Synthesis and Characterization of SAPO-34 Nanoparticles For CO_2 Capture

by

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2012

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____
(DR YEONG YIN FONG)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD SAIFUDDIN BIN ZULKAPLE

ABSTRACT

Synthesis of SAPO-34 nanocrystals which has been recently considered as a challenging task was successfully performed by sonochemical method using TEAOH as structure directing agent (SDA). The products were characterized by scanning electron microscope (SEM), transmittance electron microscope (TEM), X-ray diffraction (XRD), and Fourier transform Infrared (FTIR). From TEM results, the average crystal size of the final product prepared sonochemically is 25 nm that is much smaller than that of synthesized under hydrothermal condition and the morphology of the crystals changes from uniform spherical nanoparticles to spherical aggregates of cube type SAPO-34 crystals respectively. In a sonochemical process, a huge density of energy for crystallization is provided by the collapse of bubbles which formed by ultrasonic waves. The fact that small SAPO-34 crystals could be prepared by the sonochemical method suggests a high nucleation density in the early stages of synthesis and slow crystal growth after nucleation. After the characterization, SAPO-34 particles were tested for its CO_2 adsorption characteristic. The effect of particle size on its adsorption behaviour was studied using CO_2 physisorption analyzer. The CO_2 adsorption isotherm results show that the size and crytallinity of SAPO-34 are important factors on the adsorptions of CO_2. The smaller the size of SAPO-34 particles, the higher the adsorptions of CO_2 rate. Thus, the reduction in particle size increase the surface area of the resulting SAPO-34, therefore, higher CO_2 adsorption rate was obtained.

ACKNOWLEDGEMENT

First and foremost, I give thanks and praise to God for His guidance and blessings throughout the entire course of my Final Year Project.

I wish to express my gratitude to my supervisor, Dr Yeong Yin Fong, for her guidance and support throughout completing my Final Year Project as partial fulfillment of the requirement for the Bachelor of Engineering (Hons) of Chemical Engineering.

Many figures had provided immeasurable amount of guidance, ideas, assistance, support and advice. Without help from these people, this Final Year Project may not be that meaningful and successful. Greatest appreciation is expressed to them.

My acknowledgement would be incomplete without giving credit to Universiti Teknologi PETRONAS, especially Chemical Engineering Department which has equipped students with essential skills for self-learning.

Finally, I would like to thank my family. They have been a wonderful source of encouragement and joy to me and also not to forget the fellow colleagues. Their help was tremendous gift to me. May God bless all of us and only He, the Almighty could repay all my debts to them.

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CHAPTER 1

1. INTRODUCTION

1.1 Background study

Carbon dioxide is one of the main contributors to global warming. Consequently, there is increasing interest in removing CO_2 in order to combat the greenhouse gas effect. Moreover, low concentration and traces of CO_2 are also undesirable in some gas streams such as the natural gas well (Lackner, 2009).

Adsorption is considered to be a competitive method for CO_2 removal in comparison to other technologies, provided that highly selective adsorbents with high CO_2 capacity are available (Aaron et al, 2005). Adsorption using microporous materials such as zeolites has attracted considerable attention because of the compatibility of the pore sizes with the dimension of many simple molecules (Hirota et al, 2012).

In the recent years, there have been increasing interests on the study of SAPO-34 in gas separation. SAPO-34, (SixAlyPz) O_2, a type of silicoaluminophosphate microporous zeolite, is of particular interest in separation, catalytic, and adsorption technologies because of its chemical and thermal stability, unique shape selectivity, molecular sieving properties, and atomically ordered 0.38 nm pore structure (Venna et al, 2008). Separation of carbon dioxide and hydrogen from different gases using SAPO-34 has been extensively reported in the literature review. Properties such as fairly strong Brønsted acidity, adsorption of desired components, and excellent shape selectivity make SAPO-34 an ideal active absorbent in CO_2 removal. Ashraf et al, 2010, reported that the SAPO-34 adsorption capacity of CO_2 is 14 mmol/g at 273K and 3000 kPa. This is because of the kinetic diameter of CO_2 (0.33 nm) compared to CH_4 (0.38 nm), therefore CO_2 can enter through the pore mouth of SAPO-34 crystals with diameter of 0.38 nm. (Ashraf et al, 2010)

1.2 Problem statement

Natural gas reserves are typically contaminated with as high as 70% CO_2 and N_2, but the pipeline specification for natural gas requires a CO_2 concentration below 2-3% (IPCC, 2005). CO_2 must be removed because it reduces the heating value and energy content of the gas, and it is acidic and corrosive in the present of water (IPCC, 2005).

SAPO-34 have been shown to be highly selective for CO_2/CH_4 separations even at high feed pressures, because CO_2 preferentially adsorbs in the SAPO-34 pores and CH_4 (0.38 nm kinetic diameter) diffuses more slowly than CO_2 (0.34 nm kinetic diameter) since it is similar in size to the SAPO-34 pore (0.38 nm). The control of the size of SAPO-34 crystals is a very important factor in improving the CO_2 adsorption activity and lifetime of the absorbent. This research will be focusing on the synthesis of SAPO-34 nanoparticles by manipulating the synthesis parameters such as the temperature and duration to obtain the suitable nanosized adsorbent for CO_2 capture.

1.3 Objectives of project

1. To synthesize nanosized SAPO-34 by manipulating the synthesis parameters using the ultrasonic pretreatment and hydrothermal synthesis.
2. To characterize the SAPO-34 nanoparticles using scanning electron microscope (SEM), transmittance electron microscope (TEM), X-ray diffraction (XRD), and Fourier transform Infrared (FTIR).
3. To study the CO_2 adsorption characteristic of the synthesized SAPO-34.

1.4 Scope of study

This research focuses on the development of SAPO-34 using ultrasonic pretreatment and hydrothermal heating. SAPO-34 nanoparticles were characterized for their properties such as morphology, and crystallinity using scanning electron microscope (SEM) and X-ray diffraction (XRD). The synthesis parameters including the ultrasonic time and crystallization duration were manipulated during the synthesis process in order to obtain nanosized SAPO-34. The resultants particles will be tested for their CO_2 adsorption behavior using physisorption analyzer. The effects of the particles size of SAPO-34 on the overall adsorption properties were studied.

1.5 Relevancy and Significance of project

Adsorption process is an economic and effective method with wide usage in separation of gaseous mixtures. Appropriate adsorbent selection is one of the main and important steps in effective adsorption processes. Nowadays, microporous materials are being studied as good alternatives in separation processes (Yang, 1997). Molecular sieves such as zeolites and zeo-types (silicoaluminophosphate) nonporous materials apart from their high thermal, mechanical and chemical stability, have the unique property that only molecules with a smaller kinetic diameter than the pores' diameter can diffuse into the channels of the adsorbents, therefore they can act as sieving to the gaseous mixtures. Zeolites have an inorganic crystalline structure with uniform pore size distribution (Vansant, 1990).

For the targeted application of carbon dioxide purification from methane, the proposed work may have an important economic impact in reducing considerably the separation costs associated with natural gas pre-treatment and reduction of greenhouse gases emissions respectively.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Removal of carbon dioxide

Carbon dioxide (CO_2) is a naturally occurring chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It appears as a gas at standard temperature and pressure. CO_2 is a non-toxic and non-flammable fluid, it has a high chemical stability as it has a very low energy level compared to other carbon compounds (Lackner, 2009).

CO_2 is the main component of greenhouse gasses, and its accumulation in the environment leads to global warming issues. Current commercial carbon dioxide capture system in plant s can reduce CO_2 emmision by 80-90% / KWh, with 85-95% capture efficiency (Baker, 2002). Natural gas wells are typically contaminated with as high as 70% of CO_2. To be transported in pipelines, natural gas must meet strict specification with respect to CO_2 content as it must be removed to below 2-3% (Nikulshina et al, 2009). CO_2 also reduces the heating value of natural gas, and it is acidic and corrosive in the presence of water within the transportation and storage systems (Baker, 2002). Thus the use of such gas fields is only acceptable if the addition CO_2 is separated and sequestered. From the environmental and energy perspective, it is important to separate and recycle CO_2 from light gasses such as CH_4 and N_2. The technology most widely used for CO_2 removal is amine adsorption and low-temperature distillation but this technology is complex and costly (Baker, 2002).

2.2 Zeolites

Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores (Bell et al, 2001). There are nearly 50 different types of zeolites with varying physical and chemical properties. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite.

Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tonnes per annum. Zeolites are mainly use in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Applications are in agriculture, animal husbandry and construction has also been recently reported (Bell et al, 2001)

Zeolites have been used as an adsorbent to separate CO_2 from CH_4 at high pressure. They are ideal for this separation because of their mechanical, and chemical stability, superior thermal, stability at high CO_2 pressures, and good erosion resistance (Bell et al, 2001).

The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. It is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others component behind (Bell et al, 2001).

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity (Bell et al, 2001).

2.3 Synthesis of SAPO-34

SAPO-34 $(Si_xAl_yP_z)O_2$ is a type of silicoaluminophosphate microporous zeolite, used in separation, catalytic, and adsorption technologies (Venna, 2008). This is mainly due to its chemical and thermal stability, unique shape selectivity and molecular sieving properties, SAPO-34 have been shown to be highly selective for CO_2/CH_4 separations even at high feed pressures. The kinetic diameter of the gas component is the key parameter in its ability to diffusion into the pores of the adsorbents (Bennet et al, 1983). It should be noted that SAPO-5, SAPO-41, SAPO-11, etc. are one-dimensional and have a pore size larger than 0.38 nm and would let both CO_2 and CH_4 move through the pores, without any separation (Bennet et al, 1983). CO_2 preferentially adsorbs in the SAPO-34 pores and CH_4 (0.38 nm kinetic diameter) diffuses more slowly than CO_2 (0.34 nm kinetic diameter) since it is similar in size to the SAPO-34 pore (0.38 nm) (Ashraf et al, 2010). Another reason of CO_2 good adsorption on SAPO-34 is its surface properties and especially characteristics of CO_2 and CH_4. Methane is a non-quadrapole molecule, whereas CO_2 has a strong quadrupole moment and because of the shape and electrostatic interactions, higher adsorption capacity can be observed. On the other hand, it can be said that the more positive charges in the crystal structure of SAPO-34 and the more heterogeneity of the surface could be a dominant factor in attractive forces with CO_2.

SAPO-34 has been prepared by several synthetic routes; for example, Lok and co-workers (1984) first reported the hydrothermal synthesis of SAPO-34 using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent. Different structure-directing agents such as morpholine, piperidine, diethylamine, triethylamine, isopropylamine, TEAOH−dipropylamine, and TEAOH−cyclohexylamine have been employed to prepare SAPO-34 (Wang et al, 2004). The van Heyden (2008) group synthesized the SAPO-34 crystals smaller than 300 nm from colloidal solutions containing tetraethylammonium ion as a structure-directing agent (SDA). Crystals measuring 100 nm were obtained under hydrothermal conditions by using a microwave oven (van Heyden et al, 2008). A polymer assisted dry gel conversion has been reported by Yao et al (2005); in their method, the SAPO-34 nanocrystals were successfully formed from a precursor gel containing polyacrylamide, but SAPO-34 crystals larger than several micrometers in size were also formed simultaneously.

Other synthetic approaches for SAPO-34 involve different heat treatment methods such as two-stage temperature varying hydrothermal synthesis (Vistad, et al, 2003), microwave synthesis (Heyden, et al, 2008), the vapor phase transport method (Yao, et al, 2008), and the incorporation of different metals (Himeno et al, 200&). However, the control of the crystal size of SAPO-34 with high surface area, high crystallinity, homogeneity, and preferential adsorption capacities over light gases is still challenging. SAPO-34 with small crystal size and narrow particle size distribution potentially leads to larger-accessible surface area, reduced diffusion resistance, and increased adsorption capacity phases, which may impact positively its performance in functional applications such as gas separation (Poshusta, et al, 2000) and heterogeneous catalysis (Walton, 2006).

Herein, this research will be focusing on the synthesis of SAPO-34 nanoparticles by using the ultrasonic pretreatment and hydrothermal heating to obtain the suitable nanosized adsorbent for CO_2 capture. The effect of the particles size of SAPO-34 on the overall adsorption properties was studied.

CHAPTER 3

3. METHODOLOGY

3.1 Research methodology

In this research, three main experimental works were conducted as shown in Figure 1. The tasks started from the synthesis of SAPO-34 nanoparticles, using an efficient ultrasonic procedure. The morphology and particle size of the synthesized SAPO-34 were modified with the aid of ultrasound power. Initial gel prepared using TEAOH as structure-directing agent was irradiated by ultrasound waves. In the present work, the ultrasonic time and the crystallization time were manipulated in synthesizing SAPO-34.

The next step is to characterize the SAPO-34 nanoparticles for their crystallinity, morphology, surface area and particle size using different physical and chemical technique such as field emission scanning electron microscope (FESEM), transmittance electron microscope (TEM), X-ray diffraction (XRD), and Fourier transform Infrared (FTIR).

Lastly, the resulting SAPO-34 particles were tested for its CO_2 adsorption characteristic. The effect of particle size on its adsorption behaviour was studied using CO_2 physisorption analyzer.

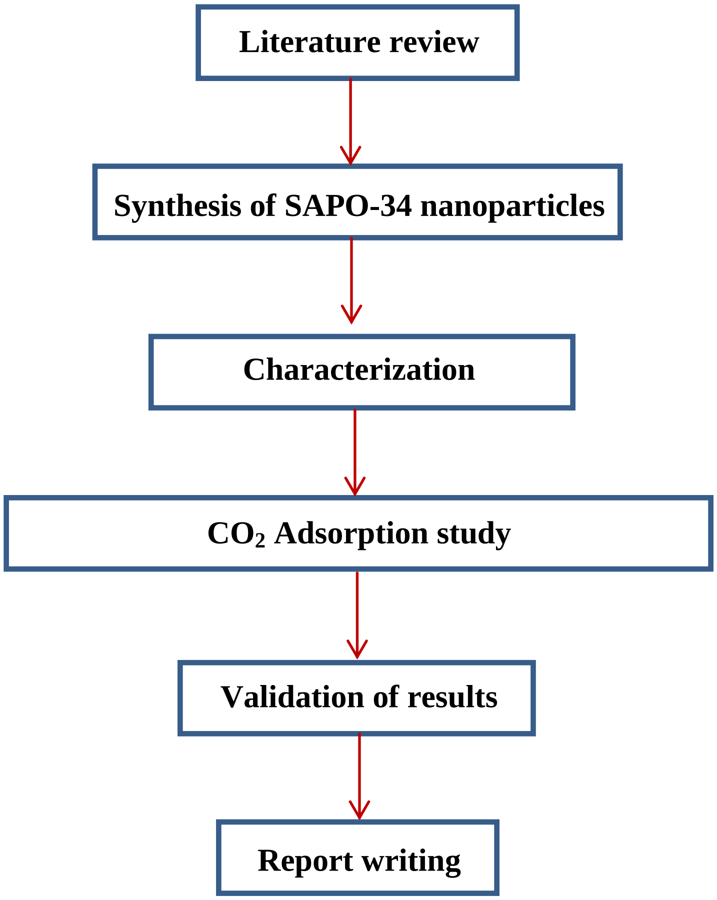

Figure 1: Process flow chart of the current research activity

3.1.1 Experimental Procedures

The experimental procedure is outline as follows:

1) First, aluminium isopropoxide ($Al(i\text{-}C_3H_7O)_3$, >99.99%) was added into a solution containing phosphoric acid (H_3PO_4, 85wt%) and deionized water.
2) The mixture was stirred for 2 hours under vigorous stirring until a homogenous solution is formed.
3) Ludox AS-40 colloidal silica (SiO_2, 40wt%) was then added and the resulting solution was stirred for 3 hours.

4) Tetraethylammonium hydroxide ($(C_2H_5)_4NOH$, 35wt%) was added and the mixture ~~is~~ was stirred for 0.5 hours.
5) Finally, dipropylamine ($C_6H_{15}N$, 99%,) was added.
6) Then the mixture was irradiated with ultrasound. The sonication temperature was controlled by using the water bath.
7) The final gel was transferred to an autoclave and was heated in an oven.
8) After synthesis, the seeds were centrifuged and wash with deionized water. The step was repeated for 3 times.
9) SAPO-34 seeds were dried in an oven for overnight.
10) The SAPO-34 seeds were then calcinated with protherm furnace at 550^oC for 6 hours prior to use.

3.1.2 Characterization Method

The synthesized SAPO-34 nanoparticles were characterized using

- Field emission scanning electron microscope (FESEM)
- Transmittance electron microscope (TEM)
- X-ray diffraction (XRD)
- Fourier transform Infrared (FTIR).

- A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. Magnification of 500x – 5000x is used.

- The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. TEM use electrons as "light source" and their much lower wavelength make it possible to get a resolution a thousand times better than with a light microscope.

- FTIR is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FTIR

Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. Wavelength of 4000cm^{-1} to 400cm^{-1} is used.

- Powder X-ray diffraction (XRD) at room temperature was performed in transmission mode using monochromatized CuKα_1 radiation of wavelength λ = 1.5406 Å. Samples were filled into thin-walled silica glass capillaries which were left unsealed.

Table 1 summarized the equipment used for characterization study in the present research work and their characterizing properties.

Equipment	**Properties**
Field emission Scanning electron microscope (FESEM)	Morphology of the sample
Transmittance electron microscope (TEM)	Particle size of the sample
X-ray diffraction (XRD)	Verify the sample structure
Fourier transform infrared (FTIR)	Structure of the sample

Table 1: List of Equipments

3.1.3 CO$_2$ Adsorption Study

The CO$_2$ adsorption characteristic of the resultant SAPO-34 particles is studied using physisorption analyzer. Carbon dioxide physisorption isotherms were measured at room temperature on a BELSORP volumetric instrument. Samples were outgassed in vacuum for at least 24 hours before the sorption measurements.

3.2 Gantt Chart

The activities Gantt Chart for the present project is shown in Table 2.

Semester	**FYP I, Semester 1 (May 2012)**														**FYP II, Semester 2 (September 2012)**													
Period (Week)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Preliminary Research Work • Literature review on the SAPO-34 nanoparticles synthesis • To define the reserach methodology of the project	■	■	■	■	■	■	■	■	■	■																		
Preparation of Extended Proposal							■																					
Preparation of Interim Oral Presentation								■	■																			
Preparation and Submission of Interim Report										■	■	■	■	■														
Synthesis of SAPO-34 nanoparticles based on different parameters (temperature and ultrasonic pre pre-treatment duration)															■	■	■	■	■	■	■	■	■	■				
Characterization study (FESEM, TEM, XRD, FTIR)																						■	■	■				
CO_2 adsorption study																								■	■	■		
Report writing																						■	■	■	■	■	■	

Table 2: Gantt Chart for FYP 1 and FYP 2

3.3 Key milestone

The key milestones of the current project are summarized in Table 3 and Table 4.

Table 3: Milestone for FYP 1

No	**Activities**	**Week**
1	Information Gathering (Literature Review)	3-10
2	Submission of extended proposal	7
3	Proposal Defense	8-9
4	Submission of interim report	14

Table 4: Milestone for FYP 2

No	**Activities**	**Week**
1	Conducting experiments	1-12
2	Submission of progress report	8
3	Pre-SEDEX	11
4	Submission of draft report	12
5	Submission of dissertation (soft bound)	13
6	Submission of technical paper	13
7	Oral presentation	14
8	Submission of project dissertation (hard bound)	15

CHAPTER 4

4. RESULT AND DISCUSSION

4.1 Synthesis of SAPO-34 Particles

Table 5 shows the SAPO-34 samples synthesized in the present study. The experiments were conducted by manipulating the crystallization time in the range from 0.5-1.5 h and the ultrasonic time ranging from 15-30 min. The crystallization time and ultrasonic time are manipulated in order to study the effect of these two synthesis parameters on the size of the resulting SAPO-34 particles.

Sample no	Ultrasonic time (min)	Heating conducted in an oven	
		Temperature (^oC)	Time (min)
S1	15	200	90
S2	15	200	60
S3	15	200	30
S4	30	200	30

Table 5:SAPO-34 samples synthesized in the present work

4.2 Characterization

4.2.1 X-ray diffraction (XRD)

The XRD patterns of the resultants SAPO-34 are shown in Figure 2. The XRD patterns for samples 1 and 4 matches well with those XRD patterns of SAPO-34 reported in literature. The characteristic peaks of SAPO-34 structure at 2θ = 9.5°, 20.5°, 22.3°, 23°, 30.7° and 35.5° can be observed in Figure 2 for Sample 1 and Sample 4. These results show that SAPO-34 particles were successfully form by applying ultrasound wave synthesis.

Heating the initial gel after ultrasonic treatment stabilizes SAPO-34 phase. The typical XRD diffraction patterns corresponding to the structure of SAPO-34 can be observed for both Sample 1 and Sample 4, but the intensities of these peaks vary according to the ultrasonic applying route. As shown in Figure 2, the intensities of the diffraction peaks obtained for Sample 1 and Sample 4 was higher than that of those peaks obtained for Sample 2 and Sample 3. This result indicates that the crystallinity of Sample 1 and Sample 4 was higher than that of the crystallinity of Sample 2 and Sample 3. The different in the crystallinity was mainly attributed to the mechanisms for ultrasonic action and the crystallization time. Applying ultrasonic before heating the initial gel in an oven can become the nucleation stage that results in a large number of nuclei at much lower supersaturation levels. The subsequent heating treatment allowed the growth of nuclei to finally form crystalline SAPO-34 particles.

The XRD patterns of Sample 2 and Sample 3 demonstrates that the samples mainly consist of amorphous phase. Weak peaks emerge at 2θ = 9.5º and 20.5º, suggesting that the appearance of a very small amount of SAPO-34 crystals. These results show that, with adequate ultrasonic pretreatment and heating time, highly crystalline SAPO-34 particles were obtained. In this study, ultrasonic time of 30 minutes and heating duration of 30 minutes could result in highly crystalline SAPO-34 particles. As compare to the conventional study of synthesis of SAPO-34, this method has significantly reduced the synthesis duration from 24 h to only 30 minutes.

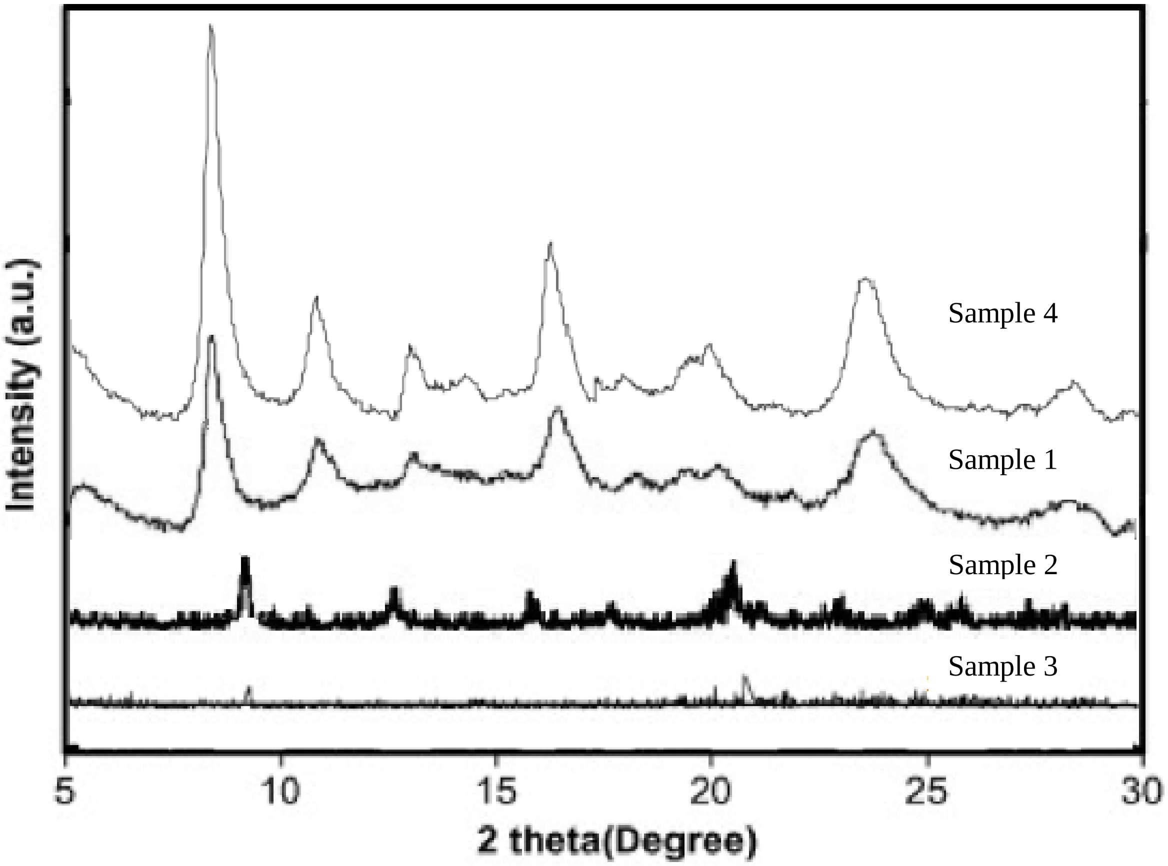

Figure 2: XRD patterns of SAPO-34 samples

4.2.2 Field Emission Scanning Electron Microscope (FESEM) & Transmittance Electron Microscope (TEM)

The FESEM images of Sample 1 and Sample 4 are shown in Figure 3 and Figure 4 respectively. For both samples, cubic crystals were observed, suggesting that high crystallinity SAPO-34 was obtained with the presence of relatively small quantity amount of amorphous phase.

Figure 5 shows the TEM images of the samples. The average crystal size of Sample 1 was 25-27 nm and the average crystal size for Sample 4 was 16-20 nm. This result indicates that the increase in ultrasonic duration coupled with the reduction in heating duration reduces the particle size of SAPO-34.

By applying ultrasonic pretreatment in the synthesis of SAPO-34 nanoparticles is found to dramatically alter the morphology and size of the product. In this case, uniform nanoparticles with average size of about 25 nm for Sample 1 and 18 nm for Sample 4 are formed instead of cubic crystals. The obtained particles are homogeneous in nano-scale and possess rough external surfaces with irregular shape. The type of driving force in the synthesis plays a crucial role in the shape and size control of nanosized SAPO-34 crystals. If compare to conventional heating method, much smaller crystal size of SAPO-34 were obtained by using ultrasonic-assisted hydrothermal method. This result could be due to the increase in number of crystal nuclei by the ultrasonic treatment. Ultrasonic can initiate seeding and control subsequent crystal growth. This is due to cavitation bubbles themselves acting as nuclei for crystal grows and to the disruption nuclei already present within the medium thus increasing the number of nuclei in the medium. Also collapsing of bubbles in acoustic cavitation occurred in less than a nanosecond and so, prevents the organization and agglomeration of particles (Askari et al, 2012).

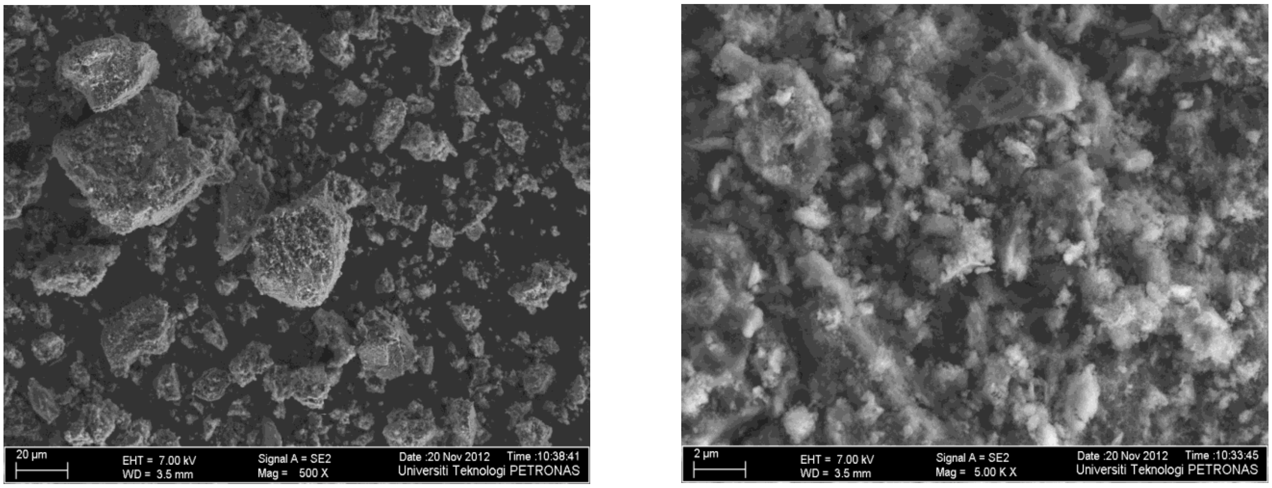

Figure 3: FESEM images of Sample 1

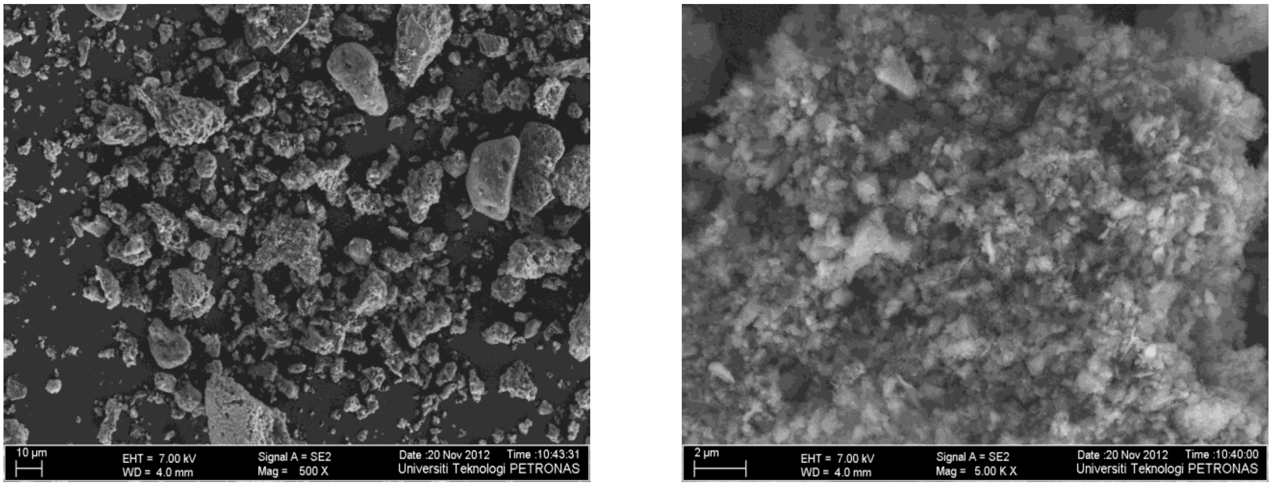

Figure 4: FESEM images of Sample 4

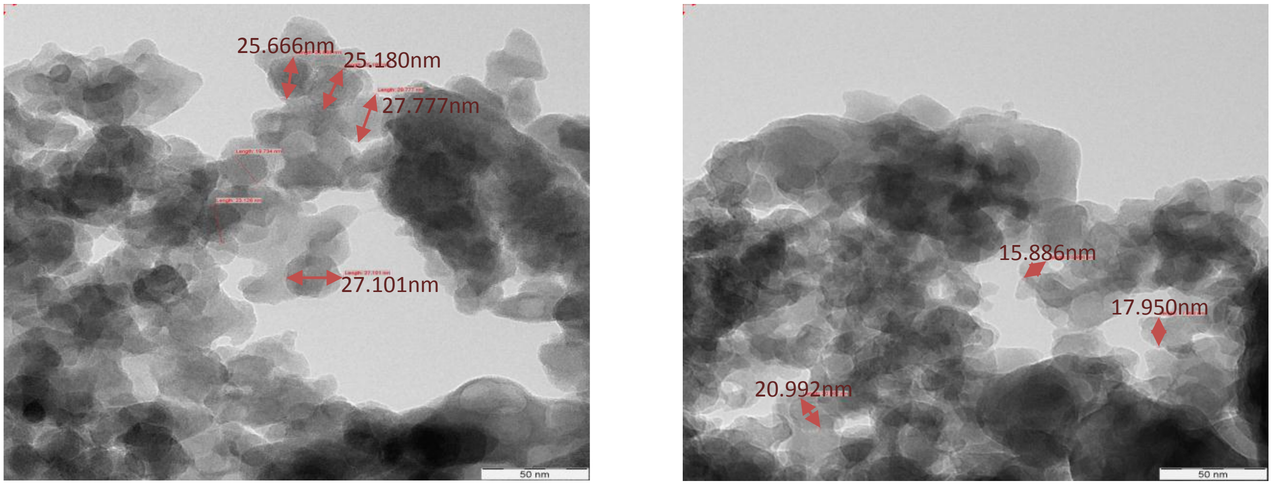

Figure 5: TEM images of (a) Sample 1 and (b) Sample 4

4.2.3 Fourier transform infrared (FTIR)

In order to further confirm the structure of the resulting SAPO-34 samples, the FTIR testing was conducted. Figure 6 show the FTIR spectrum obtained for Sample 1 and Sample 4. The framework vibrations at 480, 635, 730 and 1100 were observed for both samples, which are corresponding to T–O bending of silicon tetrahedra, T–O bending in D6 rings, T–O–T symmetric stretching and asymmetric stretching of TO_4 tetrahedra, respectively, matches well with those of SAPO-34 FTIR patterns reported in the literature (Salmasi et al, 2011).

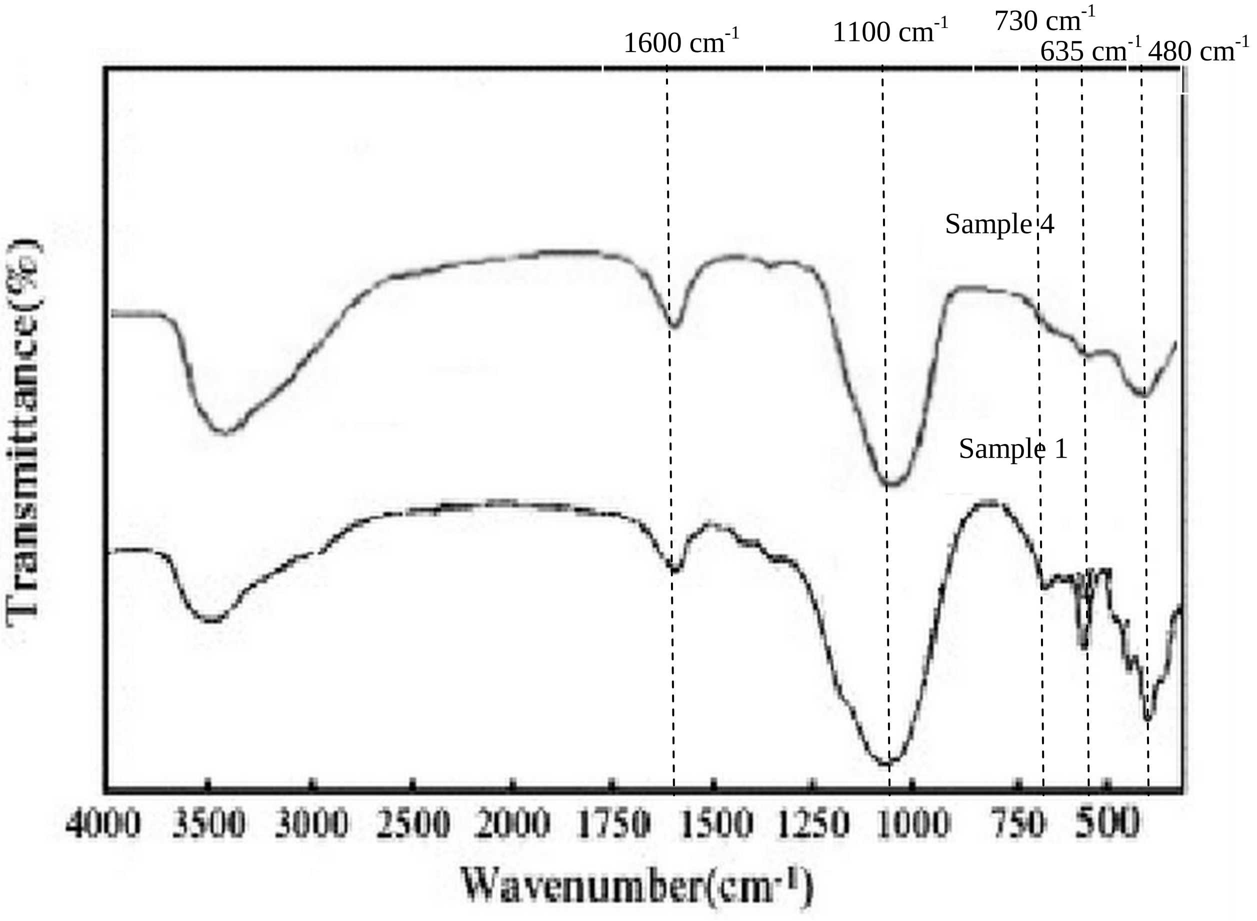

Figure 6: FTIR patterns of SAPO-34 Sample 1 and Sample 4

4.3 CO_2 Adsorption Isotherm

Figure 7 shows the CO_2 adsorption isotherm of Sample 1 and Sample 4. Based on the results, both Sample 1 and Sample 4 represent good performance in adsorption process. As shown in Figure 14, CO_2 adsorption capacity of Sample 4 is higher than that of Sample 1. This result shows that SAPO-34 particles with higher crystallinity and lower particles size showed higher CO_2 adsorption rate. At $p/p_o = 0.8$, CO_2 adsorption capacity of Sample 1 is 0.9 cm^3/g while for Sample 4, 1.9 cm^3/g was obtained. In additions, the surface area for Sample 4 is higher than the surface area of Sample 1.

The reduction in particle size could increase the surface area of the resulting SAPO-34, therefore, higher CO_2 adsorption rate was obtained for Sample 4. Furthermore, the increase in crystallinity of SAPO-34 increases the CO_2 adsorption site which resulted in the increase in amount of CO_2 adsorbed in SAPO-34.

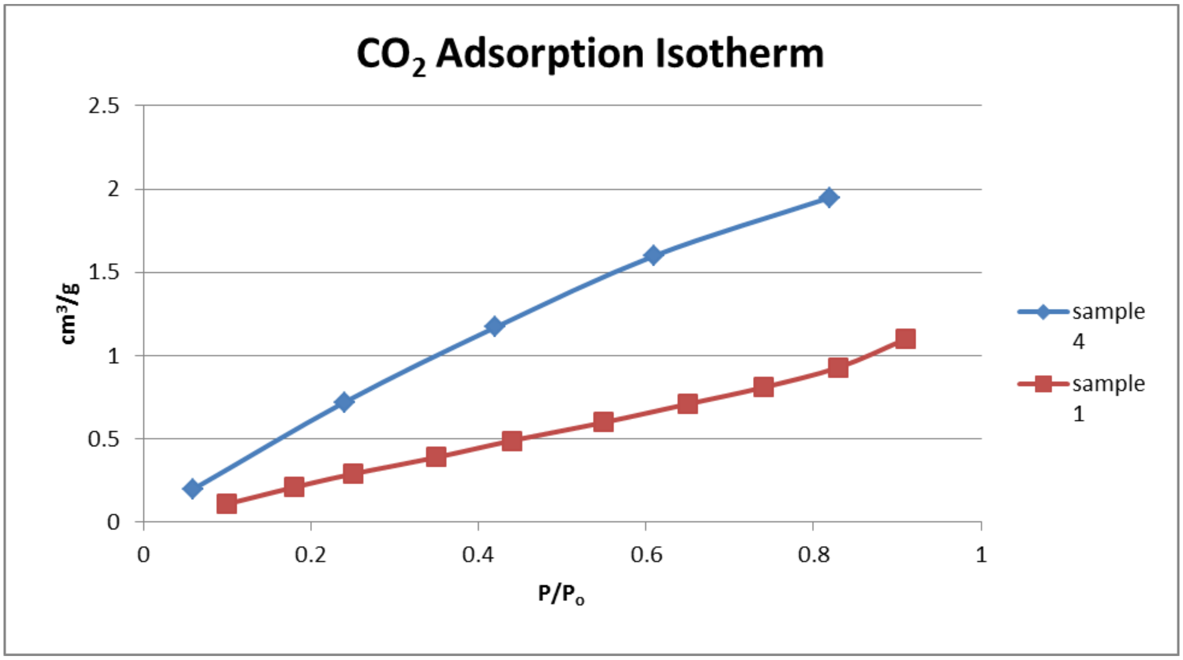

Figure 7: Comparison of adsorption isotherm for Sample 1 and Sample 4

CHAPTER 5

5. CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

SAPO-34 nanocrystals of 17nm-30nm were successfully synthesized by ultrasonic procedure using TEAOH as structure directing agent. The particles were characterized by XRD, FESEM, TEM, and FTIR. Contrary to hydrothermal method which required at least 24 h for synthesis of fully crystalline SAPO-34, sonochemical-assisted hydrothermal synthesis method leads to lower synthesis duration of only 1-2 h in order to obtained a fully crystalline SAPO-34 particles in the nanosize range.

Comparing to hydrothermal synthesis, this novel technique is time saving and more efficient in producing SAPO-34 nanopaticles. The fact that SONO-SAPO-34 nanopaticles can be prepared by the sonochemical method suggests a high nucleation density in the early stages of synthesis and slow crystal growth after nucleation.

In a sonochemical process, a huge density of energy for crystallization is provided by the collapse of bubbles which formed by ultrasonic waves. Collapsing of bubbles occurred in less than a nanosecond resulting in a high rate of temperature decrease, which prevents the organization and agglomeration of particles and leads to smaller size crystals. These results suggest that this unconventional method is a very useful technique for the synthesis of SAPO-34 nanocrystals in a high yield.

Based on the results of characterization, the ultrasonic time and the crystallization time are important factors in synthesizing of nano-sized SAPO-34 particles. The ultrasonic time of 15 minutes with crystallization time of 1.5 hours can produce nano-sized SAPO-34. Also 30 minutes of ultrasonic time and 0.5 hours of crystallization time produced the smallest SAPO-34 particles.

The crystallinity and the size of SAPO-34 are important factors in the CO_2 adsorption. The smaller the particles size, the higher the adsorption capacity because of the increase in the surface area. In addition, increase in crystallinity of the materials, the higher the CO_2 adsorption capacity.

5.2 Recommendations

During the experiment, there might be some errors occur as follow:

1. Human error during preparation of sample weight and also in determining the stirring power (rpm). There are slight different from each sample to another because no stirring power is recorded.
2. The ultrasonic frequency is unknown and cannot be set. Also the temperature of the water bath is not consistence because no temperature control.
3. The physisorption analyzer might not be functioning ideally prior to the adsorption analysis because of the equipment initialization step and also pressure inconsistency.

Based on the knowledge gain in this work, the following recommendations for future studies are made:

1. Using digital magnetic stirrer plate that is able to set the desired stirring power (rpm) and time (min) digitally.
2. Clean the oven before using it for crystallization of the sample to avoid any contaminations to the sample.
3. Able to understand and use the overall equipment procedures for any input of changing the parameters, for example, temperature ramping and etc.
4. Vary the parameters of interest for better comparison in any condition.
5. Reduce in time interval from one procedural step to another.

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