

# Progress in Seed-assisted Synthesis of (Silico)Aluminophosphate Molecular Sieves

ZHANG Xiaosi<sup>1,2</sup>, YANG Miao<sup>1</sup>✉, TIAN Peng<sup>1</sup> and LIU Zhongmin<sup>1</sup>✉

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**A**luminophosphate (AIPO) and silicoaluminophosphate (SAPO) molecular sieves are an important class of open-framework crystalline materials with wide applications thanks to their molecular-scale selectivity, moderate/strong acidity and excellent (hydro)thermal stability. In recent decades, the manufacturing of new microporous solids with ordered structures has been widely investigated and many effective methods have been developed, which enriches the material types and broadens their applications beyond the traditional use as catalysts and adsorbents. However, the development on the synthesis of AIPO/SAPO molecular sieves is still insufficient and lags behind the needs of applications. Herein, we summarize the work on the seed-assisted synthesis of AIPO/SAPO molecular sieves compared with the zeolite synthetic system, aiming to prompt the synthesis and application of AIPO/SAPO molecular sieves.

**Keywords** Seed-assisted synthesis; AIPO/SAPO molecular sieve; Crystallization mechanism

## 1 Introduction

Aluminophosphate (AIPO) and silicoaluminophosphate (SAPO) molecular sieves, firstly reported by Union Carbide Corporation<sup>[1,2]</sup>, are an important class of open-framework crystalline materials possessing abundant and regular microporous architectures. Given their special properties like zeolites including rich microporosity, molecular-scale shape selectivity and high (hydro)thermal stability, AIPO/SAPO molecular sieves are being found more and more new applications in both traditional and emerging fields<sup>[3–6]</sup>. For instance, AIPO-18 is a suitable candidate to separate N<sub>2</sub> from CH<sub>4</sub><sup>[7,8]</sup>. AIPO-LTA is a promising material in zeolite-water-adsorption energy storage and transformation<sup>[9]</sup>. Due to the isomorphous substitution of Si atoms into the AIPO framework, SAPO molecular sieves hold medium-strength acidity, which are desired industrial catalysts candidates. SAPO-34 is well-known as the methanol to olefins (MTO)

catalyst, which has taken the lead in realizing industrial production<sup>[10,11]</sup>. Also, SAPO-11, as an excellent catalyst support for the hydro-isomerization of *n*-paraffin, has been widely used to produce high octane gasoline blending components<sup>[12,13]</sup>. Despite so many potential applications, it is still full of challenges in the rational design and synthesis of AIPO/SAPO molecular sieves. There are only about 45 known AIPO and 40 known SAPO molecular sieve structures among 255 known zeolite topologies up to now<sup>[14,15]</sup>. Notably, not all AIPO frameworks can be successfully introduced into Si atoms to obtain SAPO form and catalytic activity. The Si content of SAPO molecular sieve seems to have a preferred range also depending on their topology type. It is even more unachievable for Si atoms to infinitely replace skeleton atoms, realizing the transformation from SAPO molecular sieves to zeolites. Continuous effort is devoted to developing various synthetic approaches including ionothermal synthesis<sup>[16,17]</sup>, assembly, disassembly, organization and reassembly (ADOR) strategy<sup>[18]</sup>, microwave-assisted<sup>[19]</sup>, solvent-free synthesis<sup>[20]</sup>, (multiple-template) aminothermal synthesis<sup>[21–23]</sup>, and intercrystalline conversion<sup>[24,25]</sup>. Moreover, a zeobank including three parts, *i.e.* synthesis database<sup>[26,27]</sup>, AIPO structure database<sup>[28]</sup> and hypothetical zeolite structure database<sup>[29]</sup> has also been built up with the aim to investigate the relationship between varied reaction factors and the resulting structure features, and provide important foundation and guidance for the rational design and synthesis of AIPO/SAPO materials. However, compared with the development of aluminosilicate zeolitic materials, the achievement in the synthesis of (silico)aluminophosphate is still limited. What is worse, some strategies used very popularly in the synthesis of zeolites are not always applicable in the synthesis of AIPO/SAPO molecular sieves. There are some obvious differences between the two synthetic systems, such as alkalinity.

Seed assistance is such a strategy, which has been widely used in the synthesis of zeolite to enhance the crystallization rate, suppress the impurity phase and control the crystal size<sup>[30]</sup>. Seed-directed synthesis (SDS) has been developed as an efficient method to synthesize some important zeolites, including beta(\*BEA)<sup>[31]</sup>, ZSM-34(OFF/ERI intergrowth)<sup>[32]</sup>,

✉ YANG Miao  
yangmiao@dicp.ac.cn

✉ LIU Zhongmin  
liuzm@dicp.ac.cn

1. National Engineering Laboratory for Methanol-to-Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China;

2. University of Chinese Academy of Sciences, Beijing 100049, P. R. China

RUB-13(RTH)<sup>[33]</sup>, ZSM-12(MTW)<sup>[34]</sup> and mordenite(MOR)<sup>[35]</sup>, etc., in the absence of organic structure directing agent(OSDA). Crystal seeds were called “the third type of SDA” by Xiao *et al.*<sup>[36]</sup>. The zeolite synthesis with the assistance of zeolite seeds or zeolite seeds solution has been systematically reviewed<sup>[37]</sup>. In addition, a working hypothesis for broadening framework types of zeolites by seeding without OSDA was proposed by Okubo *et al.*<sup>[38]</sup>. Based on this hypothesis, NES-type zeolite was successfully synthesized *via* introducing EUO-type zeolite as seed without OSDA<sup>[39]</sup>. While as a special case, our group<sup>[40]</sup> reported the synthesis of high-silica ZSM-35 (FER structure, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=29.0) using non-calcined MCM-49 (MWW structure, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=19.1) as seed. It is worth noting that there are no common composite building units(CBUs) between the frameworks of FER and MWW. It is indicated that similarity in the local atomic connection between the seeds and target zeolite, even without the common CBUs, would have the possibility to lead to a successful synthesis.

Additionally, as an extension of the seed-directed route, interzeolite conversion from FAU(faujasite) or BEA(beta) parent materials to high-silica MFI(ZSM-5), CHA(chabazite), STF(SSZ-35) and MTW(ZSM-12) zeolites without OSDA was also realized<sup>[41–49]</sup>. While interzeolite transformation from high framework density to low framework density could only be realized in the presence of more suitable OSDA<sup>[50–52]</sup>. These successful examples provide more opportunities for the design and synthesis of zeolite materials. Unfortunately, the related synthesis in AIPO/SAPO system is rarely reported<sup>[24,25]</sup>.

In this review, we try to summarize the work on the seed-assisted synthesis of AIPO/SAPO molecular sieves with the aim to provide a full profile about this field. The growth of molecular sieve membrane by seeding<sup>[53]</sup> is excluded herein since our main target is focused on the modification of crystalline phase, composition and crystal morphology. Although introducing seeds into AIPO/SAPO synthetic system could accelerate crystallization, widen crystallization phase region, inhibit impurity, and even decrease crystal size, it is always impossible to replace the OSDA altogether. Moreover, whether the seed works or not seems to strongly depend on its physicochemical properties. So, the selection of crystal seed is crucial to ensure the success of synthesis. The insights on how and what kind of seed can help such a low alkalinity hydrothermal crystallization system will be discussed.

## 2 Synthesis of AIPO/SAPO Molecular Sieves with Isostructural Seeds

### 2.1 Promoting the Crystallization of Molecular Sieves by Seed Assistance

The early reports on the use of seeds to promote the

crystallization of AIPO/SAPO molecular sieves are few. A mixture seed containing AIPO-41 was claimed to be necessary for the hydrothermal crystallization of pure AIPO-41 phase<sup>[54]</sup>. Later in 1996, pure AIPO-41 was synthesized in a mixed water-alcohol system without any seed<sup>[55]</sup>. Strohmaier *et al.*<sup>[56]</sup> reported the synthesis of SAPO-EMM-3 by introducing AIPO-EMM-3 as seed. Less than 1%(mass fraction) AIPO-EMM-3 seed was added, which consists of platelet shaped crystals of dimension 0.5–2 μm and <0.05 μm thick. By doing this, pure SAPO-EMM-3 could be prepared reproducibly at SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> levels up to 0.80, and the competitive phases of SAPO-17 and SAPO-31 could be inhibited effectively. Moreover, the SEM micrograph of SAPO-EMM-3 showed agglomerates of very small crystals. Another example reflecting the power of seeding is the synthesis of silicoaluminophosphate ECR-40 with an MEI topology. Its structure contains uncommon Al-O-Al connections imparting very strong acidity to the material. ECR-40 was first synthesized by Vaughan *et al.*<sup>[57]</sup> using either tris-(2-hydroxyethyl)methyl ammonium(THMA<sup>+</sup>) or bis-(2-hydroxyethyl)dimethylammonium(BHDMA<sup>+</sup>) ions as the template. The crystallization unusually took 24–57 d at 160–170 °C. In 2015, Hong *et al.*<sup>[58]</sup> reported that five OSDAs, THMA<sup>+</sup>, BHDMA<sup>+</sup>, (2-hydroxyethyl)trimethylammonium (HTMA<sup>+</sup>), bis(2-hydroxyethyl)methylamine(BHMA) and bis-(2-hydroxyethyl)ethylamine(BHEA), could direct ECR-40A-E phases in a hydrothermal environment, respectively. While except ECR-40A synthesized by THMA<sup>+</sup>, ECR-40 or UZM-22 seed was essential for all the other syntheses of ECR-40B-E, and the crystallization time could be shortened to 12–16 d. Recently, dual-template directed aminothermal synthesis was developed to complete the crystallization of ECR-40 within 2 d<sup>[23]</sup>. The strong alkaline aminothermal environment combining with the dual OSDAs, *N,N*-diethyl ethanolamine (DEEA) and *N,N,N*-trimethylbutylammonium chloride (BTMACl), and fluoride mineralizing agent promotes the crystallization. The role of seed seems less indispensable for AIPO/SAPO synthesis, however, the crystal seed still plays a role in promoting crystallization when no more suitable crystallization conditions are found.

Solvent-free route for the synthesis of zeolites was first reported by Xiao *et al.*<sup>[20]</sup> in 2013, where water appeared only as a reactant dose. Seeding is helpful for such a system, and titanosilicate zeolites with MFI and \*BEA structures were synthesized under solvent-free condition<sup>[59]</sup>. Afterwards, Zhao *et al.*<sup>[60]</sup> synthesized solvent-free triclinic AIPO-34 under the assistance of seed. The introduction of seed crystal could decrease the formation of prephase obviously, and AIPO-34 phase became a major product. Additionally, the template consumption was reduced much although its absence was impossible.

Considering that many kinds of aluminosilicate molecular

sieves have been successfully synthesized without OSDA with the assistance of seed<sup>[37]</sup>, the OSDA-free synthesis of AIPO/SAPO crystalline phase has ever been tried, although few have been successful<sup>[61]</sup>. It is because that the inorganic raw materials usually need alkaline conditions to dissolve and then participate in crystallization, but strong alkali hydroxide is not suitable for the crystallization of AIPO/SAPO materials. The compensation of negative charges of the aluminophosphate-based network produced by the introduction of  $Me^{n+}$ ,  $Si^{4+}$ , etc., normally requires protonated OSDAs<sup>[62]</sup>. AIPO-H3 is a common impurity phase in many AIPO molecular sieve syntheses<sup>[63]</sup>, which contains an equal ratio of tetrahedrally Al(T) and octahedrally Al(O) coordinated aluminum. Its OSDA-free synthesis is a rare successful case, and the gel composition of aluminophosphate  $Al/P \geq 1.0$  and seed are necessary<sup>[64]</sup>. Without the addition of seed crystals, variscite and metavariscite were crystallized from aluminophosphate gels even with  $Al/P > 1.0$ . The addition of the organic template seems to delay the crystallization even with the help of the seed. Possibly, the crystallization route has been changed when organic template is introduced. Tian *et al.*<sup>[65]</sup> investigated the effect of organic template dosage, phosphorus source, and crystal seed on the synthesis of SAPO-34 molecular sieve in triethylamine (TEA) hydrothermal system. Amorphous material or dense phase aluminium phosphate was always the final product if organic template is absent. But the impurity of SAPO-5 was inhibited, and the crystallinity of the SAPO-34 could be improved by adding seed crystal. They demonstrated that the organic template was the key substance for the formation of SAPO-34, while the crystal seed could only partially replace the role of organic template. In addition, their results show that the addition of conventional SAPO-34 crystal as seed cannot change the morphology of SAPO-34 product. It means that the seed used to reduce the crystal size has to be carefully selected. The related discussion will be involved in Section 2.2.

## 2.2 Modifying the Crystal Morphology by Seed Assistance

Since SAPO-34 and SAPO-11 are the SAPO materials with an important application background, many investigations on the modification of their crystal morphology have been carried out with the aim of optimizing their catalytic performance.

### 2.2.1 SAPO-34

It has been long recognized that SAPO-34 with a small grain has better MTO catalytic performance since the shortened diffusion pathway length and the enlarged external surface may enhance the use efficiency of active centers, reduce the

side reactions and enhance the coke capacity<sup>[66–68]</sup>. But, SAPO-34 with a small crystal size was only synthesized by using expensive organic template tetraethyl ammonium hydroxide (TEAOH) in the early years<sup>[69,70]</sup>. TEAOH is believed to have strong basicity and initiate more nuclei to hit the aim. As above mentioned, it is difficult to add large SAPO-34 crystals as seed to decrease the crystal size<sup>[65]</sup>. Zhu *et al.*<sup>[71]</sup> prepared low silica SAPO-34 by using conventional SAPO-34 as seeds and the only Si source. The product crystal size is over 10  $\mu m$ , presenting the irregular cubic shape and coarse surface. The optimal catalytic MTO performance is mainly attributed to the decreased Si content of SAPO-34.

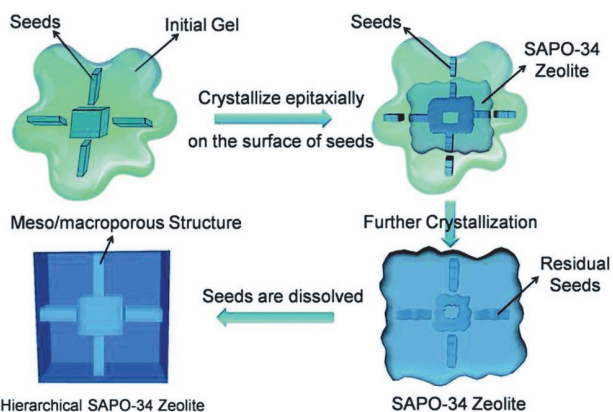
In 2014, a post-synthesis milling and recrystallization method was developed to prepare nanoscale SAPO-34 (50–350 nm in size) with a TEA template<sup>[72]</sup>. This method is also applicable for the synthesis of other SAPO materials including SAPO-5 and SAPO-35. After that, the milled SAPO-34 was widely used as an effective seed to assist the synthesis of SAPO-34 in various synthetic systems. Qiao *et al.*<sup>[73]</sup> synthesized special Si-enriched nano SAPO-34 crystals with the assistance of milled SAPO-34, and etched them to realize the preparation of hollow SAPO-34 single crystal. Gao *et al.*<sup>[74]</sup> synthesized SAPO-34 nanocrystals (*ca.* 200 nm) with a quite low silica content at a low temperature with the assistance of milled SAPO-34 seed. And the particle size gradually dropped with the increase in the amount of seed. Wang *et al.*<sup>[75]</sup> achieved the fast fabrication of nanosized mesoporous SAPO-34 single crystal with the assistance of milled SAPO-34 precursor and the mesoporous [3-(trimethoxysilyl)propyl] octadecyldimethylammonium chloride (TPOAC). As shown in Table 1, the crystallization phase region, micro to meso porosity and Si content of SAPO-34 products are wide-range tunable with the assistance of seed, which enables the optimized SAPO-34 with satisfied MTO catalytic property and excellent hydrothermal stability. Furthermore, Wu *et al.*<sup>[76,77]</sup> synthesized a series of SAPO-34 nanocrystals with various multiple functional templates under the assistance of milled SAPO-34 seed.

In parallel, SAPO-34 molecular sieve with a nanosheet-like morphology (*ca.* 200 nm) was also demonstrated to be an effective seed to control the crystal size of SAPO-34 by Yu and co-workers<sup>[78]</sup>. Nano-sized hierarchical SAPO-34 with intracrystalline meso-macroporosity was synthesized under the assistance of this kind of seed and with TEA as the template. And 8% (mass fraction) seed was charged in the gel, which led to a remarkably decreased crystal size, a higher crystallinity, and an improved solid yield compared to the conventional counterpart. Such a small-sized seed acts as the original nuclei to accelerate crystallization and decrease crystal size due to the Ostwald ripening mechanism. As shown in Fig.1, they demonstrated that the nanosheet-like seeds are covered inside

**Table 1 Synthesis conditions<sup>a</sup>, compositions and textural properties of mesoporous SAPO-34s**

Sample	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Precursor <sup>b</sup> /(%, mass fraction)	Product composition Si/Al/P	S <sub>BET</sub> <sup>c</sup> /(m <sup>2</sup> ·g <sup>-1</sup> )	S <sub>mic</sub> <sup>d</sup> /(m <sup>2</sup> ·g <sup>-1</sup> )	S <sub>ext</sub> <sup>d</sup> /(m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>mic</sub> <sup>d</sup> /(cm <sup>3</sup> ·g <sup>-1</sup> )	V <sub>mes</sub> <sup>e</sup> /(cm <sup>3</sup> ·g <sup>-1</sup> )
SP34-MS-1	0.2	49.8	0.106/0.515/0.379	521	438	83	0.20	0.21
SP34-MS-2	0.4	47.6	0.128/0.504/0.368	532	406	126	0.19	0.27
SP34-MS-3	0.6	10.7	0.130/0.500/0.370	517	374	143	0.17	0.22
SP34-MS-4	0.6	21.4	0.140/0.495/0.365	557	427	130	0.20	0.18
SP34-MS	0.6	45.5	0.148/0.488/0.364	567	455	112	0.21	0.17
SP34-MS-5	0.6	64.3	0.150/0.486/0.364	580	488	72	0.23	0.13

a. The initial gel molar composition is 2.3DEA:1.0Al<sub>2</sub>O<sub>3</sub>:1.0P<sub>2</sub>O<sub>5</sub>:0.2—0.6SiO<sub>2</sub>:150H<sub>2</sub>O, crystallization condition: 200 °C, 4 h. The silica source is a 1/3 molar ratio mixture of TPOAC/TEOS; b. calculation based on the inorganic oxides content; c. total surface area is determined by the BET equation; d. micropore surface area, volume and external surface area are determined by the *t*-plot method; e. mesopore volume is determined from the adsorption isotherm by the BJH method. Reprinted with permission from Ref.[75], Copyright 2016, Royal Society of Chemistry

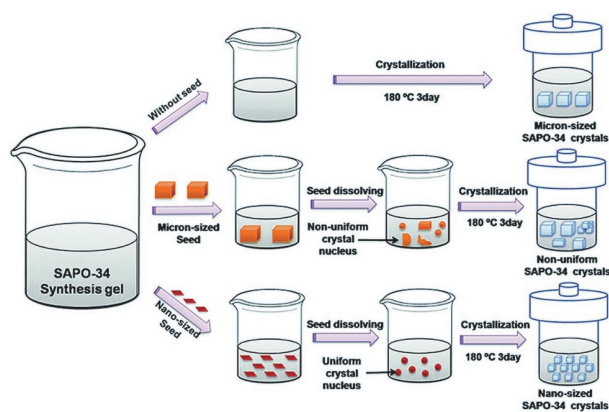
**Fig.1 Schematic of the process for the formation of nano-sized hierarchical SAPO-34 zeolites**

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of the initial gel and etched into fragments by the gel firstly. And then the SAPO-34 zeolites crystallize epitaxially on the surface of seeds. Within the further process of crystallization, the seed crystals are continually dissolved in the gel phase introducing more void spaces. As a result, the hierarchical SAPO-34 zeolites with meso/macro-porous are finally obtained.

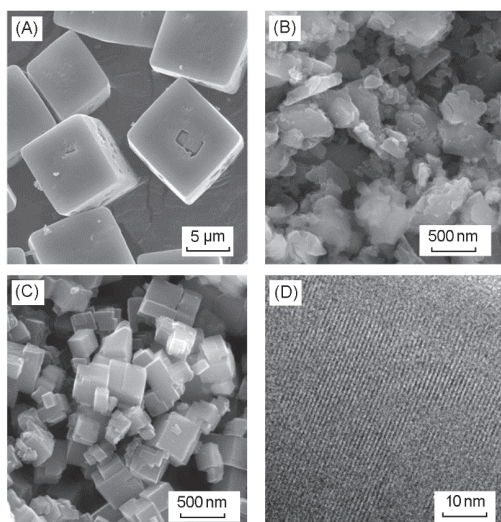
In addition, Yu *et al.*<sup>[79]</sup> demonstrated that only nano-sized SAPO-34 seeds could facilitate the formation of uniform nano-sized SAPO-34 crystals within morpholine(MOR) as the sole template. Based on the experimental results, they proposed the possible process for the formation of nano-sized SAPO-34 zeolites, as shown in Fig.2. Subsequently, under the assistance of seed with a nanosheet-like morphology (*ca.* 200 nm), a nano-sized hierarchical SAPO-34 catalyst was obtained, where the TEA/Al<sub>2</sub>O<sub>3</sub> molar ratio was as low as 2.0<sup>[80]</sup>. It is implied that adding nanosized seed into the gel can help decrease the template consumption.

A continuous flow process for preparation of crystalline microporous AIPO-5, SAPO-5 and SAPO-34 was developed by Okubo and coworkers<sup>[81,82]</sup> with the assistance of seed. The addition of a milled seed, the pretreatment of Al and Si sources by mechanical milling, and the employment of a high temperature condition were found to be the critical factors that

**Fig.2 Schematic of the possible process for the formation of nano-sized SAPO-34 zeolites**

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could be contributed to the enhancement of crystallization rate of SAPO-CHA. Owing to the feature of rapid heating, the tubular reactor demonstrated itself as a facile and precise platform to control over the phase selection between SAPO-CHA and SAPO-AFI by tuning the crystallization kinetics. They also highlighted the importance of the seed size. The 10-min-milled seed showed a higher efficiency in accelerating the crystallization rate than did the reference raw crystal seed. The seed with a smaller size could provide a larger external surface, where newly formed crystals could grow. As a result, the SAPO-34 product presents the conventional morphology but with a crystal size smaller than 1 μm(Fig.3)<sup>[82]</sup>. Also, Sun *et al.*<sup>[83]</sup> realized the fast synthesis of nano-sized SAPO-34 with high crystallinity within 10 min through seeding and tubular reactor heating. They demonstrated that the fast heat transfer of the tubular reactor and the rapid nucleation induced by the addition of SAPO-34 seeds greatly accelerated the crystallization of SAPO-34. Zeng *et al.*<sup>[84]</sup> reported that the solvent-free synthesis of hierarchical SAPO-34/18 was successful by adding 1%(mass fraction) SAPO-34 seed crystals to the solid mixture. Also, the oil-bath heating system was used here. They highlighted that the ultrafast crystallization kinetics was the synergy of ammonium salt(homogeneous mineralizing effect), oil-bath heating(ultrafast heat transfer), and seeding(enhanced nucleation and reduction of induction



**Fig.3 SEM images for the reference SAPO-CHA seed before ball milling and the 10-min-milled seed, respectively(A, B) and SEM and TEM image for the SAPO-CHA product synthesized for 10 min with the addition of 10%(mass fraction, based on  $\text{Al}_2\text{O}_3$ ) of the 10-min-milled seed(C, D)**

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period). In addition, Zhang *et al.*<sup>[85]</sup> showed that the SAPO-34 molecular sieves prepared using a liquid crystal seed containing a SAPO-34 precursor exhibited a smaller crystal size, weaker acidic strength, and higher selectivity to light olefins in MTO in comparison with the one synthesized with seed powder. Actually, researchers have done much work on the post-treatment of seeds. Wang *et al.*<sup>[86]</sup> treated micrometer-sized SAPO-34 seeds by MOR, by which the uniform nano-sized SAPO-34(200–500 nm) was synthesized with MOR as the sole template. In Zhao's work<sup>[87]</sup>, mechanical milling and  $\text{H}_3\text{PO}_4$  chemical etching were adopted to activate solubility and dispersibility of raw SAPO-34 seeds. The resultant samples are all pure SAPO-34 phase, despite one of them is already amorphous phase etched by 0.0001 mol/L  $\text{H}_3\text{PO}_4$ . The structure of seeds seems to have no influence on the phase selectivity of the products. They concluded that the smaller nano-sized seeds could be uniformly dispersed and easily dissolved in the reaction gel to form regular crystal nuclei, which was favorable for the formation of nano-sized products. Also, an improved solvent-free approach was developed to synthesize SAPO-34 catalysts with an enhanced MTO reaction performance, in which  $\text{H}_3\text{PO}_4$  solution-etched seed crystals could modulate the physico-chemical properties of SAPO-34 crystals<sup>[88]</sup>.

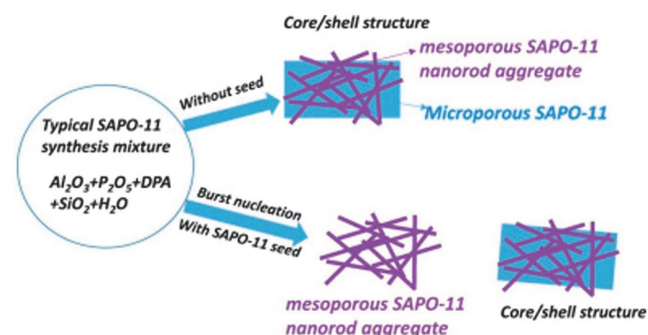
### 2.2.2 SAPO-11

Among the catalytic materials explored for *n*-alkane isomerization, SAPO-11 molecular sieve as an acidic carrier of bifunctional catalysts has attracted much attention due to its

outstanding isomerization performance<sup>[89–91]</sup>. However, its one-dimensional 10-membered-ring channel system(0.39×0.63 nm) can only produce mono-branched isomers<sup>[92–94]</sup>, and di-branched isomers with higher research octane numbers (RONs) are hardly formed. The active sites near the pore mouths of SAPO-11 could be contributed to the formation of di-branched isomers and the number of pore mouths is closely related to the external surface area of SAPO-11. So, much effort has been made to decrease the crystal size of SAPO-11 and increase its external surface.

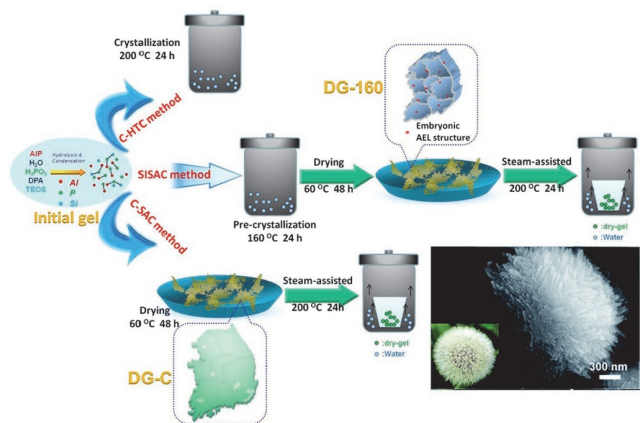
Li *et al.*<sup>[95]</sup> first prepared a silanized SAPO-11 seed in the presence of triethoxy(propyl)silane(Pr-TES) at 120 °C for 4 h, and then SAPO-11 molecular sieve with a smaller particle size (*ca.* 1 μm) was synthesized with the assistance of this hydrophobic seed. Compared with conventional SAPO-11, the product possesses a much more external specific surface area, a larger pore volume and more suitable acidity, resulting in much better activity and higher isomers selectivity. In 2015, Fang *et al.*<sup>[96]</sup> synthesized a hierarchical SAPO-11 molecular sieve with a mesopore volume up to 0.40 cm<sup>3</sup>/g with 2%–10% (mass fraction) SAPO-11 seed. The product SAPO-11 shows a nanorod morphology with an ultra-small diameter of 5 nm. As depicted in Fig.4, the formation of hierarchical SAPO-11 with a core(microporous SAPO-11)/shell(mesoporous SAPO-11 aggregate) structure is an integrated effect of the burst nucleation and the special rod shape of SAPO-11 nanocrystal. They demonstrated that the role of SAPO-11 seed was to promote the nucleation by increasing the surface area of the liquid-solid interface.

To synthesize SAPO-11 with more external acid sites, Yi *et al.*<sup>[97]</sup> have designed a novel synthetic route named seed-induced steam-assisted conversion(SISAC method, shown in Fig.5), which intensifies the interaction between the seed and dry gel. The aluminosilicophosphate gel was pre-crystallized at 160 °C for 24 h, and the intermediate with an embryonic AEL structure was obtained during this low-temperature hydrothermal process. Under this condition, the obtained gel with abundant nuclei of SAPO-11, denoted as DG-160, was



**Fig.4 Schematic representation of the generative process of SAPO-11**

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**Fig.5 Synthesis route of SAPO-11 by three methods(the inset at the down-right panel is the multi-branched dandelion-like product by SISAC method)**

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subjected to the SAC process. The multi-branched dandelion-like SAPO-11(the inset at the down-right panel in Fig.5) was fully crystalline and exhibited more acidity, an external surface and a mesopore volume. They proposed that the nanoscale interactions between seed(DG-160) and amorphous structure played a vital role for the formation of dandelion-like SAPO-11.

### 2.2.3 Other SAPO Materials

Besides SAPO-34 and SAPO-11, some other nanoscale SAPO materials including SAPO-5<sup>[72]</sup>, SAPO-35<sup>[72]</sup> and DNL-6<sup>[98]</sup> have ever been synthesized through the seed assistance strategy. The synthetic strategy is quite similar so only one example herein is highlighted. Nano-DNL-6 with a particle size of *ca.* 150 nm can be obtained when a milled DNL-6 seed is introduced into a reactant gel without the cationic surfactant. Comparatively, using the as-synthesized micrometer-size DNL-6 as the seed can only achieve a mixture of DNL-6 and SAPO-34, and the particle size is larger. It is indicated that the milled precursor can widen the crystalline phase region of DNL-6 and promote its nucleation. The crystallization process and the mechanism of seeding seem to be basically similar.

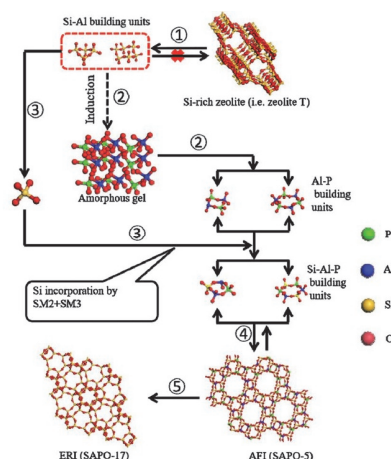
From the above work, we can briefly conclude that both nanoscaled crystal and ball-milled one or embryo with broken structural units can be used as a seed to decrease the crystal size, widen the crystallization phase region, and adjust the product composition and morphology. This is because that the seed like this could be dispersed and dissolved more easily in the synthetic gel to provide a large external surface area for booming nucleation, which favors more opportunities for the formation of target crystal structure and decreases crystal size.

## 3 Synthesis of AIPO/SAPO Molecular Sieves with Heterostructural Seeds

The synthesis of zeolites by using heteronuclear seeds normally requires common composite building units(CBUs) between seed and targeted product<sup>[38]</sup>. Some seeded syntheses even without the common CBUs were also reported, and the similarity in the local atomic connection between the seeds and target zeolite was the successful reason<sup>[40]</sup>. The report on the synthesis of AIPO/SAPO molecular sieves with heterostructural seeds is relatively rare.

Jin *et al.*<sup>[99]</sup> reported that the pure-phase ERI-structure AIPO-17 and SAPO-17 crystals were prepared as fast as several hours with the aid of isomorphous(AIPO-17) and heterogeneous(zeolite T, SSZ-13 and SAPO-34) seeds. The latter contain some vital building units promoting nucleation, which also provide silica source for the crystallization of SAPO-17. The possible mechanism of heterogeneous zeolite-induced nucleation was proposed as schematically shown in Fig.6. They demonstrated that the dissolution-reconstruction processes occurred in two processes: (1) the dissolution of seeds followed by a rearrangement to SAPO-type building units, and (2) the dissolution of SAPO-5 framework followed by the construction of SAPO-17 framework.

SAPO-34 and SAPO-18 are two materials holding similar double-6-ring(*d6r*) units. Core-shell molecular sieves comprised of SAPO-34 core and AIPO-18 shell were also synthesized by adding micron-sized SAPO-34 into the AIPO-18 nanocrystalline synthesis system<sup>[100]</sup>. Recently, Wang and coworkers<sup>[101]</sup> reported that adding SAPO-34 crystal seeds to the SAPO-18 aminothermal system resulted in the formation of hierarchical SAPO-18/34 intergrowth zeolites(for 1%–5% seed crystals, based on inorganic oxides in the initial synthesis gel) and pure SAPO-34 zeolite(for 7% seed crystals),



**Fig.6 Possible mechanism of heterogeneous zeolite-induced nucleation of SAPO-17**

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respectively, depending on the amount of seed. The obtained SAPO-18/34 intergrowths and SAPO-34 zeolites had a larger external surface area, a higher mesopore volume, and more strong acid sites than the single phase SAPO-18.

In addition, some zeolite/SAPO composite materials were also synthesized. Li *et al.*<sup>[102]</sup> synthesized ZSM-5/SAPO-5 composite molecular sieves by an embedding method. Through adding SAPO-5 crystal as seed, the crystallinity of the composite molecular sieve increased and the particles were mainly in an elliptic morphology. Wang and coworkers<sup>[103]</sup> synthesized a catalyst support, MOR/SAPO-11 composite zeolite, by a hydrothermal method with MOR acting as the seed for crystallization. It is noted that the MOR zeolite particles are uniformly and tightly covered by SAPO-11 molecular sieves, resulting in a core/shell structure. Chemical bonding of MOR and SAPO-11 brought in more weak B-acidic sites. As a result, Pt@MOR/SAPO-11 exhibited a higher isomerization activity than the Pt-loaded pristine MOR or the physical mixture of MOR and SAPO-11. Recently, Li's group<sup>[104]</sup> developed a novel strategy to improve the hydrothermal stability of Cu-SSZ-13 with SAPO-34 as seed. The experiment results showed that the introduction of SAPO-34 enhanced the distribution of the Al tetrahedron in the CHA framework, as well as influenced the type and stability of the isolated Cu<sup>2+</sup> ions as the major active sites for NH<sub>3</sub>-SCR. Subsequently, Li *et al.*<sup>[105]</sup> reported that H-type SAPO-34 molecular sieves were synthesized directly in the Na-free system using Cu/SSZ-13 as the core and TEA as the template. In the meantime, our group<sup>[106]</sup> used Cu-SSZ-13 as Cu source, part of Si/Al source and seed to assist the crystallization of Cu-SAPO-34. As a result, a Cu-CHA composite with interlaced SAPO and aluminosilicate parts was synthesized, which exhibits a high NH<sub>3</sub>-SCR activity in a wide temperature window and a robust resistance against both steaming at 800 °C and soaking in 80 °C water.

## 4 Summary and Outlook

This review summarizes the seed-assisted synthesis of AIPO/SAPO molecular sieves, and highlights the role of seed in promoting crystallization and modifying the crystal morphology. Although the effect of crystal seeds on AIPO/SAPO crystallization seems to be less indispensable than that in aluminosilicate system, and the template cannot be replaced thoroughly, its effect on regulating crystalline phase and morphology is still obvious and effective, and the investigation on the seed-assisted synthesis of AIPO/SAPO materials still deserves attention. The way, in which the crystal seed plays its role is different from that of aluminosilicate system due to the weaker alkalinity and different crystallization mechanism of AIPO/SAPO molecular sieve. But

the introduction of crystal seed can still shorten the induction period to accelerate the secondary nucleation and enhance the crystallization rate, induce the crystallization toward given a zeolite structure and ensure the phase purity, decrease the template consumption, widen the crystallization phase region, facilitate the formation of nano-sized molecular sieves, and tune the textural and acidic properties of the products. Notably, the dissolution of seed is very important, which offers enough external surface or solid-liquid interface of gel for nucleation. As a result, both ball-milled crystals and X-ray amorphous embryonic zeolite(or nano-sized crystals) have been evidenced as effective seeds.

It is worth noting that the seed-assisted synthesis of AIPO/SAPO molecular sieve has not been fully developed yet, and the role of seed is far from being fully elucidated. We hope that this review will shed some light on the synthesis of AIPO/SAPO materials, prompt the synthesis of AIPO/SAPO molecular sieves with novel structures, provide an impetus for the development of efficient synthesis strategies, and prompt the industrial application of AIPO/SAPO molecular sieves.

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## Conflicts of Interest

The authors declare no conflicts of interest.

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