

**SYNTHESIS OF SILICOALUMINOPHOSPHATE
ZEOLITE CATALYSTS DIRECTED BY
BENZYLTRIMETHYLAMMONIUM HYDROXIDE
TEMPLATE FOR THE CHEMICAL
PRODUCTION OF BIOFUEL ADDITIVES**

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UNIVERSITI SAINS MALAYSIA

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HYDROXIDE TEMPLATE FOR THE CHEMICAL
PRODUCTION OF BIOFUEL ADDITIVES**

by

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**Thesis submitted in fulfilment of the requirements
for the degree of
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LIST OF SYMBOLS

%	Percent
Å	Angstrom (1×10^{-10} m)
Al	Aluminum
Al ₂ O ₃	Aluminum oxide
AlO ₂ ⁻	Aluminate ion
°C	Degree Celsius
Ca ²⁺	Calcium ion
CH ₃ COOH	Acetic acid
Cu ²⁺	Copper(II) ion
H ⁺	Hydrogen ion
H ₂ O	Water
H ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric acid
K ⁺	Potassium ion
kJ mol ⁻¹	Kilojoule per mole
Mg ²⁺	Magnesium ion
mmol g ⁻¹	Millimole per gram
Mn ⁴⁺	Manganese(IV) ion
N ₂	Nitrogen gas
Na ⁺	Sodium ion
NH ₃	Ammonia
nm	Nanometer (1×10^{-9} m)
P	Phosphorus
P ₂ O ₅	Phosphorus pentoxide

pH	Potential of hydrogen
Si	Silicon
Si/Al	Silicon-to-aluminum ratio
SiO ₂	Silicon dioxide

LIST OF ABBREVIATIONS

1-PyH	1-Propylpyridinium hydroxide
[PPy]Br	1-Propylpyridinium bromide
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BTMAOH	Benzyltrimethylammonium hydroxide
CL	Condenser lens
CP	Hexadecylpyridinium chloride
CTA	Hexadecyltrimethylammonium bromide
D _{av}	Average pore size from BJH adsorption curve
DEA	Diethylamine
DFE	Difurfuryl ether
DR	Dubinín-Radushkevich
DPA	Dipropylamine
EL	Ethyl levulinate
EP	Ethyl pyruvate
FA	Furfuryl alcohol
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GC-FID	Gas chromatography with flame ionization detection
GC-MS	Gas chromatography mass spectrometry
h	Hour(s)
HF	Hierarchical factor
HK	Horváth-Kawazoe

IPA	Isopropylamine
IUPAC	International union of pure and applied chemistry
IZA-SC	International zeolite association
NH ₃ -SCR	Ammonia-selective catalytic reduction
NLDFT	Non-local density functional theory
MeSAPO	Metallosilicoaluminophosphate
mg	Milligram(s)
min	Minute(s)
MOR	Morpholine
MTO	Methanol to olefin
OL	Objective lens
OPA	2-Oxopropanoic anhydride
PA	Pyruvic acid
PP	Piperidine
SAPO	Silicoaluminophosphate
S _{BET}	Total surface area
S _{ext}	External surface area
SF	Saito-Foley
S _{micro}	Micropore surface area
TEA	Triethylamine
TEAOH	Tetraethylammonium hydroxide
TG/DTG	Thermogravimetric and differential thermal analysis
TMA	Trimethylamine
TOF	Turnover frequency
TON	Turnover number

TP	Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride
TPA	Tripropylamine
TPD	Temperature-programmed desorption
V_{meso}	Mesopore volume
V_{Tot}	Total pore volume
XRD	X-ray diffraction

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Appendix E	GC-MS spectrum of EP, the esterification product of PA and EtOH.
Appendix F	GC-MS spectrum of OPA, the esterification side product of PA and EtOH.

**MANGKIN ZEOLIT SILIKOALUMINOFOSFAT DITEMPLAT OLEH
TRIMETILBENZILAMMONIUM HIDROKSIDA BAGI PENGHASILAN
BAHAN TAMBAH BIOBAHAN API**

ABSTRAK

Zeolit silikoaluminofosfat (SAPO) adalah mangkin yang sangat berguna. Biasanya, ia disintesis dengan sebatian ammonium kuaterner alifatik sebagai acuan organik. Namun, benziltrimetilammonium hidroksida (BTMAOH) yang mengandungi kumpulan berfungsi siklik sebagai acuan masih belum dikaji. Kajian ini melaporkan penghabluran SAPO-34 dan SAPO-20 menggunakan BTMAOH dengan mengikuti pembentukannya. BTMA^+ menunjukkan peranan sebagai pengarah struktur dan pengisi liang yang berkesan di mana SAPO-34 dan SAPO-20 tulen dengan sifat permukaan yang unik (dari segi luas permukaan, keliangan, keasidan) terbentuk selepas 24 dan 42 jam pada $180\text{ }^{\circ}\text{C}$. Berbanding dengan SAPO-20, SAPO-34 bersaiz liang lebih besar menunjukkan sifat pemangkinan yang lebih baik (penukaran 100%, hasil etil levulinat 72.5%) dalam etanolisis furfural alkohol dengan bantuan gelombang mikro. Mangkin SAPO-34 adalah stabil dan boleh dikitar semula, dan boleh dijadikan sebagai mangkin berkos efektif untuk pelbagai tindak balas petrokimia. Kerja ini juga mengkaji penyediaan SAPO-5 berstruktur hierarki menggunakan pelbagai surfaktan, iaitu dimetiloktadesil[3-(trimetoksisilil)propil] ammonium klorida (TP), heksadesiltrimetilammonium bromida (CTA) dan heksadesilpiridinium klorida (CP). Keputusan menunjukkan sebatian ionik ini berinteraksi dengan reagen tak organik semasa penghabluran, dan seterusnya mengubah sifat morfologi (saiz dan bentuk

hablur) dan struktur (keliangan dan keasidan) SAPO-5. Antara sampel SAPO-5 hierarki, TP-SAPO-5 dengan faktor hierarki tertinggi ($HF = 0.074$) dan keasidan kedua tertinggi (0.73 mmol g^{-1}) adalah mangkin terbaik bagi penghasilan etil piruvat melalui pengesteran. Selepas pengoptimuman parameter, prestasinya (penukaran 92.0%, kepilihan 85.9%) setanding dengan mangkin HCl dan H_2SO_4 (penukaran 88-92%, kepilihan 84-92%) dan lebih baik berbanding zeolit H-Y, H-MOR dan SAPO-34 (penukaran 56-100%, kepilihan 67-76%). TP-SAPO-5 boleh diguna semula sehingga lima kitaran, menjadikannya mangkin hijau dan unggul untuk penukaran produk biojisim.

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ABSTRACT

Silicoaluminophosphate (SAPO) zeolites are very useful catalysts. Usually, they are synthesized with aliphatic quaternary ammonium compounds as organic template. However, benzyltrimethylammonium hydroxide (BTMAOH) containing cyclic functional group as a template has not been studied. Here, the crystallization of SAPO-34 and SAPO-20 zeolites using BTMAOH is studied by following their evolutionary formation. The BTMA⁺ has shown its effective structure-directing and pore-filling roles whereby pure SAPO-34 and SAPO-20 with unique surface properties (surface area, porosity, acidity) are formed after 24 and 42 h at 180 °C. Compared with SAPO-20, SAPO-34 with larger pore size exhibits better catalytic activity (conversion 100%, ethyl levulinate (EL) yield 72.5%) in microwave-assisted furfuryl alcohol (FA) ethanolysis. The spent SAPO-34 catalyst is stable and recyclable, offering it as a cost-effective catalyst for various petrochemical reactions. This work also studies the preparation of hierarchical SAPO-5 using various surfactants, namely dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (TP), hexadecyltrimethylammonium bromide (CTA) and hexadecylpyridinium chloride (CP). The results show that these ionic compounds experience interactions with inorganic reagents during crystallization, which in turn altering the morphological

(crystal size and shape) and structural (porosity and acidity) properties of SAPO-5. Among hierarchical SAPO-5 samples, TP-SAPO-5 with the highest hierarchical factor ($HF = 0.074$) and second highest acidity (0.73 mmol g^{-1}) is the best catalyst for producing ethyl pyruvate (EP) *via* esterification. After parametric optimization, its performance (conversion 92.0%, selectivity 85.9%) is comparable to homogeneous HCl and H_2SO_4 catalysts (conversion 88-92%, selectivity 84-92%) and much superior than H-Y, H-MOR, SAPO-34 zeolites (conversion 56-100%, selectivity 67-76%). The hierarchical TP-SAPO-5 is also reusable for up to five reaction cycles, making it as a green and excellent catalyst for biomass product conversion.

CHAPTER 1

INTRODUCTION

1.1 General introduction

Zeolites are microporous solids that are widely used in adsorption, ion exchange and catalysis due to their high surface area, medium-strong acidity, high hydrothermal stability and excellent molecular sieve properties (Pérez-Botella et al., 2022). Zeolites are usually composed of several TO_4 ($T = \text{Si, P or Al}$) tetrahedral units connected together and form a framework with a three-dimensional porous structure. To date, the International zeolite association (IZA) has approved 256 different types of zeolite frameworks (IZA-SC, 2025). Among them, Silicoaluminophosphate (SAPO) zeolites have been widely studied because of their broad industrial prospects, unique pore shapes and sizes.

SAPO zeolites are usually hydrothermally synthesized in one-pot in the presence of organic templates. Typically, after uniformly mixing the silica source, alumina source, phosphorus source, organic template and water in a certain proportion (adjusting the pH if needed), the resulting hydrogel is crystallized at high temperature (90-200 °C) for a certain period of time (Kordala and Wyszowski 2024). After crystallization, SAPO zeolites with specific crystal shape are obtained. Besides, by altering the aging time, crystallization time, heating temperature, type and amount of organic template, type and concentration of silica, alumina and phosphorus sources, water content, pH of hydrogel, many SAPO zeolites with very high purity can be synthesized that are very useful for industrial applications (Rimaz et al., 2022).

SAPO zeolites have made great achievements in the catalytic reactions such as in methanol to olefin (MTO) (Sun et al., 2018), selective catalytic reduction of NO_x with NH_3 (Wang et al., 2024), esterification of levulinic acid (Ma et al., 2022), ethanolysis of Furfuryl alcohol (FA, Guo et al., 2020), etc.

The research is driven by the need to optimize the synthesis and functional properties of SAPO molecular sieves to enhance their catalytic performance and applicability. Despite their promising features, the formation mechanism of SAPO zeolites remains unclear, particularly concerning the time dependence of the organic template method and the influence of soft template approaches involving amphiphilic molecules on crystal morphology. Addressing these gaps can facilitate better control over pore architecture, structural stability, and activity, leading to more tailored and efficient SAPO-based materials for various industrial applications. Hence, it is a great interest to synthesize SAPO zeolites catalysts and use them in the chemical production of biofuel additives.

1.2 Problems statement

The synthesis of zeolites and SAPO-type molecular sieves traditionally relies heavily on the use of organic templates, such as quaternary ammonium compounds and amines, quaternary phosphonium, and metal complexes, which serve as structure-directing agents, pore fillers, and charge-balancing species (Luan et al., 2024). Among these, quaternary ammonium cations are particularly notable for their effectiveness in guiding framework formation due to strong electrostatic interactions with the inorganic building units, thus influencing the resulting pore architecture and

framework stability. However, the application of specific organic templates containing cyclic functional groups, such as benzyltrimethylammonium hydroxide (BTMAOH), remains underexplored. While BTMAOH could offer distinct advantages owing to its structural features, its role as an organic template in the synthesis of SAPO zeolites and the mechanisms by which it influences phase selectivity, crystallization pathway, and framework stabilization are not yet fully understood.

Another challenge lies in achieving hierarchical structures with mesoporosity alongside microporous frameworks, which can enhance mass transfer, improve catalytic performance, and extend material lifetime. Surfactants and mesopore-forming agents are often introduced to generate hierarchical architectures, yet their effects during the crystallization process and their interactions with organic templates like BTMAOH have not been comprehensively studied.

This work utilizes BTMAOH as an organic template to synthesize three SAPO zeolites: SAPO-20, SAPO-34, and hierarchical SAPO-5 using surfactant mesopore-forming agents. First, the study investigates the formation of SAPO-20 and SAPO-34 whereby the crystallization is monitored at different time intervals. This approach not only examines the progressive evolution of these zeolites from amorphous solid but also investigates the phase transformation of SAPO-34 into pure SAPO-20. In another study, the study compares the effects of various surfactants on the hierarchical structure of SAPO-5. The surfactants serve as mesopore-forming agents and their interactions during the crystallization of SAPO-5 are also studied. Next, the zeolite catalysts are used and tested in ethanolysis of furfuryl alcohol (FA) to produce ethyl levulinate (EL), and esterification of pyruvic acid (PA) to produce ethyl pyruvate (EP).

1.3 Research objectives

The research objectives of this research are:

- i. To study the formation process of SAPO-34 and SAPO-20 using BTMAOH as the organic template.
- ii. To study the catalytic performance of SAPO-34 and SAPO-20 in ethanolysis of FA.
- iii. To explore the effects of various surfactants on the formation of hierarchical SAPO-5 structures via a soft-templating technique.
- iv. To study the catalytic performance of hierarchical SAPO-5 in esterification of PA.

1.4 Overview of the thesis

This thesis consists of six chapters, covering the research background, literature study, experimental procedures, research findings, conclusion and future recommendations.

Chapter 1 introduces zeolites, focusing on the definition, synthesis and applications of SAPO-type zeolites. This chapter also introduces the problem statement, objectives and overview of this study.

Chapter 2 is a comprehensive literature review, which briefly introduces the types of zeolites. It also focuses on describing the current research, synthesis methods, and applications of SAPO-5, SAPO-20, and SAPO-34.

Chapter 3 describes the experimental methods used in this study, including the detailed procedure to study the synthesis of SAPO-20 and SAPO-34. In addition, the synthesis protocol of preparing hierarchical SAPO-5 is described. Next, the instruments and acquisition parameters used for characterizing SAPO zeolites and catalytic reactions are also described.

Chapter 4 reports the time-dependent crystallization evolution of SAPO-34 and SAPO-20 zeolites using BTMAOH template. The crystallization process at different times is monitored using various characterization methods, and the crystallization mechanism is proposed. In addition, the catalytic behavior of these two SAPO zeolites in the alcoholysis of FA to EL is also studied. Lastly, their catalytic performance is also compared with other homogeneous and heterogeneous catalysts.

Chapter 5 reports the results of soft-templating synthesis of hierarchical SAPO-5 for enhanced esterification of PA with ethanol. In this study, three surfactants are used as mesoporegens, namely TP, CTA and CP. The hydrothermally synthesized hierarchical and parent SAPO-5 are characterized with various methods to study their crystallinity, porosity, morphology and surface acidity before their catalytic behaviors are studied in the esterification of PA to EP. Besides, the catalytic performance of hierarchical SAPO-5 is also compared with other homogeneous and heterogeneous catalysts.

Chapter 6 concludes the findings of the study. Furthermore, the chapter also lists out the suggestions for the future work of this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Zeolites

Zeolites are a family of crystalline microporous aluminosilicates. They are composed of corner-sharing tetrahedral units of SiO_2 and AlO_2^- , forming three-dimensional frameworks with pores and channels of different sizes and shapes (Figure 2.1). The zeolite framework has a negative charge due to the substitution of Si with Al. In order to balance the surface charge, non-framework cations such as H^+ , Na^+ , K^+ , Ca^{2+} or Mg^{2+} are added. These cations can be exchanged with other ions in solution, giving zeolites their ion-exchange properties. Zeolites also have reversible physi- and chemisorbed water without collapsing their structures upon sorption process, making them useful for dehydration and rehydration applications.

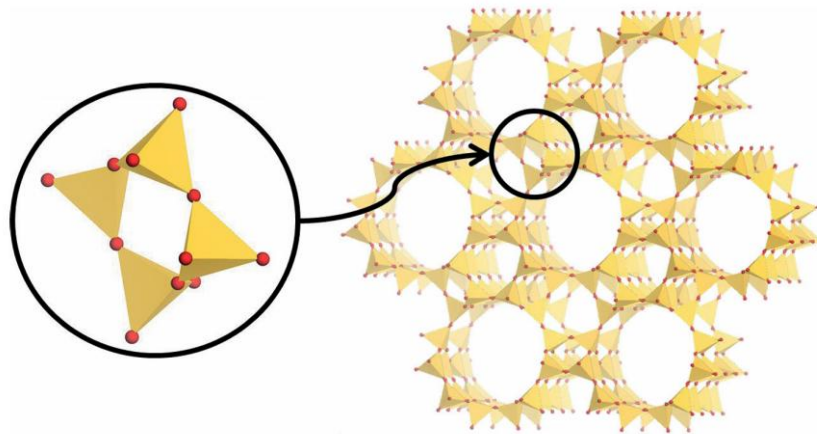


Figure 2.1 The structure of zeolite that is composed of tetrahedral TO_4 units, where T can be Si, Al or P (Daniel 2017).

Zeolites can be classified based on their framework structures, which are assigned three-letter codes by the International zeolite association (IZA). So far, there

are more than 160 types of framework structure have been identified by IZA (Al-Jubouri and Holmes 2017). Some of the common types of zeolites are Faujasites (FAU), Mobil Number Five (MFI), Mordenite (MOR), Linde Type A (LTA) and Chabazite (CHA) (Figure 2.2).

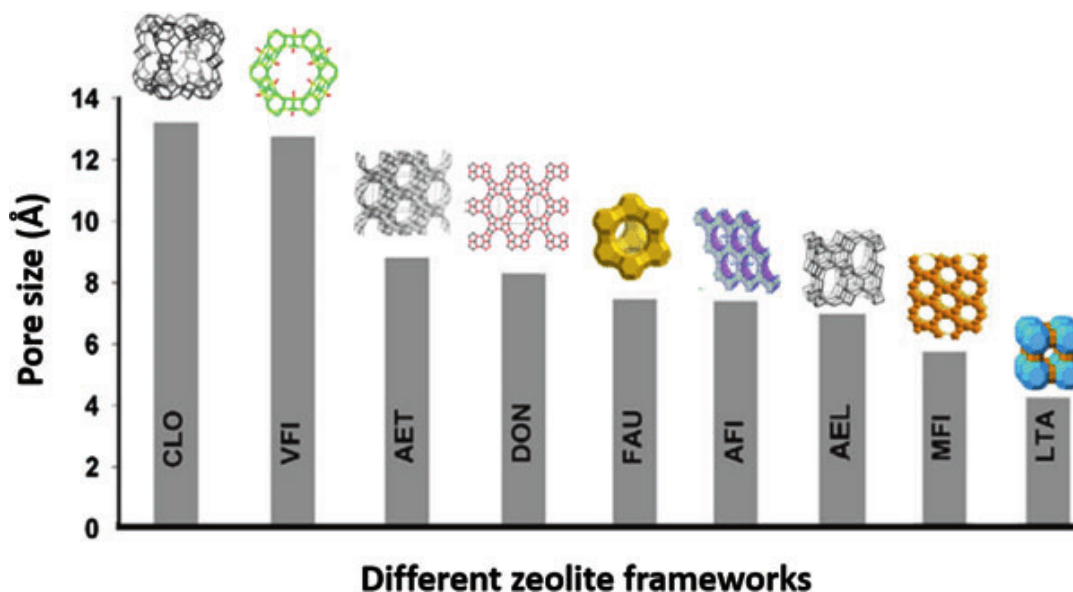


Figure 2.2 Some common types of zeolites with their respective pore sizes (Schwanke et al., 2017).

Faujasites (framework code: FAU) have a cubic or rhombohedral symmetry. These materials belong to large pore zeolites as they have 12-membered ring pore sizes with a pore diameter of 0.74 nm (Dib et al., 2022). As a result of their large microporosity, FAU-type zeolites are very widely used in catalytic cracking of petroleum (Van Borm et al., 2012) and gas separation (Wang et al., 2023). The examples of FAU zeolites are X and Y typed zeolites (Garcia et al., 2018).

Mobil Number Five (MFI) is another important zeolite. This type of zeolite has an orthorhombic symmetry and belongs to medium pore zeolite family. They have

10-membered ring pore sizes and a pore opening of 0.55 nm (Garcia et al., 2018). MFI-type zeolites are used in catalytic conversion of methanol to hydrocarbons (Wang et al., 2018), alkylation of aromatics, and shape-selective catalysis (Qian et al., 2019). Some examples of MFI zeolites are ZSM-5 (Grand et al., 2017) and silicalite (Isabel Dı'az 2004).

Mordenite belongs to MOR family and it is a 12-membered ring and large pore zeolite. It has a monoclinic symmetry and a pore size of 0.67 nm (Yao et al., 2020). Mordenite can be found naturally as rock and it can also be synthesized in the laboratory. Mordenite zeolite is very useful in catalytic cracking, hydrocracking and isomerization of hydrocarbons thanks to its large and accessible micropores besides its strong acidity (Yao et al., 2020).

Linde Type A (LTA) is a small pore zeolite (0.42 nm) made up of 8-membered ring. It has a cubic symmetry and its crystal shape can easily be recognized as cubical morphology. An example of LTA-typed zeolite is zeolite A that has a Si/Al ratio of 1.0 (Kumar et al., 2018). Due to its very high cation exchangeability, zeolite A is used in water softening (Lahnafi et al., 2023), detergent formulation (Koohsaryan et al., 2020) and gas separation (Eduardo et al., 2022).

Chabazites (CHA topology) are another very important small pore zeolite (0.38 nm). This type of zeolite is constructed by 8-membered ring and has a rhombohedral symmetry (Debost et al., 2023). Chabazites can also be found naturally near volcanic area and some can be prepared in the laboratory. In industry, chabazites are used in selective catalytic reduction of NO_x (Koohsaryan et al., 2020), methanol to olefin

conversion (Yang et al., 2017) and gas separation (Lee et al., 2019). Some examples of CHA zeolites are chabazite, SAPO-34 and SSZ-13 (Zang et al., 2022).

The classification of zeolites based on framework codes, membered ring sizes and dimensions is summarized in Table 2.1.

Table 2.1 Several common zeolite classifications based on framework code and ring size.

Zeolites framework codes	Membered ring size	Pore dimension (nm)
FAU	12	0.74
MFI	10	0.55
MOR	12	0.67
LTA	8	0.42
CHA	8	0.38

2.2 SAPO zeotype materials

Silicoaluminophosphate (SAPO) zeolites are another class of zeolites that have similar framework structures as aluminosilicate zeolites. Due to the presence of phosphorus atom, these materials display different chemical and physical properties as compared to their aluminosilicate counterparts (Figure 2.3) (Eduardo et al., 2022). SAPO zeolites have higher hydrothermal stability and higher selectivity but lower acidity than the conventional aluminosilicate zeolites. However, the frameworks of

SAPO zeolites are very flexible. They can be incorporated with other elements (such as iron, cobalt, titanium, zinc, etc.) to further modify their physicochemical properties (Hartmann and Kevan 1999). The resulting materials are called metallosilicoaluminophosphate (MeSAPO). So far there are about 40 types of SAPO zeolites. Some examples of SAPO zeolites are SAPO-5 (AFI), SAPO-11 (AEL), SAPO-20 (SOD), SAPO-34 (CHA) and SAPO-41 (AFO).

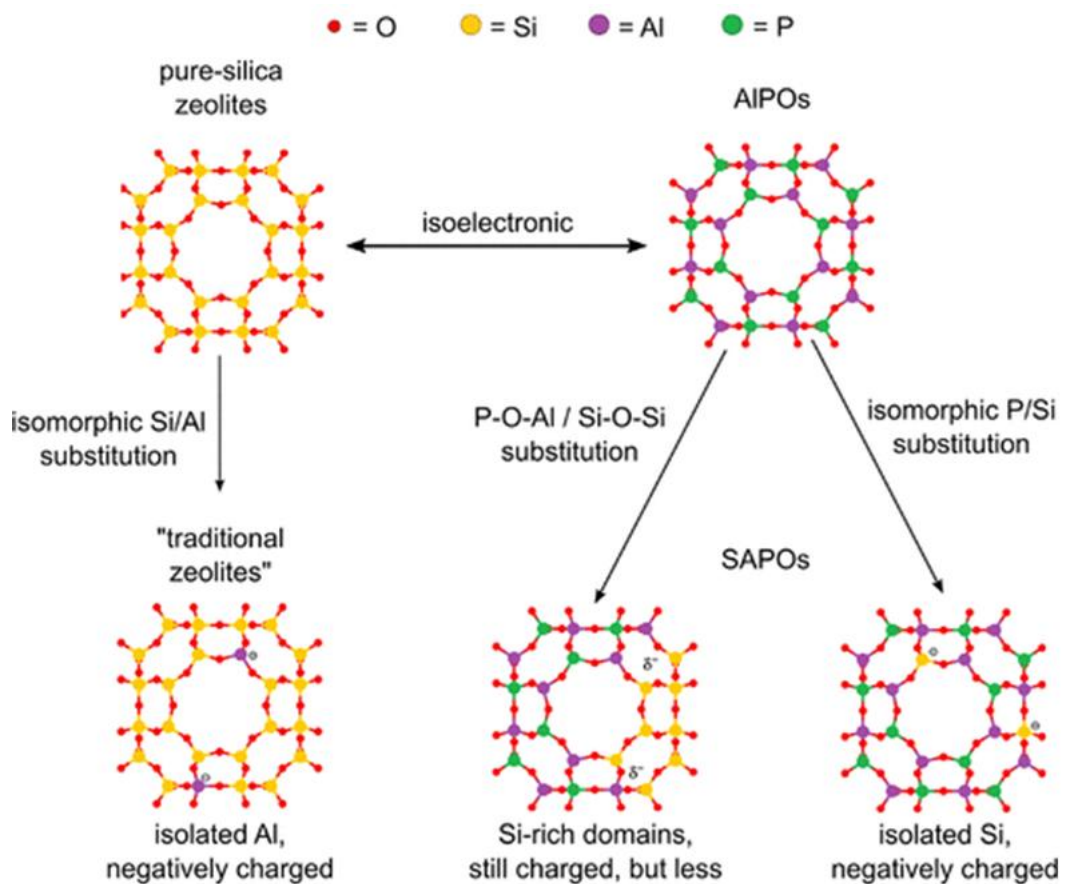


Figure 2.3 SAPO and aluminosilicate zeolites (Eduardo et al., 2022).

2.2.1 SAPO Number 5 (SAPO-5)

SAPO-5 is the most famous SAPO zeotype material. It has a hexagonal structure with a framework topology of AFI. Its structure is composed of one-

dimensional pore channel system made up of 12-membered ring. The zeolite pore size is considerably big (0.74 nm) allowing most of the molecules to diffuse into the micropores (Figure 2.4) (Machoke et al., 2015).

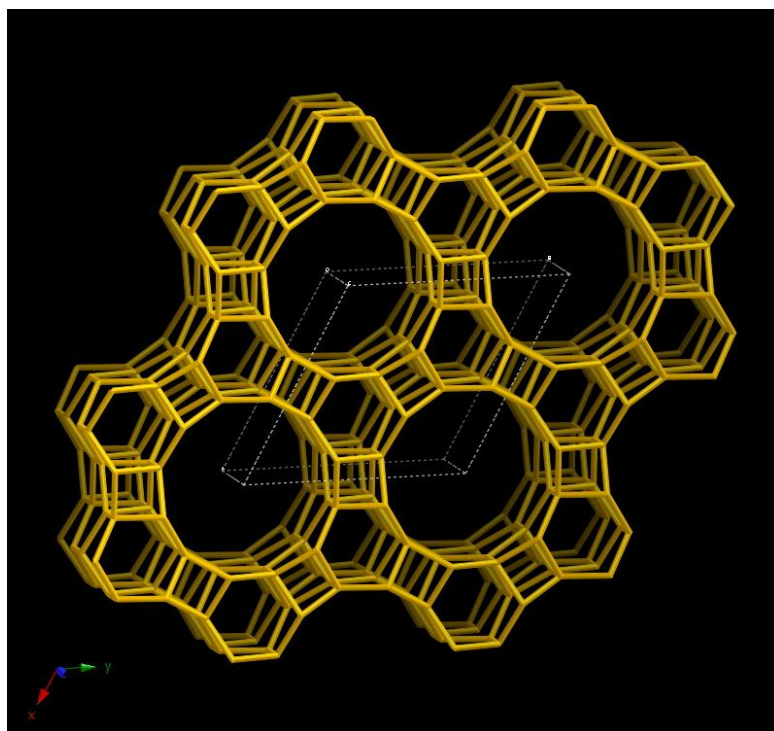


Figure 2.4 AFI pore structure (IZA-SC 2025).

SAPO-5 can be synthesized through hydrothermal crystallization in the presence of a gel mixture containing silica, alumina, phosphorus source, water and organic template. Typically, the templates used are triethylamine (TEA) (Liu et al., 2014), tetraethylammonium hydroxide (TEAOH) (Wang et al., 2021), tripropylamine (TPA) (Kornatowski et al., 1992), dipropylamine (DPA) (Seelan and Sinha 2004) or diethylamine (DEA) (Wang et al., 2003). For crystallizing SAPO-5, the hydrogel mixture should be in the pH range of 4-6 and is heated at 150-200 °C for 3-12 h. The synthesis conditions, such as the composition of the gel, pH, aging time, crystallization

temperature and time, can affect the crystal size, shape, purity and morphology of SAPO-5.

Xiao et al. studied the effect of aging time and crystallization time on the synthesis of SAPO-5 (Xiao et al., 1995). Their team fixed the initial sol composition as $1\text{Al}_2\text{O}_3: 1\text{P}_2\text{O}_5:2\text{SiO}_2:1\text{TEA}:70\text{H}_2\text{O}$, and extended the aging time. With increasing the aging time and reducing the crystallization time, the morphology of SAPO-5 molecular sieve is changed from large crystal rods to small crystal spheres.

Utchariyajit et al. found that when the initial sol composition was fixed as $1\text{Al}_2\text{O}_3: 2\text{P}_2\text{O}_5:0.2\text{SiO}_2:1.5\text{TEA}:750\text{H}_2\text{O}$, extending the aging time generates more crystal nuclei, thereby producing smaller SAPO-5 crystals with short hexagonal prism shape (Utchariyajit and Wongkasemjit 2010). However, if the aging time is too long, the impurity quartz phase and SAPO-34 are co-crystallized.

Yu et al. studied the effect of crystallization temperature on the synthesis of SAPO-5 (Yu et al., 2011). They found that the activation energy for growing SAPO-5 molecular sieve in different axial directions is quite different (a-axis: 64 kJ mol^{-1} and c-axis: 100 kJ mol^{-1}). High temperature ($200\text{ }^\circ\text{C}$) is not conducive for the formation of SAPO-5 nuclei where nucleation is only favored at low temperature ($140\text{ }^\circ\text{C}$). Also, they realized that changing the crystallization temperature significantly affects the purity, crystallinity and morphology of SAPO-5.

Finger et al. studied the effect of amount of TEA template in SAPO-5 crystallization (Finger et al., 1991). By increasing the content of TEA, the nucleation rate of SAPO-5 is enhanced, hence shortening the crystallization time. In addition, the

yield of SAPO-5 solid is increased where SAPO-5 crystals with intergrown rose-shape as new morphological shape are obtained.

The effect of template content on morphological change is also confirmed by Xiao et al. where they found that when they increase the TEA content, the cross-section of SAPO-5 changes from square to hexagonal, and finally to circular (Xiao et al., 1995). Further increasing the organic template content, however, produces SAPO-34 as side product.

Aluminum source is another factor that affects the crystallization of SAPO-5. Wen et al. used microwave-assisted ionothermal method to study the effect of aluminum source on the morphology of SAPO-5 (Wen et al., 2017). The results showed that the morphology of SAPO-5 synthesized with aluminum isopropoxide as the aluminum source was hexagonal prisms and nanoparticle agglomerates, while the morphology of SAPO-5 synthesized with aluminum acetate as the aluminum source was columnar with different aspect ratios. At the same time, smaller mesoporous volume was produced when aluminum isopropoxide was used as the aluminum source.

The pH of initial sol is another important factor controlling the particle size distribution and product yield of SAPO-5. Roldán et al. study the effects of different initial gel pH values (5-9) on the Si incorporation efficiency on AlPO (Roldán et al., 2007). The study found that in samples synthesized at low pH content, not all Si^{4+} ions were incorporated into the AlPO-5 framework. In some cases, large amount of unreacted amorphous silica and silicon-free AlPO-5 phases existed as physical

mixtures. However, when the pH was around 9 and an appropriate amount of silica was added in the starting gel, Si^{4+} was effectively incorporated into the AFI framework.

2.2.2 SAPO Number 20 (SAPO-20)

SAPO-20 is a small pore SAPO material having SOD framework structure (Figure 2.5). Normally, it has a rhombic icosahedral morphology and its structure consists of a three-dimensional channel system composed of 6-membered rings. The pores of SAPO-20 zeolite are very small (0.3 nm) and only very small molecules can diffuse into them (Zhang et al., 2021).

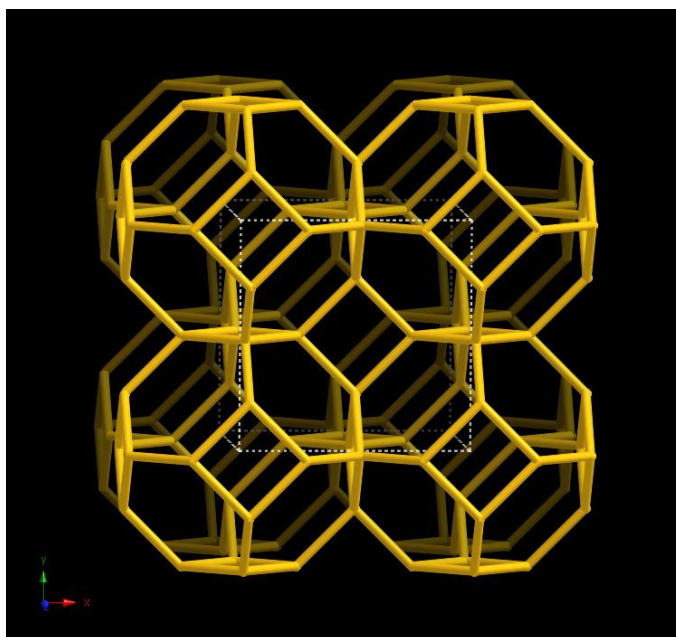


Figure 2.5 SOD pore structure (IZA-SC 2025).

SAPO-20 can only be crystallized in the presence of organic templates such as trimethylamine (TMA) (Turrina et al., 2016), isopropylamine (IPA) (Zhang et al., 2021) and TEAOH (Dong et al., 2020). The crystallization temperature suited for the growth

of SAPO-20 is 200 °C for 24 h (Malla and Komarneni 2011). Due to its very small micropore opening, its sodalite structure has been used in adsorption and dye removal (Klunk et al., 2019, Gilani et al., 2021).

2.2.3 SAPO Number 34 (SAPO-34)

SAPO-34 is a type of SAPO zeolite that has a chabazite (CHA) structure (Figure 2.6). It has three-dimensional pore channel system with 8-membered ring pores and a pore diameter of 0.38 nm (Xu et al., 2021).

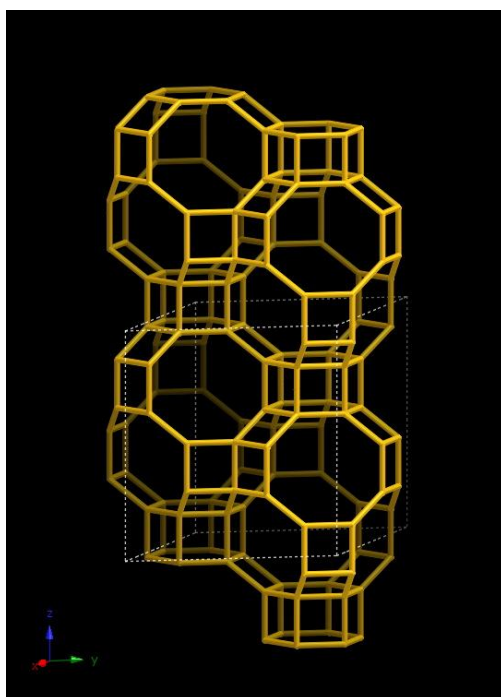


Figure 2.6 CHA pore structure (IZA-SC 2025).

SAPO-34 is usually synthesized under hydrothermal conditions in the presence of TEAOH (Hu et al., 2023). Besides that, SAPO-34 crystallized using DEA (Liu et al., 2008), TEA (Xu et al., 1990), 1-Propylpyridinium hydroxide (1-PyH) (Ma et al., 2022), piperidine (PP) (Dumitriu et al., 1997) and morpholine (MOR) (Sun et al., 2020)

as organic templates have also been reported. Normally, the crystallization of SAPO-34 takes place at 150-220 °C within 48 h (Ghavipour et al., 2023). Similar to SAPO-5, the physicochemical properties and formation of SAPO-34 are governed by the synthesis conditions (e.g. hydrogel composition, pH, aging, crystallization temperature and time).

Wang et al. hydrothermally synthesized the hierarchical SAPO-34 molecular sieve by modulating the Si/Al molar ratio of the gel precursor (Wang et al., 2023). By increasing the Si/Al ratio from 0.20 to 0.67, the morphology of the SAPO-34 crystals gradually changed from discrete ultra-small nanocrystals to dense polycrystalline aggregates. It was shown in the MTO reaction that SAPO-34 molecular sieves with low silicon content (Si/Al = 0.20) exhibited better catalytic performance than those with high silicon content (Si/Al = 0.67), with the catalytic life extended by about 2.5 times and the selectivity for ethylene and propylene has increased by about 10%. At the same time, when the catalyst with low silicon content was pretreated with NH₃ flow, the selectivity of ethylene and propylene has increased by 18.1% in the initial stage.

Aghaei et al. synthesized SAPO-34 by using high-temperature (300 °C, 3 h) and conventional (200 °C, 24 h) hydrothermal methods and the effects of crystallization time and crystallization temperature on the physicochemical properties and catalytic performance of SAPO-34 were studied (Aghaei and Haghighi 2015). The findings showed that the crystallization time and temperature affected the crystallinity, phase purity and grain size. In addition, the crystallization temperature had greater

effect than crystallization time on the crystallite size. In addition, nucleation also tended to occur using high temperature hydrothermal method, forming SAPO-34 with smaller crystallite size (400 nm) which is active in MTO reaction (conversion 94%, 90% selectivity).

2.3 Synthesis techniques of SAPO materials

2.3.1 Hydrothermal method

Hydrothermal method is a synthesis technique to prepare SAPO zeolites where water is used as a solvent under high temperature and pressure. In this method, the crystallization of SAPO zeolites is controlled by the temperature and pressure of the hydrothermal system, where both factors affect the solubility and reaction rates of the system (Marzpour et al., 2016).

Typically, the hydrogel made up of silicon, aluminum and phosphorus sources mixed with water is prepared. The organic template is then added to the hydrogel and stirred until a homogeneous mixture is obtained. In some cases, an aging process is required where this treatment is important to obtain crystals with smaller size and high crystallinity. The resulting mixture is then transferred to a sealed a Teflon-lined stainless steel autoclave and heated at a certain temperature (140-210 °C) for a certain time (1-72 h) under autogenous pressure (Figure 2.7). During hydrothermal process, nucleation and crystal growth occur in the synthesis mixture.

Hydrothermal synthesis benefits from its ability to produce well-crystallized and pure materials with controlled morphology, making it suitable for synthesizing

various materials. However, its main weaknesses include long reaction times and high energy consumption due to prolonged heating. Additionally, it can result in variability in crystal size and shape, affecting product consistency. Despite these drawbacks, hydrothermal methods remain valuable for their effectiveness in fabricating high-quality crystalline materials.



Figure 2.7 A stainless-steel autoclave used for hydrothermal synthesis of zeolites.

Solvothermal synthesis is different from hydrothermal synthesis because the solvent used is not water but an organic solvent. Hence, its synthesis and crystallization process are completely different from the hydrothermal one considering different hydrophilic-hydrophobic interactions. In 1985, Bibby et al. first published an article in Nature magazine reporting the synthesis of sodalite zeolite using non-aqueous solvents (ethylene glycol and propanol) in an autoclave (Bibby and Dale 1985). The synthesis can be done because the organic solvents have low boiling point and can exert high vapor pressure than hydrothermal synthesis at similar temperature, whereby high pressure is favored for crystallization of zeolites. Since then, AlPO-5 and AlPO-11

zeolites synthesized through solvothermal synthesis have successfully been reported (Yang et al., 2011).

Sinha et al. reported the crystallization of SAPO-31 using aqueous and non-aqueous (ethylene glycol) media (Sinha and Seelan, 2004). The results showed that the samples synthesized from non-aqueous medium had high surface acidity due to high Si^{4+} substitution and less formation of silica island. In addition, the SAPO-31 zeolite prepared in non-aqueous media showed high XRD crystallinity that contributes to high surface area and high acidity as compared to the sample synthesized in aqueous media (Figure 2.8).

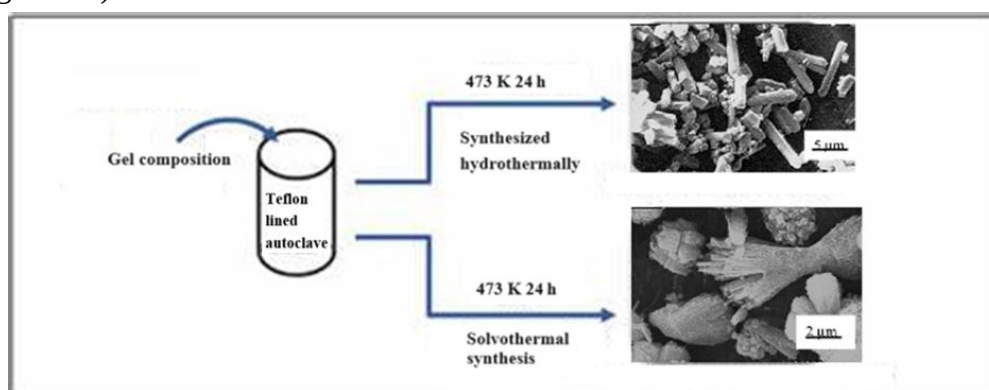


Figure 2.8 Comparative solvothermal and hydrothermal syntheses of SAPO-31 zeolite (Sinha and Seelan 2004).

2.3.2 Microwave heating

Microwave heating is another well-known method for crystallizing SAPO zeolites. It is based on the fact that microwave irradiation can generate electromagnetic waves that can penetrate the synthesis mixture and induce dipolar polarization and ionic conduction of the molecules (Amini et al., 2021). The dipolar polarization and ionic conduction can cause rapid and uniform heating of the synthesis mixture, which

can accelerate the hydrolysis and polycondensation of the Si, Al and P tetrahedral units that form the SAPO framework (Figure 2.9) (Wang et al., 2023).

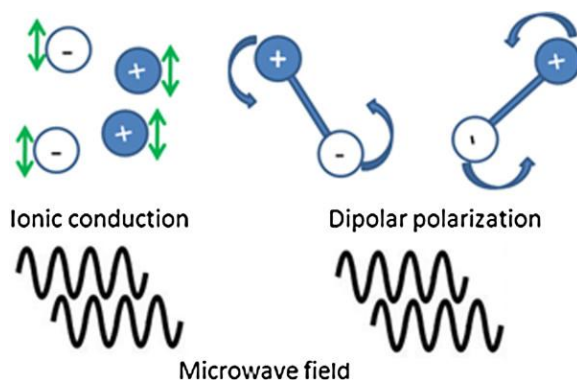


Figure 2.9 Two mechanisms to induce microwave heating (Gude et al., 2013)

The crystallization process of SAPO zeolites can be controlled by the microwave power (Zeng et al., 2021). For example, high microwave irradiation power can lead to high temperature and pressure in the synthesis, which favors the formation of more crystalline zeolites. In contrast, low microwave power leads to low temperature and pressure, which slows down the formation of zeolites, viz. slow crystallization rate. Furthermore, the microwave power, heating temperature and time also affect the crystal size, shape, purity and surface properties of SAPO zeolites.

Shalmani et al. synthesized nano-sized SAPO-34 zeolite by manipulating the synthesis conditions under microwave-assisted hydrothermal conditions (Shalmani et al., 2012). The results showed that the heating time plays a crucial role in controlling the shape and size of nanocrystals, while aging time and microwave power have negligible effect. In addition, more viscous initial gel is beneficial for preparing pure SAPO-34 with smaller crystals. Also, high microwave power has positive influence on crystallizing SAPO-34 with smaller size.

In addition, Gharibeh et al. studied the effects of microwave and conventional oven heatings on nucleation and growth of SAPO-11 (Gharibeh et al., 2008). The results show that microwave synthesis only spends 2 h at 175 °C to complete the crystallization process instead of 15 h if oven heating is used. In addition, microwave heating can enhance the nucleation and growth of SAPO-11 thanks to the fast and uniform heating. As a result, the microwave energy promotes nucleation, producing SAPO-11 of smaller size with narrower size distribution compared to that prepared using conventional heating.

2.3.3 Dry gel synthesis (steam-assisted crystallization) method

The dry gel synthesis method is different from the hydrothermal method because the dry precursor gel is separated from the template aqueous solution, whereby they are separated by a vessel (Figure 2.10) (Vattipalli et al., 2018). During heating, the vapor of organic template interacts with the dry gel and converts the amorphous dry gel into a zeolitic crystalline solid.

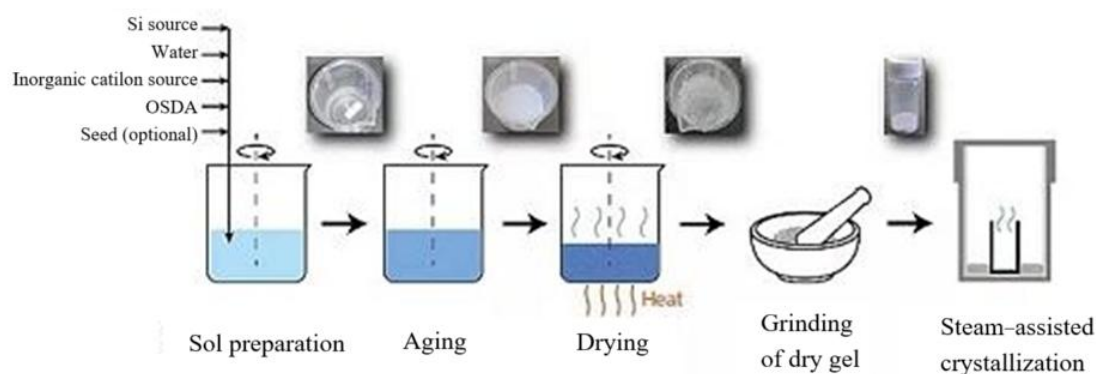


Figure 2.8 Preparation of SAPO zeolite using dry gel synthesis (steam-assisted crystallization) method (Vattipalli et al., 2018).

Hirota et al. synthesized SAPO-34 nanocrystals by using dry gel method where TEOAH served as a structure-directing agent (Hirota et al., 2010). The results showed that this method produced high nucleation density and slow crystal growth rate was also observed, leading to the formation of SAPO-34 nanocrystals (approx. 75 nm). The resulting SAPO-34 was also compared with that synthesized using hydrothermal method and found that the latter method produced larger crystals.

Table 2.2 summarizes all the methods for synthesizing SAPO zeolites where the advantages and disadvantages of each method are listed.

Table 2.2 Advantages and disadvantages of the zeolite synthesis methods.

Synthesis method	Advantages	Disadvantages
Hydrothermal method	Simple process, low cost	Uneven distribution of crystal size
Microwave heating	Short crystallization time, high crystallinity, relatively uniform particle size	Microwave technology is currently difficult to industrialize
Solvothermal method	Synthesis of high-silicon molecular sieves	Need to recycle organic solvents and templates
Dry gel method	High output, low waste liquid	The process is relatively complex

2.4 Catalytic applications of SAPO

2.4.1 Methanol to olefin

Methanol to olefin (MTO) is a process that converts methanol to light olefins, such as ethylene and propylene, which are valuable petrochemical products. The catalytic performance of SAPO catalysts for MTO reaction can be evaluated by several parameters, such as the conversion of methanol, the selectivity and yield of olefins, the lifetime and stability of catalyst, and the coke formation and deactivation of catalyst (Chen et al., 2012). Among the SAPO catalysts, SAPO-34 has been reported to have the best catalytic performance for MTO reaction, due to its CHA structure with 8-

membered ring pores that has a pore opening of 0.38 nm (Figure 2.9) (Liu et al., 2023). SAPO-34 can achieve a high conversion of methanol (>90%), high selectivity (>80%) and high yield of olefins (>0.7 g/g) (Figure 2.11). In addition, SAPO-34 also shows a very long lifetime (>100 h) and stability with a low coke formation (<10% decline after each run) (Yang et al., 2021).

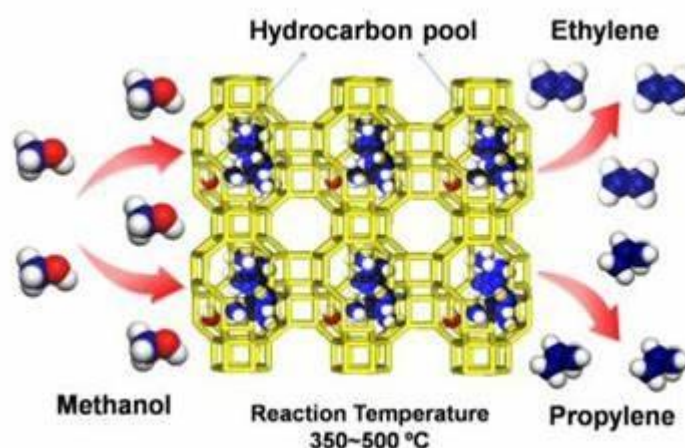


Figure 2.9 The picture shows the reaction process of methanol to olefin catalyzed by SAPO-34 (Sun et al., 2018).

SAPO-11 and SAPO-18 have also been used as catalysts for MTO reaction, but their catalytic performance is lower than that of SAPO-34 (Soundararajan et al., 2001, Zhong et al., 2019). SAPO-11 and SAPO-18 can achieve a moderate conversion of methanol (60-80%) and selectivity (60-70%) with a yield of 0.4-0.5 g/g. Both catalysts, however, show a shorter lifetime (<50 h) and lower stability (>20% decline) due to high coke formation (Said and Zaky 2019).

Recently, several efforts have been made to improve the catalytic performance of SAPO-type catalysts in MTO reaction. For example, Ji et al. synthesized nanosized low-silicon SAPO-34 zeolite (600-800 nm) with hierarchical hollow structures in the