The state-of-the-art synthetic strategies for SAPO-34 zeolite catalysts in methanol-to-olefin conversion

Qiming Sun¹, Zaiku Xie² and Jihong Yu¹,³,*

ABSTRACT

Methanol-to-olefin (MTO) conversion has proven to be one of the most successful non-petrochemical routes for producing light olefins. Silicoaluminophosphate (SAPO) zeolite SAPO-34 is one of the best industrial catalysts for MTO conversion, but suffers from rapid deactivation due to the inherent diffusion bottleneck limited by the narrow eight-ring pore openings. To improve the MTO performance, considerable synthetic efforts have been devoted to decrease the crystal size of zeolites or introduce secondary larger pores in zeolite crystals to form hierarchical structures. This review mainly focuses on presenting the state-of-the-art synthetic strategies for nanosized and hierarchical SAPO-34 catalysts with excellent MTO performance. Furthermore, the industrialization of SAPO-34 catalysts for the MTO reaction, and some current problems and future prospects for the synthesis of SAPO-34 catalysts, are also pointed out. We expect that this review can not only shed some light on the preparation of SAPO-34 catalysts, but also stimulate the future development of high-performance SAPO-34 catalysts to meet the increasing demands of the chemical industry.

Keywords: methanol-to-olefin, zeolites, SAPO-34, hierarchically porous structure, nanocrystals, heterogeneous catalysis

INTRODUCTION

Light olefins, such as ethylene and propylene, have been widely used as important raw materials for various chemicals in the chemical industry. However, the shortage of oil resources has forced researchers to develop an alternative technology for the preparation of light olefins that is independent of oil resources [1,2]. The methanol-to-olefin (MTO) process has proven to be a successful non-petrochemical route for the production of light olefins from abundant non-oil resources, such as natural gas, coal and even biomass using methanol as the intermediate. Thus, the MTO reaction can act as a bridge between the non-petroleum chemical and modern petrochemical industries [3]. Over the last 40 years, the fundamental research and industrial applications of the MTO reaction have received great attention from many institutions and companies. In 2010, the first 600 000 ton/year MTO unit in the world was successfully built up and brought on stream in China, which is regarded as a significant milestone for the conversion of coal to light olefins [4].

Because of their excellent shape selectivity, appropriate acidity, and superior thermal and hydrothermal stability, crystalline zeolites with ordered microporous architectures have been widely used as the most important solid heterogeneous catalysts in a number of industrial processes [5–11]. Silicoaluminophosphate (SAPO) zeolite SAPO-34, with its CHA framework structure, has proven to be the most ideal catalyst for MTO conversion to produce ethylene and propylene. The SAPO-34 zeolite possesses a large CHA cage (0.94 nm in diameter) and a small eight-ring pore (0.38 nm) opening, as well as moderate acidity, which can induce very high selectivity of ethylene and propylene (>80%) in MTO reactions with complete conversion of methanol [12]. In general, the reaction temperature of MTO conversion is in the range of 350–500°C. The schematic representation of MTO conversion over the SAPO-34 catalyst is shown in Scheme 1. Based on the proposed hydrocarbon pool mechanism, polymethylbenzenium ions are formed during the reaction, which act as the important reaction intermediates for olefin production [13].
However, these polymethylbenzenium ions can further turn into bulk organic species as coke deposition accommodated in the large cavities connected by narrow channels, thus covering the active sites of catalysts and leading to their rapid deactivation during methanol conversion. This is indeed the main problem associated with SAPO-34 catalysts [14]. To overcome the inherent diffusion limitations and retard coke deposition, various synthetic strategies have been developed in recent years, and considerable efforts are focused on the reduction of crystal sizes of the catalysts or the introduction of secondary larger pores into the zeolite crystals to form hierarchical structures. The nanosized and hierarchical SAPO-34 catalysts demonstrate significant advantages in the enhancement of mass transfer and decrease of coke formation rate as compared with their traditional microporous counterparts with larger crystal sizes.

There have been several excellent reviews about the MTO reactions concerning both fundamental research and commercial processes [3,4,13–18]. However, most of the reviews have focused on mechanistic research into MTO catalysis, the influencing factors on the catalytic behavior of MTO over different zeolitic catalysts and the diffusion and deactivation of MTO catalysts, as well as the industrial investigation of methanol conversion. In view of the significance of synthesizing SAPO-34 zeolite as the most important commercial catalyst in MTO units, in this review, we will present state-of-the-art synthetic strategies for the preparation of nanosized and hierarchical SAPO-34 catalysts with excellent MTO performance. The industrialization of SAPO-34 catalysts for the MTO reaction, and some current limitations as well as future prospects for the synthesis of SAPO-34 catalysts, have also been discussed.

Scheme 1. A schematic representation of MTO conversion over the SAPO-34 catalyst.

SYNTHESIS OF HIGH-PERFORMANCE SAPO-34 CATALYSTS

Synthetic methods for nanosized SAPO-34 catalysts

Diffusion limitations cause not only the decrease of catalytic lifetime, but also the low selectivity of light olefins during MTO reactions. Many previous studies have revealed that SAPO-34 catalysts with smaller crystal sizes show advantages in improving mass transfer and inhibiting coke formation in MTO catalytic reactions, and thus exhibit superior MTO catalytic performance [19–22]. In recent years, some synthetic approaches have been developed to synthesize nanosized SAPO-34 crystals, such as the mixed-template, concentrated or dry gel, microwave-assisted, ultrasound-assisted, and recrystallization and seed-assisted synthetic methods. The nature underlying these strategies for preparing nanosized SAPO-34 crystals is the promotion of fast and abundant nucleation in the initial precrystallization stage and/or retardation of crystal growth in the process of crystallization.

Mixed-template synthetic method

Up to now, more than 20 types of organic templates have been utilized to synthesize SAPO-34 catalysts. Among these templates, tetraethylammonium hydroxide (TEAOH), morpholine (MOR), triethylamine (TEA) and diethylamine (DEA) are the most commonly used templates. The choice of templates significantly affects the particle sizes and physicochemical properties of as-synthesized zeolites. In general, compared with other templates, TEAOH tends to direct the synthesis of smaller SAPO-34 crystals. However, the high cost of TEAOH may limit the practical large-scale production of catalysts in industry. Using mixed templates, for example adding more than two templates into the synthesis gel to direct the formation of zeolites, has proven to be an effectively low-cost way to synthesize SAPO-34 catalysts with small crystal size [23,24].

Lee et al. [25] prepared the spherical aggregation of nanosized SAPO-34 crystals using TEAOH and MOR as mixed templates. Compared with using a single MOR template, utilizing a mixed template could reduce particle sizes. Moreover, the catalyst obtained using a mixture of 75% MOR and 25% TEAOH gave the longest lifetime, reaching up to 840 min (450°C, weight hourly space velocity (WHSV) = 1 h⁻¹). Ye et al. [26] also studied the synthesis of SAPO-34 catalyst using different combinations of TEAOH and DEA as mixed templates. The authors found that adding some TEAOH into the DEA synthetic
gel could decrease the SAPO-34 crystal size in comparison with using DEA as the sole template. The catalyst using a mixture of 50% TEAOH and 50% DEA gave the longest lifetime (545 min) at 425°C in a MTO reaction. Subsequently, Wang et al. [27] synthesized small SAPO-34 crystals (1.4 μm) with a mixed template of TEA/TEAOH. The molar ratios of TEAOH/TEA in the synthetic gel greatly affected the chemical composition, crystal morphology, crystal size and silicon incorporation in SAPO-34 catalysts. Among the obtained catalysts, SAPO-34 catalysts synthesized with TEAOH/TEA = 0.1 possessed larger surface area, more suitable acidity, smaller crystal size and higher catalytic activity than those synthesized with a single template. Recently, Masoumi et al. [28] systematically investigated the synthesis of SAPO-34 catalysts in a tri-templating agent (TEAOH, TEA and MOR) system. The catalyst prepared with the composition of MOR/TEA/TEAOH = 0.5/0.5/1 exhibited a higher yield of light olefins than those synthesized with single and dual templates due to its higher crystallinity, smaller crystal size and higher surface area. Although many efforts have recently been made in the exploration of mixed-template synthetic methods, it is still highly desirable that the ratio of different templates in the synthesis gel be further optimized in future research, especially with regard to decreasing the consumption of TEAOH for the synthesis of nanosized SAPO-34 catalysts with excellent MTO performance.

Concentrated or dry gel conversion method

Besides templates, the concentration of synthetic gels can also greatly affect the morphology and physicochemical property of SAPO-34 catalysts [29]. Hirota et al. [30] synthesized SAPO-34 nanocrystals by a dry gel conversion (DGC) method using TEAOH as the template. The average crystal size of the obtained SAPO-34 catalysts was 75 nm, which was smaller than that prepared using the hydrothermal method using the same template. The reduced crystal sizes obtained by the DGC method can be ascribed to the high nucleation density in the early stages of synthesis and slow crystal growth after nucleation. Similarly, Askari et al. [31] synthesized SAPO-34 nanoparticles (less than 500 nm) by the DGC method using MOR as the template and investigated the effect of synthetic parameters on the crystallinity, shape and particle size of SAPO-34. It was found that increasing the crystallization time and gel drying temperature was beneficial for the crystallization of SAPO-34 nanoparticles. Moreover, the DGC method can remarkably reduce the crystallization time and the formation of fully crystalline SAPO-34 nanocrystals required only 6 h. Similar to the DGC method, the concentrated gel conversion method is also an alternative simple route for reducing crystal size, because the concentrated synthesis gel is beneficial for the interaction between the inorganic raw materials and organic template, leading to fast and abundant nucleation in the initial pre-crystallization stage. Recently, Sun et al. [32] synthesized nanosheet-like SAPO-34 crystals with 20 nm in thickness and different silicon contents under hydrothermal conditions using the concentrated gel conversion method (Fig. 1). The concentrated gel synthesis system not only accelerated the nucleation forming nanosized crystals, but also improved the product yield up to 90%. Significantly, SAPO-34 nanosheets with the lowest silicon content exhibited the longest catalyst lifetime so far (1206 min, WHSV = 2 h⁻¹) and a lower coking rate (0.06 mg/min) in a MTO reaction than previously reported catalysts tested under similar conditions.

Microwave-assisted synthetic method

Compared to conventional hydrothermal synthesis, the microwave heating process displays several advantages, such as efficient use of energy, facile morphology and phase control, as well as rapid and homogenous nucleation rates, which are favorable for fast and energy-efficient production of small zeolite crystals with uniform size distribution. Heyden et al. [33] synthesized cube-like SAPO-34 nanoparticles that were 100 nm in diameter by means of a microwave hydrothermal treatment using colloidal precursor solutions. Recently, Yu et al. [34,35] synthesized nanosized SAPO-34 catalysts with different crystal morphologies in the reaction system of Al₂O₃-P₂O₅-SiO₂-TEAOH-H₂O under microwave conditions. The raw materials and compositions of synthetic gels significantly affected crystal morphology. Nanosheet-like SAPO-34 crystals with a size of ~280 x 40 nm can be obtained using colloidal silica or SiO₂ powder as the silica source, but when the tetraethylorthosilicate (TEOS) is used as the silica source, uniform 80 nm spherical aggregations composed of SAPO-34 crystals of ca. 20 nm can be formed (Fig. 2). Moreover, the crystallization time of SAPO-34 by the microwave-assisted synthetic method can be also reduced to 1 h, which significantly improves synthesis efficiency. Recently, Álvaro-Muñoz et al. [36] also prepared nanocrystalline SAPO-34 catalysts using dilute zeolitic precursor solutions by the microwave-assisted hydrothermal synthetic method. The use of microwave irradiation not only shortened the crystallization time from days to several hours, but also...
resulted in a lower level of silicon incorporation, leading to slightly lower acidity.

**Ultrasonic-assisted synthetic method**

Sonochemical synthesis by ultrasonic irradiation is a new method for the synthesis of nanocrystals, which is simple and efficient, and the particle size of the obtained products can be easily controlled by changing the ultrasound-related variables. Different from other traditional chemical methods, sonochemistry is based on acoustic cavitation, that is, the formation, growth and collapse of bubbles in the solution can significantly influence the crystallization kinetics and the formation of nuclei. Askari et al. [37] synthesized SAPO-34 nanocrystals using TEAOH as a template by an ultrasonic pretreatment method. The obtained SAPO-34 catalysts exhibited spherical aggregated morphology and the average particle size was ca. 50 nm (Fig. 3), which was much smaller than that synthesized under conventional hydrothermal conditions. Moreover, use of the ultrasonic-assisted synthetic method can remarkably reduce the crystallization time to 1.5 h. As compared with the SAPO-34 catalysts with larger crystal sizes synthesized by the conventional hydrothermal method, the nanosized SAPO-34 catalyst exhibited a more than twice-prolonged catalytic lifetime, due to the improved diffusion efficiency and decreased acidity [38]. The ultrasonic-related parameters, such as ultrasound...
power intensity, ultrasonic irradiation time, sonication temperature and sonotrode size, had an influence on the physicochemical characteristics of SAPO-34 catalysts [39,40]. In particular, the ultrasonic power was the most important parameter affecting the crystallinity and morphology of the products. The increase of ultrasonic power, its duration and the sonication temperature were favorable for decreasing the mean particle sizes of SAPO-34 catalysts and forming more uniform spherical nanoparticles.

Recrystallization and seed-assisted synthetic method

Beside the methods mentioned above, in recent years, other novel synthetic strategies have also been developed for the preparation of nanosized SAPO-34 catalysts. Yang et al. [22] developed a post-synthesis milling and recrystallization method to prepare small cube-like SAPO-34 crystals that were 50–350 nm in size (Fig. 4). Firstly, micrometer-sized SAPO-34 was synthesized using DEA as the template, and then the SAPO-34 precursor was calcined followed by milling using a planetary ball mill. Finally, the milled SAPO-34 was hydrothermally recrystallized and showed remarkably improved MTO performance as compared with the unmilled counterpart. The milled SAPO-34 precursor with the smaller particle size was the key factor for the generation of nanosized SAPO-34 crystals, which can act as the initial nuclei in favour of the subsequent crystallization. The fast crystallization process can keep the nanosized morphology of the milled SAPO-34 precursor unchanged and finally lead to the formation of small SAPO-34 crystals. Subsequently, this synthetic method was further developed to synthesize other nanosized and hierarchical zeolites [41,42].

The seed-assisted synthetic method has been widely used for the synthesis of aluminosilicate zeolites. Very recently, Sun et al. [43] successfully synthesized nanosized hierarchical SAPO-34 catalysts with high crystallinity and product yield via the seed-assisted method. The addition of seeds acting as the original nuclei can accelerate crystallization and decrease crystal size due to the Ostwald ripening mechanism. Significantly, compared to the conventional micronsized SAPO-34 zeolites, the nanosized hierarchical SAPO-34 zeolites showed superior performance in the MTO reaction with 4-fold prolonged catalytic lifetime and remarkably improved selectivity of ethylene and propylene reaching up to 85.0% (WHSV = 2 h⁻¹, T = 673 K).

In general, it takes one or several days to crystallize SAPO-34 zeolite under hydrothermal conditions, which consumes much energy and increases the synthetic cost. Thus, there is a significant need to reduce the crystallization time of SAPO-34 catalysts. Recently, Sun et al. [44] successfully synthesized nanosized SAPO-34 catalyst in 10 min by rapidly heating the reaction gel in a stainless steel tubular reactor with an outer diameter of 12.0 mm and an inner diameter of 9.0 mm combined with the seed-assisted method. The obtained SAPO-34 catalysts possessed high crystallinity and nanosheet-like morphology as shown in Fig. 5. The remarkably reduced synthesis time of SAPO-34 catalysts was attributed to the fast heat transfer of the stainless steel tubular reactor and rapid nucleation induced by the addition of SAPO-34 zeolite seeds. Importantly, the nanosized SAPO-34 catalysts synthesized in the minute time scale exhibited superior performance in the MTO reaction compared to counterparts synthesized by the conventional hydrothermal method for 12 h. This method could be realized as an efficient mass production route for the synthesis of nanosized SAPO-34 catalysts using a continuous flow reactor that meets the demand of future large-scale industrial applications.

Synthesis of hierarchical SAPO-34 catalysts

To further enhance the mass transfer, reduce the coke formation rate and improve the MTO catalytic performance, considerable efforts have also been devoted to creating larger secondary pores (>2 nm) to form hierarchically porous SAPO-34 catalysts. Introducing mesopores or macropores into the microporous SAPO-34 zeolite crystals can greatly enhance the intracrystalline mass transport efficiency for the reactant and products and decrease the deactivation rate, thus prolonging catalyst lifetime. In addition, the introduction of hierarchical structure can usually decrease the acidity of SAPO-34 catalysts and further enhance their catalytic performance. In recent years, several methods have been successfully developed for the synthesis of hierarchical SAPO-34 catalysts,
including the hard-templating, soft-templating and post-treatment methods. The approaches for the preparation of hierarchical SAPO-34 catalysts are briefly summarized in Table 1.

### Hard-templating method
Jacobsen et al. [45] reported the first example of the generation of hierarchical zeolites by the hard-templating method using nanocarbon as the mesoporous template. Since then, various hard templates have been employed to synthesize hierarchical aluminosilicate zeolites [46]. More recently, Schmidt et al. [47] introduced hierarchical pores into the SAPO-34 zeolites using carbon nanoparticles and carbon nanotubes as secondary templates. The authors found that the mesopores created by carbon nanoparticles were located inside the crystals, but that the additional pores were not connected to form a 3D mesopore network, which showed almost no improvement for the diffusion limitation. In contrast, the use of carbon nanotubes led to mesopores that were accessible from the outside of the particles, which enhanced the MTO performance. Subsequently, several hierarchical SAPO-34 catalysts were also synthesized using carbon nanotubes as hard templates, and the hierarchical SAPO-34 catalysts obtained exhibited enhanced MTO activity compared with conventional microporous catalysts [48–50]. In addition, some other hard templates were also employed for the synthesis of hierarchical SAPO-34 zeolite, such as polystyrene spheres [51] and aqueous rapeseed pollen extract [52]. Recently, Gong et al. [52] reported a new synthetic route to prepare hierarchical SAPO-34 constructed by numerous nanosheets with 10–40 nm thickness using rapeseed pollen extract as the synthesis solution. With the increase of rapeseed pollen suspension in the starting synthesis gels, the amount of SAPO-34 nanosheets increased and their shape became much curlier.

### Soft-templating method
Besides the hard-template method, the soft-templating method is an alternative approach to synthesize hierarchical zeolites. During the crystallization process, the self-assembled supermolecular materials and/or surfactant molecules as soft templates interact with the reactant raw materials to direct the formation of meso/macroporous structures in zeolites. Compared to hard templates, soft templates are more widely used because soft templates are more flexible and adjustable, which is beneficial for the control of the hierarchical structure and morphology of zeolites. Among the soft templates, organosilane surfactants are most commonly used to fabricate the hierarchical SAPO-34 catalysts [41,53–58]. Recently, Sun et al. [56] synthesized hierarchical SAPO-34 catalysts using MOR as a microporous template and [3-(trimethoxysilyl)propyl]-octa-decyl-diethylammonium chloride (TPOAC) as the mesopore director through a one-step hydrothermal crystallization. The hierarchical SAPO-34 crystals were micronsized cubic aggregates composed of nanocrystallites with the sizes of the individual nanocrystals ranging from 100 to 500 nm. The proposed assembly pathway of nanocrystallites into micrometer-sized hierarchical porous SAPO-34 crystals is shown in Fig. 6. The TPOAC surfactant plays two roles in the formation of hierarchical SAPO-34 catalysts: (i) the long-chain hydrophobic organic tails of the TPOAC surfactant are convolved to form mesoscale micelles directing the mesoporous structure; (ii) the TPOAC surfactant caps the surface of nanocrystals, thus restricting the further growth of the nanocrystals and forming the cube-like agglomerates with some intervoid space. Subsequently, Wang et al. [57] synthesized the spherical self-assembly of SAPO-34 nanosheets by using the same organosilane surfactant (TPOAC) as the mesoporegen, and DEA as the microporous template. Wang et al. [41] very recently also fabricated uniform dice-like particles in a size range of 300–500 nm consisting of a large number of 20–50 nm nanocrystals with abundant holes, by adding an amount of milled SAPO-34 precursor into the TPOAC-containing synthesis gel to accelerate the crystallization of the microporous structure. The introduction of a suitable amount of milled
SAPO-34 precursor together with the quaternary ammonium-type organosilane would be the key to make the crystallization of microporous and mesoporous structures match well. Some other works have also demonstrated that TPOAC can effectively direct the formation of hierarchical SAPO-34 catalysts using TEAOH as a microporous template [53,54].

Apart from the organosilane surfactants, some other soft templates have been employed to prepare hierarchical SAPO-34 catalysts, such as cetyltrimethylammonium bromide (CTAB) [59,60], polyethylene glycol (PEG) [61,62], polyethylenimine (PEI) [63], organophosphorous surfactant [64] and dimethyloctadecyl[(3-(trimethoxysilyl)propyl] ammonium chloride [65]. Kong et al. [60] fabricated hierarchical SAPO-34 catalysts via the hydrothermal crystallization method with CTAB as a mesoporous generating agent. The results showed that, with the increase of CTAB in the synthesis gel, the amount of mesopores in the hierarchical SAPO-34 catalysts was increased but the acidic strength and concentration decreased gradually. Cui et al. [61] synthesized hierarchical cross-like SAPO-34 catalysts with different pore size distributions ranging from 10 to 50 nm via hydrothermal synthesis with PEG-2000 as the mesoporous agent. Recently, Wang et al. [63] synthesized hierarchical SAPO-34 catalysts with uniform mesopores using a PEI dendrimer (mol wt = 70,000) as a mesoporous directing agent under conventional hydrothermal conditions. The PEI chains extended in the synthesis gel and thus uniform mesopores could be formed along the interconnecting linear chains of PEI. Very recently, a novel soft template of organophosphorous surfactant ([2-(diethoxylphosphono)propyl]hexadecylmethylammonium bromide (DPHAB)) was employed to synthesize hierarchical SAPO-34 catalysts with various special morphologies using TEAOH, DEA and TEA as templates [64]. Among the investigated templates, TEAOH showed the best cooperation with the organophosphorous surfactant in directing the formation of nanosized mesoporous SAPO-34.

Post-treatment method

There are a number of post-treatment approaches for the upgradation of conventional aluminosilicate zeolites, such as acid/base leaching, demetallation by steaming and etching in fluoride medium [66]. However, compared with the synthesis of the hierarchical aluminosilicate zeolites, fabricating the hierarchical SAPO zeolites using post-treatment methods is more difficult due to the unstable framework structure under acidic or alkaline conditions. Verboekend et al. [67] post-treated a series of SAPO zeolites, such as SAPO-5, SAPO-11 and SAPO-34, by various acid and base treatments for the formation of hierarchical structures. The authors found that SAPO zeolites amorphized strongly in aqueous NaOH, but crystallinity was preserved in the presence of organic bases. In acid media, SAPO-11 remained fully crystalline, while SAPO-34 strongly amorphized. The phenomena of high resistance in alkaline media and low stability in acid media of

Figure 5. TEM images of nanosized SAPO-34 samples synthesized at different times by fast heating the reaction gel in a stainless steel tubular reactor as compared with samples synthesized by conventional heating. S: with seed; N: without seed; Oil: oil heating; and Oven: oven heating. Scan bar: 500 nm. Adapted from [44] © 2015 The Royal Society of Chemistry.
Table 1. Summary of various synthetic methods for the synthesis of hierarchically porous SAPO-34 zeolites.

<table>
<thead>
<tr>
<th>Hierarchical template/Method</th>
<th>Microporous template</th>
<th>Structure/morphology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard-templating method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon nanoparticles</td>
<td>Mixed template (MOR and TEAOH)</td>
<td>Isolated mesopores are located inside the particle</td>
<td>[47]</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>Mixed template (MOR and TEAOH)</td>
<td>Connecting mesopores accessible from the outside of the particle</td>
<td></td>
</tr>
<tr>
<td>Multiwall carbon nanotube with a diameter of about 10-20 nm</td>
<td>TEAOH</td>
<td>Ni and Co-containing hierarchical SAPO-34 catalysts with mesopore in the range of 10-40 nm.</td>
<td>[48]</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>DEA</td>
<td>Sub-micrometer-sized cubic crystals containing nonuniformed mesopores.</td>
<td></td>
</tr>
<tr>
<td>Dry gel conversion method</td>
<td>TEA</td>
<td>30–50 μm microspheres containing macropores (ca. 1.9 μm)</td>
<td>[51]</td>
</tr>
<tr>
<td>Polystyrene spheres</td>
<td>TEA</td>
<td>Blooming flower-like spherical morphology (10-16 μm) constructed with curlier and rose petals-like nano-sheets (10-40 nm)</td>
<td>[52]</td>
</tr>
<tr>
<td>Rapeseed pollen extract</td>
<td>TEA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soft-templating method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organosilane surfactant (TPOAC)</td>
<td>MOR</td>
<td>Micrometer-sized cubic crystals consist of small cube-like nanocrystals (100-500 nm) containing small mesopores (2–5 nm) and larger mesopores (ca. 30 nm)</td>
<td>[56]</td>
</tr>
<tr>
<td>Organosilane surfactant (TPOAC)</td>
<td>DEA</td>
<td>Sphere-like SAPO-34 zeolites consisting of interpenetrating nanosheets with the thickness around 50 nm.</td>
<td>[57]</td>
</tr>
<tr>
<td>Organosilane surfactant (TPOAC)</td>
<td>DEA</td>
<td>Uniform dice-like particles in the size range of 300–500 nm consist of a large number of 20–50 nm nanocrystals with abundant holes</td>
<td>[41]</td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide (CTAB)</td>
<td>Tetramethylammonium hydroxide (TMAOH) and MOR</td>
<td>Aggregates of plate-like morphology with mesopores about 3 nm.</td>
<td>[59]</td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide (CTAB)</td>
<td>Mixed template (TEA and TEAOH)</td>
<td>Cubic-like morphology (1-2 μm) with coarse surface.</td>
<td>[60]</td>
</tr>
<tr>
<td>Polyethylene glycol (PEG-2000)</td>
<td>TEA</td>
<td>Cross-like SAPO-34 catalysts enriched mesopores ranged from 10 to 50 nm.</td>
<td>[61]</td>
</tr>
<tr>
<td>Polyethyleneimine (PEI, (Mw = 70 000)</td>
<td>TEA</td>
<td>A regular array orientated uniform mesopores in the range from 2.0-3.0 nm</td>
<td>[63]</td>
</tr>
<tr>
<td>Organophosphorous surfactant-assistant (DPhAB)</td>
<td>TEAOH and TEA</td>
<td>Micrometer-sized spherical aggregation consisted of nanosized SAPO-34 crystals</td>
<td>[64]</td>
</tr>
<tr>
<td>Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMOD)</td>
<td>TEAOH</td>
<td>Rod-like and elongated shapes of the mesopores well-connected within the microporous network.</td>
<td>[65]</td>
</tr>
<tr>
<td>Post-treatment method</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Leaching in acid media (HCl, H4EDTA, and Na2H2EDTA)</td>
<td>Supplied by ACS Material</td>
<td>Strongly amorphous.</td>
<td>[67]</td>
</tr>
<tr>
<td>Leaching in NaOH solution</td>
<td>Supplied by ACS Material</td>
<td>Strongly amorphous.</td>
<td>[67]</td>
</tr>
<tr>
<td>Leaching in organic bases (TEAOH or DEA)</td>
<td>Supplied by ACS Material</td>
<td>Preserving the crystallinity during base treatment.</td>
<td></td>
</tr>
<tr>
<td>Leaching in dilute HF acid with NH4F</td>
<td>TEAOH</td>
<td>A mosaic structure of nano-particles (10 and 40 nm) of rectangular shape at the crystal faces.</td>
<td>[68]</td>
</tr>
<tr>
<td>Leaching in HF-NH4F containing solutions under ultrasonic condition</td>
<td>TEAOH</td>
<td>Rough surface and amounts of mesopore and/or macropore in the crystals</td>
<td>[69]</td>
</tr>
<tr>
<td>Leaching in TEAOH solution</td>
<td>TEA</td>
<td>An hourglass-like, touching triangles pore pattern on the four side surfaces and many mesopores (80–150 nm) on the crystal surface.</td>
<td>[70]</td>
</tr>
<tr>
<td>Recreating in TEAOH solution or HCl solution</td>
<td>TEAOH and TMEDA as templates and fully milled SAPO-34 powder as seeds</td>
<td>Hollow cubic-like morphology with wall thickness about 30 nm treated in NaOH and 30 nm treated in HCl, respectively.</td>
<td>[71]</td>
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</table>
Table 1. Continued.

<table>
<thead>
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<tr>
<td>Other method</td>
<td></td>
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</tr>
<tr>
<td>Natural layered material kaolin as raw materials</td>
<td>TEA</td>
<td>Sphere-like particle composed of decussate zeolite slice units about 60 nm thick.</td>
<td>[72]</td>
</tr>
<tr>
<td>Mesoporous materials (SBA-15) as silica source</td>
<td>TEA</td>
<td>Layered bulk particle with size of 15 μm with straight hexagonal arrayed mesopore</td>
<td>[73]</td>
</tr>
<tr>
<td>Decreasing silicon/Al ratio to 0.05</td>
<td>TEA</td>
<td>X-shaped hollow cubic crystal with plentiful 50 to 500 nm macro pore openings</td>
<td>[74]</td>
</tr>
<tr>
<td>Al-rich method coupled with the use of the polyethylene glycol 2000 polymer</td>
<td>TEA</td>
<td>Center-hollowed morphology with a butterfly like boundary and many macro holes on their surfaces.</td>
<td>[75]</td>
</tr>
<tr>
<td>Introducing NaF with the ratio of F/silicon=0.02–0.1</td>
<td>TEA</td>
<td>Floral morphology composed with flake-like zeolites.</td>
<td>[76]</td>
</tr>
<tr>
<td>In situ growth-etching by excess HF</td>
<td>TEA</td>
<td>Central-holed rhombohedral crystals (5–10 mm) comprised intracrystalline parallel macrochannels of ca. 100 nm</td>
<td>[77]</td>
</tr>
<tr>
<td>Dry gel conversion of the amorphous silicoaluminophosphate monolith combined with Poly (ethylene oxide) (PEO, Mₙ=1,000,000)</td>
<td>TEAOH</td>
<td>Spherical aggregates (7 μm) consist of cubic SAPO-34 crystals with thickness in the range of 400-600 nm and length in the range of 1.2-1.5 μm.</td>
<td>[79]</td>
</tr>
<tr>
<td>Dry gels containing gelatin by a vapor-phase transport method</td>
<td>TEA</td>
<td>X-shaped hollow cubic crystal containing highly loose and porous fibrous structure</td>
<td>[80]</td>
</tr>
<tr>
<td>Adding nanosized sheet-like SAPO-34 seeds</td>
<td>TEA</td>
<td>Nanosized cubic-like hollow crystals (300-800 nm) with intracrystalline mesopores and macropores (25–200 nm).</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Figure 6. Proposed assembly pathway of cubic hierarchical porous SAPO-34 crystals aggregated by small cubic nanocrystals assisted by the organosilane surfactant. Adapted from [56] © 2014 The Royal Society of Chemistry.
SAPO-34 are attributed to the relatively high silicon content in the catalysts. Recently, Chen et al. [68] developed a facile approach for the preparation of hierarchical SAPO-34 crystals via post-synthesis fluoride etching. The NH$_4$F and HF could dissolve the interface between crystalline domains and direct the hierarchical zeolite with a system of straight intersecting mesopores, as shown in Fig. 7. Subsequently, this fluoride etching method can be expanded to obtain other hierarchical SAPO-34 catalysts by using different microporous templates, such as morpholine and triethylamine [69].

Other hierarchical SAPO-34 catalysts with unique hollow morphology can also be synthesized by post-treatment methods. Recently, Liu et al. [70] prepared hierarchical SAPO-34 crystals using a facile TEAOH etching post-treatment method. After etching by TEAOH solution, the scattered pores on the top and bottom surfaces and the hourglass-like hollow macroporous pattern on the four side surfaces can be observed by transmission electron microscope (TEM) measurement. In addition, Qiao et al. [71] synthesized hollow SAPO-34 crystals with a shell thickness of 30–50 nm and good crystallinity via selective etching of their precursor under controlled alkaline or acid conditions. Experimental results showed that the silicon gradients in the crystals played an important role in the generation of a hollow structure with a silicon-rich external surface. For base or acid treatment, the crucial microenvironments for a well-preserved crystal shell were the enriched silicon–Al domains and silicon islands at the outer layers of crystals, respectively.

Other methods

Besides the methods described above, some other approaches have also been developed to prepare the hierarchical SAPO-34 catalysts. Zhu et al. [72] reported a one-step method to synthesize nanosheet-like hierarchical SAPO-34 zeolites using cheap and natural layered kaolin as the raw material without adding any mesoporous templates. The layered kaolin not only acted as the source of silicon and aluminium, but also induced zeolite growth via its layered structure. Similarly, Liu et al. [73] synthesized a layered hierarchical SAPO-34 with mesopores (7-30 nm) by using as-synthesized mesoporous SBA-15 as the silica source. Modulating the composition of the initial synthetic gel can also generate the hierarchical structure. Li et al. [74] reported a simple method to prepare a hierarchical SAPO-34/18 zeolite with an intergrowth CHA/AEI crystal structure by decreasing the ratio of silicon/Al to 0.11–0.12 in the starting gel. Recently, Sun et al. [75] synthesized a tri-level hierarchically porous SAPO-34 zeolite with intracrystalline micro-meso-macroporosity in an Al-rich gel with the use of PEG-2000 polymer under hydrothermal conditions. The proposed process forming the tri-level hierarchical SAPO-34 zeolite is illustrated in Fig. 8. In the process of crystallization, the PEG micelles are embedded into the zeolite crystal directing the mesoporous structure. Meanwhile, the superfluous aluminium in the SAPO-34 zeolite framework produces more defects and terminal groups, leading to the formation of macropores. The central parts with intergrowth structure of the hierarchical crystals are more easily etched during the process of crystallization, leading to the formation of a hollow morphology.

The F$^-$ ion can also be used to direct the formation of hierarchical structures. Liu et al. [76] synthesized a mesoporous floral SAPO-34 using a conventional hydrothermal method in the presence of NaF using the ratio of F/silicon = 0.02–0.2. The formation of mesoporous SAPO-34 was attributed to the eroding effect of fluoride ions. Xi et al. [77] developed a facile one-step hydrothermal synthesis of hierarchically macroporous SAPO-34 through the etching effect of HF. In general, HF acts as the mineralizer in the synthetic process of zeolites, while, in this work, the excess HF is introduced in the synthetic system. The superfluous HF acted not only as a mineralizer to improve the crystallinity of the SAPO-34 zeolite, but also as a chemical etching agent to form the intracrystalline parallel nanometer-sized macrochannels and central-holed morphology, as shown in Fig. 9. In general, the syntheses of zeolites generally requires an excess of reactant materials to afford a moderate product yield. After the generated zeolite products are separated from the reaction mixtures, the mother-liquors are usually discarded as waste. Xi et al. [78] have further developed a facile and ‘green’ route via the recycling of waste mother-liquors to synthesize hierarchical SAPO-34 catalysts. The excess HF and TEA used in the synthetic system were effectively used and
further enhanced the yield of SAPO-34. Importantly, the synthesized catalysts remained high MTO catalytic performance after three recycles of mother-liquors, which was comparable to the initially prepared catalyst.

On the other hand, DGC and vapor-phase transport (VPT) methods are an effective method to synthesize hierarchical SAPO-34 catalysts, which may generate some defects during the crystallization process due to the non-uniform gel compositions. Yang et al. [79] prepared a hierarchical SAPO-34 monolith with macro/mesoporous structure by the DGC of the amorphous SAPO monolith combined with poly(ethylene oxide) and propylene oxide. The macropores of the hierarchical SAPO-34 were constructed by interconnected spherical aggregates of cubic SAPO-34 crystals and the mesopores were formed by the close stacking of cubic SAPO-34 crystals. Subsequently, Gong et al. [80] reported hollow SAPO-34 cubic crystals with a hierarchical internal structure prepared from dry gels containing gelatin using a VPT method. The cubic crystals showed unique butterfly-like X-shaped black spots on their faces under light. Zheng et al. [81] also synthesized hierarchical SAPO-34 catalysts comprised of crystallites (< 100 nm) with well-connected mesopores in a dry gel system. 1,2,3-hexanetriol was introduced into the synthesis gel as a growth inhibitor to hinder the aggregation of primary nanocrystallites.

The solvent-free synthetic method is also a facile way to introduce mesoporosity into SAPO-34 crystals [82–84]. Recently, Jin et al. [84] successfully prepared a hierarchical SAPO-34 zeolite using morpholine as a template by the solvent-free synthetic method. The as-synthesized SAPO-34 showed uniform cubic morphology (10–30 μm), and some hierarchical macropores of 0.1–3 μm and mesopores of 5–50 nm existed inside the crystals. It was proposed that that the formation of meso- and macrostructures in the crystals might be related to the presence of meso- and macropores in the starting materials and the solid transformation process of zeolite crystals. By using such a synthetic strategy, Li et al. [85] also synthesized hierarchical SAPO-34 nanocrystals with significantly reduced TEAOH template consumption.

Very recently, Sun et al. [43] developed a cost-effective strategy to synthesize nanosized hierarchical SAPO-34 catalysts via the seed-assisted method. The proposed process for the formation of nanosized hierarchical SAPO-34 zeolites is shown in Fig. 10. The nanosized seed was the key to direct the
Figure 9. Low-magnification and corresponding high-magnification SEM images of the conventional (a1 and a2), hierarchically macroporous SAPO-34 synthesized with HF/Al₂O₃ ratios of 1.1 (b1 and b2), 1.9 (c1 and c2), 2.7 (d1 and d2) and internal section of the hierarchically macroporous SAPO-34 synthesized with a HF/Al₂O₃ ratio of 2.7 (e1 and e2). Adapted from [77] © 2014 The Royal Society of Chemistry.
Seeds are dissolved. SAPO-34 zeolite Hierarchical SAPO-34 zeolite Further crystallization Seeds are dissolved Residual seeds

**Figure 10.** Schematic of the formation process of nanosized hierarchical SAPO-34 zeolites via the seed-assisted method. Adapted from [43] © 2016 The Royal Society of Chemistry.

The formation of macro/mesopores, because the small seeds can be easily involved into the as-synthesized SAPO-34 crystals, and with the continuous dissolution of seeds during the synthesis process, the hierarchical structures and void spaces were eventually obtained.

**INDUSTRIALIZATION OF SAPO-34 CATALYSTS FOR THE MTO REACTION AND PERSPECTIVES FOR THE SYNTHESIS OF SAPO-34 CATALYSTS**

SAPO-34 zeolites exhibit superior catalytic performance for the MTO reaction. Great efforts have been put into fundamental research into, and industrial development of, the MTO process. Employing SAPO-34 catalyst type MTO-100, Universal Oil Products Company (UOP) corporation built a pilot plant with 0.75 t/d (ton/day) methanol feed in 1995 [86]. Then, in collaboration with Wison (Nanjing, China) Clean Energy Co., Ltd. in 2013, UOP industrialized the MTO process at a large scale with the methanol feed rate being 2300 t/d.

Dalian Institute of Chemical Physics (DICP) began research and development into the MTO process using SAPO-34 catalysts in the early 1990s. In 2004, DICP demonstrated the MTO industrial process with SINOPEC Luoyang Petrochemical Engineering Corporation in a 50 t/d pilot plant. Based on DICP MTO catalysts (DMTO), the world’s first MTO commercial plant with a 1800 kiloton (kt)/year methanol feed was built and brought into use in 2010, and the products for polymerization can be obtained. Since 2006, DICP has worldwide licensed DMTO technology over 20 sets with a total capacity of 11 Mt/a (megaton/year) ethene and propene production [4].

SINOPEC Shanghai Research Institute of Petrochemical Technology (SRPI) began MTO process research and development from 2000 using SAPO-34 catalysts [87,88]. In a 15 m³ crystallization kettle with the high-efficiency mixing approach and special static seal, SRPI successfully developed the segmental crystallization technique involving crystal seed and composite template, and template recovery techniques. The special catalyst with a nanosheet hierarchical structure was prepared [79]. Employing
this kind of SAPO-34 zeolite, SRIPT finished a 100 t/d feed MTO pilot test from 2007 to 2008. A 600 Kt/year methanol feed commercial plant was then constructed in SINOPEC Zhongyuan Petrochemical Co., Ltd., and the plant has run stably over 5 years. The evaluation results of the plant indicate that the methanol conversion is above 99%, the yield to ethylene and propylene is about 81%, and the yield to ethylene, propylene and butylene is over 91% [89]. In 2016, the largest commercial plant, with methanol consumption of 3600 Kt/year, was constructed and brought on stream in Ordos by Zhongtianhechuang Energy Co., Ltd. A 3000 t/a SAPO-34 catalyst plant (containing zeolite synthesis and catalyst manufacturing) has also been constructed in Nanjing by a Branch Company of SINOPEC Catalyst Co., Ltd.

Along with the advancement of the MTO industrialization process and the establishment of commercial MTO units, the synthesis of SAPO-34 catalysts has increasingly drawn researchers’ attention. In the last decade, many efficient synthesis strategies have been developed for the synthesis of nanosized and hierarchical SAPO-34 catalysts with excellent catalytic performance. However, during the synthesis process of SAPO-34 catalysts, there remain a number of problems that need to be solved and shortcomings that need to be overcome.

So far, the most commonly used template to prepare SAPO-34 nanocrystals remains TEAOH, which is expensive. Applying the mixed-template method can decrease the amount of expensive template agent to obtain smaller crystals, but in most cases, TEAOH is still needed in the synthesis gel if nanosized catalysts are expected. As low cost is one of the most important factors for the large-scale production of zeolites in industry, the generation of nanosized SAPO-34 catalysts using cheap templates such as TEA, DEA and MOR is a challenge. In addition, even though some synthetic methods such as DGC and VPT can fabricate SAPO-34 nanocrystals, the complicated multi-step synthesis process and relatively poor crystallization of zeolites may hinder their practical application. Some synthetic methods for nanocrystals, such as microwave-assisted and ultrasonic synthetic methods, may be easy to realize in small-scale laboratory synthesis, but their large-scale application in industry seems difficult. On the other hand, note that the decrease of crystal size sometimes causes difficulties in the separation of nanocatalysts from the reaction gels and poor crystallization, as well as poor thermal and hydrothermal stability. Hence, facile methods for the synthesis of nanocatalysts with adjustable crystal size and desirable morphology under the premise of good crystallinity need to be developed. Among various synthetic methods, the seed-assisted method might be an optimal route for the preparation of nanosized SAPO-34 due to the low synthetic cost, high product yield and excellent catalytic performance. Moreover, the introduction of seeds can also reduce the consumption of the template, and the seeds may act as a special template in the synthesis of zeolites [90].

Compared with aluminosilicate zeolites, the construction of hierarchical SAPO zeolites seems more difficult due to the relatively poor stability of the framework. It is highly desirable that more available and facile synthetic methods are developed to synthesize the hierarchical SAPO-34 catalysts. The hard-template method usually suffers from poor interaction between the hard template and synthesis gels and fails to direct the formation of hierarchical structures. The soft-template method usually depends on expensive templates for the preparation of meso/macropores. Sometimes, the introduction of soft templates may also lead to the phase separation of microporous and mesoporous materials. On the other hand, the large-scale industrial application of the post-treatment method may be hindered by its complicated synthesis procedure, reduced crystallinity, and low product yields of zeolite catalysts. It should be pointed out that the introduction of extra additives, such as soft templates, hard templates and other acidic or alkaline substances in the synthetic system, not only raises the synthetic cost but also causes environmental pollution when the occluded extra species are removed by calcination. The solvent-free method, synthesis via modulation of the composition of initial synthetic gel, as well as the seed-assisted method might become the most attractive and green synthesis approaches for the fabrication of the hierarchical structures in microporous SAPO-34 zeolite catalysts.

So far, the preparation of zeolites with controllable ordered meso/macroporous structures and the construction of interconnected micro-mesopore structures with narrow pore size distributions remains a great challenge. The precise adjustment of the hierarchically porous structure and the distribution of meso/macropores inside the catalysts are highly desirable to further improve catalytic activity and modulate the selectivity of ethylene and propylene. Moreover, precise adjustment of the silicon distributions, especially the silicon coordination environment, decreasing the silicon island contents and reducing the silicon enrichment on the surface of SAPO-34 catalysts are also important issues for the synthesis of SAPO-34 catalysts with high catalytic performance. Last, but not least, the crystallinity and stability of hierarchical zeolite catalysts also need to be considered and further improved through future synthetic efforts.
Due to urgent requirements for the sustainable development of the chemical industry [91], some cost-effective, environmentally benign and highly efficient synthetic routes for the preparation of SAPO-34 catalysts with superior MTO catalytic performance have been developed in recent years, such as the aminothermal [92–94], ionothermal [95–97] and phase-transformation synthetic methods [98]. These synthetic methods could be applied for the synthesis of nanosized and hierarchical SAPO-34 catalysts with excellent MTO performance.

CONCLUSION AND OUTLOOK

The development of the MTO industrialization process over the last decade has greatly promoted continuous progress in the synthesis of SAPO-34 catalysts. In particular, some efficient synthetic methods have been developed for the preparation of nanosized and hierarchical SAPO-34 catalysts with excellent MTO conversion. However, more facile, cost-effective and environmentally benign routes to synthesize nanosized and/or hierarchical SAPO-34 catalysts with enhanced catalytic performance are required for large-scale industrial application. Moreover, gaining precise control of crystal morphology and intracrystalline hierarchically porous structure, as well as the distribution of catalytic active sites, are important issues for the fabrication of high-efficiency SAPO-34 catalysts and modulating the selectivity of ethylene and propylene in MTO reactions. We hope that this review will shed some light on the synthesis of SAPO-34 catalysts, and provide an impetus for the development more efficient synthetic strategies for SAPO-34 catalysts to meet increasing industrial demands.

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