**Effect of Ultrasonic Pretreatment on the Formation of SAPO-34 for**

**$CO_2$ capture**


by


Mthobisi Dladla



Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)



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CERTIFICATION OF APPROVAL


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(CHEMICAL)



Approved by,



_____

(Dr Yeong Yin Fong)




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TRONOH, PERAK

September 2014

# 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.

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MTHOBISI DLADLA

# ABSTRACT

Carbon dioxide is the sole contributor towards global warming. Therefore the growing atmospheric $CO_2$ concentration and its impact on climate have motivated widespread research and development aimed at slowing or stemming anthropogenic carbon emissions. Additionally, in the natural gas processing industry, corrosive impurities known as 'acid gases', typically $CO_2$ and hydrogen sulfide ($H_2S$) are undesirable. Due to the extreme development of adsorption technology and the increase in adsorbent synthesis, it has been considered to be one of the most promising techniques for the capture of $CO_2$ from natural gas. Zeolites are considered efficient in this particular application and due to the high surface area and porosity of SAPO-34; it is predominant for $CO_2$ capture. In the present work, synthesis of SAPO-34 was successfully performed via hydrothermal synthesis for 24 h using TEAOH as structure directing agent (SDA). However, attempt to reduce the synthesis duration of SAPO-34 through ultrasonic pretreatment was not successful. The characterization studies were carried out by using scanning electron microscope (SEM), and X-ray diffraction (XRD). From XRD results, a relative crystallinity of 90% based on XRD peak intensity at $2\theta = 9.5°$ and less intense peaks at $2\theta = 21.5°$, $22.6°$, $23°$ & $35.9$ was obtained for the sample synthesized under hydrothermal conditions for 24 h without ultrasonic pretreatment The SEM micrographs showed that SAPO-34 crystals having an average crystal size of 2 µm with homogeneous size distribution were obtained. Both XRD and SEM analysis confirmed the formation of SAPO-34 under hydrothermal synthesis for 24 h without ultrasonic pretreatment. Nevertheless, samples synthesized under ultrasonic pretreatment coupled with the reduction of synthesis durations ranging from 15 min to 3 h did not show SAPO-34 structure and morphology mainly due to the systematic errors. After the characterization, SAPO-34 particles were tested for its $CO_2$ adsorption characteristics and the adsorption capacity was comparable with those results reported in the literature..

# ACKNOWLEDGEMENTS

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**CHAPTER 1**

**INTRODUCTION**

**1.1 Background of Research**

Recent studies in the field of gas separation have focused on common techniques such as adsorption, membrane separation and cryogenics with regard to their applications, especially for $CO_2$ capture from a wide variety of sources such as natural gas and in the atmosphere where it is present as a pollutant to the environment (Gupta et al., 2002). Additionally these studies have been directed on how to efficiently maximize gas separation from each technique. According to the $CO_2$ Capture Project (2008) the adsorption technique was regarded unattractive for large-scale separation of $CO_2$ owing to the low capacity and low $CO_2$ selectivity of the existing adsorbents. Nonetheless, due to the extreme development of adsorption technology and the increase in adsorbents, adsorption has been considered to be one of the most promising techniques for the capture of $CO_2$. Furthermore there is a constant synthesis of inorganic adsorbents that possess dramatically improved properties which translate into better performance (Knaebel, 2002). These inorganic adsorbents include aluminas, silicas and zeolites. Zeolites which are also called molecular sieves have been of interest among the existing adsorbents since they are a stoichiometric blend of the other two adsorbents; aluminas and silicas (Knaebel, 2002).

Moreover, this predominant feature of the zeolite group of inorganic adsorbents offers them better properties in $CO_2$ removal. 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. Furthermore, different types of molecules can enter the zeolite, while some diffuse through the channels more quickly, leaving other components behind (Bell et al., 2001). The dominant zeolites that are in commercial use for adsorption are Type A, X, and Y (Yang, 2003). Since the most essential attributes of an adsorbent for any given application include capacity, selectivity, regenerability,

kinetics, compatibility and cost, it could be presumed that zeolites possess an ample amount of these attributes however rarely will a single adsorbent be optimal in all these respects (Knaebel, 2002). Therefore, in the synthesis of zeolites using a pretreatment of the reaction mixture has been introduced which utilizes the knowledge of ultrasonic sonochemistry (Askari & Halladj, 2011). One such class of zeolites or molecular sieves is Silicoaluminophosphate (SAPO-34). SAPO-34 has been reported and applied in $CO_2/CH_4$ separation. $CO_2$ favorably adsorbs in the SAPO-34 pores and $CH_4$ diffuses more slowly than $CO_2$ since it is similar in size to the SAPO-34 pore (Ashraf et al, 2010). Furthermore, Askari & Halladj (2011) reported that SAPO-34 nanocrystals were successfully synthesized by a sonochemical method using TEAOH as a structure directing agent (SDA). However, the performance of the resulting materials on $CO_2$ adsorption is not reported. Therefore, in the present project, the effects of ultrasonic pretreatment on the synthesis of SAPO-34 and its performance on $CO_2$ capture were studied.

## 1.2 Problem statements

It is well known that the earth's rising temperature is a result of the green-house effect, caused by the increasing concentrations of $CO_2$ in the atmosphere, or what is commonly known as global warming. Additionally, it can be observed that due to an increase in the industrial sector and urbanization, the increase of $CO_2$ to the atmosphere has also increased substantially. Thus, in order to provide the alternative solution towards the treatment of the global warming crisis, $CO_2$ capture technology needs to be established. Among the existing technologies, $CO_2$ capture through adsorption process is the most attractive technology due to its advantages such as the low energy requirements and low capital cost when running pressure swing adsorption (PSA). Moreover, SAPO-34 has been identified as a potential adsorbent for $CO_2$ capture due to its properties such as high porosity and an ionic nature which gives them a high affinity for $H_2O$ and $CO_2$. Recently, ultrasonic pretreatment has been reported by Askari and Halladj (2011) for the synthesis of SAPO-34 and the synthesis duration has been successfully reduced. However, this study is still at an initial stage and more work needs to be carried out to

study the effect of ultrasonic pretreatment duration on the formation of SAPO-34 and also its performance in $CO_2$ capture.

## 1.3 Objectives and scope of study

**The objectives of the present work are as follows:**

1. To synthesize SAPO-34 by manipulating the ultrasonic pretreatment duration and synthesis time.
2. To characterize the resultant SAPO-34 using X-ray diffraction (XRD) and scanning electron microscope (SEM).
3. To study the $CO_2$ adsorption characteristics of SAPO-34 using $CO_2$ physisorption.

## 1.4 Relevancy if the project

This research focuses on the synthesis of SAPO-34 using ultrasonic pretreatment prior to hydrothermal growth. SAPO-34 was characterized for their properties such as morphology, and crystallinity using scanning electron microscope (SEM) and X-ray diffraction (XRD). The parameters including the ultrasonic duration and synthesis time were varied during the synthesis. The resultant SAPO-34 was tested for its $CO_2$ adsorption properties using physisorption analyzer.

## 1.5 Feasibility of the project within the Scope and Time Frame

The project was performed in two semesters that includes two areas of study which are i) synthesis and characterization of SAPO-34 and ii) $CO_2$ adsorption study. It will involve the use of the university laboratories and based on the aforementioned description, it is feasible to be carried out for the specified duration.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Critical Analysis of Literature

### 2.1.1 CO$_2$ Removal

Carbon Dioxide (CO$_2$) is a gas that we come across with on a regular basis. It is a colorless, odorless gas produced by burning carbon and organic compounds and by respiration. It is naturally present in air (about 0.03 percent) (Wikipedia). Additionally the concentration of CO$_2$ in the atmosphere has increased markedly in the 21st century, at a rate of 2.0 ppm/yr during 2000–2009 and faster since then (Tans & Pieter, 2009). Hence, it is generally accepted that this increase in atmospheric CO$_2$ maybe resulting in a global climate change or global warming (Drage et al., 2009).

Additionally carbon dioxide, as well as H$_2$S and other acid gases, must be removed from natural gas because in the presence of water, these impurities can form acids that corrode pipelines and other equipment (Rufford et al., 2012). It also provides no heating value and must be removed to meet gas quality specifications before distribution to gas users (Rufford et al., 2012). Furthermore the maximum level of CO$_2$ permitted in natural gas transmitted to customers by pipeline is typically less than 3% (Hubbard, 2010). Thus, natural gas is only useful when the additional CO$_2$ is removed. Hence from the viewpoints of energy and the environment it is important to separate CO$_2$ from natural gas.

### 2.1.2 Existing CO$_2$ removal technologies

Kerry (2006) reported that from the beginning of the industrial application of air separation by low temperatures, it was clear that contaminants such as water and carbon dioxide had to be eliminated. Gas or vapor component separation from the gas phase is

essential in many industrial processes like the preparation of high-purity industrial gases such as oxygen, nitrogen, argon, neon, hydrogen, etc. and elimination of pollutants from vent gases to meet legislative requirements (Sinnott & Towler, 2013). There are three basic methods or techniques for gas separation namely solvent or sorbent separation (absorption and adsorption), cryogenic distillation and membrane separation (Nguyen, 2012). The comparison between these gas separation methods in $CO_2$ removal will be discussed in the following sections.

**Membrane Separation**

Matsuura (1993) reported that materials utilized for the membrane that is carrying out the membrane separation process range from organic polymeric materials to inorganic materials. Nonetheless the typical membranes applied in gas separation processes are synthetic in nature. They utilize the mechanism of permeation and it basically falls into two categories, each governed by the type of membrane involved (Isalski, 1989). The first is through non-porous or dense film membranes and the second is through porous membranes which generally contain larger voids than dense-film membranes. Fundamentally, gas separation membranes allow one component in a gas stream to pass through faster than the others. Figure 2.1 shows $CO_2$ separation using membrane technology.
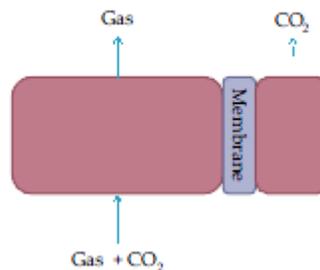


*Figure 2.1 Gas separation using membrane (Nguyen,. 2012, pg 2-3 )*

According to Harzog et. al (2009) permeation is generally pressure-driven – i.e., the feed gas is compressed and/or the permeate channel operates under vacuum and a sweep gas is employed. However due to the low partial pressure of $CO_2$ in the flue gas, this constitutes a major challenge for the membrane-based separation compared to liquid absorbents or solid adsorbents that are thermally regenerated (i.e., heated to remove the captured $CO_2$). Additionally the $CO_2$ Capture Project (2008) stated that much development is required before membranes could be used on a large scale for $CO_2$ capture in power stations.

**Cryogenics Distillation**

In cryogenic distillation, the feed gas is compressed to high pressure, cooled, and then chilled until the gas is partially liquefied and distillation can be implemented (shown in Figure 2.2) (Sinnott & Towler, 2013). $CO_2$ can be separated from other gases by cooling and condensation. According to the $CO_2$ Capture Project (2008) cryogenic separation is widely used commercially for streams that already have high $CO_2$ concentrations (normally >90%) but it is not applied for more dilute $CO_2$ streams. However in a study done by Letcher (2008), it is stated that cryogenic distillation does not seem to be currently considered as an alternative for $CO_2$ capture, probably because of anticipated high costs when diluted streams are used. Conclusively cryogenic distillation is not an attractive process to be considered as far $CO_2$ capture is concerned.



*Figure 2.2 Gas Separation by cryogenic distillation (Nguyen, 2012, pg 2-3 )*

**Solvent/Sorbent Separation**

Solvent or sorbent separation is divided into two separation processes namely the absorption and adsorption processes.

Absorption or solvent extraction is the assimilation of molecules into a solid or liquid substance, with the formation of a solution or a new compound (Kerry, 2006). According to Sinnot and Towler (2013) a component is removed from a gas by contacting the gas with a solvent that dissolves the component selectively. For instance in absorption process of separating $CO_2$ and other components of flue gas which is a by-product of combustion of fossil fuel in power stations, the flue gas is contacted with a liquid absorbent (or solvent) that has b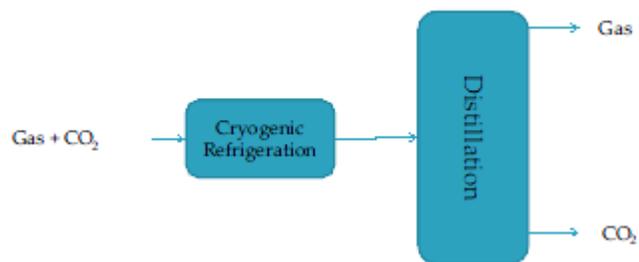een selected because carbon dioxide dissolves in it more readily than nitrogen – i.e., it is selective for $CO_2$. This process takes place in scrubbers in which turbulent flow promotes rapid $CO_2$ transfer from gas to liquid. Differences in density make it easy to separate the emerging gas and liquid (Hezrog et al, 2009). Conventional technologies in recovering $CO_2$ include absorption by aqueous amines. Amine scrubbing technology was established over 60 years ago in the oil and chemical industries, for removal of hydrogen sulphide and $CO_2$ from gas streams. However utilization of this process is energy intensive and expensive when used for large volumes of dilute gas and this is mainly due to the high heat capacity of water and use of temperature swings to induce $CO_2$ desorption (Hicks et all, 2008). Thus, gas adsorption which is an alternative of gas absorption for $CO_2$ capture is required.

Adsorption is the bounding of molecules of a gas, liquid, dissolved substances, or of particles to the surface of a solid (Kerry, 2006). The separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another is involved (Walter & Weber, 1989). Furthermore it is a surface phenomenon which in principle occurs at any given pressure and temperature for all chemical species known to be in existence. The adsorbing phase or solid with internal or external surfaces exposed to the molecules of a gas or liquid phase where the molecules of a gas stick or adsorb is called the adsorbent (Keller, 2005). There is a wide variety of organic and inorganic adsorbents which have various applications in adsorption processes however in this particular report the focus will be on those efficient for $CO_2$ capture. According to the

CO2 Capture Project (2008) solid adsorbents, such as zeolites and activated carbon, can be used to separate $CO_2$ from gas mixtures. Adsorption is probably the most widely used method in gas separation (Sinnot & Towler, 2013). Moreover, commercial $CO_2$ capture technology that exists today is very expensive and energy intensive. Improved technologies for $CO_2$ capture are necessary to achieve low energy penalties. Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of $CO_2$ from gas streams. Hence PSA technology has gained interest due to low energy requirements and low capital investment costs (Siriwardane et al., 2001). Figure 2.3 shows the adsorption process for $CO_2$ capture.

## Separation with Solvents/Sorbents
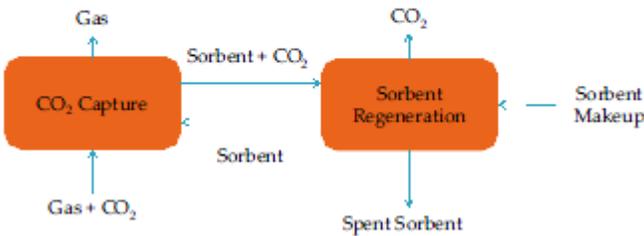


*Figure 2.3 Gas separation with solvents/sorbents (Nguyen, 2012,)*

**Adsorption Principles**

**Surface Interactions**

Surface adsorption is largely the result of binding forces between the individual atoms, ions or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interaction (Walter & Weber, 1985). There are four principle types of adsorption namely exchange, physical, chemical and specific. Moreover in this report since a solid adsorbent is under study, the focus will be on physical adsorption or physisorption rather than all of the others. Furthermore, in physisorption systems adsorbed molecules are weakly bound, often by van de Waals and/or dispersion forces due to induced dipole-dipole interactions. Van de Waals forces of interaction cause surface atoms to be more reactive and to attract gas, solid and liquids to satisfy the imbalance of atomic forces

Surface area determinations involve creating the conditions required to adsorb an average monolayer of gas molecules onto a sample. By extending this process so that gas is allowed to condense in the pores, the sample's fine pore structure can be evaluated.

**2.1.3. Adsorbents**

For any particular application where adsorption is the potential process of choice, there exists a number of possible alternative adsorbents and a number of details of the application which affect the engineer's selection. Additionally the performance of any adsorptive separation is directly determined by the quality of the sorbent (Yang, 2003). According to Knaebel (2002) adsorption capacity is the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of the adsorbent and it is the most important characteristic of an adsorbent. Furthermore an adsorbent must have high internal volume which is accessible to the adsorbate. Selectivity is also another important factor which is the ratio of the capacity of one component to that of another at a given fluid concentration (Knaebel, 2002).

There are various adsorbents available currently and some are still under research and development. Only four types of generic sorbents have dominated the commercial use of adsorption: activated carbon, zeolite, silica and activated alumina (Yang, 2003) and available for industrial purpose. Furthermore, in several excellent reviews on $CO_2$ capture by adsorption (Choi et al., 2009, 2010; Sayari et al., 2011), it can be understood that to develop an appropriate $CO_2$ capture adsorbent should satisfy (1) low-cost raw materials, (2) low heat capacity, (3) fast kinetics, (4) high $CO_2$ adsorption capacity, (5) high $CO_2$ selectivity and (6) thermal, chemical, and mechanical stabilities under extensive cycling (Yu et al., 2012). Table 2.1 shows commercial adsorbents and their typical applications, as well as their $CO_2$ adsorption capacities. Hence it can be observed that silica gel and activated alumina do not have values for $CO_2$ adsorption capacity due to the fact that they are not efficient as $CO_2$ adsorbents.

**Table 2.1: Typical applications of commercial adsorbents (Crittenden & Thomas, 1998, pg 28-2 ), (Lee, et. al, 2004, pg314), (Yu, et. al, 2012, pg759) and (Keller & Stuart, 2005, pg26 – 30), .**

| Type | Typical Applications | $CO_2$ adsorption capacity/ mmol.g$^{-1}$ |
|---|---|---|
| Silica Gel | Drying of air and technical gases and liquids<br>Removal of volatile organic compounds | 0.89 |
| Activated alumina | Dehydration agent<br>Air separation (N$_2$, O$_2$)<br>Gas purification | 0.87 |
| Activated carbon | Removal of organic substances (VOCs) from air and technical gases<br>Purification of natural gas, biogas, syngas and others (H$_2$S, $CO_2$) | 3.9 |
| Zeolite | Removal of $CO_2$ from (CH$_4$, N$_2$) gas mixtures<br>Drying of gases<br>Sweetening sour gases and liquids | 4.5 |

| | Separation of solvent systems | |
| | Pollution control. | |

Silica gel is a partially dehydrated polymeric form of colloidal silicic acid with the formular $SiO_2.nH_2O$ (Crittenden & Thomas, 1998). Silica gel is also the most widely used desiccant because of its large capacity for water and ease in regeneration (Yang, 2002).. Accordingly, ordered mesoporous silica may be a candidate for $CO_2$ capture because of its high surface area, high pore volume, tunable pore size and good thermal and mechanical stability. However the $CO_2$ adsorption capacities are not high enough, especially, at atmospheric pressure, to allow their practicability (Yu et al., 2012). The surface comprises mainly SiOH and SiOSi groups and, being polar, it can it can be used to adsorb water, alcohols, phenols, amines, etc. however it is not efficient as a $CO_2$ adsorbent (shown in Table 2.1).

Activated alumina is a porous high area form of aluminium oxide with the formula $Al_2O_3.nH_2O$ (Crittenden & Thomas, 1998). It has higher surface polarity than silica gel and has both acidic and basic characteristics. It is used mainly as a desiccant for warm gases including air but in many commercial applications it has now been replaced by zeolitic material (Crittenden & Thomas, 1998).

Activated carbons comprise elementary microcrystallites stacked in random orientation and are made by the thermal decomposition of various carbonaceous materials followed by an activation process (Crittenden & Thomas, 1998). According to Knaebel (2002) the base materials that comprise activated carbons include: wood, coal, peat, coconut shells, saran, recycled tires and others. Additional activation produces a distribution of internal pores, and affects the carbon surface generally to enhance its adsorptive capacity. However, the weak $CO_2$ adsorption of carbonaceous materials in a range of 50–120°C leads to high sensitivity in temperature and relatively low selectivity in operation (Yu et al., 2012).

Zeolites are porous crystalline aluminosilicates which comprise assemblies of SiO4 and AlO4 tetrahedra joined through the sharing of oxygen atoms (Crittenden &

Thomas, 1998). Fundamentally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores (Bell et al, 2001). More than 150 synthetic zeolite types are known (Yang, 2003). Cavities (or cages) are contained within the framework of a zeolite and are connected by regular channels (pores) which are of molecular dimensions and into which adsorbate molecules can penetrate (Crittenden & Thomas, 1998). As a result of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tonnes per annum (Bell et al, 2001).

Zeolites are able to separate gas mixtures effectively based on size. In other cases different types of molecules enter the zeolite, but some diffuse through the channels more quickly, leaving other components behind (Bell et al, 2001). The adsorption efficiencies of zeolites are largely affected by their size, charge density, and chemical composition of cations in their porous structures (Yu et al., 2012). Type A, X and Y remain the dominant zeolites and molecular sieves that are in commercial use for adsorption and ion exchange (Yang, 2003). However other various kinds of adsorbents and membranes such as MCM-41, b-zeolite, ZSM-5,silicoaluminophosphate-34, (SAPO-34), and zeolite T have been used specifically to study the separation of $CO_2$ from $CH_4$. (Salmasi et al., 2013).

### 2.1.4 Comparison of zeolites

SAPO-34 $(Si_xAl_yP_z)O_2$ is a type of silicoaluminophosphate microporous zeolite or molecular sieve, used in separation, catalytic, and adsorption technologies (Venna, 2008). Shown in Figure 2.4 is a   SAPO-34 is a cage-type molecular sieve with framework structure similar to the chabazite zeolite which naturally occurring and has a three-dimensional pore system with ellipsoidal cages interconnected via 8-membered ring windows with pore apertures of 0.38 nm x 0.38 nm (Salmasi, 2013). Since $CO_2$ has a kinetic diameter of 0.33nm the pore aperture of SAPO-34 allows to easy diffusion through the crystal structure easily(Salmasi, 2013). The key parameters of an adsorbent's capability to peform adsorption are the pore size and surface area (Rivera-

Ralmos, 2008). Shown in Table 2.2 are different types of zeolites and their surface areas. Thus when these zeolites are compared, it can be seen that SAPO-34 has the highest surface area. Additionally, as compared to SAPO-34, SAPO-5, SAPO-41, SAPO-11 are one-dimensional and have a pore size larger than that of SAPO-34 and would let both $CO_2$ and $CH_4$ move through the pores, without any separation (Bennet et al, 1983). Thus this feature makes SAPO-34 more attractive for $CO_2$ capture than other microporous zeolites.

**Table 2.2:  Zeolites and their respective surface areas (Salmasi et. al., 2013, pg 1070 & Zhao et al., 2007, pg 357)**

| Zeolites | BET surface area ($m^2/g$) |
|---|---|
| SAPO-34 | 502 |
| T-type zeolite | 352 |
| Zeolite 13X - N | 482 |
| Zeolite 13X - K | 443 |
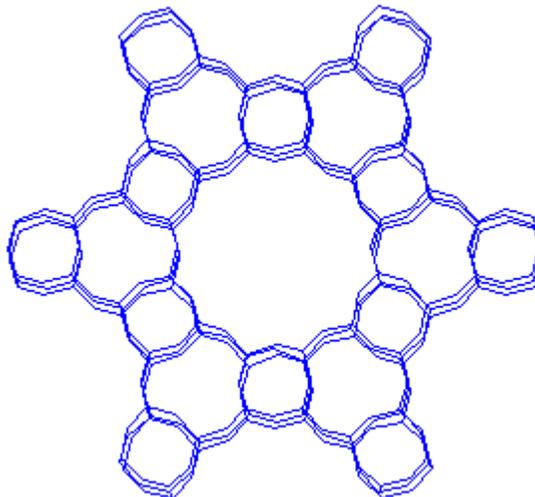


**Figure 2.4: SAPO-34 framework structure (Taken From: http://www.upv.es/~gsastre/img/fig01.gif)**

## 2.2 Formation of SAPO-34

SAPO-34 is mainly synthesized hydrothermally using different templates or structure directing agents such as TEAOH, morpholine, piperidine, triethylamine, isopropylamine, TEAOH−dipropylamine, and TEAOH−cyclohexylamine (Wang et al., 2004). Additionally, Lui at al. (2007) successfully synthesized SAPO-34 using dimethylamine as a template. SAPOs have considerable potential as acidic catalysts which play different key roles such as adsorption in sorption reactions and membrane (Askari & Halladj, 2011). Moreover, sonochemical assisted hydrothermal synthesis of samples leads to form fully crystalline SAPO-34 taking only 1.5hr, whilst for hydrothermal method at least 24 hr of synthesis time is required to obtain fully crystalline SAPO-34 (Askari & Halladj, 2011).

This research will be focusing on the synthesis of SAPO-34 by using the ultrasonic pretreatment prior to hydrothermal growth. The resultant SAPO-34 will be characterized and it performance in CO2 adsorption will be tested.

## 2.3 Relevancy and recentness of the literature

The references of this project report are taken from various journals of Chemical Engineering and dissertations and books from different authors from 1983 − 2014. The titles covered included those of $CO_2$ separation from natural gas, gas separation using membrane, cryogenic distillation and solvent and sorbent, adsorbent technology, ultrasonic pretreatment of SAPO-34 nanoparticles.

# CHAPTER 3

# METHODOLOGY

## 3.1 Research Methodology

To achieve the objectives of this project, three experimental works were conducted. Firstly, the synthesis of SAPO-34 was carried out with the aid of ultrasonic pretreatment. Secondly, hydrothermal synthesis was employed. The crystallization time was manipulated in all synthesis procedures respectively. Thereafter the synthesized SAPO-34 was characterized for its morphology, crystallinity, surface area and particle size using different analytical techniques such as X-ray diffraction (XRD) and Scanning electron microscope (SEM).

Finally, the resulting SAPO-34 zeolite was tested for its $CO_2$ adsorption property. The adsorption behavior of the resulting SAPO-34 was studied using $CO_2$ physisorption analyzer.

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│    Literature Review    │
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│    Synthesis of SAPO-34 │
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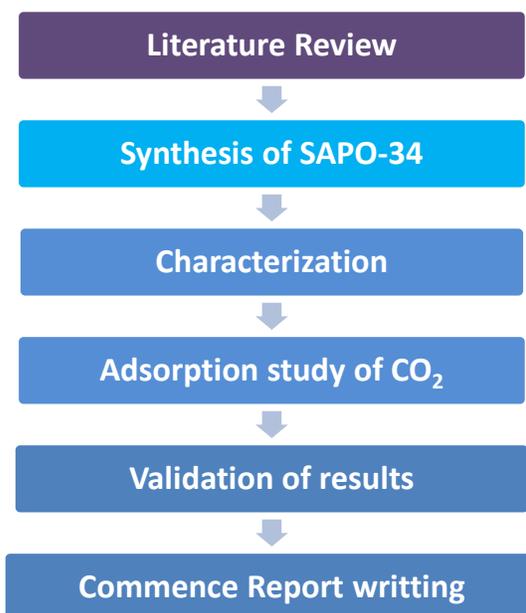
**Figure 3.1: Project Methodology**

### 3.2 Experimental Procedure

The experimental procedure is defined as follows (Askari & Halldj, 2011):

a. First, aluminium isopropoxide (Al(i-C$_3$H$_7$O)$_3$, >99.99%) was added into phosphoric acid (H$_3$PO$_4$, 85wt%). Tetraethylammonium hydroxide (TEAOH, 20wt%) was used as SDA.

b. Aluminium isopropoxide was firstly mixed with template (TEAOH) and deionized water. The mixture was stirred for 1 hour under vigorous stirring until a homogenous solution was formed.

c. Silica source (TEOS) was then added and stirred. Finally, with continuous stirring, phosphoric acid (85wt% in water) was added dropwise to the above solution.

d. The initial gel was further stirred and then irradiated with ultrasound at a frequency of 24kHz. The initial gel was then irradiated with ultrasound at a frequency of 40 kHz (SOLTEC, Model 2400EP) and the sonication temperature was maintained at a temperature of 50 °C

e. Then the mixture was irradiated with ultrasound with the duration varied from 30 min – 90 min. The sonication temperature being controlled by using the water bath.

f. The final gel was transferred to an autoclave and heated in an oven at 200°C. The synthesis time will be varied from 1.5h-3h.

g. After synthesis, the solid product was recovered and centrifuged and wash with deionized water. The step was repeated 3 times.

h. SAPO-34 solid particles were dried in an oven at 110°C.

i. The SAPO-34 solid particles were then calcined at 550°C for 5 hours to remove the organic template molecules. Table 3.1 shows the samples that were synthesized in the present work

**Table 3.1: Synthesis conditions of SAPO-34**

| Sample | Ultrasonic pretreatment duration (min) | Synthesis time (hr) |
|---|---|---|
| S1 | 30 | 1.5 |
| S2 | 30 | 3 |
| S3 | 60 | 1.5 |
| S4 | 60 | 3 |
| S5 | 90 | 1.5 |
| S6 | 90 | 3 |
| S7 (reference sample) | 0 | 24 |
| S8 | 15 | 1.5 |
| S9 | 15 | 3 |

## 3.3 Characterization Method

The synthesized SAPO-34 particles will be characterized using equipment shown in Table 3.2:

**Table 3.2: Equipment used for characterization**

| Equipment | Function |
|---|---|
| Scanning electron microscope (SEM) | Crystal size & morphology of the sample |
| X-ray diffraction (XRD) | Crystallinity of the sample |

## 3.4 Equipment used for synthesis of SAPO-34

Table 3.3 shows equipment used for synthesis of SAPO-34.

**Table 3.3: Equipment used for synthesis of SAPO-34**

| Equipment |
|---|
| Ultrasonicator (SOLTEC) |

| Teflon-lines stainless steel autoclave (30 ml) |
| Oven |
| Centrifuge |
| Hot plate stirrer |

## 3.5 Chemicals used for experimentation

Table 3.4 shows the chemicals to be used for synthesis of SAPO-34

**Table 3.4: List of chemicals used**

| Chemicals | Formula |
|---|---|
| Aluminum isopropoxide | $Al(O-i-_3H_7)_3$ |
| Phosphoric acid | $H_3PO_4$ |
| Tetraethylammonium hydroxide | $C_4H_{13}NO$ |
| Tetraethyl orthosilicate | $SiC_8H_{20}O_4$ |
| Distilled water | $H_2O$ |

## 3.6 $CO_2$ Adsorption Study

The $CO_2$ adsorption characteristic of the resultant SAPO-34 particles will be studied using BELSORP physisorption analyzer.

## 3.7 Project Activities

The project activities are summarized in Figure 3.2

```
|→  Project Topic Selection

|→  Research Work

|→  Project Background

                                    Scope of Study
|→  Problem Statement
                                    Project Objectives

|→  Literature Review

                                    Synthesis
                                      ▪ hydrothermal
                                      ▪ ultrasonic
|→  Methods                          Characterization

                                      • XRD
                                      • SEM

                                    CO₂ adsorption study

|→  Results and Discussion

|→  Conclusion and Recommendations
```
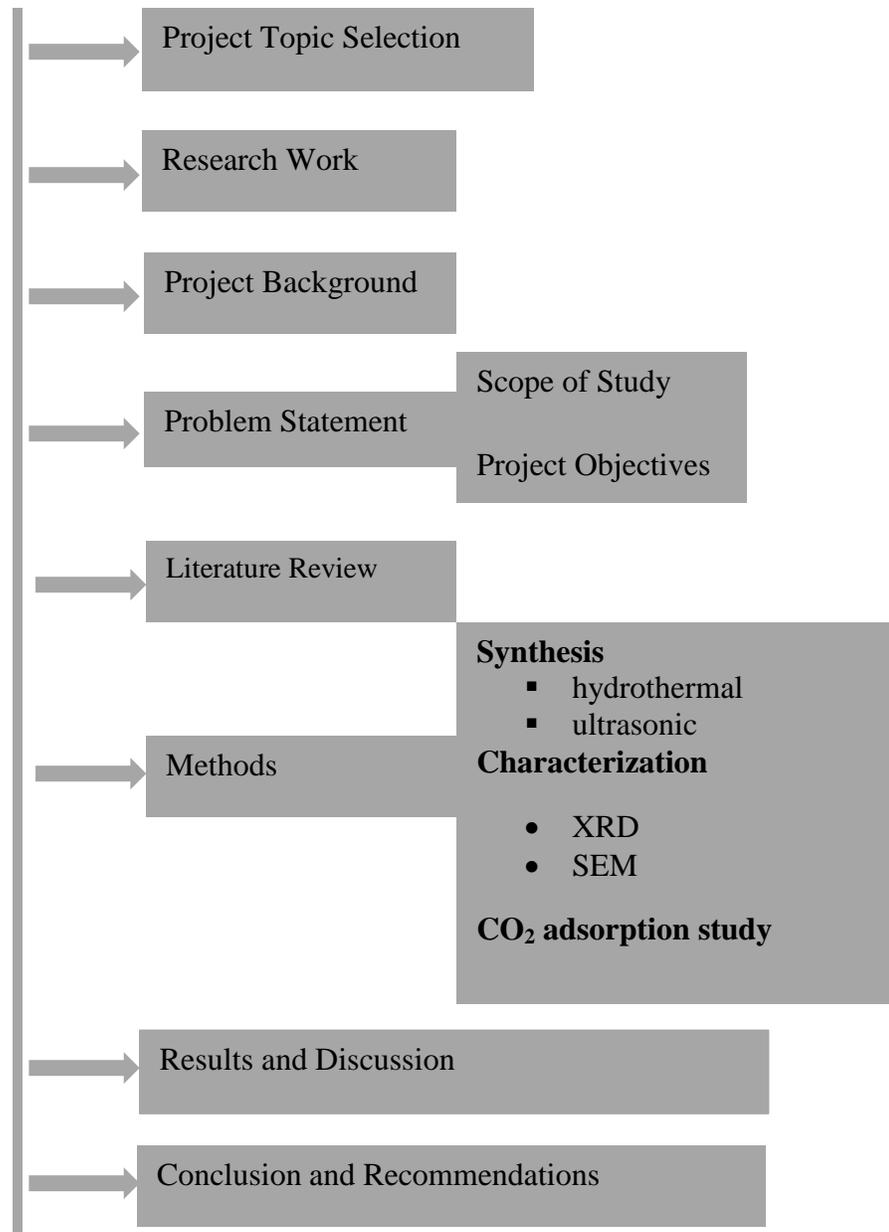
**Figure 3.2: Project Activities**

## 3.8 Gantt Chart

The Gantt chart for all the activities is shown in Table 3.5

**Table 3.5:  Gantt chart for FYP I & FYP II**

| | Scope of Work (FYP I) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Selection of Project Topic | ▓ | ▓ | | | | | | | | | | | | | FYP I |
| 2 | Preliminary Research Work | | ▓ | ▓ | ▓ | ▓ | ▓ | ▓ | | | | | | | | |
| 3 | Submission of Extended Proposal | | | | | | ▦ | | | | | | | | | |
| 4 | Proposal Defense | | | | | | | | ▓ | ▓ | | | | | | |
| 5 | Project work continues | | | | | | | | | | ▓ | ▓ | ▓ | | | |
| 6 | Submission of Interim Draft Report | | | | | | | | | | | | | ▦ | | |
| 7 | Submission of Interim Report | | | | | | | | | | | | | | ▦ | |
| | **Scope of Work (FYP II)** | | | | | | | | | | | | | | | |
| 1 | Continuation of Project Work | ▓ | ▓ | ▓ | ▓ | ▓ | ▓ | ▓ | | | | | | | | FYP II |
| 2 | Submission of Progress Report | | | | | | | | ▦ | | | | | | | |
| 3 | Continuation of Project Work | | | | | | | | | ▓ | ▓ | | | | | |
| 4 | Poster Presentation | | | | | | | | | | | ▦ | | | | |
| 5 | Draft Report Submission | | | | | | | | | | | | ▦ | | | |
| 6 | Dissertation Submission (Soft Copy) | | | | | | | | | | | | | ▦ | | |
| 7 | Technical Paper Submission | | | | | | | | | | | | | ▦ | | |
| 8 | Presentation of VIVA | | | | | | | | | | | | | | ▦ | |
| 9 | Dissertation Submission (Hard Copy) | | | | | | | | | | | | | | ▦ | |

## 3.9 Key Milestones

The key milestones of the project are shown in Table 3.6

**Table 3.6: Key Milestones for FYP I and FYP II**

| | Activities | Week | Section |
|---|---|---|---|
| 1. | Information Gathering/Literature Review | 3-10 | |
| 2. | Submission of Extended Proposal | 7 | |
| 3. | Proposal Defense | 8-9 | **FYP I** |
| 4. | Submission of Interim Report | 14 | |
| 5. | Conducting experimentation | 1-12 | |
| 6. | Submission of Progress Report | 8 | |
| 7. | Pre-SEDEX | 11 | |
| 8. | Submission of draft report | 12 | |
| 9. | Submission of dissertation (soft bound) | 13 | **FYP II** |
| 10. | Submission of Technical Paper | 13 | |
| 11. | Oral Presentation | 14 | |
| 12. | Submission of project dissertation (hard bound) | 15 | |

## 4.1 Synthesis of SAPO-34

The synthesis of SAPO-34 was conducted using a designed experimental procedure where the hydrothermal synthesis and ultrasonic pretreatment times were varied in order to study their respective effects on $CO_2$ adsorption and synthesis time. Table 4.1 shows the completed nine experiments of the synthesis of SAPO-34 using different ultrasonic pretreatment duration and hydrothermal heating duration. Figure 4.1 show the picture of the sample powders.

**Table 4.1: Synthesis Conditions of SAPO-34**

| Sample | Ultrasonic pretreatment duration (min) | Synthesis time (hr) |
|---|---|---|
| S1 | 30 | 1.5 |
| S2 | | 3 |
| S3 | 60 | 1.5 |
| S4 | | 3 |
| S5 | 90 | 1.5 |
| S6 | | 3 |
| S7 (reference sample) | 0 | 24 |
| S8[1] | 15 | 1.5 |
| S9[1] | | 3 |



**Figure 4.1: Synthesized SAPO-34 samples**

---

[1]Extra samples for investigating irradiation duration.

## 4.2 Characterization

### 4.2.1.   X-Ray Diffraction Analysis

X-Ray Diffraction is a tool used for identifying crystallinity of the samples. The XRD patterns of the Reference sample (S7) are shown in Figure 4.2. The XRD patterns of the Reference sample (S7) closely resemble the patterns of SAPO-34 reported in the literature by Askari & Halladj (2011) (Figure 4.3). The patterns reflect a relative crystallinity of 90% based on XRD peak intensity at $2\theta = 9.5°$. Additionally, the characteristic peaks of SAPO-34 can also be observed at $2\theta = 21.5°$, $22.6°$, $23°$ & $35.9°$. Therefore, 24 h of the synthesis time is required to obtain fully crystalline SAPO-34 under hydrothermal conditions.

However the samples pretreated using sonication show different XRD patterns from literature (Figure 4.2). The patterns show a highly amorphous structure which does not seem to reflect the crystalline structure of SAPO-34. According to Askari & Halladj (2011), applying sonication before hydrothermal heating should result in high crystallinity SAPO-34 as well as reduce the hydrothermal synthesis time. Nevertheless in this work, there was a failure with regards to obtaining fully crystalline SAPO-34 when ultrasonic pretreatment was implemented. Such a failure can be attributed to a systematic error. Since using the same synthesis procedure, SAPO-34 was obtained under hydrothermal conditions it therefore stands to reason that the failure is connected to the ultrasonication variables. By changing ultrasound related variables, an easy control of the size of particles can be achieved. Thus, the variables influence the physicochemical phenomena related to nucleation and crystal growth, occurring during crystallization (Askari & Halladj, 2011). Additionally sonochemical reactions and their products can be affected by various parameters. Some of these effecting parameters are: frequency and power of ultrasonic waves, time of exposure to irradiation, solution temperature, type of solution, reaction vessel diameter, and the kind of noble gas used in the reaction environment (Talebi et. al, 2010).

Furthermore, a study conducted by Nanzai, et. al, (2009) revealed that the formation of $H_2O_2$ and chloride ion, from the sonolysis of pure water and 1,2,4-trichlorobenzene aqueous solution, was affected by the reaction vessel diameter. Hence, these yields increased as the reaction vessel diameter increased. However such parameters were not investigated in the present work. Additionally ultrasound frequency can affect the sonication process as reported by Okitsu, et. a.(2005). Moreover, the effect of this parameter could be predominant as the frequency of the ultrasonicator is unknown and cannot be set, thus it could vary largely when compared to the required frequency of 24 kHz (Askari & Halladj, 2011).

Sonication of the precursor gel should achieve high nucleation density in the early stages of synthesis and slow crystal growth after nucleation. However the duration of sonication is critical in the formation of this type of sample (Muller et. al, 2005) suggesting that longer exposure to ultrasound could affect the product being synthesized. According to Muller et. al (2005), when sonication is performed without interruption for longer periods of time, larger particles are re-formed; this does not seem to be due to the sonication itself but rather an effect of the heating of the solution. Hence, the key observation is that solution heating indicates that there is an optimum duration for sonication to initiate growth and refine the particle size (Muller et. al. 2005). It then stands to reason that uncontrolled temperature conditions could affect the resulting sample. Therefore two extra samples were synthesized by 15 minutes ultrasonic duration and hydrothermal synthesis durations of 1.5 h and 3 h in order to study the effects of time exposure to ultrasound. However the resulting XRD patterns closely resembled the other pretreated samples suggesting that the error was due to a different factor and not ultrasound duration.
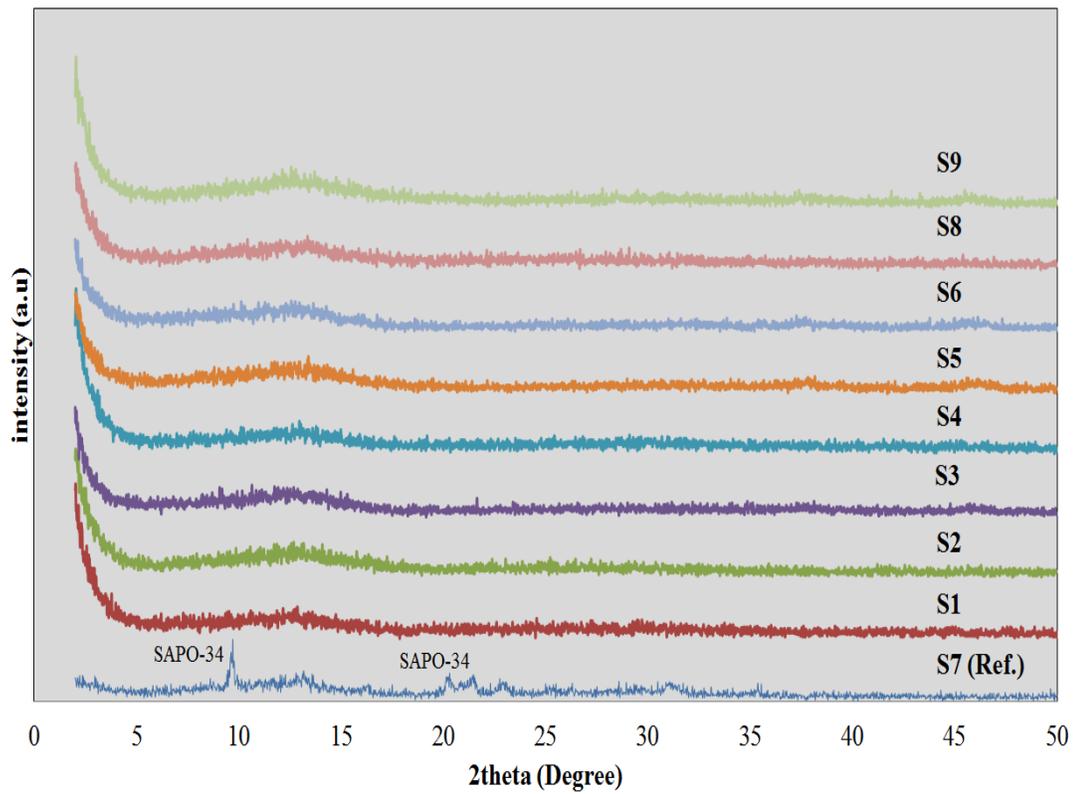
**Figure 4.2: XRD patterns for SAPO-34 samples synthesized in the present work**
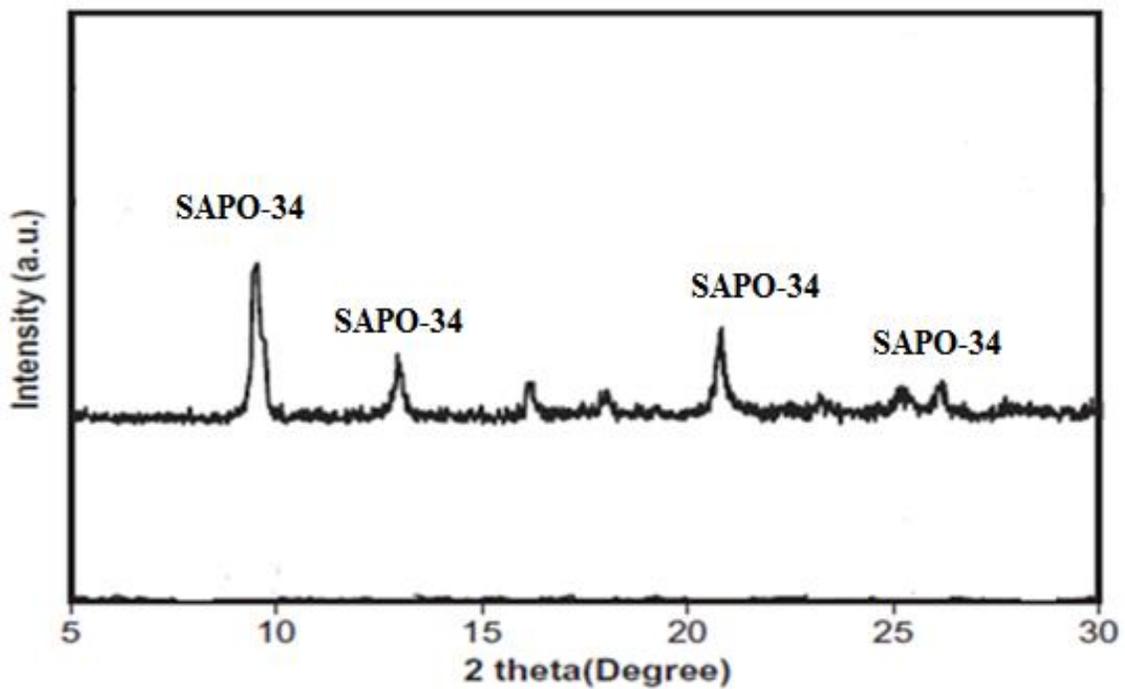


**Figure 4.3: XRD pattern for hydrothermally synthesized SAPO-34 (Askari & Halladj, 2011).**

### 4.2.2.   Scanning Electron Microscope – Crystal Size & Morphology

The SEM image of the Reference sample (S7) is shown in Figure 4.4. The image shows a slight amorphous phase however the morphology and crystallinity highly resemble that of SAPO-34 found in literature. Furthermore cubic crystals can be seen so the formation of SAPO-34 is confirmed. Referring to Figure 4.4, SAPO-34 cube type crystals having an average crystal size of 2 μm with homogeneous size distribution are formed after crystallization time of 24 h without ultrasonic pretreatment.

The SEM images of SAPO-34 samples pretreated with ultrasound are shown in Figure 4.5. The SEM images show that the morphology and crystal size of each sample were highly diverse from the SEM image expected for SAPO-34 when compared to the images obtained from the reference samples (S7) as well as those images obtained for SAPO-34 reported in the literature. There is little nucleation that can be observed from the images and the samples consist of a highly amorphous phase. Moreover, this is expected since the XRD patterns of the same samples showed peaks not equivalent to those of SAPO-34 samples. Hence it can be concluded that the resulting product is not crystalline SAPO-34, but amorphous materials. This observation, as has been aforementioned is attributed to a failure in the ultrasonic pretreatment of the sample.
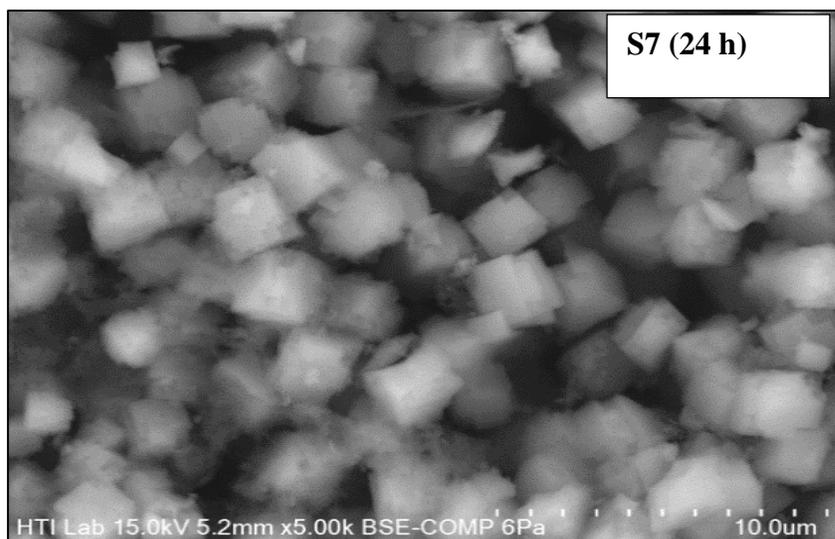


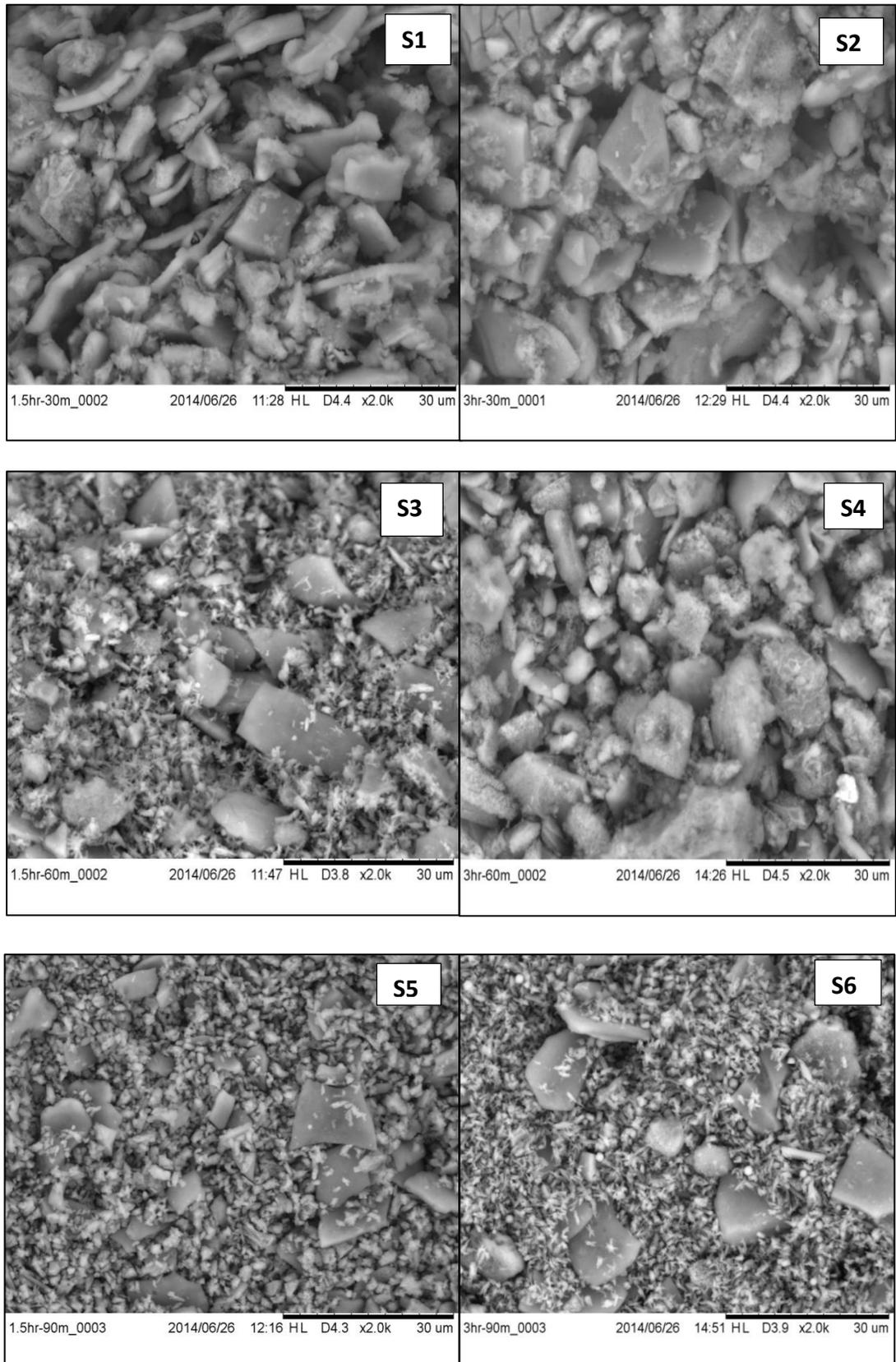**Figure 4.4: SEM image of Reference sample (S7)**

**Figure 4.5: SEM image of SAPO-34 samples with different ultrasonic & crystallization times**

## 4.3. CO$_2$ Adsorption Isotherm

Figure 4.5 shows the CO$_2$ adsorption isotherm of the Reference Sample (S7) and it reflects substantial adsorption. However when compared to the study done by Kim. et. al (2012) by applying the same temperature conditions (298 K) the adsorption isotherm shows lower adsorption capacity (can be seen in the comparison of Figure 4.6 & Figure 4.7). Nonetheless this can be explained by studying the Si/Al ratio of the precursor gel and its effects on the adsorption capacity of the resultant SAPO-34 powder. This relationship between Si/Al ratio and the CO$_2$ adsorption is as a result of the SAPO-34 structure, which is generally considered to be formed by substituting silicon for phosphorous in AlPO$_4$, which has a neutral framework and exhibits no ion exchange capacity. However, as reported by Li et al., (2007), when SAPO-34 membranes are ion exchanged after preparation, the CO$_2$/CH$_4$ selectivity increases. Thus by utilizing silicon instead of AlPO$_4$ a significant amount of ion exchange is achieved which affects selectivity. Therefore, since a SAPO-34 membrane has closely related properties to that of a SAPO-34 adsorbent; it can be assumed that the effects of the Si/Al ratio on the membrane will be similar in the adsorbent.

According to Li, et. Al (2007), CO$_2$ adsorption isotherms at 295 K (Figure 4.8) show that the amounts of CO$_2$ adsorbed significantly increase with decreasing Si content. Therefore, when SAPO-34 is prepared using low Si/Al gel molar ratio, better adsorption performance will be obtained compared with the SAPO-34 prepared using higher Si/Al gel molar ratio In this particular study, the Si/Al gel molar ratio used is 0.3. Thus when referring to Table 4.2, the first powder sample (P1) has a similar gel molar ratio in Al$_2$O3 and SiO$_2$ to the Reference Sample and the crystal ratio is 0.21. Since only this particular molar ratio has an effect on the adsorption, the other ratios can be neglected. Table 4.3 shows the different gel ratios which correspond to the adsorption isotherms (Figure 4.7). Ultimately when referring to Figure 4.8 it can be seen that the performance closely resembles the one obtained when analyzing the Reference sample, assuming the 3 K (298 K – 295 K) temperature difference in the adsorption operating conditions has insignificant effects and is therefore negligent. However the adsorption

amount found in Figure 4.8 is 10 times the amount obtained for the reference sample. Nonetheless when the results are compared to those of a study conducted by Padeyash, et. al (2013) (Figure 4.9) using a similar gel mole ratio as in this paper, the resulting adsorption isotherm is even more similar to that obtained from the adsorption analysis of Reference Sample (S7). However the adsorption performance ought to differ from experimental $CO_2$ ($N_2$) physisorption since separation of gas mixtures ($CO_2/CH_4$) largely depends on selectivity.

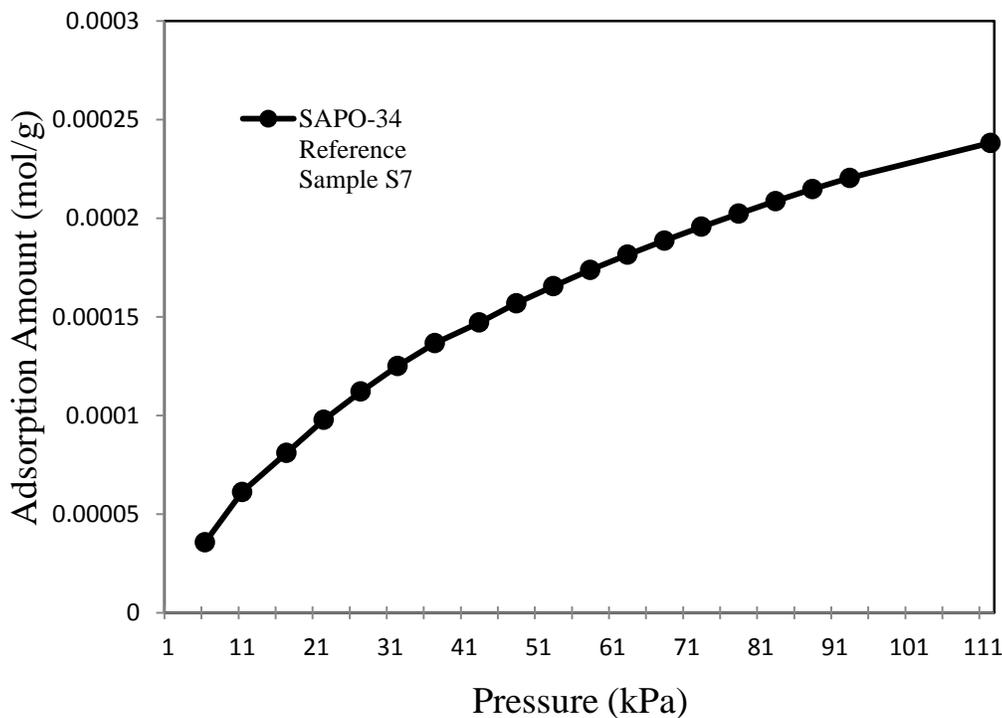## SAPO-34 Adsorption Isotherm (S7)



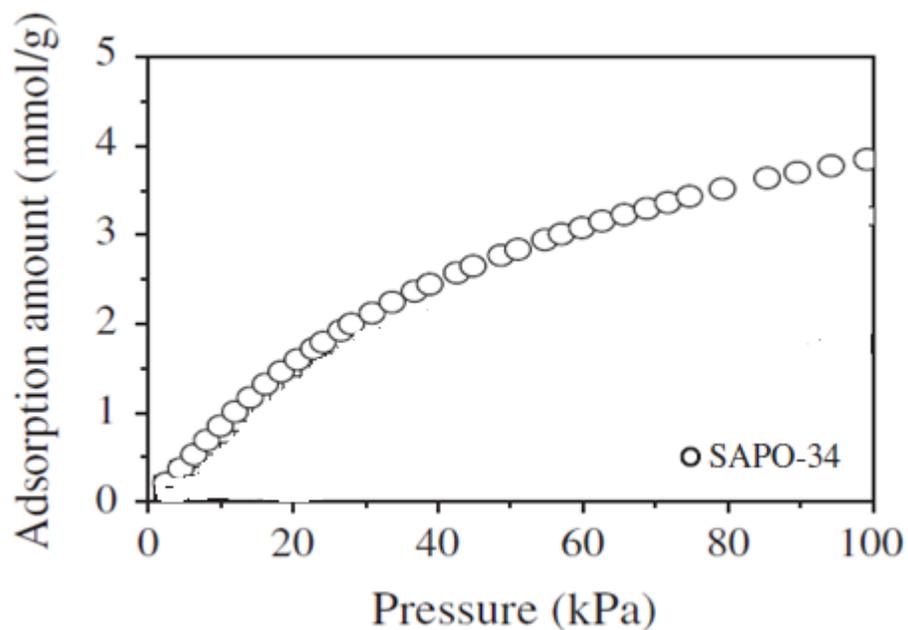**Figure 4.6: Adsorption Isotherm (298 K) for Reference Sample (SAPO-34)**

**Figure 4.7: Adsorption Isotherm (298 K) for SAPO-34 (Kim, et. al (2012) Mesaporous SAPO-34 with Amine Grafting for $CO_2$ capture, pg 518)**

**Table 4.2: Gel and Crystal Compositions for SAPO-34 powders ((Li, et. al (2007) SAPO-34 membranes for $CO_2/CH_4$ separations: Effect of Si/Al ratio, pg 313)**

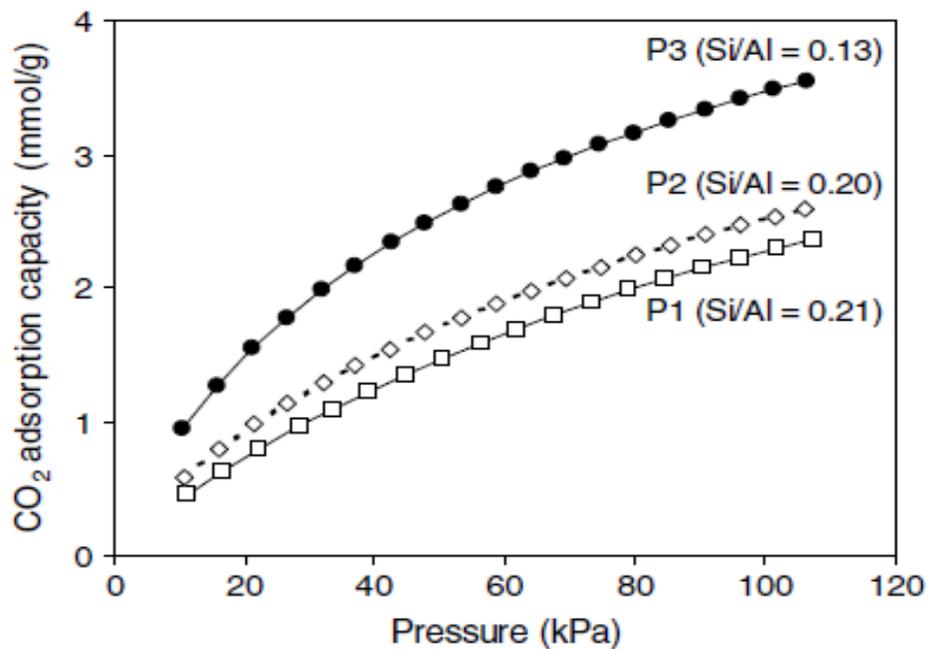| Powder | Gel mole ratio ($Al_2O_3:P_2O_5:SiO_2:$ TEAOH:$H_2O$) | Crystal Composition | Si/Al ratio | |
|---|---|---|---|---|
| | | | **Gel** | **Crystal** |
| **P1** | **1:1:0.6:1.2:55** | **$(Si_{0.11}Al_{0.51}P_{0.38})O_2$** | **0.3** | **0.21** |
| P2 | 1:1:0.4:1.2:55 | $(Si_{0.096}Al_{0.47}P_{0.43})O_2$ | 0.20 | 0.20 |
| P3 | 1:1:0.3:1.2:55 | $(Si_{0.061}Al_{0.48}P_{0.46})O_2$ | 0.15 | 0.13 |

**Figure 4.8: CO$_2$ Adsorption Isotherms (295 K) for SAPO-34 at various Si/Al crystal ratios (Li, et. al (2007) SAPO-34 membranes for CO$_2$/CH$_4$ separations: Effect of Si/Al ratio, pg 313)**
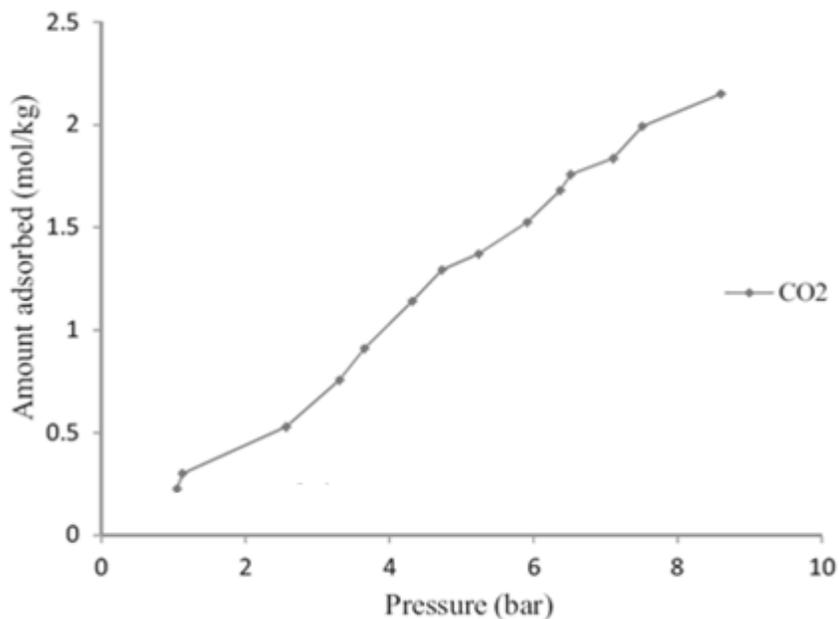


**Figure 4.9: CO$_2$ Adsorption Isotherms (300K) for SAPO-34 (Paydeyash, et. al (2013), pg 1338)**

# CHAPTER 5

## 5. CONCLUSION & RECOMMENDATIONS

### 5.1. Conclusion

In conclusion, SAPO-34 crystals were successfully synthesized via hydrothermal synthesis for 24 hr using TEAOH as structure directing agent. The particles were characterized by XRD and SEM. Both the XRD patterns and SEM images of the reference sample confirmed the successful synthesis of SAPO-34. The sonochemical-assisted hydrothermal synthesis method should lead to lower synthesis duration than 24 hours however, in this study SAPO-34 particles could not be obtained when pretreating with ultrasound. Since the molar quantities and gel-preparation procedure was similar for both hydrothermal synthesis and ultrasonic pretreatment, the failure could therefore be attributed to sonication and not sample preparation since successful results were obtained under hydrothermal synthesis.

Even though SAPO-34 could not be obtained under ultrasonic pretreatment, it was discovered that a few sonication parameters can affect the resulting product. The parameters such as frequency and power of ultrasonic waves, time of exposure to irradiation, solution temperature, type of solution, reaction vessel diameter, and the kind of noble gas used in the reaction environment; of which most were not investigated since they are beyond the scope of this study. Nevertheless the time of exposure to irradiation was investigated by decreasing the sonication time to 15 minutes and the results proved that the ultrasonic duration was not the predominant factor contributing to the failure.

The reference sample showed reasonable $CO_2$ adsorption even though literature shows a higher adsorption performance. $CO_2$ adsorption largely depends on the crystallinity and size of SAPO-34. The adsorption of SONO-SAPO-34 could not be studied since the synthesis could not be achieved. Therefore a study of the effect of ultrasound parameters should be done to investigate factors contributing to this failure.

**5.2. Errors & Recommendations**

### 5.2.1.   Experimental Errors

1. Human error is expected in the sample-preparation stage.

- Weight of reactants will differ from sample to sample but with insignificant affects.

- Stirring speed of the mixture, since no definite speed is determined.

2. The ultrasonic frequency is unknown and cannot be set which could also affect the resulting sample.

3. The temperature of the water bath is not consistent which could also affect sample preparation.

4. The ideal functioning of the physisorption analyzer might not be up to standard prior to the adsorption analysis.


### 5.2.2.   Recommendations

1. Obtaining information regarding the stirring power (rpm) that should be used in the mixing of reactants.

2. Utilize sonication equipment where the frequency is known and can be set or varied.

3. Availability of apparatus and equipment for synthesis & characterization should be maximized.

4. A study of aforementioned parameters.

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