

**AFI MOLECULAR SIEVES FORMATION
TEMPLATED BY IMIDAZOLIUM-BASED IONIC
LIQUIDS UNDER IONOTHERMAL AND
HYDROTHERMAL CONDITIONS**

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UNIVERSITI SAINS MALAYSIA

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by

GHOY JIA PEI

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURES

AlPO	Aluminophosphate
AlPO-5	Aluminophosphate number 5
BET	Brunauer-Emmet-Teller
[bzm]Cl	1-Benzyl-2,3-dimethylimidazolium chloride
[bzm]OH	1-Benzyl-2,3-dimethylimidazolium hydroxide
[dhm]OH	3-(2,3-Dihydroxylpropyl)-1,2-dimethylimidazolium hydroxide
D ₂ O	Deuterium oxide
FeAPO	Ferroaluminophosphate
FeAlPO-5	Ferroaluminophosphate number 5
FeNKX-2	Ferroaluminophosphate number 2
FTIR	Fourier transform infrared
¹ H NMR	Proton nuclear magnetic resonance
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IL	Ionic liquid
IUPAC	International Union of Pure and Applied Chemistry
IZA	International Zeolite Association
MeAPO	Metalloaluminophosphate

NKX-2	Aluminophosphate number 2
[pm]Br	1-Propyl-2,3-dimethylimidazolium bromide
[pm]OH	1-Propyl-2,3-dimethylimidazolium hydroxide
SBU	Secondary building units
S_{BET}	Specific BET surface area
SDA	Structure-directing agent
SEM	Scanning electron microscopy
$S_{\text{micropore}}$	Micropore surface area
TPAOH	Tetrapropylammonium hydroxide
TPAF	Tetrapropylammonium fluoride
TEA	Tetraethylamine
TEAOH	Tetraethylammonium hydroxide
TG/DTG	Thermogravimetric and derivative thermogravimetric analysis
UV-Vis	Ultraviolet-visible
V_{total}	Total pore volume
XRD	X-ray diffraction

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**PEMBENTUKAN AYAK MOLEKUL JENIS AFI YANG DIACUANKAN
OLEH CECAIR IONIK BERASASKAN IMIDAZOLIUM DALAM
KEADAAN IONOTERMAL DAN HIDROTERMAL**

ABSTRAK

Feroaluminofosfat (FeAPO-5) dan aluminofosfat (AlPO-5) yang memiliki topologi AFI masing-masing telah disintesis melalui kaedah ionotermal dan hidrotermal. Kaedah ionotermal dijalankan dengan menggunakan 1-benzil-2,3-dimetilimidazolium klorida, [bzm]Cl, sebagai agen pengarah struktur sementara kaedah hidrotermal dijalankan dengan menggunakan 1-benzil-2,3-dimetilimidazolium hidroksida ([bzm]OH), 1-propil-2,3-dimetilimidazolium hidroksida ([pm]OH) dan 3-(2,3-dihidroksipropil)-1,2-dimetilimidazolium hidroksida ([dhm]OH) sebagai agen pengarah struktur. Pembentukan FeAPO-5 di bawah keadaan ionotermal dengan menggunakan H_3PO_3 sebagai sumber fosforus dianalisa secara spektroskopi dan mikroskopi termasuk fenomena yang melibatkan proses induksi, nukleasi dan penghabluran. Hasil kajian menunjukkan pemerbadanan kation Fe^{3+} telah meningkatkan kadar penghabluran FeAPO-5. Semasa proses penghabluran, fasa perantaraan ferumaluminofosfit FeNKX-2 terbentuk sebelum transformasi kepada fasa FeAPO-5 berlaku. Peningkatan kadar penghabluran feroaluminofosfat FeAPO-5 dapat dijelaskan dengan kehadiran kation Fe^{3+} yang bertindak sebagai media pemindahan elektron perantaraan dan menggalakkan pembebasan kation fosforus P^{5+} dari takungan kation fosfit P^{3+} yang diperlukan untuk penghabluran FeAPO-5. Suatu mekanisme penghabluran FeAPO-5 juga dicadangkan berdasarkan hasil kajian eksperimen yang diperolehi. Sintesis hidrotermal AlPO-5 telah dijalankan dengan menggunakan agen pengarah struktur berasaskan

imidazolium yang mengandung kumpulan berfungsi yang berbeza. Hasil kajian menunjukkan molekul agen pengarah struktur yang mengandung kumpulan berfungsi yang berbeza dan saiz molekul mempengaruhi kadar penghabluran, tahap penghabluran, morfologi dan peratusan hasil hablur AIPO-5. Penggunaan [dhm]OH yang mempunyai kumpulan berfungsi diol sebagai agen pengarah struktur didapati menghasilkan hablur AIPO-5 yang mempunyai kadar penghabluran, tahap penghabluran dan peratusan hasil hablur yang paling tinggi berbanding dengan penggunaan [bzm]OH dan [pm]OH sebagai agen pengarah struktur yang mengandung kumpulan berfungsi yang kurang berkutub.

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ABSTRACT

Ferroaluminophosphate (FeAPO-5) and aluminophosphate (AlPO-5) molecular sieves of AFI topology have been successfully synthesized under ionothermal and hydrothermal conditions, respectively. The former approach employed 1-benzyl-2,3-dimethylimidazolium chloride ([bzm]Cl), as a structure-directing agent (SDA) while the latter used 1-benzyl-2,3-dimethylimidazolium hydroxide ([bzm]OH), 1-propyl-2,3-dimethylimidazolium hydroxide ([pm]OH) and 3-(2,3-dihydroxypropyl)-1,2-dimethylimidazolium hydroxide ([dhm]OH) as the SDAs. The formation of FeAPO-5 under ionothermal condition using H_3PO_3 as a phosphorus source was investigated by spectroscopy and microscopy analyzes where the phenomenon involved induction, nucleation and crystallization processes. The results obtained showed that the incorporation of Fe^{3+} has enhanced the crystallization rate of FeAPO-5. During the crystallization process, FeNKX-2 intermediate was first obtained prior to phase transformation to FeAPO-5. The fast crystallization rate of FeAPO-5 was explained by the presence of Fe^{3+} as an intermediary electron-transfer medium promoting the fast release of phosphorus nutrient, P^{5+} , from phosphite, P^{3+} , a reservoir that required for the crystallization of FeAPO-5. A possible mechanism for the growth of FeAPO-5 crystals *via* new synthesis route was also proposed based on the experimental results and time-dependent studies. The hydrothermal synthesis of AlPO-5 was investigated by using

imidazolium-based SDAs containing three different functional groups. The results showed that the SDA molecules containing different functional groups of different polarity and molecular size had a significant effect on the rate of crystallization, degree of crystallinity, morphology and solid yield of the AlPO-5 crystals produced. The AlPO-5 crystals which were synthesized by using [dhm]OH, which had polar diol functionality, was found to have the highest rate of crystallization, the highest degree of crystallinity and highest solid yield compared to the case of using [pm]OH and [bzm]OH which contained less polar functional groups.

CHAPTER 1

INTRODUCTION

1.1. General introduction

Aluminophosphate zeotype materials (AIPO-*n*) are a group of microporous minerals with a neutral framework composed of alternating AlO_4 and PO_4 tetrahedrals [1]. Most of these aluminophosphate materials are found to have novel frameworks, such as AIPO-5, AIPO-18, AIPO-41, etc. AIPO-5 with AFI topology, for example, is one of the most famous zeotype microporous solids that have attracted great attention owing to its advantages such as large micropores (pore opening 7.3 Å) and outstanding thermal stability [2]. This crystalline solid comprises hexagonal morphology having one-dimensional channels and enclosed by 12-membered ring channels. Isomorphous substitution of metal cations in the framework of AIPO-*n* yields another zeotype material called metalloaluminophosphate, MeAPO-*n* [3, 4]. Unlike AIPO-*n* solids, MeAPO-*n* materials have negatively charged framework. Thus, these materials contain the characteristics of both zeolites and aluminophosphates, which give them unique catalytic, ion-exchange and adsorbent properties [5].

Normally, AIPO- and MeAPO-based crystalline solids are synthesized under a hydrothermal or ionothermal condition in the presence of organic structure-directing agents (SDAs) [6]. The SDA, which is added during the synthesis, plays a very important role in directing the formation of a specific crystalline framework structure where the SDA must fit well in the micropores in order to stabilize the produced framework. Thus, a suitable SDA is required to achieve this goal. Besides, SDA is also important in controlling the nucleation and crystal growth processes of

these microporous materials. This is because different SDA molecules have different polarity, pH, and molecular size, and hence the presence of these molecules will affect the chemical environment during the hydrothermal synthesis.

Synthesis of AlPO-*n* and MeAPO-*n* materials is also affected by the use of initial reactants. Usually, phosphoric acid (H₃PO₄, or called orthophosphoric acid) is used as a phosphorus source while pseudoboehmite and aluminum isopropoxide are commonly employed as the aluminum sources in the synthesis of both microporous materials. The use of a different source of reactants plays a significant role in the nucleation and crystallization processes, and, therefore, influences the growth and morphology of the final products.

1.2. Problem statements

Hydrothermal and ionothermal syntheses of AlPO-*n* and MeAPO-*n* molecular sieves using H₃PO₄-containing route are widely reported. Nevertheless, the formation of these zeotype materials under ionothermal condition using phosphorous acid (H₃PO₃) as phosphorus source has not been yet studied so far.

In addition, SDA molecules have different polarity, functional groups, and molecular size. The presence of these polar molecules in the synthesis precursor surely will affect the chemical environment during the hydrothermal synthesis. So far, no work has been carried out on the study of the effect of changing the functional groups of SDA on altering the formation and physico-chemical properties of AlPO-*n* materials. Both of these problems (effect of H₃PO₃ and SDA), hence, are worth to be further explored.

1.3. Objectives of study

The objectives of the project are summarized as follows:

- a) To study the formation of FeAPO-5 zeotype materials using phosphorous acid (H_3PO_3) as phosphorus source under ionothermal condition.
- b) To monitor the crystallization process throughout the synthesis process using microscopy and spectroscopy techniques.
- c) To propose the growth mechanism for FeAPO-5 in ionic liquid from the novel H_3PO_3 -containing route.
- d) To study the effects of the use of SDAs with different functional groups on the crystallization process and on the physico-chemical properties of AlPO-5 material.

1.4. Scope of thesis

The outline of the thesis is as follows: Following this introductory chapter, Chapter 2 presents an elaborated and a detailed background which relates to the studied project including a general introduction of AlPO-*n* and MeAPO-*n* materials, their synthesis methods and crystalline framework formation study.

Chapter 3 focuses on the formation of FeAPO-5 crystals under ionothermal condition. In this study, H_3PO_3 was used as a phosphorus source. The synthesis was performed at 170 °C and the induction, nucleation and crystallization processes of FeAPO-5 were investigated using spectroscopy and microscopy analyzes. A possible mechanism for the growth of FeAPO-5 crystals *via* new synthesis route was then proposed based on the experimental results and time-dependent studies.

The findings obtained through the study of the effect of SDAs on the hydrothermal crystallization AFI-type of molecular sieves are discussed in Chapter 4.

More detailed descriptions which involved the influences of SDAs on the morphology, rate of crystallization and degree of crystallinity of AlPO-5 are provided in this chapter.

Chapter 5, which is the last chapter of this dissertation, presents the summary of the findings for this project and some recommendations for the future works.

CHAPTER 2

LITERATURE REVIEW

2.1. Porous materials

Porous materials are solids permeated by interconnected or non-interconnected pores. According to the IUPAC definition, porous materials can be divided into microporous (< 2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm) materials based on their pore diameters [7]. A simplified picture of representative porous materials with different pore sizes and the corresponding pore size distributions are shown in Figure 2.1. Synthetic zeolites are classified as ordered microporous solids and they have been commercially utilized on a large scale in industries [8]. In past few decades, porous materials are becoming more important due to their wide applications in ion exchange, catalysis and separation processes [9, 10, 11]. Typically, zeolites and zeotype materials are of high demands and extensive researchers have been carried out to commercially produce them.

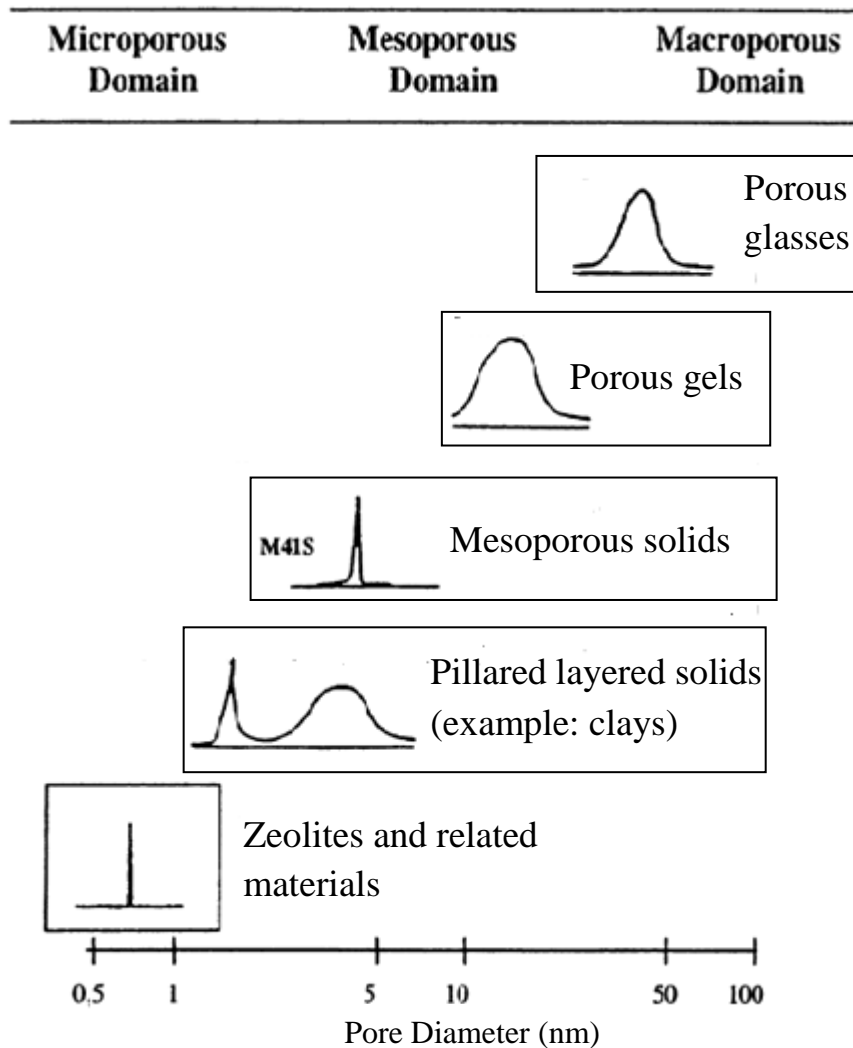


Figure 2.1. Examples of micro-, meso-, and macroporous materials showing pore size domains and typical pore size distributions [7].

2.2. Zeolite and zeotype materials

2.2.1. Zeolites

A Swedish mineralogist, Cronstedt, discovered the first zeolite mineral, stilbite in 1756 and began the history of zeolites [12]. This mineral has been called as ‘zeolite’ (derived from two Greek words, *zeo* and *lithos*, meaning “to boil” and “a stone”) because a large amount of steam was observed when this mineral was heated. Zeolites are an essential family in microporous materials. Normally, the term ‘zeolite’

refers to a crystalline aluminosilicate or silica polymorph based on corner-sharing TO_4 ($\text{T} = \text{Si}$ and Al) tetrahedra forming a three-dimensional framework with the uniform pore of molecular dimensions.

Today, the term ‘zeolite framework’ usually refers to a corner sharing a network of tetrahedrally coordinated atoms [12]. The term ‘zeolite’ has a broader meaning, which comprises all microporous silica-based solids showing crystalline walls, including those materials where the fraction of Si atoms has been substituted by trivalent (Al , Fe , B , Ga ,...) or tetravalent (Ti , Ge ,...) metal ions [7]. Their structural formulae are determined based on the crystallographic unit cell [13].

The aluminosilicate zeolites, which are constructed from SiO_4 tetrahedra and AlO_4 tetrahedra, have an anionic framework as shown in Figure 2.2. The negative charge of the framework is balanced by the extra-framework cations located in the channels and cages of a zeolite structure [12]. The general formula of zeolites can be considered as $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O}$, where M is an alkali or alkaline earth cation, n is the valence of the M cation, w is the number of water molecule per unit cell, x and y are the total numbers of tetrahedra per unit cell [7].

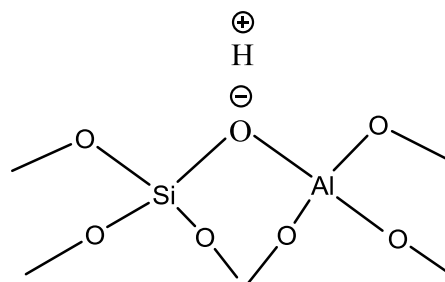


Figure 2.2. Zeolite framework with alternating AlO_4 and SiO_4 tetrahedra (if $\text{Si}/\text{Al} = 1$), where charge deficiency from Al^{3+} leads to the formation of a Brønsted acid site on a neighboring oxygen.

2.2.2. Aluminophosphate materials (AlPO-*n*)

Zeotype molecular sieves are a family of solids showing identical structure to zeolites but possess different elements composition in them. Wilson et al. reported the main breakthrough of a new class of aluminophosphate molecular sieves in 1982 [14]. AlO_4 and PO_4 tetrahedra alternate in the framework of aluminophosphate molecular sieves [15]. When the Al and P atoms in the framework are substituted by other elements such as Be, B, Ge, Si, Cr, Mn, Fe and Co, it is known as isomorphic substitution and the resulting materials are called metalloaluminophosphates (MeAPO-*n*) [4].

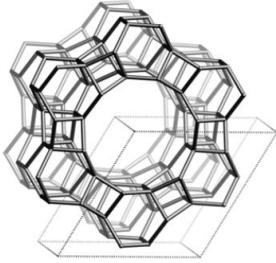
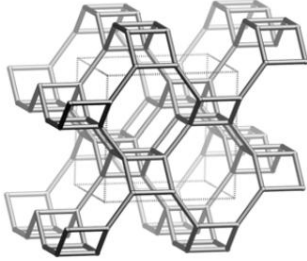
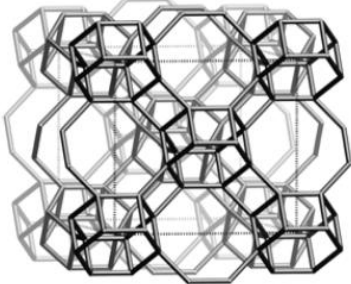
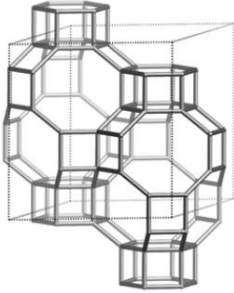
There are three types of isomorphous substitution mechanism (SM) of Al and P occurring in AlPO-*n*. The first substitution mechanism (SM I) involves the aluminum substituted with valence atoms +1, +2 and +3 resulting the Me–O–P bond (Me = Metal). The second substitution mechanism (SM II) is for phosphorus replaced by valence elements +4 or +5 to form Me–O–Al bond. The third substitution mechanism (SM III) is the substitution of pairs of adjacent Al and P atoms [3].

The bonding concept in AlPO-based materials has been elucidated by Flanigen et al. [13]. They observed that the Al–O–P, Si–O–Si, Si–O–Al, Me–O–P, and Me–O–P–O–Me linkages are likely to be appeared in the framework while the linkages P–O–P, P–O–Si, Al–O–Al, Me–O–Al, and Me–O–Me are unfavorably existed in the framework due to thermodynamically unfavorable.

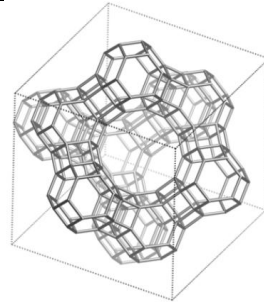
2.2.3. Nomenclatures, secondary building units (SBUs) and framework structures of AlPO-*n* materials

Members of the AlPO-*n* family are distinguished and named according to the protocol set by the Commission of the International Zeolite Association (IZA). This material is designated AlPO-*n* where *n* is a number representing a particular structure type, followed by an IUPAC three letter framework code for a known framework topology irrespective of composition. For example, AlPO-5 is given the code AFI (**AlPO Five**), AET (**AlPO Eight**) for AlPO-8 and AEL (**AlPO Eleven**) for AlPO-11 (Table 2.1). This concept of naming is applied to all aluminophosphates. However, some of the aluminophosphates may have zeolite analogues such as AlPO-34 (CHA named after zeolite **chabazite**), AlPO-37 (FAU named after zeolite **faujasite**) and AlPO-43 (GIS named after zeolite **gismondine**). Thus, the naming of these aluminophosphates is different from the others. Today, there is 206 framework type codes have been proposed [16]. AlPO-*n* crystalline materials can be built up from preformed building blocks, called secondary building units (SBUs) (Figure 2.3) [7]. These SBUs which contain up to 16 T-atoms (T = P and Al atoms) with an assumption that the whole framework is made up of one type of SBU only. The SBUs are always non chiral, with the oxygen atoms omitted and represented by the presence of a single straight line between two T atoms [17].

Table 2.1. Structure frameworks and pore sizes of several AIPO-*n* materials [16].

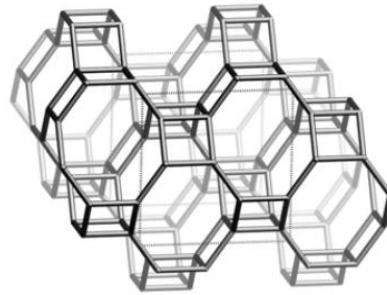
AIPO-<i>n</i> (Structure type)	Frameworks and channels
<p><i>n</i> = 5 (AFI)</p>	 <p>Pore size = 7.3 Å Channels: [001] 12 7.3 x 7.3*</p>
<p><i>n</i> = 12 (ATT)</p>	 <p>Pore size = 4.2 × 4.6 Å Channels: [100] 8 4.2 x 4.6* ↔ [010] 8 3.8 x 3.8*</p>
<p><i>n</i> = 18 (AEI)</p>	 <p>Pore size = 3.8 × 3.8 Å Channels: {[100] 8 3.8 x 3.8 ↔ [110] 8 3.8 x 3.8 ↔ [001] 8 3.8 x 3.8}***</p>
<p><i>n</i> = 34 (CHA)</p>	 <p>Pore size = 3.8 × 3.8 Å Channels: [001] 8 3.8 x 3.8***</p>

$n = 37$
(FAU)



Pore size = 7.4 Å
Channels: $\langle 111 \rangle$ **12** 7.4 x 7.4***

$n = 43$
(GIS)



Pore size = 3.1 × 4.5 Å
Channels: $\{[100]$ **8** 3.1 x 4.5 \leftrightarrow $[010]$ **8** 2.8 x 4.8 $\}$ ***

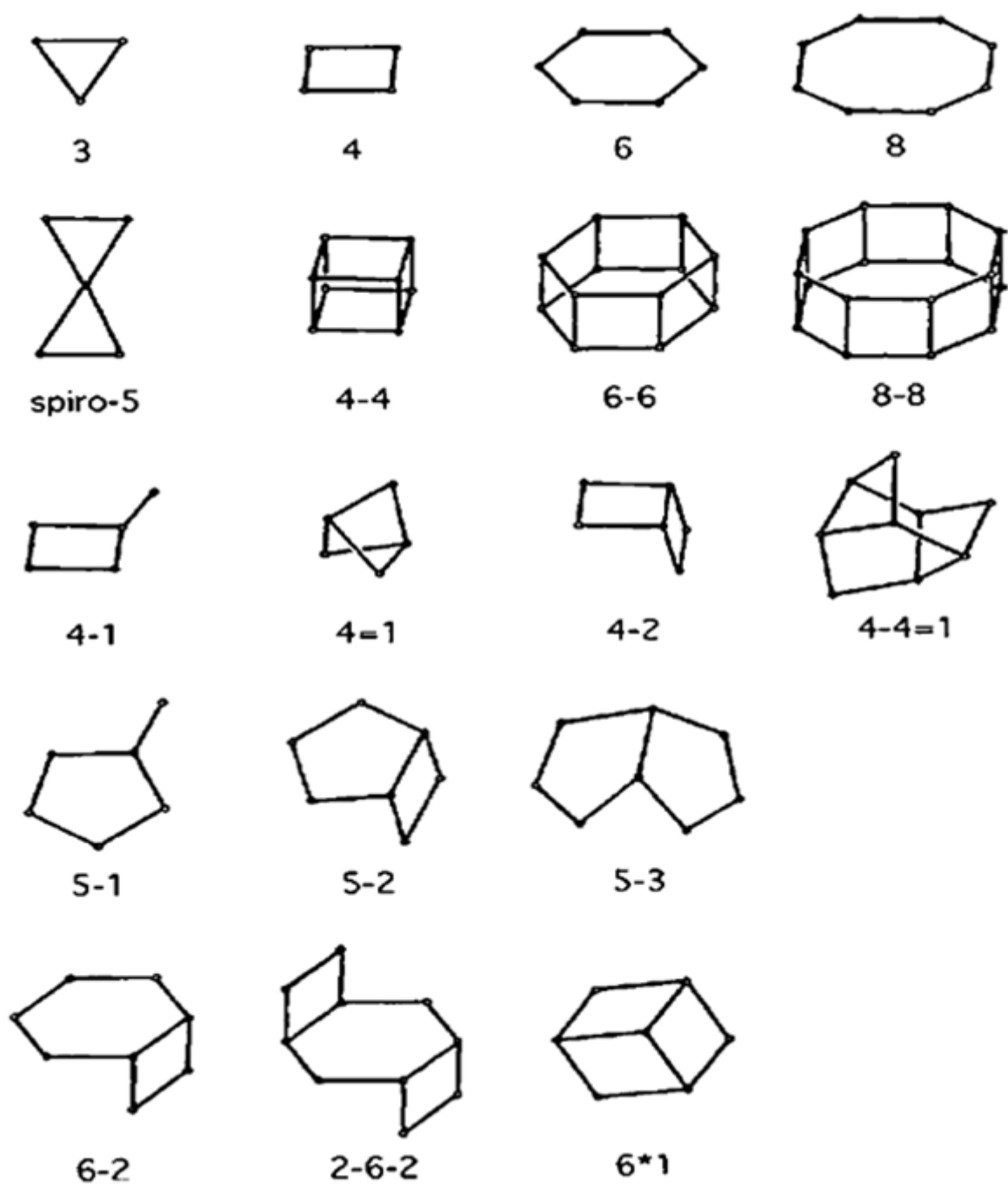


Figure 2.3. Secondary building units (SBUs). The SBU codes are given below the structures [18].

2.3. Framework substitution: aluminophosphate derivatives

Metal substituted aluminophosphates (MeAPO-*n*) have a wide-ranging of applications in different acid catalyzed reactions. The incorporation of metals ions into the framework of AlPO-*n* is considered as a remarkable advancement of their use in industrial processes. Fe-containing molecular sieves, for example, have attracted well-known interest because of their special catalytic properties in a series of reactions, especially in redox catalysis [19].

Ren et al. reported that iron substituted aluminophosphate (FeAPO-5) can be used as a catalyst for benzene hydroxylation with the selectivity of more than 85% and the Fe³⁺ ions are tetrahedrally coordinated in the catalyst [20]. The iron atoms which are tetrahedrally coordinated in the framework of the AlPO-5 structure are exceptionally good catalysts for numerous oxidation reactions such as selective oxidation of cyclohexane in air, and Aerial oxidation of cyclohexane for the production of adipic acid with molecular oxygen as an oxidant [21, 22].

Besides that, it has been reported that incorporation of different type metal ions into MeAPO-*n* framework can affect the morphology of the synthesized MeAPO-*n* crystals. Tian et al. reported Cr³⁺ and Ti⁴⁺ substituted MeAPO-*n* crystals show completely different morphologies [23]. The Cr-AFI crystals showed a novel flower-like morphology whereas Ti-AFI crystals showed a kiwi-fruit-like morphology. It is believed that different isomorphic substitution mechanisms of transition metal ions in the MeAPO-*n* crystals may be resulted to different growth behavior of the MeAPO-*n* crystals and different morphology from the others [23].

2.4. Preparation of AlPO-*n* materials

Synthesis of AlPO-*n* materials relies on the control of numerous reaction variables such as preparation method, reactant gel composition, type of structure directing agent (SDA) used, heating time and temperature. Since most of these reaction variables are not independent of one another, it is not easy to assess the effect of varying any one of them. Synthesis methods of zeolite materials and the factors governing the crystallization process are described in the following sub-sections.

2.4.1. Hydrothermal synthesis

The solvent interaction between reacting species is very essential to the molecular sieve synthesis. In general, during the synthesis of AlPO-*n* molecular sieves, water is used and the synthesis is called hydrothermal synthesis. The term hydrothermal generally refers to the reactions involving aqueous solvents under high pressure and high temperature (above 100 °C) conditions. During hydrothermal synthesis, water serves as a space filler to stabilize the porous lattice of zeolites and AlPO-*n* materials. Besides that, it is also used in hydrolysis and reformation of T–O–T bonds (T = P and Al). Thus, the chemical reactivity is enhanced and the mixture viscosity is decreased in the presence of water.

AlPO-*n* materials are hydrothermally synthesized at a temperature between 100–250 °C from a reaction mixture containing sources of aluminum (typically aluminum hydroxide hydrate, aluminum isopropoxide or pseudo-boehmite), phosphorous (generally phosphoric acid) and an organic amine or a quaternary ammonium salt under autogeneous pressure. In the synthesis of AlPO-*n* and MeAlPO-*n* material, a solution of the metal salt (usually in the form of acetate or

sulfate) and/or silica (silica sol or colloidal silica) are also added into the reactive mixture (Figure 2.4). The reaction medium produced usually is weakly acidic or neutral (pH = 4–7).

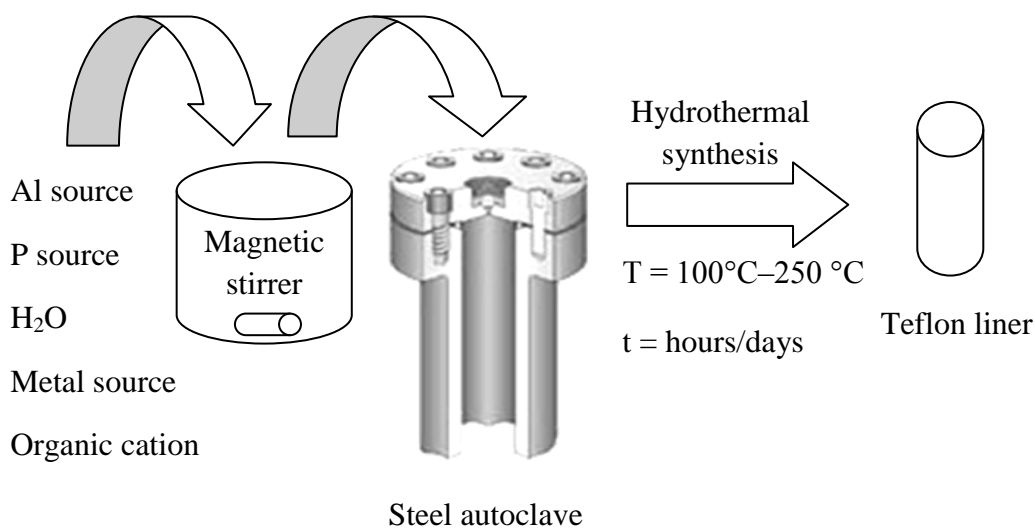


Figure 2.4. Schematic illustration of the hydrothermal synthesis of AlPO-*n* materials; the starting materials are mixed together to form a gel which is then transferred to a steel autoclave containing a Teflon liner, and is heated at a particular temperature (T) for a certain period of time (t).

2.4.2. Solvothermal synthesis

The non-aqueous route or solvothermal synthesis is another possible route to synthesize AlPO-*n* molecular sieves. Basically, this route uses organic solvent rather than water. The organic solvents are classified into four groups based on their tendency to hydrogen bond interaction. The typical organic solvents that have been used in the synthesis of AlPO-*n* material are hexanol, propanol, pyridine, glycerol and glycol [24]. In addition, these molecular solvents also produce significant

autogenous pressure at an elevated temperature which can enhance the crystallization rate of AlPO-*n* materials [25].

2.4.3. Ionothermal synthesis

Ionothermal synthesis uses ionic liquids (ILs) as both solvent and structure-directing agent in the synthesis of AlPO-*n* materials. Compared with the hydrothermal and solvothermal methods, ionothermal synthesis technique can avoid the application of volatile solvents and hence, allowing the reactions take place at near ambient pressure where the safety concerns can be eliminated. As a result, it leads to a new formation of materials frameworks (Figure 2.5). Since there are no other solvents added to the reaction mixture, there are no other molecules present to act as space fillers during the ionothermal synthesis. So, ionothermal synthesis ideally removes the competition between template-framework and solvent-framework interactions which are facing in hydrothermal and solvothermal syntheses [24].

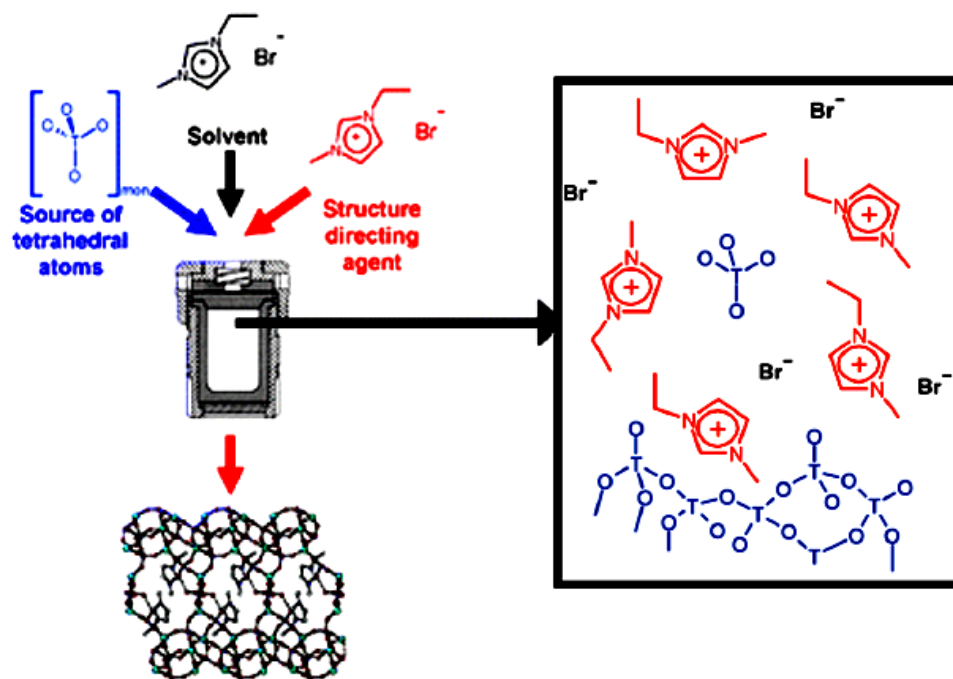


Figure 2.5. Schematic illustration of the synthesis of AlPO-*n* zeotype materials under ionothermal synthesis [25].

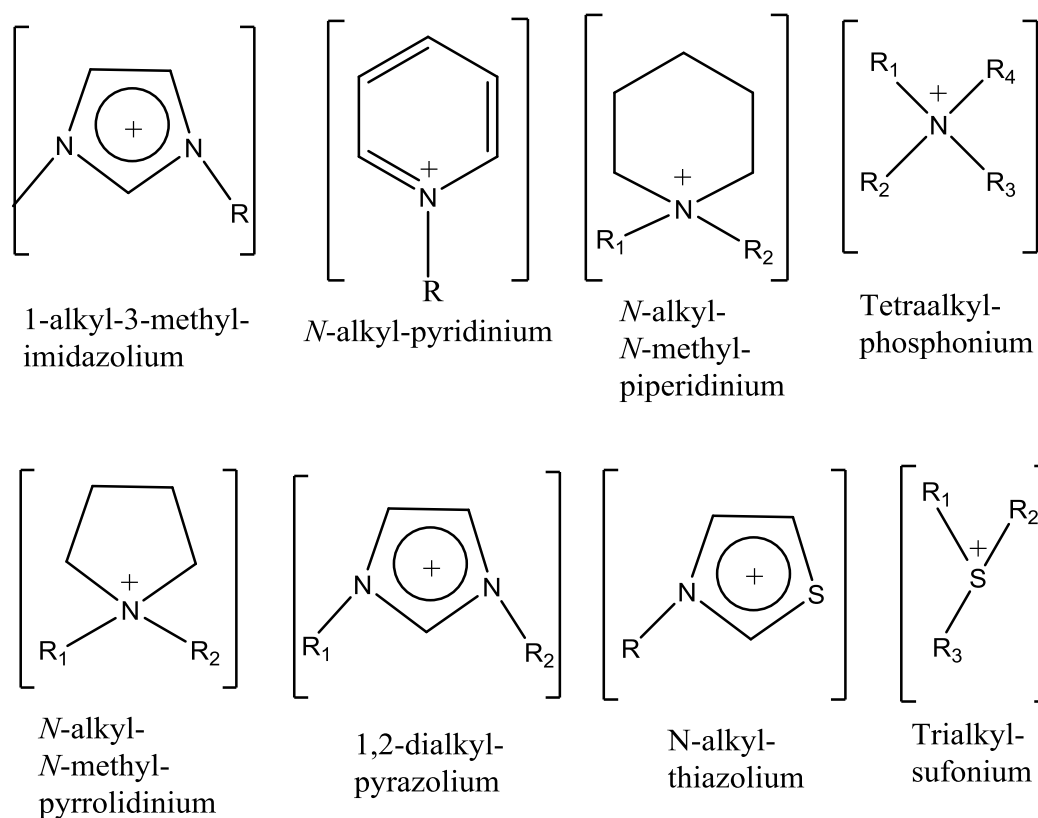
2.5. Structure-directing agents (SDAs)

The synthesis of molecular sieves usually requires the presence of organic molecules, such as amines or quaternary ammonium ions, in the synthesis mixture. The addition of organic molecules is typically necessary to direct the crystallization of a certain microporous structure, and so they are called structure-directing agents (SDAs) or templates. Many efforts have been making in designing and employing the novel organic templates with different molecular size, geometry and polarity in the synthesis of new porous materials. These organic molecules are usually encapsulated within the zeolite framework during the crystallization process, where their chemical identity is retained. It is believed that they can stabilize a particular framework type *via* filling the void space and *via* non-bonding interactions between

organic and inorganic components [26]. The capability of a molecule to direct the crystallization of a certain AlPO-*n* crystals depends on the nature of these interactions. However, this template-framework interaction is still not yet clearly understood [27].

Studies discover that one “template” can be used to form multiple structures framework. For example, dipropylamine can be used to form 10 different AlPO-*n* structures such as AlPO-11, AlPO-31, SAPO-34 and AlPO-41 [28]. Furthermore, multiple “templates” can be used to form one structure. The AlPO-5 crystal can be formed by using different templates [29] such as tetrapropylammonium hydroxide (TPAOH) [30], tetrapropylammonium fluoride (TPAF) [31] and guanidinium hydroxide [32]. In general, tetrapropylammonium hydroxide (TPAOH) is a typical template used in the synthesis of AlPO-5 [12].

The role of these molecules has been described as a structure-directing effect which is referring to the close relationship between the size and shape of the organic cation and the size and shape of cavities formed within the framework. This template effect indicates that the organic molecules organize the inorganic tetrahedral units into a particular geometric topology around themselves throughout the gelation or nucleation process [33]. In fact, these organic species plays the following roles in the formation of specific channels and cages: i) space filling, ii) structure directing, and iii) true templating [34]. Several groups of organic cations which are commonly used in the formation of structure directing agent (SDA) are shown in Figure 2.6.



$R_{1,2,3,4} = \text{CH}_3(\text{CH}_2)_n$, ($n = 1, 3, 5, 7, 9$); aryl; etc.

Figure 2.6. Examples of cations most commonly used as the structure-directing agents (SDAs) [35].

The space filling role of an organic cation is obvious when the AlPO-5 crystals can be prepared by using several different templates. The precise nature of the organic species is not of importance showing its role as a space-filler to simply prevent water molecules entering the channels and cages of the framework. As a result, a decrease in the unfavorable energetic interactions between the water molecules and the growing zeolite framework takes place [36].

The structure-directing role of an organic cation suggests that a specific structure can be directed only by a specific organic species and cannot be synthesized

by the use of any other templates. There is a very high correlation between the size and the shape of the organic molecules used. The size and shape of the framework pores produced are due to an optimized arrangement for maximizing the van der Waals contacts between the framework and the organic species without ionic interactions [37-39].

A “true template” occurs when the structure of a material uses the geometric and electronic configurations that are unique to the organic molecule, and upon calcination, the shape of the pore is said to retain the shape of the organic molecule. A few studies have shown that the shape of the template plays an important role in determining the framework due to strong guest-host interaction, and that true templating has taken place [40, 41].

Overall, the organic species are found to play some important roles during the synthesis of molecular sieve materials through:

- promoting the formation of nanoporous materials,
- accessing more metastable states by stabilizing the voids of the molecular sieve materials,
- influencing the degree of metal-ion substitution of the framework in MeAPOs (positive charge from template charge balances with the negative charge from metal ion), and
- increasing the nucleation and modifying the crystal growth rates.

The crystallinity, morphology and particle size of AlPO-*n* and MeAPO-*n* materials are influenced by many factors such as initial gel composition, the type of cations (organic and/or inorganic) used, the type and/or amount of reagent sources (i.e. alumina source, phosphorus source and template) and the reaction conditions (i.e. crystallization time, heating temperature, pressure, pH and agitation) [42-45].

Among these factors, the type of template has more pronounced effects. The elemental composition and morphology of a specific zeotype may alter using different types of templates [46]. For example, Emrani et al. used two different types of templates (triethanolamine and tetraethylammonium hydroxide), as organic structure directing agents in the synthesis of SAPO-34. Their results revealed that using different templates produced different particle size, crystallinity, and purity of SAPO-34 [46].

In addition, the morphology of a crystal is determined by the growth rate of the crystal faces which have different surface energies during the crystallization process [47, 48]. An addition of organic or inorganic additives into the reaction system can change the relative surface energies of different crystal faces, and thus changing the morphology of the resulting crystals [49, 50].

2.5.1. Effect of aluminum source

It is believed that the source of Al can change the pH value of the starting gel and plays a significant role in forming the crystalline phase [51]. Many experiments have been carried out to investigate the effect of synthesis parameters on the size of crystals, pore size, and purity of AIPO-*n* molecular sieves. Sadeghian et al., who synthesized AIPO-5 crystals by altering the precursor gel composition, found that the use of aluminum isopropoxide as the aluminum source can synthesize a better morphology of AIPO-5 crystals compared with the use of aluminum hydroxide. The synthesized AIPO-5 crystals have high purity and high crystallinity when aluminum isopropoxide was used [51].

2.5.2. Effect of phosphorus source

Synthesis of AlPO-*n* and MeAPO-*n* materials is also influenced by the use of initial reactants. Most of the molecular sieves materials are synthesized by using phosphoric acid (H₃PO₄) as a phosphorus source. A study on the effect of phosphorus source was carried out by [Chen et al. \[52\] using a mixture of H₃PO₄ and H₃PO₃ as the phosphorus sources to promote the crystallization of SAPO-41 and AlPO-41. It was reported in the study that the crystallization period for AlPO-41 and SAPO-41 had effectively been reduced.](#) It is believed that the transformation of phosphorus from P(III) to P(V) plays an important role during the crystallization process.

2.6. Synthesis mechanism

Understanding how porous crystalline materials (e.g. zeolites and their related structures) are formed from a precursor gel is important since it can lead to a more rational approach towards design and synthesis of new molecular sieves.

The synthesis of AlPO-*n* is found to proceed *via* three stages. The first stage involves pre-nucleation (induction), followed by nucleation and the last stage is crystal growth. Pre-nucleation involves the initial dissolution of the solid starting reagents (Al and P precursors and SDA) by the solvent water to form an amorphous aluminophosphate. The precursor gel is then heated in an oven under autogenous pressure for a particular period of induction time. This is followed by nucleation where the dissolved particles aggregate and form nuclei which serve as the nucleation sites. Finally, the nuclei grow larger with time and form the molecular sieve structures [38].

The exact mechanism for the crystallization process of AlPO_n crystal remains not fully understood due to the complexity of the reactions which occur throughout the heterogeneous synthesis mixture during the crystallization process. Currently, there are two main crystallization mechanisms have been proposed, namely (a) solution-mediated transport mechanism and (b) solid hydrogel transformation mechanism. It is clear that in any particular case the true mechanism could lie somewhere between these two extremes, or could proceed *via* a combination of both. These two mechanisms differ by the presence of liquid component during the crystallization process.

Kerr et al. proposed the solution-mediated transport mechanism in the middle of the 1960s according to their studies on the crystallization of zeolite A (Figure 2.7) [53]. This mechanism involves partially or completely dissolution of the aluminosilicate/aluminophosphate gel in the solution phase to form active silicate, phosphate, and aluminate ionic species. The dissolved ionic species are then transported to the nucleation sites *via* a solution-mediated diffusion where re-crystallization in the solution occurs to form the structure of the molecular sieve material and crystal growth subsequently takes place.

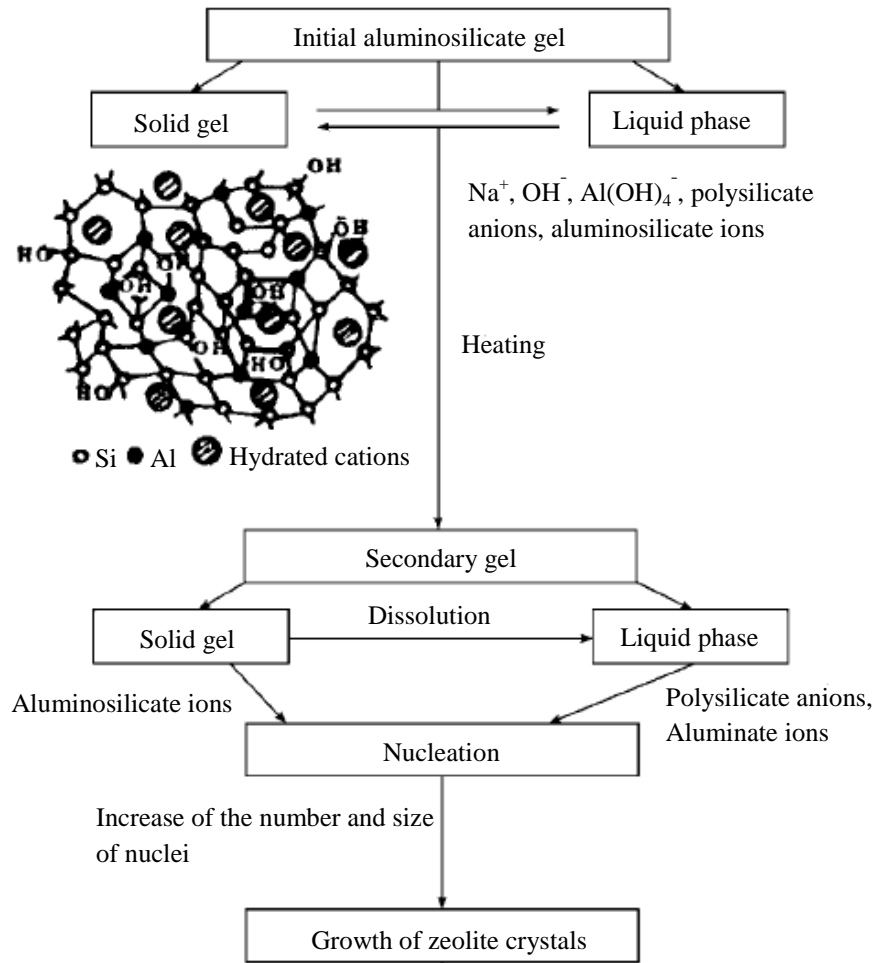


Figure 2.7. Illustration of solution-mediated transport mechanism [12].

Breck and Flanigen in 1968 proposed the solid hydrogel transformation mechanism as illustrated in Figure 2.8. This mechanism is completely different from the solution-mediated transport mechanism as the liquid component or solid gel does not involve in the crystallization process [36]. This mechanism suggests that the structure of molecular sieve is obtained by structural rearrangement of the framework of solid phase aluminosilicate/aluminophosphate hydrogel formed from the condensation of silicate, phosphate and aluminate ions occur in the early stage of