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Synthesis of zeolite SSZ-24 using a catalytic amount of SSZ-13 seeds

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SSZ-24 proved to be a zeolite with poor synthesis reproducibility and slow crystallization rate. The present study deals with the preparation of SSZ-24 by a seed-assisted approach. SSZ-13 and SSZ-24 zeolites are employed as seeds and the impact of seeds content on the formation of SSZ-24 studied. Both types of zeolite accelerate the zeolite nucleation, shorten crystallization time, and lead to the formation of pure and highly crystalline SSZ-24. However, the use of SSZ-13 seeds is more efficient in terms of rapid crystallization and crystallinity level. Pure and highly crystalline SSZ-24 is readily obtained even though the amount of SSZ-13 seeds has been decreases to a "catalytic level", i.e. 0.3 wt.%. The higher seeding power of SSZ-13 seeds is attributed to the presence of framework Al, which stabilizes structural elements that promote the SSZ-24 nucleation.

Introduction

Zeolites are extensively used in different areas of the chemical industry, such as shape selective catalysis, gas adsorption and separation, and ion exchange.¹⁻⁶ Crystalline structure and chemical compositions determine the properties and practical applications of a zeolite. However, the use of a particular zeolite does not depend solely on its properties. The production conditions in terms of operational simplicity, short production time and reactants employed are often decisive for the large-scale use of a particular zeolite. Hence, the optimization of synthesis parameters that lead to a more efficient and low-cost zeolite synthesis deserves particular attention.

It is almost 60 years since the first seeded zeolite synthesis was reported.⁷ In the 1960s, Kerr investigated the factors affecting the formation of zeolites A, B, and X using 10-15 wt.% seeds.^{7,8} Later, Mirskii proposed a kinetic model of zeolite formation in the presence of seeds.⁹ Kacirek employed seeds to achieve the separation of nucleation and growth, the amount of the added faujasite seeds nuclei with respect to the whole amount of the crystalline products was 2.5 to 3.0 wt. %.¹⁰ Seeds are commonly used when zeolite synthesis reproducibility is poor since the seeded synthesis is less sensitive to the reactants and crystallization conditions used.

Further, the seed-assisted approach is used to reduce the cost

and enable the development of environmentally friendly production processes of relevant zeolites.^{11,12} Important issues as the reduction of the synthesis time, elimination of impurities, controlling the particle size are also positively influenced by seeding.¹³⁻²⁰ Seeding is also commonly employed in the preparation of zeolite membranes and 3D structures.²¹ The seed content in zeolite synthesis vary between 5 and 15 wt.% approximately, and the use of 1 to 3 wt.% is scarcely reported.

SSZ-24 is a high-silica, large-pore molecular sieve isostructural with AIPO-5 (AFI) aluminophosphate.²² SSZ-24 was first synthesized by Zones et al. using 1-trimethylammonioadamantane as structure directing agent (SDA).²³ The crystallization of SSZ-24 is substantially longer in respect to the most of high silica zeolites. Typically, the synthesis of SSZ-24 requires more than 10 days at 150 °C using N, N, N-trimethyl-1-adamantanamine cation as an organic structure-directing agent.²³⁻²⁶

Over past decades, many efforts have been made to optimize the crystallization of zeolite SSZ-24. Zones et al. synthesized boron-containing SSZ-24 by using a calcined form of boron-substituted zeolite beta ([B]-BEA) as primary silica sources.²⁷ Lobo and Davis reported the synthesis of [B]-SSZ-24 using N(16)-methylsparteinium (MeSPA) as SDA and sodium borate as the source of boron.²⁸ In the later case, the calcined [B]-BEA did not work as precursors for [B]-SSZ-24 synthesis. Maekawa et al. studied the phase transformation of [Al]-BEA to [Al]-SSZ-24 by using MeSPA as OSDA.^{29,30} Valtchev et al. reported a synthesis of zeolite SSZ-24 with 5 wt.% seeds.³¹ Peng et al. reported a fast synthesis of zeolite SSZ-24 at 210 °C in 60 min by fast heating in a stainlesssteel tubular reactor with 10 wt.% SSZ-24 seeds.³² However, such fast synthesis

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method involved special equipment and a series of complicated and time consuming pre-treatment steps before the hydrothermal treatment, which limits its practical application. For instance, 2 days stirring at room temperature was required for homogenization of the gel followed by an aging step at 95 °C for 3 days and then synthesis in an oil bath at 210 °C for 60 min.

Here we report the use of catalytic amounts of seeds for rapid synthesis of zeolite SSZ-24. Two types of seeds, zeolite SSZ-24 and SSZ-13, were employed. The structure similarity, i.e. the abundant presence of 6-rings, in the AFI- (SSZ-24) and CHA- (SSZ-13) type structures is the reason to employ SSZ-13 and compare its performance in respect to the SSZ-24 seeds. The ultimate goal of this study is to reduce both the mass of seeds used and the crystallization time, which would bring substantial practical advantages. To the best of our knowledge, no other synthesis of SSZ-24 under autogenous pressure hydrothermal conditions reported to date is shorter than 1 day and required only a catalytic amount of seeds.

Experimental

Materials

All chemicals and materials used are from commercially available sources and employed without further purification. Potassium hydroxide (KOH 98%, Aladdin Chemistry), Lithium hydroxide (LiOH 98%, Sigma-Aldrich), Sodium hydroxide (NaOH 98%, Aladdin Chemistry), Cesium hydroxide (CsOH 50 wt.% in water, Adamas-beta), N,N,N-trimethyl-1-adamantammonium hydroxide (TMAD 25%, Xikai Industry), Deionized water, Aluminum metal powder (99.5%, Aladdin Chemistry), Colloidal silica (Ludox HS-40, 40 wt.% SiO₂, Sigma-Aldrich) and fumed silica (SiO₂, Sigma-Aldrich). The zeolite Beta with Si/Al=15, which was used as a silicic acid-alumina source in the synthesis of SSZ-13, was purchased from Changchun Third Party Pharmaceutical Technology. A home-made SSZ-24 and SSZ-13 were used as seeds without prior calcination.

Conventional hydrothermal synthesis of SSZ-24

The reference SSZ-24 sample, denoted CS (conventional synthesis), was obtained from a gel with composition 0.1TMAD: 0.15KOH: 1SiO₂: 44H₂O. In a typical synthesis, 1.5 g fumed silica, 0.21 g KOH, and 1.51 g TMAD were mixed with 18.9 g H₂O under stirring.²⁴ The resulting gel was charged into a Teflon-lined stainless-steel autoclave and hydrothermally treated at 150 °C for 22 days. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C. The sample was calcined at 550 °C (at 60 °C·h⁻¹ ramp) in air flow for 6 h.

Synthesis of SSZ-13 and SSZ-24 seeds

SSZ-13 was prepared according to reference 33 and used for seeding. The SSZ-13 seeds used in this study were prepared from a gel with molar composition 1SiO₂:0.05Al₂O₃:0.18K₂O:0.31TMAD:30H₂O, where 1.7 g zeolite beta and the TMAD solution were mixed (solid/liquid weight

ratio = 0.14) under stirring for 2 h at room temperature. The autoclave was heated at 150 °C for 24 h. After the crystallization step, the solid product was collected by vacuum filtration and washed thoroughly with deionized water until a near neutral pH and then dried overnight at 60 °C.

The SSZ-24 seeds used in this study were prepared from a gel with molar composition 0.06TMAD: 0.1NaOH: SiO₂: 21.1H₂O, where 0.3 wt.% of SSZ-13 seeds prepared according to the procedure described above were added. In a typical synthesis, 4.4 g colloidal silica (Ludox HS-40), 0.1 g sodium hydroxide and 0.005 g SSZ-13 seeds were mixed with 1.6 g TMAD solution under stirring, the autoclave was heated at 100 °C for 1 h and at 180 °C for 22 h. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C. Both SSZ-24 and SSZ-13 seeds were used without prior calcination.

Synthesis of zeolite SSZ-24 using SSZ-24 seeds

The synthesis of SSZ-24 was studied in the presence of KOH and NaOH.

KOH system: Synthesis gel was prepared according to the following composition 0.1TMAD: 0.15KOH: 1SiO₂: 44H₂O and 5 wt.% of SSZ-24 seeds. The seed content (in wt.%) is calculated on the SiO₂ basis in the starting gel. In a typical synthesis, 1.5 g fumed silica, 0.21 g KOH, and 1.51 g TMAD were mixed with 18.9 g H₂O under stirring. 0.075 g SSZ-24 seeds were added into the above gel. The synthesis was performed in a Teflon-lined stainless-steel autoclave and hydrothermally treated at 150 °C for 24 h and 72 h. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C.

NaOH system: Synthesis gel was prepared according to the following composition 0.06TMAD: 0.10NaOH: xSiO₂: 21.1H₂O, when x is 1.76 mole, the mass of seeds added was 0.0, 0.3, 1.2, 3.0 (wt.%); when x is 1.20 mole, the mass of seeds added was 4.2 (wt.%). The seed content (in wt.%) is calculated on the SiO₂ basis in the starting gel. In a typical synthesis, 4.4 g colloidal silica (Ludox HS-40) and 0.1 g NaOH was mixed with 1.6 g TMAD solution under stirring. 0.07 g SSZ-24 seeds were added into the above gel. The gel was then mixed vigorously for 10 min. The resulting reaction mixture was charged into a Teflon-lined, stainless-steel autoclaves. Before the hydrothermal treatment, the mixture was aged at 100 °C for 1 h. Then autoclaves were heated statically under autogenous pressure for 22 h at 180 °C. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C. The sample was calcined at 550 °C (at 60 °C·h⁻¹ ramp) in air flow for 6 h and denoted as S24-Y, where S24 represents synthesis in the presence of SSZ-24 seeds, and Y is the numerical order of a series of experiments at variable syntheses conditions, as shown in Table 1.

Synthesis of zeolite SSZ-24 using SSZ-13 seeds

Similar to the previous part, the synthesis of SSZ-24 was studied in the presence of KOH and NaOH.

KOH system: Synthesis gel with composition 0.1TMAD: 0.15KOH: 1SiO₂: 44H₂O and 5 wt.% of SSZ-13 seeds was prepared. The seed content (in wt.%) is calculated on the SiO₂ basis in the starting gel. In a typical synthesis, 1.5 g fumed silica, 0.21 g KOH, and 1.51 g TMAD were mixed with 18.9 g H₂O under stirring. 0.075 g SSZ-13 seeds were added into the above gel. The synthesis was performed in a Teflon-lined stainless-steel autoclave and hydrothermally treated at 150 °C for 24 h and 72 h. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C.

NaOH system: Synthesis gel was prepared using the following composition xTMAD: yNaOH: SiO₂: zH₂O, where x = 0 – 0.08, y = 0 – 0.3, z = 21.1 – 28.7 (moles); and the seed content was varied between 0.0 and 9.0 wt.% (Table 2). The seed content (in wt.%) is calculated on the SiO₂ basis in the starting gel. In a typical synthesis, 4.4 g colloidal silica (Ludox HS-40) and 0.1 g NaOH was mixed with 1.6 g TMAD solution under stirring. The 0.005 g seeds were added into the gel. The gel was then mixed vigorously for 10 min and charged into a Teflon-lined stainless-steel autoclave. Before the high temperature hydrothermal treatment, the mixture was aged at 100 °C for 1 h. Then autoclaves were heated statically under autogenous pressure for 22 h at 180 °C. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C. The sample was denoted as S13-X, where S13 represents synthesis in the presence of SSZ-13 seeds, and X is the numerical order of a series of experiments at variable syntheses conditions, as shown in Table 2.

Influence of the alkaline metal (Li, Na, K, Cs) on the synthesis of SSZ-24: Synthesis gel was prepared according to the following composition 0.06TMAD: 0.1MOH: SiO₂: 21.1H₂O, M = Li, Na, K, Cs, and 0.3 wt.% of SSZ-13 seeds. The gel was then mixed vigorously for 10 min and then charged into Teflon-lined stainless-steel autoclaves. Before the high temperature hydrothermal treatment, the mixture was aged at 100 °C for 1 h. Then autoclaves were heated statically under autogenous pressure for 22 h at 180 °C. The final product was collected by vacuum filtration and washed with deionized water until a near neutral pH and dried overnight at 60 °C.

Crystal growth kinetics of SSZ-24: The relative crystallinity of the samples prepared at different period of crystallization were determined by XRD analysis using the peak area at 7.42° 2θ in relative to the reference SSZ-24 sample (CS). For more accurate analysis, the XRD patterns of the calcined samples were used.

The yield of SSZ-24 was calculated by the following equation:

$$\text{yield (\%)} = \frac{\text{SSZ-24 (g)}}{\text{Si source (g) + seeds (g)}} \cdot 100$$

Characterization

Powder X-ray diffraction (PXRD) analysis was performed on a PANalytical B.V. Empyrean powder diffractometer at 40 kV and 40 mA using Cu Kα radiation (λ = 1.5418 Å) over the range of 2θ = 4.0 – 40.0°. Thermogravimetric analysis (TGA) was performed using a SHIMADZU DTG-60 thermal analyser system from 30 to 650 °C under an air atmosphere at a heating rate of 10 °C min⁻¹. A JEOL JSM6700 scanning electron microscope was used to study the morphology of the samples. Elemental analysis of the sample was measured by Energy Dispersive X-Ray Fluorescence Spectrometer (EDX) operated at JEM-2100F. Nitrogen and carbon dioxide physisorption analyses were performed with a Quantachrome Autosorb-iQ analyzer with ultra-high-purity nitrogen gas (99.999% purity) at 77 K and CO₂ gas (99.999% purity) at 273 K and 298 K. The calcined samples were analyzed after degassing at 300 °C. The specific surface areas (S_{BET}) were obtained using the Brunauer-Emmett-Teller (BET) equation. The microporous volume (V_{mic}, cm³ g⁻¹) and external surface area (S_{ext}, m² g⁻¹) were obtained from the t-plot based on the Harkins-Jura equation.

Results and discussion

3.1 Conventional hydrothermal synthesis of SSZ-24

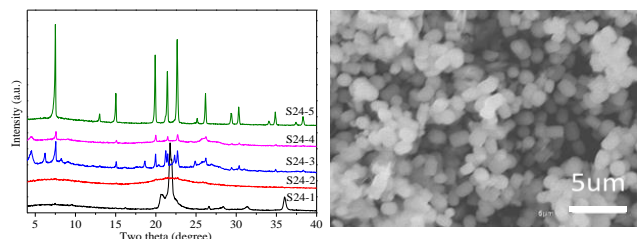
Our preliminary study of SSZ-24 crystallization was based on the gel composition reported in reference 24. A highly crystalline SSZ-24 was obtained after 22 days crystallization at 150 °C (Fig. S1). The addition of 5 wt.% SSZ-24 seeds to this system did not show the expected positive effect in term of substantially improved crystallization rate. After 24 h crystallization amorphous and unidentified phase was found in the solid, while after 72 h traces of SSZ-24 with a large amount of amorphous material was observed (Fig. S2). In contrast, the addition of 5 wt.% SSZ-13 seeds to the system resulted in crystalline product after 72 h of synthesis (Fig. S3). However, in a mixture of SSZ-24, SSZ-13 and SSZ-31 was synthesized. Thus, further optimization of the initial gel was required in order to obtain pure SSZ-24.

3.2 Synthesis of zeolite SSZ-24 using SSZ-24 seeds

We have studied the performance of SSZ-24 seeds in the formation of pure and highly crystalline AFI-type zeolite in a NaOH system. Table 1 shows the synthesis conditions and the obtained products. The synthesis containing below 1.2 wt.% seeds did not yield a crystalline product (Run S24-1, S24-2). At higher seeds loading, i.e. 3.0 wt.%, SSZ-24 and crystoballite type SiO₂ were formed (Run S24-4). A pure SSZ-24 was obtained after the increase of seeds content to 4.2 wt.% while decreasing the SiO₂ content in the gel to 1.20 mole (Run S24-5). XRD pattern (Fig. 1 left) and SEM micrograph (Fig. 1 right) of S24-5 showed that a pure zeolite SSZ-24 was obtained and the crystals were relatively uniform in size. However, a careful SEM inspection indicated that some impurities were present in the sample. The amount of these impurities is below 3 wt.% since no other crystalline phase was detected in the XRD pattern of the solid. It should also be mentioned that the preliminary aging at 100 °C is indispensable to obtain pure SSZ-24. Without preliminary aging the formation of SSZ-31 as an impurity is observed (Fig. S4).

Table 1 Synthesis conditions and products of seeded SSZ-24 synthesis at 180 °C for 22 h.

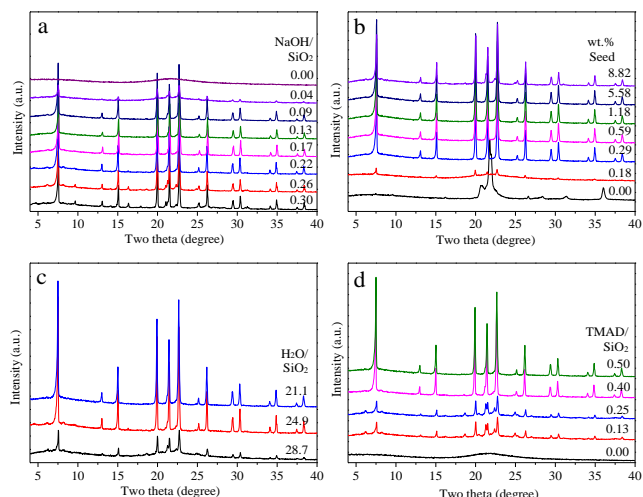
Run	Synthesis conditions				Product(s) Crystalline phase(s)
	SiO ₂ (mole)	Seeds (wt.%)	NaOH/ SiO ₂	TMAD/ SiO ₂	
S24-1	1.76	0.0	0.10	0.06	Amorphous
S24-2	1.76	0.3	0.10	0.06	Amorphous
S24-3	1.76	1.2	0.10	0.06	SSZ-24, SiO ₂ , SSZ-31
S24-4	1.76	3.0	0.10	0.06	SSZ-24, SiO ₂
S24-5	1.20	4.2	0.10	0.06	SSZ-24

**Fig. 1** XRD pattern (left) and SEM micrograph (right) of SSZ-24 obtained by using SSZ-24 as seed.

3.3 Synthesis of zeolite SSZ-24 using SSZ-13 seeds

Structure similarities between SSZ-24 and SSZ-13, i.e. the abundant presence of 6 member rings units, inspire us to try the use of SSZ-13 seeds in the synthesis of SSZ-24.

All important factors controlling SSZ-24 crystallization were studied. First, we have investigated the impact of sodium on the formation of SSZ-24 in NaOH system in the presence of 0.6 wt. % SSZ-13 seeds. The experimental conditions and the results are summarized in Table 2 (Run S13-1 to S13-8) and the XRD patterns are presented in Fig. 2a. When NaOH/SiO₂ ≥ 0.26, mixed phases of zeolite SSZ-13, SSZ-24, SSZ-31 were formed (Run S13-1, S13-2). Pure well crystalline SSZ-24 was obtained at 0.04 ≤ NaOH/SiO₂ ≤ 0.13 (Run S13-5, S13-6, S13-7). It is worth noting that NaOH is crucial in SSZ-24 synthesis since without it (NaOH/SiO₂ = 0) AFI-type material was not formed (Run S13-8).

**Fig. 2** XRD patterns of SSZ-24 synthesized at different content of NaOH (a), SSZ-13 seeds (b), Water (c) and TMAD (d).

The impact of seed content was studied in experiments S13-9 to S13-15 (Table 2). The XRD patterns are presented Fig. 2b. Pure SSZ-24 phase was constantly obtained even at seed content as low as 0.3 wt.% (Run S13-11). Noteworthy, at seed content of 0.2 wt.% still SSZ-24 can be observed in the product, but the amount of crystalline material was very low. Also, the crystallization rate decreased substantially. On the other hand, the use of 0.3 wt.% seeds (Run S13-11), resulted in SSZ-24 materials with 90% crystallinity. No crystallization was observed in the non-seeded system (Run S13-9). In the introduction section, it was pointed out that the zeolite synthesis required ≥ 3-5 wt.% seeds. The reduction of the seed content below 3 wt.% is rarely reported. The present study showed that upon optimization of the synthesis conditions, the mass of seeds could be reduced below 1 wt.% in respect to the silica content in the gel. Such a low seed content we consider as a “catalytic” since it is negligible with respect to

Table 2 Conditions of SSZ-24 synthesis with SSZ-13 seed at 180 °C for 22 h and the corresponding products.

Run	Synthesis conditions (mole ratio)				Product (s)	
	Seed (wt.%)	NaOH/SiO ₂	TMAD/ SiO ₂	H ₂ O/ SiO ₂	Phase (s)	Crystallinity (%)
S13-1	0.6	0.30	0.08	24.9	SSZ-13, SSZ-24, SSZ-31	-
S13-2	0.6	0.26	0.08	24.9	SSZ-13, SSZ-24, SSZ-31	-
S13-3	0.6	0.22	0.08	24.9	SSZ-24, SSZ-31	-
S13-4	0.6	0.17	0.08	24.9	SSZ-24, SSZ-31	-
S13-5	0.6	0.13	0.08	24.9	SSZ-24	92
S13-6	0.6	0.09	0.08	24.9	SSZ-24	88
S13-7	0.6	0.04	0.08	24.9	SSZ-24	28
S13-8	0.6	0.00	0.08	24.9	Amorphous	-
S13-9	0.0	0.09	0.08	24.9	Layered silicate	-
S13-10	0.2	0.09	0.08	24.9	SSZ-24	17
S13-11	0.3	0.09	0.08	24.9	SSZ-24	82
S13-12	0.6	0.09	0.08	24.9	SSZ-24	88
S13-13	1.2	0.09	0.08	24.9	SSZ-24	89
S13-14	6.0	0.09	0.08	24.9	SSZ-24	92
S13-15	9.0	0.09	0.08	24.9	SSZ-24	92
S13-16	0.3	0.09	0.08	28.7	SSZ-24	43
S13-17	0.3	0.09	0.08	21.1	SSZ-24	90
S13-18	0.3	0.09	0.06	21.1	SSZ-24	91
S13-19	0.3	0.09	0.04	21.1	SSZ-24, SSZ-31	-
S13-20	0.3	0.09	0.02	21.1	SSZ-24, SSZ-31	-
S13-21	0.3	0.09	0.00	21.1	Amorphous	-

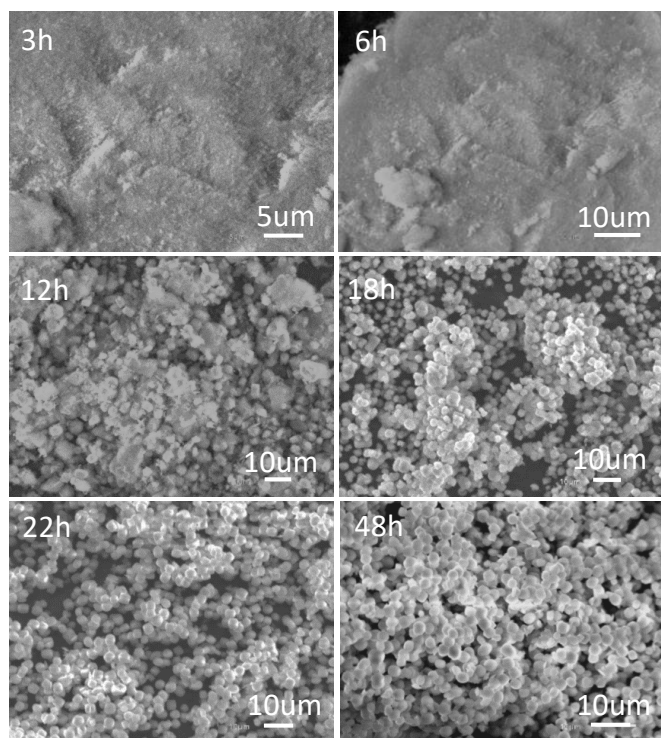


Fig. 3 SEM micrographs of the series of samples S13-18 after 1, 3, 6, 12, 18, 22 and 48 h of hydrothermal synthesis.

the mass of the gel.

The water content had a pronounced effect on the seeded SSZ-24 synthesis (Table 2, S13-11, S13-16, S13-17). For instance, as water content was increased to $\text{H}_2\text{O}/\text{SiO}_2=28.7$, the crystallinity of SSZ-24 decreased to 43% (Run S13-16), while the crystallinity reached 90% (Run S13-17) when the water content decreased to $\text{H}_2\text{O}/\text{SiO}_2 = 21.1$ (Fig. 2c).

The effect of TMAD on the synthesis of SSZ-24 was studied in the series S13-17 to S13-21 synthesis (Table 2). When TMAD/SiO_2 mole ratio ≥ 0.06 (Run S13-17 and S13-18), a pure SSZ-24 was obtained. SSZ-31 was present as an impurity when $\text{TMAD}/\text{SiO}_2 < 0.06$ (Run S13-19 and S13-20) and only amorphous was found in the TMAD-free system (Run S13-21). The crystal growth kinetics of SSZ-24 in SSZ-13 seeded system was followed by SEM (Fig. 3). After 12 h large amorphous particles and crystals, the later are not well shaped, can be seen. The crystals are much better shaped after 18 h, but still some amorphous can be observed in the solid product. No traces of amorphous material are seen in the product after 22 h crystallization. The extension of the crystallization time to 48 h resulted in larger crystals, which is a consequence of the Ostwald ripening.

In general, the use of SSZ-13 seeds in the crystallization of SSZ-24 is much more efficient with respect to the genuine SSZ-24 seeds. Often the crystal size and morphological feature influence the seed performance. However, the employed SSZ-13 and SSZ-14, where fairly similar in morphology. Therefore, the seeding power of SSZ-13 is likely to be related to their composition. Hence we consider that the Al-containing SSZ-13 is more stable under conditions employed. More precisely, the

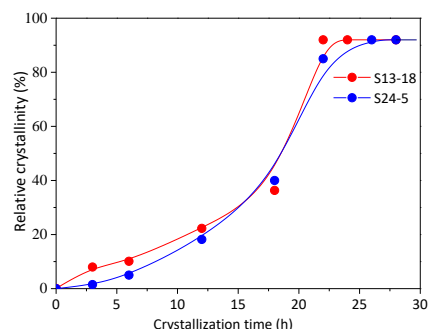


Fig. 4 Crystal growth kinetics of SSZ-24 synthesized with SSZ-13 (S13-18) and SSZ-24 (S24-5) seeds.

framework aluminum is providing a stable configuration which retains the structure elements that promote the formation of SSZ-24. On the contrary, the all-silica SSZ-24 was readily dissolved in basic medium and lost its seeding power. In order to gain more insight into the phase transformation during the crystallization process, we have studied the crystal growth kinetics of SSZ-24 at 180 °C (Fig. 4). The relative crystallinity of the calcined samples was determined by the peak area at $7.42^\circ 2\theta$ under XRD patterns (Fig. S5) in relative to the reference SSZ-24 sample (CS). The reaction rate of using SSZ-13 (Run S13-18) as seeds is higher and a complete crystallization was obtained after 22 h, faster than the one using SSZ-24 (Run S24-5) as seeds (28 h). Consider the conventional synthesis of SSZ-24 required 22 days.²⁴ The employment of seeds, as shown in the present study, improves substantially the crystallization rate of SSZ-24.

Generally, zeolites are synthesized in the presence of alkali metal cations, which influence not only the crystallization rate and framework Si/Al ratio but also the crystal size and

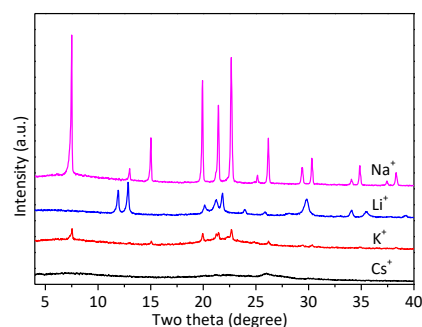


Fig. 5 XRD patterns of SSZ-24 synthesized with different alkaline metal cations at 180 °C for 22 h.

morphology.^{34,35} Since alkali metal cation plays an essential role in the zeolite synthesis, the effect of Li^+ , Na^+ , K^+ , Cs^+ on the formation of SSZ-24 were studied. Sodium is the most widely used alkali cation in zeolite synthesis. It promotes the formation of a number of zeolites and contributing to a rapid crystal growth rate.³⁷ Potassium is also largely used in zeolite

synthesis with more pronounced structure specificity. In contrast, Li^+ and Cs^+ hardly promote the crystallization of zeolite structures.³⁸ A previous study showed that pure SSZ-24 was obtained from the K-TMAD system, while the replacement of K^+ with Na^+ would lead to bi-phases product.³⁶ However, when as-synthesized SSZ-13 seeds were used, the Na-containing system yielded highly crystalline SSZ-24 within 24 h. The crystallinity of K-SSZ-24 was lower with respect to Na-SSZ-24 (Fig. 5) and the increase of K^+ content hindered the formation of SSZ-24 (Fig. S6a). The extension of the reaction time of K^+ -containing system to 2 days resulted in highly crystalline SSZ-24, however zeolite SSZ-31 was formed as a side product (Fig. S6b). In contrast, SSZ-24 was constantly obtained in Na^+ system even after 3 days of synthesis, revealing the essential role of the alkaline cation in SSZ-24 synthesis. In summary, SSZ-24 was successfully obtained in the presence of Na^+ and K^+ , while Li^+ yielded an unknown phase and in the case of Cs^+ no crystalline product was found (Fig. 5).

For the sake of comparison the characteristics of the two best SSZ-24 samples obtained with SSZ-13 (S13-18) and SSZ-24 (S24-5) seeds were compared. Both samples showed X-ray crystallinity higher than 90%. Thermogravimetric (TG) analysis showed similar weight losses, 12.6 wt.% and 12.9 wt.% for S13-18 and S24-5, respectively (Figure S7). The amount of TMAD (300 – 650 °C) in the two samples is approximately 10 wt. %. The weight loss in the low temperature range (30 – 250°C) attributed to the physisorb water release is a little lower for S13-18 (1.9 wt.%) in respect to S24-5 (2.4 wt.%).

Nitrogen adsorption-desorption analysis of S13-18 and S24-5 samples measured at 77 K showed Type I isotherms (Fig. 6a) with a sharp uptake at a low pressure of $P/P_0 < 0.05$, which is characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) equation was applied over the $0.05 < P/P_0 < 0.25$ range of the isotherms. The micropore volume ($0.13 \text{ cm}^3\text{g}^{-1}$) of S13-18 are substantially higher in respect to S24-5 ($0.10 \text{ cm}^3\text{g}^{-1}$). We attribute the higher micropore volume to the higher crystallinity of SSZ-13 seeded sample (Table 3).

Table 3 Comparison of physicochemical properties of S13-18 and S24-5 samples.

Samples	Seed (wt.%)	Yield/ %	$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	$V_{\text{mic}}/\text{cm}^3\text{g}^{-1}$	Si/Al
S24-5	4.2	61	407	0.10	299
S13-18	0.3	80	413	0.13	196

Conclusions

In summary, we have developed a seed-assisted synthesis method for rapid crystallization of highly crystalline SSZ-24. The synthesis time was substantially shortened from 22 days in conventional synthesis to 22 h in our seeded system. This result was obtained with a catalytic amount (0.3 wt.%) of seeds, which make the synthesis particularly attractive for practical use. The reduction of the crystallization time and seed content was achieved without compromising the crystallinity (> 90 %) of the product. Thus the seed-assisted synthesis, with appropriate aging and selection of alkaline metal cations, directs the rapid crystallization of SSZ-24 and prevents the formation of undesired phase. This study illustrates that the seeded approach can properly address the crystallization of the most challenging zeolite.

Conflicts of interest

There are no conflicts to declare.

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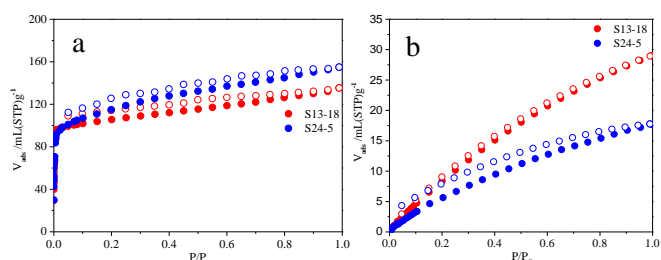


Fig. 6 N_2 physisorption isotherms (a) and CO_2 adsorption isotherms (b) of S13-18 and S24-5 samples at 77 K and 273 K respectively.

S13-18 showed also a substantially higher CO_2 adsorption than S24-5 (Fig. 6b). According to the elemental analysis (Table 3), the Si/Al ratio of S13-18 is 196 while S24-5 is 299. Both zeolites are almost all-silica materials, and thus impact of the framework composition on the adsorption properties is not expected.

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