SYNTHESIS AND CHARACTERISATION OF MICROPOROUS AlPO-5 MOLECULAR SIEVES TEMPLATED BY NOVEL IMIDAZOLIUM-BASED STRUCTURAL DIRECTING AGENTS

by

DAMIEN KHOO YIYUAN

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURES

Abbreviations/ symbols	**Descriptions**
AFI	Aluminophosphate-5
[bmim]OH	1-Butyl-3-methylimidazolium hydroxide
[dhpdm]OH	3-(2,3-Dihydroxylpropyl)-1,2-dimethylimidazolium hydroxide
[edmim]Br	1-Ethyl-2,3-dimethylimidazolium bromide
[emim]OH	1-Ethyl-3-methylimidazolium hydroxide
^{13}C NMR	Carbon-13 nuclear magnetic resonance
^{1}H NMR	Proton nuclear magnetic resonance
AlPO	Aluminophosphate
BET	Brunauer-Emmet-Teller
CP/MAS	Cross-polarization magic angle spinning
DMSO	Dimethyl sulphoxide
D_2O	Deuterium oxide
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
IL	Ionic liquid
MB	Methylene blue
NMR	Nuclear magnetic resonance
S_{BET}	Specific BET surface area
SDA	Structure-directing agent
$S_{micropore}$	Micropore surface area
TBAOH	Tetrabutylammonium hydroxide

Abbreviations/ symbols	Descriptions
TEA	Tetraethylamine
TEAOH	Tetraethylammonium hydroxide
TG/DTA	Thermogravimetric and differential thermal analysis
TPA	Tetrapropylamine
TPAOH	Tetrapropylammonium hydroxide
UV-Vis	Ultraviolet-visible
V_{total}	Total pore volume
XRD	X-ray diffraction

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SINTESIS DAN PENCIRIAN PENAPIS MOLEKUL MIKROLIANG AlPO-5 YANG DIACUANKAN OLEH AGEN PENGSTRUKTURAN BARU BERASASKAN IMIDAZOLIUM

ABSTRAK

Penapis molekul mikroliang aluminolfosfat (AlPO) telah disintesis melalui kaedah hidroterma dan kaedah ionoterma. Sintesis melalui kaedah hidroterma menggunakan 3-2(2,3-dimetilimidazolium hidroksida), [dhpdm]OH, sebagai suatu agen pengstrukturan (SDA) baru sementara kaedah ionoterma dijalankan dengan menggunakan 1-etil-2,3-dimetilimidazolium bromida, [edmim]Br, cecair ionik sebagai agen pengarah dan pelarut. Kedua-dua kaedah ini dikaji dengan mengoptimakan keadaan sintesis iaitu suhu dan tempoh sintesis dan kepekatan molar SDA, nisbah P_2O_5/Al_2O_3 dan H_2O dalam gel sintesis. Hasil kajian mendapati pelbagai morfologi hablur AlPO-5(AFI) yang memiliki topologi AFI diperoleh hasil daripada pengunaan keadaan sintesis yang berbeza. Kaedah sintesis hidroterma yang menggunakan [dhpdm]OH telah menghasilkan hablur yang berbentuk turus jalur, gumpalan prisma heksagon, setong heksagon dan rod silinder. Di samping itu, sintesis melalui kaedah ionoterma menggunakan [edmim]Br pula menghasilkan gumpalan hablur berbentuk kepingan heksagon dan hablur bijian yang berbentuk heksagon.

Kajian terhadap [dhpdm]OH dan [edmim]OH yang terkurung di dalam mikroliang AlPO-5 dijalankan dengan kaedah spektroskopi FT-IR dan analisis TG/DTA. Molekul [dhpdm]OH didapati berinteraksi kuat dengan rangka AlPO-5 dan menyebabkan molekul organik tersebut hanya dapat dikeluarkan daripada mikroliang AlPO-5 pada suhu yang lebih tinggi berbanding dengan [edmim]Br. Bagi

mengaplikasikan penapis molekul mikroliang AlPO-5, molekul organik di dalam mikroliang AlPO-5 dikeluarkan untuk menghasilkan bahan yang berliang. Molekul organik, [dhpdm]OH, dikeluarkan melalui kaedah pengkalsinan AlPO-5 pada suhu yang tinggi dan kaedah pengoksidaan Fenton. Kaedah kedua didapati lebih menjimatkan tenaga dan merupakan kaedah yang lebih berkesan untuk mengeluarkan molekul organik [dhpdm]OH.

Cubaan untuk menggunakan penapis molekul mikroliang AlPO-5 tersebut untuk menjerap pewarna larutan metilena biru telah dijalankan. Kajian tersebut mendapati bahawa AlPO-5 dapat menyingkirkan 16% metilena biru.

SYNTHESIS AND CHARACTERISATION OF MICROPOROUS AlPO-5 MOLECULAR SIEVES TEMPLATED BY NOVEL IMIDAZOLIUM-BASED STRUCTURAL DIRECTING AGENTS

ABSTRACT

Microporous aluminophosphate (AlPO) molecular sieves have been successfully crystallised under hydrothermal and ionothermal syntheses. The former approach engaged 3-(2,3-dihydroxypropyl)-1,2-dimethylimidazolium hydroxide, [dhpdm]OH, as a new structure-directing agent (SDA). The ionothermal synthesis was carried out by using 1-ethyl-2,3-dimethylimidazolium bromide, [edmim]Br ionic liquid, as both solvent and structure-directing agent. Both methods were investigated by optimising the synthesis conditions such as crystallisation time and temperature and molar concentrations of SDA, P_2O_5/Al_2O_3 ratio and H_2O in precursor gels. The results obtained showed different morphologies of well-defined AlPO-5 (AFI) crystals with AFI topology under different synthesis conditions. Hydrothermal treatment using [dhpdm]OH produced crystals with column-strip, aggregated hexagonal prism, hexagonal barrel and narrow cylindrical rod structures. On the other hand, ionothermal treatment using [edmim]Br ionic liquid yielded aggregated and spheroidal hexagonal thin-plate crystals.

Supramolecular study of [dhpdm]OH and [edmim]Br molecules in the AlPO-5 microporous materials are conducted using FT-IR spectroscopy and TG/DTA analysis. The [dhpdm]OH molecules were found to have very strong interaction with the AlPO-5 framework as these molecules could only be removed from the AlPO-5 micropores at a higher temperature compared to the case of [edmim]Br. In order for

the AlPO-5 to be used for further purposes, the SDA was removed from the pore cavity of the AlPO-5 framework to create microporous void space. Porous AlPO-5 in this study was prepared from a selected hydrothermal-treated AlPO-5 molecular sieve by calcination which required a high temperature and a combustion-free method known as Fenton-liked oxidation process. It was found that the more energy-saving Fenton-liked oxidation method was a more effective technique to remove [dhpdm]OH organic template.

The synthesised porous AlPO-5 molecular was used to remove dye pollutants. The synthesised AlPO-5 molecular sieves were able to remove 16% methylene blue dye solution.

CHAPTER 1

INTRODUCTION

1.1. General introduction

With the rapid advancement and development of nanotechnology, the emergence of nanosized materials in the market has received tremendous demands from industries of various fields. Addressing to the needs of today's market, extensive research has been mobilised to produce scalable and economical nanomaterials; one of which zeolitic materials. Zeolites and zeotypes molecular sieves are groups of microporous minerals which have been widely used in a variety of industrial applications such as catalysts in the oil refining and petrochemical industry, as ion-exchange beds in domestic and commercial water purification as well as in gas separation, as adsorbents in wastes treatment industry, and as hosts for drug delivery system in biochemical and biomedical industry. Over the decades, these aforementioned materials are produced hydrothermally and ionothermally (most recent approach), but with the lack of a full understanding to the formation mechanism for these materials. Though the recipes to prepare these materials are found empirically, it is still not possible to intentionally create new framework.

It is hypothesised that, the nucleation and growth process of these microporous materials depend on the solvent and structure-directing agent participated in the process. The flexibility and rigidity of the structure-directing agents influence the framework structures to which the zeolitic materials adapt. The confirmation of the organic template must be able to direct the precursors into forming a specific

framework and fits well in order to stabilise the achieved framework. Therefore, it is very crucial to find a suitable organic template to selectively-direct the crystallisation of the aforementioned microporous materials.

1.2. Objectives of study

This study was carried out to explore new alternative approaches to synthesis microporous AlPO materials through a self-prepared novel imidazolium-based SDA which contains a diol functional group. Thus, two organic SDAs were utilised in the synthesis of AlPO materials *via* the hydrothermal and ionothermal methods. This study was aimed to investigate the morphological versatility of AlPO materials through optimisation of different synthesis conditions such as heating time and concentrations of precursors and SDA. Conventional organic template removal method *via* calcination method requires a lot of energy, thus making it less environmental friendly. This study aimed to propose the microwave-assisted Fenton-liked oxidation process as a organic template removal method which requires less energy and the method is time-saving.

1.3. Scope of thesis

The research presented in this thesis aims to address the development in the synthesis field of crystalline microporous aluminophosphates (AlPO) materials through the interactions between a self-prepared novel imidazolium-based structure-directing agent and precursors of microporous AlPOs. As it is more common for organic molecules such as amines (tetraethylamine, tetrapropylamine) and quaternary amines (tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide) to be used as structure-directing

agent (SDA) in the hydrothermal synthesis of AlPOs, efforts to produce other alternatives of SDA are also emphasised.

Following the success of imidazoles ([emim]OH and [bmim]OH) in crystallising AlPOs, this research focused on the use of self-designed imidazolium based organic molecule, 3-(2,3-dihydroxylpropyl)-1,2-dimethylimidazolium hydroxide, ([dhpdm]OH), in preparing AlPO materials. At this juncture, different chemical compositions are optimised to hydrothermally synthesise AlPO have been used to investigate the effects of different synthesis parameters such as prolonged heating time, concentration of precursors and SDA on the frameworks structures and morphologies of the crystallised materials. Through an evaluation of the preparation techniques, insight is provided into the candidacy of [dhpdm]OH to participate as a structure- directing agent in the development of versatile AlPO morphologies. This thesis also presented a "greener" approach known as the ionothermal synthesis in the presence of ionic liquid, 1-ethyl-2,3-dimethylimidazolium bromide ([edmim]Br) to crystallise AlPO molecular sieves. Similarly, different synthesis parameters (such as prolonged heating time, concentration of precursors and SDA) were found to have large influences on the frameworks structure and morphologies of the crystallised materials.

Following this introductory chapter, Chapter 2 gives a detailed background on the concepts involving zeolitic materials, structure-directing agents and ionic liquids, hydrothermal and ionothermal syntheses, framework structures and morphologies of crystallised materials. Chapter 3 presents the experimental methodology which includes the preparation of structure-directing agents and synthesis of AlPO materials (both hydrothermal and ionothermal). The characterisation techniques for

organic templates and AlPO materials such as X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), thermogravimetry and differential thermal analysis (TG/DTA), Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (^{27}Al and ^{31}P MAS NMR) and nitrogen sorption isotherm analysis are also described in this chapter.

Further to this, the experimental results and discussion are presented in detail in Chapter 4. The findings obtained through ionothermal synthesis using[edmim]Br and hydrothermal synthesis using [dhpdm]OH are discussed at in this chapter. More detailed descriptions which involve the influences of synthesis parameters such as heating time, concentration of precursors and SDA on the crystallisation of AlPOs are also provided in this chapter. Subsequently, two template removal techniques, which are, the conventional calcination method in a muffle furnace, and the microwave-assisted Fenton-liked oxidation process are presented in the later part of Chapter 4. The similarities and differences between these two methods in terms of effectiveness and efficiency in removing the [dhpdm]OH molecules from the micropores of synthesised AlPO are also elaborated. Also, an attempt to use these porous materials in removing methylene blue pollutants is presented in the later part of this chapter.

At the end of this thesis, in Chapter 5, the findings from this study are summarised and the recommendations to future work are proposed in hope to provide a broader insight and prospect in developing the field of microporous zeolitic materials.

CHAPTER 2

LITERATURE REVIEW

2.1. Porous materials

Porous material is basically defined as a frame or matrix permeated by an interconnected network of pores filled with a fluid[1]. Generally, there are two types of pores; open pores which connect to the external surface of the material and closed pores which are isolated from the external surface area[2]. These materials with pore sizes near molecular dimensions, such as zeolite and zeotype (aluminophosphate) materials, have became an important class of inorganic crystalline materials with emerging demands of applications[3]. Open porous materials are more favourable amongst catalysis industry and bioreactors while materials with closed pores are commonly used for thermal insulation and low density structural component. Figure 2.1 shows the various classes of nanoporous materials.

According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials are classified according to their pore size[4]. Besides that, porous materials can also be classified based on their framework building blocks such as all-inorganic, hybrid organic-inorganic and all-organic porous polymers and carbonaceous materials[2].

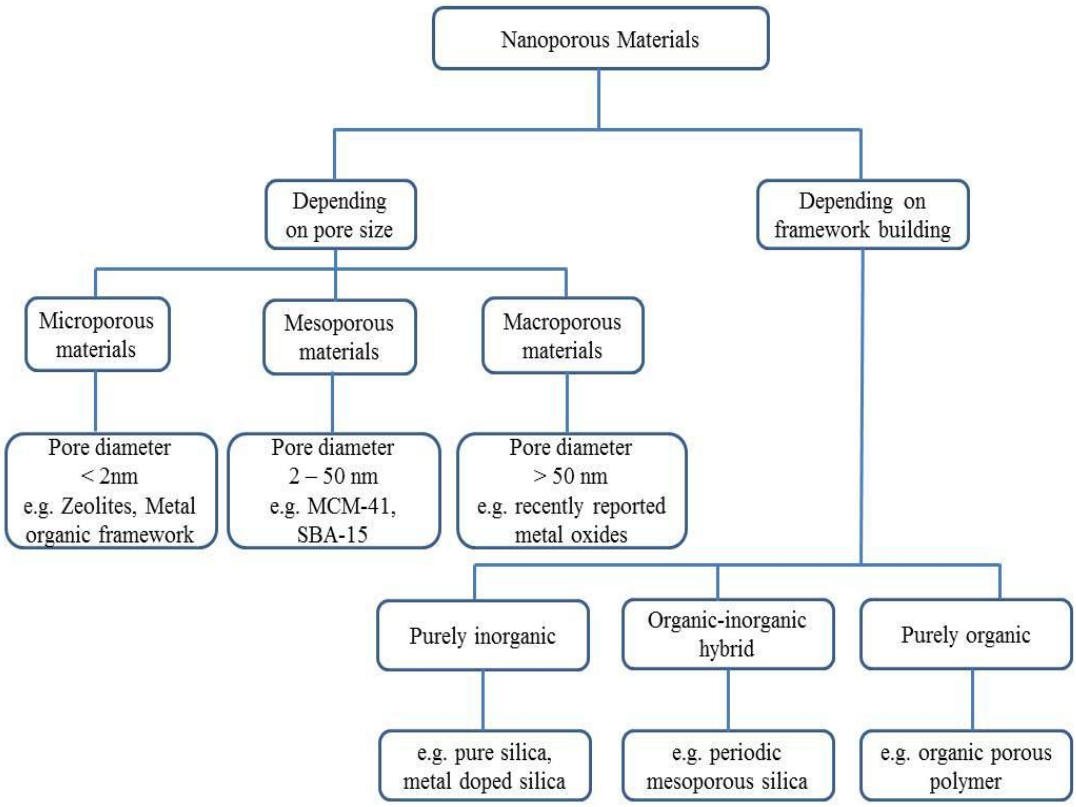


Figure 2.1. Schematic representation of the classification of nanoporous materials[2].

2.1.1. Microporous materials

Microporous materials which possess a regular network of channels and pores less than about 2 nm are the materials of interest in this thesis. These materials have very low densities and high surface areas which allow them to be applied in adsorption of gases and other small molecules[5]. As these molecular sieves exhibit shape selectivity in which the pores allow certain molecular shapes, sizes or configurations to enter the system, they are widely used in the fields of heterogeneous catalysis and separation[6, 7]. It is known that valences of elements which are stable in a tetrahedral coordination can be located in a microporous framework. This phenomenon is due to the geometric constraints of their bond

lengths and angles[8]. Currently, the most extensively studied groups of microporous materials are the aluminosilicate zeolite and aluminophosphate zeotype materials.

2.2. Zeolite and aluminophosphate (AlPO) materials

2.2.1. Zeolite materials

Derived from the Greek words “zeo” (boil) and “lithos” (stones), zeolite was first discovered about 250 years ago by Alex Fredrik Crönstedt, a Swedish mineralogist, who observed large amount of steam by heating a mineral[9]. The material was later reported to be stilbite[10]. Since then, the science of mineralogy and classification of zeolite minerals have been revolutionised. It was not until 1862 when St Claire Deville claimed to have produced levynite, the first man-made zeolite[11].

However, it was Richard Barrer who reported the first reliable natural zeolite synthesis in the 1940s, earning him the title “The Father of Modern Zeolite Science”[12]. Barrer pioneered a wide range of work pertaining to the microporous sciences: synthesis gel chemistry, diffusion in solid systems, molecular sieves adsorption, etc.[12]. Initially, he focused on investigating the conversion of known mineral phases under the action of strong salt at fairly high temperature (170 – 270 °C) in which two species which exhibit isostructural variants with unique characteristics were obtained[13]. These materials were found to have the KFI structure and led to the synthesis of ZK-5 zeolite[14]. Barrer introduced organic constituents such as alkylamines and alkylammonium salts as space filling agents, structure directing agents and templating agents in the laboratory synthesis of zeolites[15, 16]. Through this finding, it is now possible to create new zeolite frameworks that do not exist in nature.

Generally, zeolites are defined as microporous crystalline aluminosilicates which are constructed from AlO_4 and SiO_4 where Al and Si are tetrahedral atoms[17]. These atoms form cages and channels of molecular sieves ranging from about 0.2-1.5 nm in diameter (Figure 2.2a)[10]. Aluminosilicate zeolites have negatively charged framework due to the charge deficiency from Al^{3+} in contrast to Si^{4+} found in pure silica zeolites. Therefore, charge compensating cations such as H^+ are required, resulting in the formation of Bronsted acid site on a neighbouring oxygen atom[17].

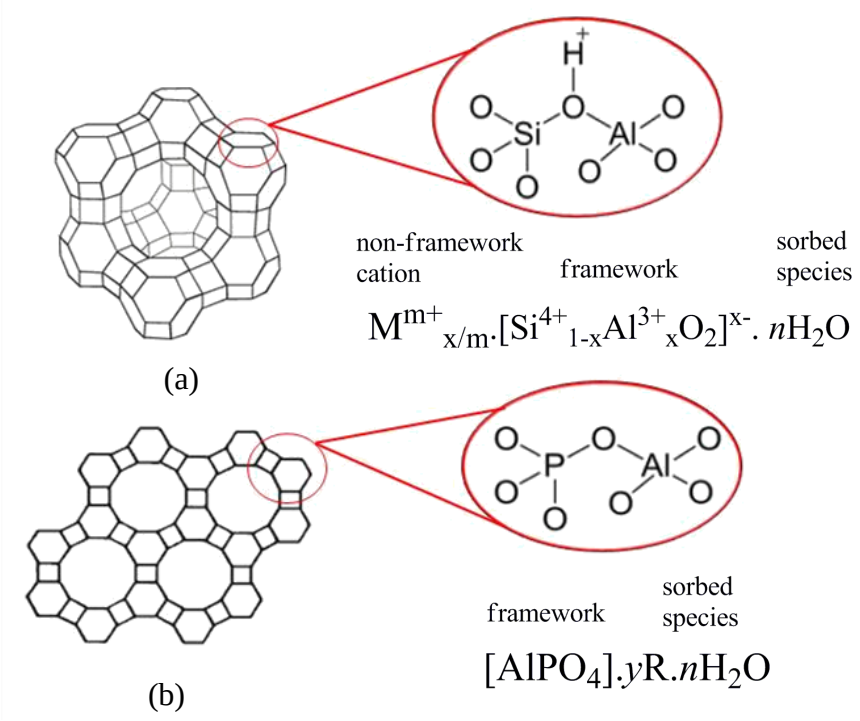


Figure 2.2. (a) Zeolite framework with alternating AlO_4^- and SiO_4 tetrahedra and (b) AlPO framework with alternating AlO_4^- and PO_4^+ tetrahedra. R denotes the organic SDA molecule occluded in the pores of AlPO material.

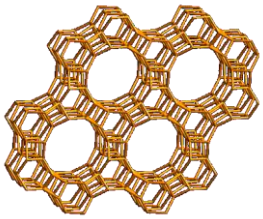
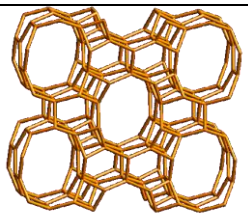
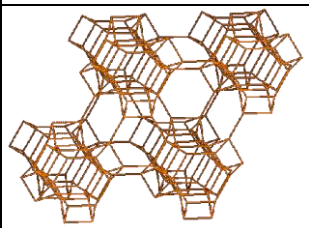
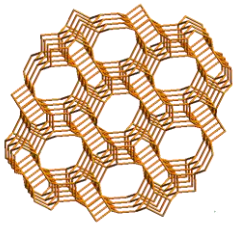
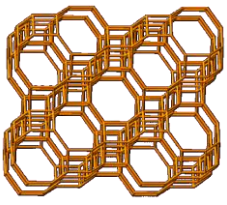
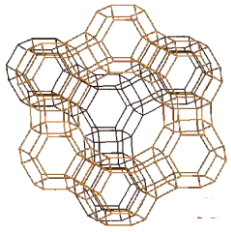
2.2.2. AlPO materials

Following the foundation laid by Barrer et al., the next decades witnessed many significant developments extended beyond aluminosilicates. It was in 1982 when Wilson et al. from Union Carbide Corporation discovered microporous crystalline aluminophosphate materials (AlPO), a new family of zeolite-related (zeotype) materials[18]. Elemental substitution of silicon for phosphorus is, ignoring topology, what distinguishes a zeolite from an AlPO. Microporous AlPO materials are not found in nature and their synthesis requires organic template such as organic amine or quaternary ammonium salts which act as structure-directing agents.

The connectivity in AlPOs network is restricted to alternating sequence of Al and P tetrahedral with TO_4 (with T = Al or P) corner-sharing units which creates cavities and channels of various diameters (Figure 2.2b)[19]. In this manner, the charge neutrality of the AlPO network is ensured as well as prevents the formation of Al-O-Al linkages which are unstable arrangements due to charge repulsion, according to the Lowenstein's rule[20]. Apart from that, P-O-P bridges which are energetically unfavourable, is also not observed in crystalline AlPO[21]. Conceptually, a neutral AlPO framework can be considered to be derived from a neutral silica zeolite by replacement of two Si^{4+} cations with one Al^{3+} and one P^{5+} cation[22].

Today, the AlPO family comprises of more than 50 structures, including 18 analogues of natural or synthetic zeolites[23]. Some of the major structures of AlPO molecular sieves crystallised with different pore sizes are listed in Table 2.1.

Table 2.1. Structure frameworks and pore sizes of several AlPO materials[23].

AlPO-*n*	**Structure type**	**Pore size (Å)**	**Framework**
n = 5	AFI	7.3	
n = 11	AEL	6.0	
n = 17	ERI	4.3	
n = 31	ATO	7.0	
n = 34	CHA	4.3	
n = 37	FAU	8.0	

2.2.3. Comparison between zeolite and AlPO materials

Despite zeolites and aluminophosphates are somewhat alike, the chemistry behind the formation of these materials is not similar. Generally, zeolites are formed mostly in alkaline medium (pH 8 ~ 14), where silanol groups may be deprotonated. Synthesis gels with low pH values may lead to the formation of dense phases of aluminosilicates. However, this condition of low acidity or neutral is favoured in the synthesis of aluminophosphates. The synthesis is usually carried out with pH values ranging from 6 to 8[24].

The source of aluminium for both zeolite and AlPO tends to be hydroxides such as aluminium alkoxide or pseudoboehmite. While AlPO relies on orthophosphoric acid as a source of phosphorus, zeolite uses various forms of silica such as fumed silica and colloidal silica. Hence, the precursor gel of AlPO tends to be around neutral and the precursor gel of zeolite is more basic. In addition, the reaction pH is also determined by the template used such as tertiary alkylamine and quaternary ammonium species.

Overall, the framework of zeolite is negatively charged, making it ready for acid catalysis. On the other hand, AlPO framework is neutrally charged and needs to be further modified to display framework catalytic ability by substituting metals such as SAPO and CrAPO[25]. Several other differences between these two materials are summarised in Table 2.2.

Table 2.2. Comparison of properties between AlPO and zeolite molecular sieves.

AlPO	Zeolite
Precursor gel contains aluminophosphate.	Precursor gel contains aluminosilicate.
Basic framework elements are Al and P (Figure 2.2b).	Basic framework elements are Si and Al (Figure 2.2a).
Phosphates degrade at low pH to simple structures. The free energy for the hydrolysis of P-O-P bond is relatively favourable.	Silicates and aluminates give a distribution of various sized anions in solution with tendency to larger structures as pH is lowered.
Avoidance of Al-O-Al and P-O-P bonds (Lowenstein's rule) reduces the structural formation to even numbered rings in an alternating form.	Existence of Si-O-Si bonds in aluminosilicate structures make possible formation of even and odd number silicate rings. However, Al-O-Al bond is avoided.

2.2.4. Nomenclature, structure building unit (SBU) and framework structure of AlPO materials

Similar to zeolites, members of the AlPO family are distinguished and named according to protocols set by the Commission of the International Zeolite Association (IZA)[23]. Each AlPO material is designated AlPO-*n* where *n* is a number indicating a specific structure, followed by a three letter framework code. For example, AlPO-5 is assigned the framework code AFI (**A**lPO **Fi**ve), ATS (**A**lPO **T**hirty-**S**ix) for AlPO-36 and AEL (**A**lPO **El**even) for AlPO-11. This concept of naming is applied to all aluminophosphates, except those having zeolite analogue such as AlPO-34 (CHA named after zeolite chabazite), AlPO-37 (FAU named after zeolite faujasite) and AlPO-43 (GIS named after zeolite gismondine). As of 2013, there are 206 framework type codes with the major structures and with some of the respective framework of AlPO materials listed in Table 2.1[23].

An AlPO structure can be described in term of building unit (Figure 2.3). Its primary building units (PBU) are composed of tetrahedral TO_4 units (T = Al, P). Each T atom can be described as 4-connected vertices (each T atom is connected to four oxygen atoms) and each oxygen atom is connected to two T atoms. Therefore, the structure of AlPOs can be described as a (4,2)-connected net. The overall AlPO framework structure is based on the secondary building units (SBU) as shown in Figure 2.3[26]. These SBUs are always non-chiral, with the oxygen atoms omitted and represented by the presence of a single straight line between two T atoms (represented by a circle) as illustrated in Figure 2.3. However, the framework composition is restricted to Al/P = 1.

The nanocrystalline material of interest in this thesis is the large pore AlPO-5 (AFI) framework as shown in Figure 2.4. Typically AFI framework is described as a one-dimensional channel consisting of a 12-ring pore opening with a diameter of 7.3 Å[27]. The hexagonal structure consists of *P6cc* space group. AlPO-5 (AFI) molecular sieve is among the most extensively studied member of the AlPOs due to their use in catalysis, separation, non-linear optics[28, 29]. Up to date, well-define AFI crystals having various morphologies have been synthesised. For example, Yates et al.[30] reported the synthesis of rod-like AlPO-5 using microemulsions. Additionally, plate-like hexagonal AlPO-5 has been reported by Kornatowski et al.[31] while nanosized AlPO-5 has also been reported by Mintova et al.[32]. The emergence of various morphologies of AlPO-5 crystals is due to the effect of water-soluble organic molecules (commonly referred to as structure-directing agent) under different synthesis conditions.

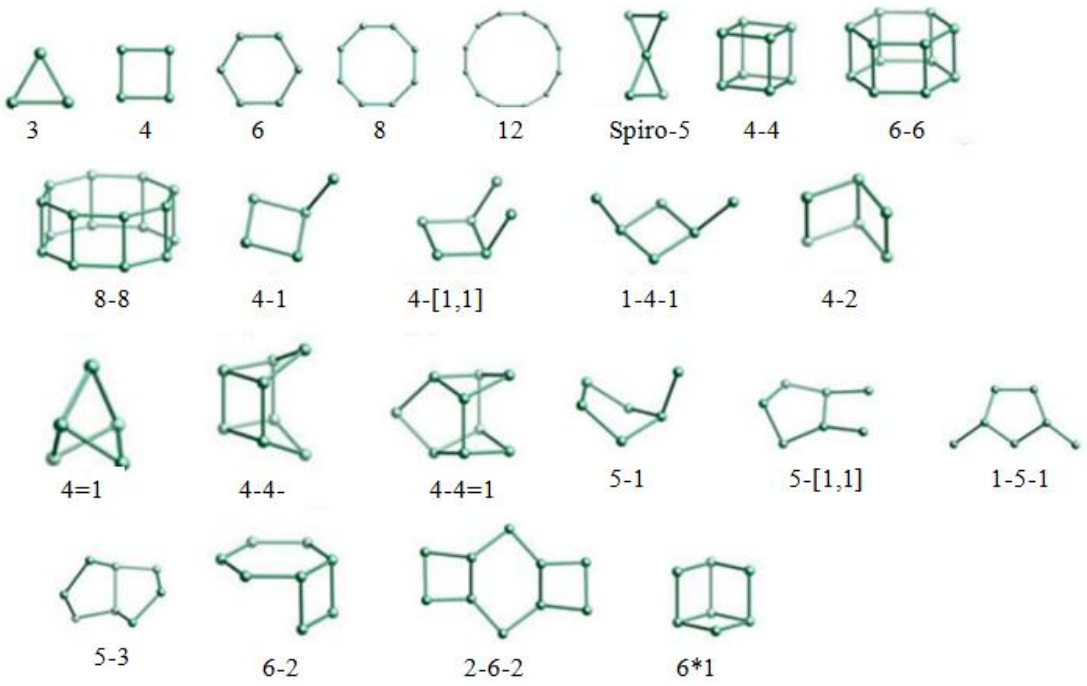


Figure 2.3. Secondary building units (SBUs) found in nanoporous materials which contain TO_4 tetrahedra[13].

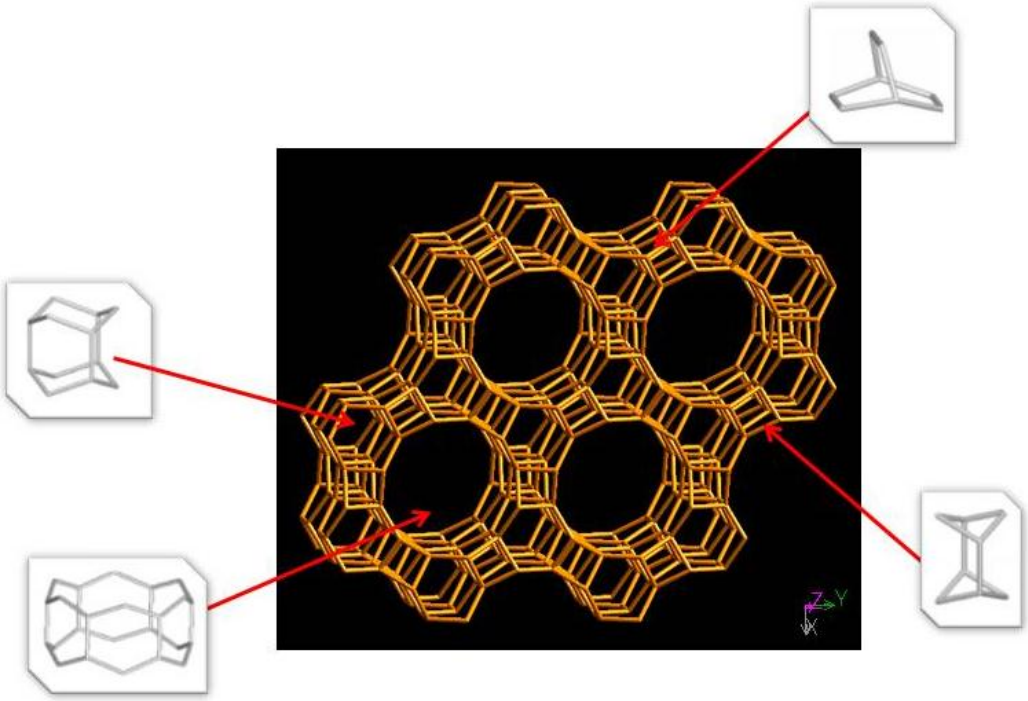


Figure 2.4. Illustration of AlPO-5 structure with AFI framework formed by arrangement of separate cages[21].

2.3. Hydrothermal synthesis of AlPO materials

Hydrothermal synthesis remains the most common approach in the synthesis of AlPO materials. In this approach, amorphous reactants containing aluminium such as aluminium isopropoxide or aluminium hydroxide hydrate and phosphorus such as orthophosphoric acid are mixed together with water as the solvent and an organic template solution which acts as structure-directing agent in a weakly acidic or weakly alkaline medium ranging from pH 4 to 10. Generally, the chemical composition of a typical reactant gel in the hydrothermal synthesis of AlPOs is expressed in the following form: $1.0Al_2O_3$: xP_2O_5: yR: zH_2O, where R is the type organic SDA and x, y and z represent the molar ratios[22]. The resulted gel mixture is then heated in a sealed autoclave at temperatures between 150 to 250 °C under autogeneous pressure for a specific period of time which could range from hours to days. Subsequently, the amorphous material in the gel mixture will undergo nucleation and crystallisation process (mechanism as described in Section 2.3.2) before the AlPOs crystals are completely formed. The crystals are recovered by filtration for micronsized crystals or centrifugation for nanosized materials, washed thoroughly with water and dried. In order to produce porous AlPOs, the organic cations occluded within the framework are removed. Several methods are proposed for the removal and they are described in Section 2.5.

The type of structure formed by the AlPOs synthesis is dependent on the control of reaction variables such as reactant gel composition and type, time, temperature, pressure, pH, type of organic SDA and history-dependent factors such as ageing, stirring, nature of mixing and order of mixing. It is evidently that changing the molar ratios of reactants used will affect the nature of the final phase formed. Hence, it is difficult to evaluate the effect of varying any one of them as

these variables are dependent of one another. Generally, changing the ratio and content of Al_2O_3 and P_2O_5 influences the product yield, framework composition and the type of structure formed. Apart from that, the water and hydroxide anion are also considered as contributing factors as they act as gel transport medium. Thus, increasing these concentrations can increase the nucleation and crystallisation rates. The degree of hydrolysis in the system is also determined by water and hydroxide concentrations. For instance, an AlPO material with a chain similar to JDF structure was formed with triethylamine as the organic template, but, increase of water concentrations favoured the formation of AlPO-5 and AlPO-15[33]. In addition, water and hydroxide concentrations also influence the pH of the reactant gel which is essential to successful crystallisation of a molecular sieve, given that aluminophosphates form in weakly acidic or weakly alkaline.

Molecular sieves are usually synthesised at temperatures between 150 to 250 °C under autogeneous pressure. Under these conditions, water has an extremely effective solvating ability which allows for the dissolution and mixing of the solid reagents to form an in homogenous gel, followed by the formation of nucleation centres which subsequently grow to form the crystalline material. Therefore, the synthesis temperature, which affects the self-generated pressure of water, directly influences the crystallisation and structure of the molecular sieve formed[34]. Figure 2.5 shows a typical illustration of the hydrothermal synthesis of AlPO materials.

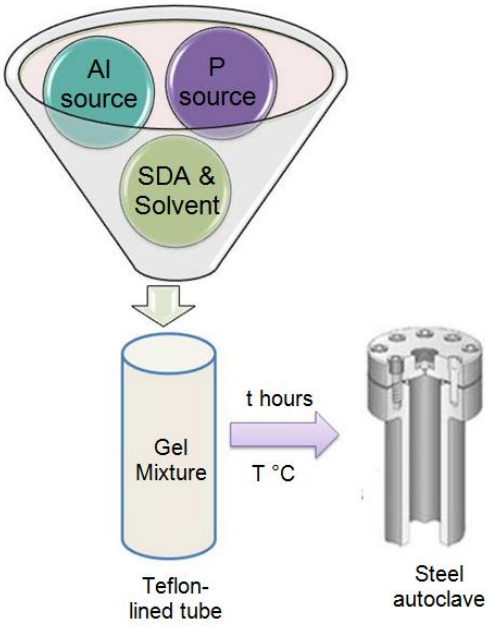


Figure 2.5. Schematic illustration of the hydrothermal synthesis of AlPO materials.

2.3.1. Structure-directing agent

Structural directing agent (SDA) is an organic additive to facilitate the synthesis of microporous materials such as zeolites and AlPOs[35]. Also known as templates, SDA are organic bases which are included in an inorganic gel medium in which the microporous framework condenses around them. Basically, organic component acts as (a) space filling agents whereby space filling refers to the organic molecules occupying the voids to help stabilise the structure against solvent water which could prevent the growing of the framework, (b) structure directing agent which implies that the SDA is responsible for one unique framework structure, (c) "true" template which occurs when the material adopts the same geometric and electronic configuration as the organic guest[36, 37]. The final structure of the framework reflects, to differing degrees, the shape of the template[38]. Hence, SDA

is a major factor in the crystallisation of molecular sieves as it dictates the size and shape of the pores in these materials.

The structure-directing effect is not as specific as one might expect. In fact, one molecule can direct the crystallisation of several different microporous structures depending on the synthesis conditions. Similarly, one microporous structure can be formed by different SDAs. For example, AlPO-5, which shows the lowest template selectivity, can be formed by at least 20 different organic molecules. Amongst the common SDAs which have successfully produced well-defined AlPO-5 crystals are amines (tetraethylamine, tetrapropylamine), quaternary amines (tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide) and imidazolium (1-ethyl-2-methylimidazolium hydroxide, 1-butyl-2-methylimidazolium hydroxide)[27, 39, 40]. Despite having the same AFI topology, these materials may possess different structural morphologies such as barrel, rod, spheroidal, hexagonal prism and column shape[27, 31, 40]. It is suggested that the type of SDAs used influences the outcome of the crystallisation[40, 41].

Nevertheless, the nature of the relationship between the structure-directing agent and the AlPO crystalline phase formed is not yet fully understood. It is fundamentally known that the organic supramolecules direct the AlPO framework structures through the organization of the inorganic tetrahedral units into a particular topology, creating the initial blocks for further crystallisation[40]. Therefore, it is still not possible to intentionally synthesise a desired structure of AlPO.

Conceptually, the actual organic-AlPO structure is the outcome of synergistic interactions between the organic cations and the inorganic components that influence the reaction pathway leading to the final outcome of the synthesis[42]. It is believed that the organic SDA influences the synthetic pathways of molecular sieves through

their interactions with the inorganic framework *via* non-covalent bonds. Therefore a suitable candidate of SDA for crystallisation of AlPO molecular sieve should fits several conditions. Among the conditions are, SDA molecules should be stabilised inside the inorganic crystalline phase *via* as many van der Waals interactions as possible. When there is a good geometrical fit in the organic-inorganic composites by van der Waals contacts, the change in the shape of the organic molecules results in different AlPO phases.

Apart from that, it is also reported that SDA should have intermediate hydrophobicity/hydrophilicity when the molecular sieve is synthesised under hydrothermal conditions[43]. Davis et al. proposed a mechanism of assembly involving inorganic-organic composite species whose formation is initiated by overlap of hydrophobic hydration spheres of both the organic and inorganic components with subsequent release of ordered water to establish intermolecular van der Waals interactions[44]. The size and rigidity of SDA also play an important role in providing sufficient room within a particular cage or pore for crystallisation. In terms of flexibility and rigidity, the SDA needs to adopt an optimum conformation in order to be ideally tight to fit in a specific molecular sieve pore. This will then allow long-range stacking sequences for layers of the crystal to grow[42]. In term of size, a bulky molecule of SDA often direct the formation of AlPOs with larger pores due to steric forces[45].

Additionally, the SDA should endure the synthesis conditions, for instance, mild basicity or acidity and high temperature during AlPO synthesis, because decomposed SDA can easily affect the structure of the synthesised product[45].

In short, organic species are found to play a key role during the synthesis of AlPO molecular sieve materials through:

- ❖ Encouraging the formation of nanoporous materials
- ❖ Accessing more metastable states by stabilising the voids of the molecular sieve materials
- ❖ Modifying the Al/P ratio and Al distribution in the gel and in the final product during the formation of AlPO materials
- ❖ Increasing the nucleation and modifying the crystal growth rates.

As such, the study of the template-framework interaction also provides an insight in controlling and synthesising AlPO-5 molecular sieves with different crystal sizes and morphologies[41].

2.3.2. Mechanism of crystallisation

The fundamental mechanism of AlPO crystallisation is considered to involve three stages; pre-nucleation, followed by nucleation and finally crystal growth as shown in Figure 2.6.

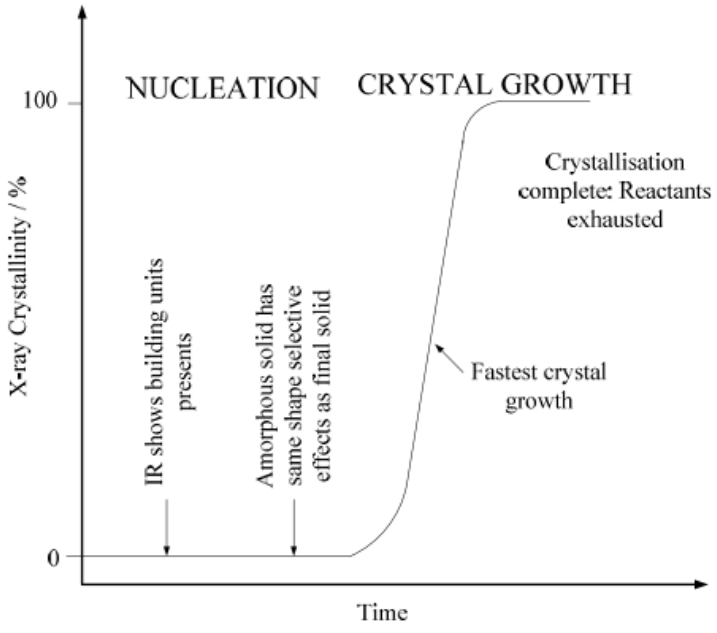


Figure 2.6. Process of crystal growth in solution[22].

The initial pre-nucleation stage involves the dissolution and thorough mixing of the starting reagents (Al and P precursors and SDA) by a solvent (usually water) to form an amorphous aluminophosphate layer. The precursor gel is then heated in an oven under autogeneous pressure for a specific period of induction time. During nucleation process, the dissolved particles aggregate and form a nuclei which serves as the crystallisation centre. Following the rapid nucleation process, the nuclei grows larger with time and forms the molecular sieve structures.

Based on this concept, several proposals regarding the crystallisation of AlPO molecular sieves had been surfaced. It has been suggested that direct solid-state transformation occurs to give the final crystalline product. In an alternative approach, Ferey et al. proposed that complete dissolution of the aluminophosphate layer occurs to produce small solution phase building units, which subsequently condensed to form the final crystalline product[46]. Ozin et al. have proposed a model for the formation of AlPO in which two- and three-dimensional structures are formed *via* hydrolysis and condensation of an initial chain structure which forms first in solution[47].

More recently, Grandjean et al. proposed a three stages, one dimensional crystallisation mechanism for hydrothermal synthesis of CoAPO-5 molecular sieves (one of the AlPO framework)[48]. According to Grandjean, the first step of AlPO formation is an initial reaction between Al and P units forming a primary amorphous phase. Moving on to the next step, a progressive condensation of linear Al-O-P chains forms a poorly ordered structure separated by template molecules up to 155 °C. Finally, there is a rapid internal reorganization of the AlPO network leading to crystallisation of the crystal structure. The crystallisation mechanism is illustrated in Figure 2.7.

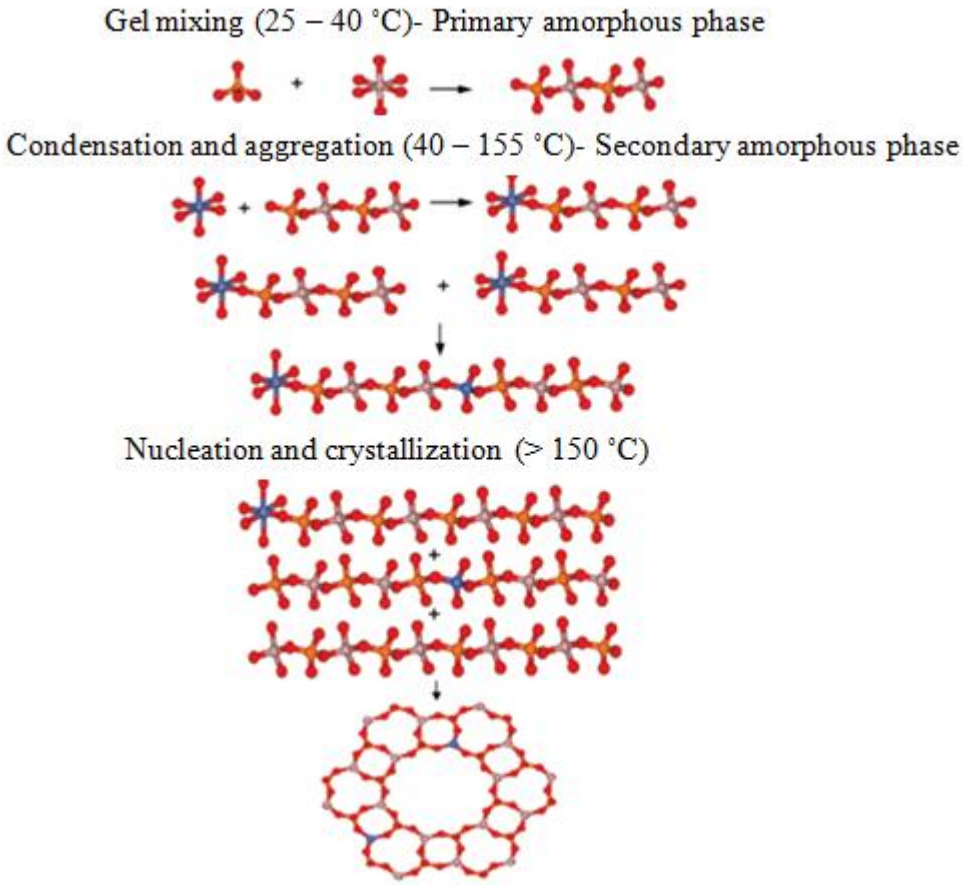


Figure 2.7. Schematic representation of the three-stage AlPO-5 crystallisation[43].

Even though the exact mechanism for the formation of zeolite and AlPO molecular sieve materials still remains unclear due to the complexity of the reactions, two other mechanisms are proposed, namely, (i) the solution-mediated transport mechanism, and (ii) the solid hydrogel transformation mechanism. These two mechanisms differ by the presence of liquid component during the crystallisation process.

2.3.2.1. Solution-mediated transport mechanism

First reported by Kerr et al., the solution-mediated transport mechanism (Figure 2.8a) involves the dissolution of the aluminosilicate/aluminophosphate gel in the solution phase to form active silicate/phosphate and aluminate ionic species[49]. These ionic species are then transported to the nucleation sites *via* solution-mediated diffusion in which re-crystallisation occur in the solution to form the structure of the molecular sieve material. Subsequently, crystal growth takes place[50]. A convincing study on this observation was reported by Ueda et al. in which zeolites Y and P were synthesised from a clear solution in the absence of solid phase hydrogel[51]. Similarly, Testa et al. managed to crystallise ZSM-5 and ZSM-11 from clear solution[52].

2.3.2.2. Solid hydrogel transformation mechanism

The solid hydrogel transformation mechanism (Figure 2.8b) which was introduced by Breck and Flanigen does not involve the dissolution of the solid gel or the liquid component[17]. This mechanism works in a way that re-organisation of the framework of solid phase aluminosilicate/aluminophosphate hydrogel formed from the condensation of silicate/phosphate and aluminate ions occurs in the early stages of crystallisation. An example of zeolites synthesised *via* this mechanism is the synthesis of ZSM-5 and ZSM-35 by Xu et al.[53]. Xu reported that an amorphous aluminosilicate gel was dehydrated at 550 °C before being treated with liquid triethylamine and ethylenediamine at 160 °C in the absence of water. Since there is no liquid phase silicate/aluminate species present, it was evidently shown that a solid phase transformation had occurred.