dioxide. It is a study on the effect of duration and temperature change to the characteristics of the produced cerium dioxide. The tests that need to be carried out are:

1) BET – surface area and porosity

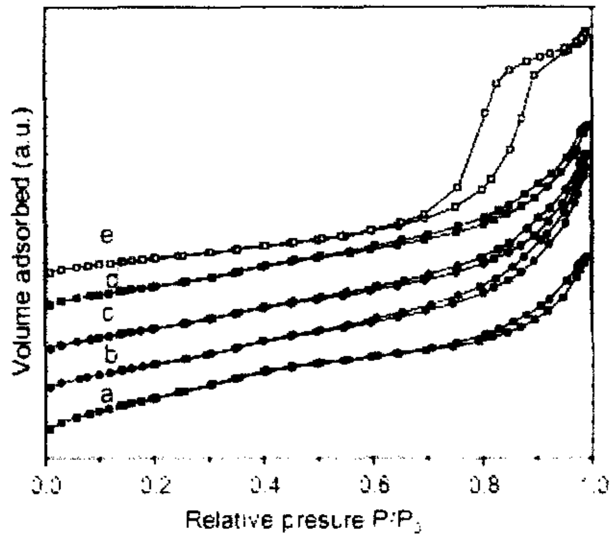

Figure 3.7 Sampe of BET analysis

2) XRD – crystal structure

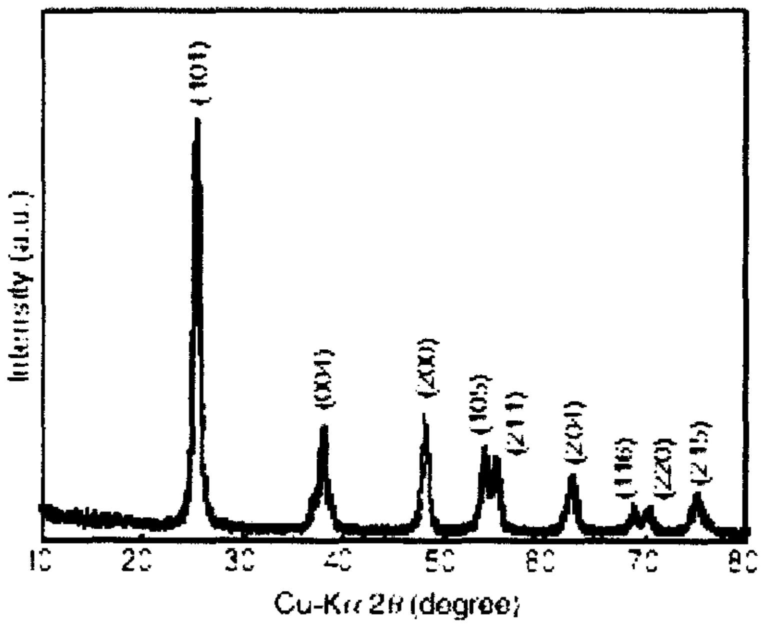

Figure 3.8 Sample of XRD analysis

3) SEM – morphology

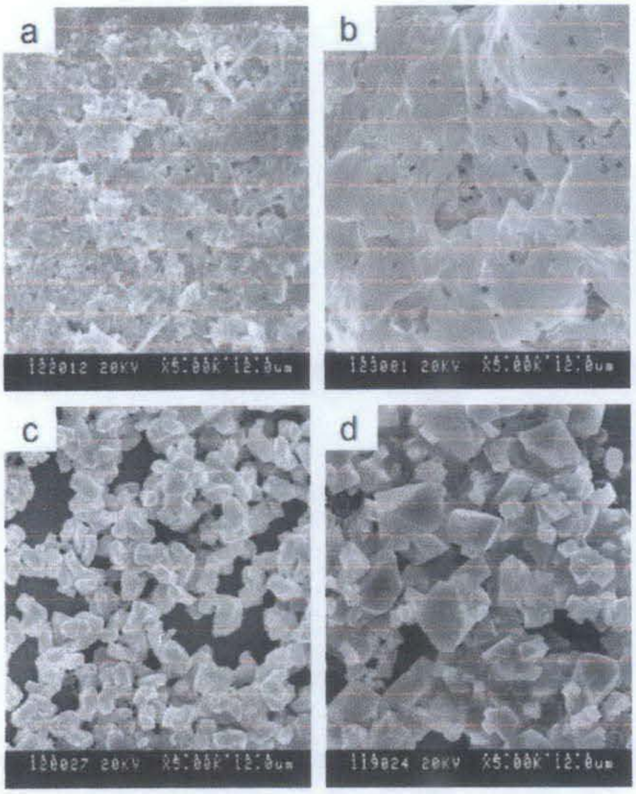

Figure 3.9 Sample of SEM imaging

The tools required tools required in this project are:

1. Hotplate magnetic stirrer

Figure 3.10 Hotplate Magnetic Stirrer

2. Beaker

Figure 3.11 Beaker

3. pH meter

Figure 3.12 pH meter

4. Fume cupboard

5. Burette

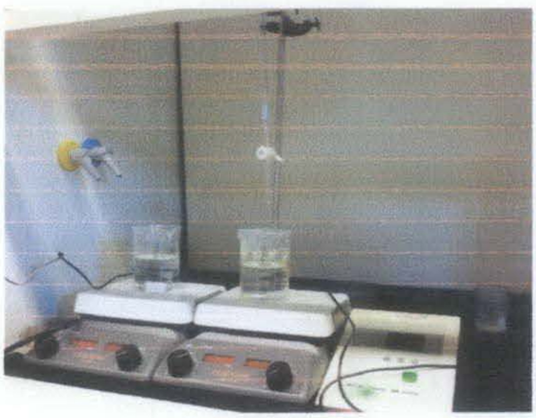

Figure 3.13 Fume cupboard and burette

3.4 Project Activities

The project activities are divided to 2 semesters. Throughout the project, there are 3 different work scope include literature research study, documentation and practical work.

3.4.1 Semester 1

Under literature research, the related research and study are performed and the necessary documents are listed. The critical analysis of the research included the comparison of the related literature review and the findings are attached for the understanding towards the objective achievement of the particular project. This review on the importance of literature review and remarks on the research objective. The extended proposal is about the review on the future research. The research is determined the feasibility in this stage and necessary improvement and adjustment is conducted to make certain on obtaining the suggested result in the research. Interim report is prepared for the wrap up on the chosen project title. It consists of the research steps from the preparation till the necessary results are obtained. The preparation is the method of synthesizing and equipment preparation such as SEM and BET.

3.4.2 Semester 2

For the next semester research planning, it is divided into two sections which are documentation and practical work. The research study begins with synthesizing mesoporous titanium dioxide using sol-gel method. The test is repeated over by different temperature and duration.. Next, for the characterization of the mesoporous cerium dioxide, X-ray diffraction (XRD) measurements were conducted. The equipment assisted in determining the position of the atoms or solid structure. The SEM also takes into measure to be used in preparing SEM images of mesoporous cerium dioxide for different temperature and duration. The documentation part included the progress report to measure the research progress over time and achievement. Then, followed by preparing the draft report for the particular research to attain a good submission of technical paper.

3.5 Project Timeline

No.	Detail/ Week	1	2	3	4	5	6	7	Mid-semester break	8	9	10	11	12	13	14
1	Selection of Project Topic	■	■													
2	Preliminary Research Work		■	■	■	■										
3	Submission of Extended Proposal Defence						●									
4	Proposal Defence									■	■					
5	Project work continues											■	■	■		
6	Submission of Interim Draft Report														●	
10	Submission of Interim Report															●

Table 3.1 FYP 1 Project Timeline

No.	Detail/ Week	1	2	3	4	5	6	7	Mid-Semester Break	8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■									
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

Table 3.2 FYP 2 Project Timeline

The important key milestones of this semester project are submission of progress report and dissertation.

3.6 Gantt Chart

3.6.1 Semester 1

	FINAL YEAR PROJECT 1/ WEEK NUMBER														
Activities	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
Topic Selection								MIDSEM BREAK							
Research related topic															
Complete literature review															
Submission of extended proposal															
Proposal Defense															
Study of method															
Study of characterization method															
Development on methodology															
Submission of Interim Draft Report															
Submission of Interim Report															

Figure 3.3 Gantt Chart for FYP 1

3.6.2 Semester 2

	FINAL YEAR PROJECT 2/ WEEK NUMBER															
Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
Initial study on synthesizing TiO_2																
Execute synthesing TiO_2																
Characteriztion study on TiO_2																
Submission of Progress Report																
Data Analysis and Report																
Pre-SEDEX																
Submission of Draft Report																
Submission of Dissertation and Technical Paper								MIDSEM BREAK								
Oral presentation																
Submission of Project Dissertation (Hardbound)																

Figure 3.4 Gantt Chart for FYP 2

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Results

Figure 4.1 First run of synthesizing

The first run of synthesizing TiO_2 brings no change in the stirred solution. The solution was stirred for whole 24 hours while maintaining its pH at 5. This may be because of the room temperature is not enough for the reaction. The activation energy needed for the reaction may not be enough. To see some results, the solution needs more days to change into gel-like form. The pH meter takes a long reading time leading to unefficiency of this experiment.

Halfway through the experiment, we discovered that if we use a larger beaker, the time takes for sol-gel to form is less than the previous smaller beaker. Therefore we can conclude that increase in surface area enhance the sol-gel formation. Using the larger beaker for all pH samples, we discovered that pH 3 sample takes the shortest time to form into sol-gel. The time taken for sol-gel to form and mass of TiO2 obtained is recorded:-

pH	Time taken (hours)
1	8
2	5
3	0.5
4	7
5	6

Table 4.1 Time taken for sol-gel formation

pH	Mass (g)
1	9.70
2	9.62
3	11.96
4	9.89
5	12.14

Table 4.2 Mass of TiO_2 acquired

4.2 Discussion

Synthesizing using sol-gel method takes a long time to produce a sample approximately one week per sample. During the experiment, several methods were tried to reduce the time consumed to form sol-gel. The first method is by increasing the beaker size and it turns out to be effective this may be because the surface area is increased and the heat is more evenly distributed to the solution. Even though by increasing temperature can speed up the sol-gel formation, however it is advised to maintain it below 70°C for a better product. Another method is to increase the rotation per minute (RPM) of the magnetic stirrer. As a result, the time consumed to sol-gel to form decrease but in a small scale.

Many obstacles come along the way of the experiment. Initially, the title of the experiment is Synthesis of Mesoporous Cerium Dioxide, but due to the late arrival of materials, the topic is changed to titanium and this delays the project for about 5 weeks. Unreliable pH meter also slows down the experiment because it takes too much time to read the sample. A new one is provided in a few weeks later. The SEM and XRD machines in the campus are currently unavailable and take time for maintenance to recover it.

CHAPTER 5 : CONCLUSION AND RECOMMENDATION

Sol-gel process has been selected to synthesize mesoporous TiO_2. The experiment will be conducted with different pH and calcinaton temperature which are pH1,2,3,4 and 5 and 450°C, 500°C and 550°C. We will study on the effect of pH and calcinations temperature to the characteristics of the mesoporous TiO_2. Hopefully this project will be completed in these 2 semesters.

The experiment may be conducted with bigger surface area to solution volume ratio to decrease time for sol-gel formation. Optimum RPM and temperature of the solution during the stirring process play a big role in sol-gel formation. $TiCl_4$ is very reactive towards the atmosphere. Therefore the experiment should be conducted in a glove box to control the humidity.

In the future, titanium dioxide that has been produced in this project may be tested for is catalytic ability. The product may also be used for another project. This topic can be widen to not only titanium dioxides but other metal oxides.

Reference

Andrianainarivelo M., Corriu R. J. P., Leclercq D., Murtin P. H.; Vioux A., (1997). Non-Hydrolytic Sol-Gel Process: Zirconium Titanate Gels, J. Mater. Chem. 7(2), Universite Montpellier II, Case 007, Place E. Bataillon, F 34095 Montpellier Cedex, France, Pp279-284,

Kim J.K.; Kim Y., Park J.W., Bae J.S., Yoon D.Y., Lee J.G., Kim J.H., Han C., (2009). Preparation Of Cuo-Ceo_2 Catalyst With Mesopore Structure For Water Gas Shift Reaction, Korean J. Chem. Eng. 26(1), Department Of Chemical Engineering, Kwangoon University, Seoul 139-701, Korea, Pp 32-35

Li Y.; Luo L., (2009), Study On The Synthesis Of Mesoporous Ceria In The Presence Of Glucose And Acrylamide, J. Chil. Chem. Soc., Institute Of Applied Chemistry, Nanchang University, Nanchang 330031, China, Pp 54

Lyons D. M., Mcgrath J. P., Morris M. A., (2003), Surface Studies Of Ceria And Mesoporous Ceria Powders By Solid-State, J. Phys. Chem. B, Department Of Chemistry, University College Cork, Cork, Republic Of Ireland, Pp 4607-4617

Lyons D. M., Ryan K. M., Morris M. A., (2002), Preparation Of Ordered Mesoporous Ceria With Enhanced Thermal Stability, J. Mater. Chem, Materials Section, Department Of Chemistry, University College, Cork, Republic Of Ireland, Pp 1207-1212

Periyat P., Baiju K. V., Mukundan P., Pillai P. K., Warrier K. G. K., (2008), High Temperature Stable Mesoporous Anatase Tio_2 Photocatalyst Achieved By Silica Addition, Applied Catalyst A: General 349, Council Of Scientific & Industrial Research, Thiruvananthapuram 695019, Kerala, India, Pp13-19,

Polshettiwar V., Baruwati B., Varma R. S., (2009), Self-Assembly Of Metal Oxides Into Three-Dimensional Nanostructures: Synthesis And Application In Catalyst, Sustainable Technology Division, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 26 West M.L.K. Drive, MS 443, Cincinnati, Ohio, Pp 728-736

Sinha A. K. , Suzuki K., (2005), Preparation And Characterization Of Novel Mesoporous Ceria-Titania, J. Phys. Chem. B, Materials Division, Toyota Central R&D Labs Inc.41-1, Aza, Yokomichi, Nagate-Cho, Aichi-Gun, Aichi-Ken 480-1192, Japan, Pp109, 1708-1714

Sorapong P., Yoshikazu S., Sommai P.A., Susumu Y., (2005), Synthesis And Characterization Of Nanoporous Nanorods, Nanowires Metal Oxides, Science And Technology Of Advanced Materials 6, Institute Of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan, Pp 224-229

Srivastava D. N., Perkas N., Zaban A., (2002), A. Gedanken, Sonochemistry As A Tool For Preparation Of Porous Metal Oxides, Pure Appl. Chem., Vol. 74, No.9, Department Of Chemistry, Bar-Llan University, Ramat-Gan-52900, Israel, Pp. 1509-1517

Xie J., Li P., Wang Y., Wei Y., (2009), Synthesis Of Needle And Flower Like Zno Microstructures By A Simple Aqueous Solution Route, Journal Of Physics And Chemistry Of Solids, College Of Chemistry And Material Science, Hebei Normal University, Shijiazhuang 050016, PR China, Pp 70, 112-116.