

Seed-Assisted Synthesis of MCM-71 Zeolite

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Abstract

MCM-71 zeolite (Mobil Composition of Matter Number 71) can be synthesized in a new condition of one-step temperature at 180 °C for 11 days. The effect of adding seed at 0.3, 0.6 and 0.9 wt.% can increase the rate of crystallization; hence, reduce the synthesis time. Sufficient amount of seed at level 0.6 and 0.9 wt.% shows marked effect. It can enhance the crystallization rate and improve the purity of MCM-71 by suppressing the mordenite formation. The well-defined rectangular-shape crystal morphology is obtained with high level of seed addition. Seed-assisted MCM-71 still exhibits the aluminium coordination of perfect tetrahedral framework and shows higher n_{Si}/n_{Al} ratio, which could improve the hydrophobic property and framework stability. The best sample with high crystallinity and purity is by seeding at 0.6 wt.%. This can reduce the synthesis time to 7 days (others reported the synthesis times of 20 and 14.83 days).

Keywords: Zeolite, MCM-71, Medium-pore Zeolite, Seed, Dewaxing

Introduction

Zeolite is crystalline microporous aluminosilicate with three-dimensionally interconnected structure. It plays an important role in industrial processes as selective adsorbent, selective ion-exchanger, and catalytically active compounds. The novel MCM-71 zeolite (Mobil Composition of Matter Number 71) was patented in 2002 [1]. It represents a new microporous material in the mordenite family [2]. This zeolite possesses a two-dimensional network consisting of straight, highly elliptical 10-MR channels (ca. 0.65 x 0.43 nm) and orthogonal sinusoidal 8-MR channels (ca. 0.47 x 0.36 nm). Its calcined form of MCM-71 has an X-ray diffraction pattern resembling that of DCM-2 [3]. This medium-pore zeolite is useful for shape-selective acid catalysis, such as dewaxing of the waxy feeds in preparation of diesel and lubricating oil basestocks [4-6] and propylene oligomerization. The high-silica MCM-71 ($n_{Si}/n_{Al} = 8$) shows excellent properties of high acid density (946 $\mu\text{mol/g}$) and high thermal stability (upto 1000 °C) [7]. This makes MCM-71 appropriate acidic catalyst in chemical conversion processes at high temperature. Moreover, the separation ability between *n*-heptane and 2-methylhexane suggests it could be interesting shape selective catalyst and adsorbent [7]. The conventional synthesis of MCM-71 has been achieved in very long synthesis time, i.e., 20 days [1] in two-step temperature and 14.83 days [7]. Even though low-cost raw materials are used similar to other commercial low-silica zeolites, e.g., A, X, and Y and no calcination process is required because its template does not act as void filler. This makes economical, reduces energy consumption, and avoids harmful gases from combustion of organic template. Therefore, this high-silica MCM-71 is considered as "green" material. However, long synthesis time is a drawback of this material because of increasing the production cost. The conventional synthesis needs at 160 °C (lower-side temperature for high-silica synthesis) which could avoid its impurity. Therefore, this work has attempted the seeding technique to shorten the synthesis time. The work contributes the synthesis condition at one-step synthesis temperature of 180 °C by using different amount of its seed (MCM-71). The effect of structural properties, purity, composition, and crystal morphology are investigated.

Materials and methods

The synthesis gel was prepared with the molar composition: 1 SiO₂: 0.05 Al₂O₃: 0.375 KOH: 0.2 C₆H₁₅NO₃: 30 H₂O. Ludox AS-30 (30 wt.% SiO₂ in H₂O) was mixed with distilled water. KOH solution (20 wt.% in H₂O) was added and the resulting mixture was stirred for 5 min. Then aluminium hydroxide (53.8

wt.% Al₂O₃) was gradually added during vigorous stirring. The resulting gel was further stirred for 0.5 h. Then triethanolamine (C₆H₁₅NO₃) (99 wt.%) was added and the gel was stirred for another 0.5 h. In case of seeding, MCM-71 in different seeding levels of 0.3, 0.6, 0.9 wt.% based on SiO₂ in the gel was added to the synthesis mixture. Then, the gel was transferred into a Teflon-lined vessel in a stainless steel autoclave. The reaction occurred at 180 °C under static condition for 3-13 d. The protonated form was carried out by ion-exchanged with 1 M NH₄NO₃ at 80 °C for 3 h (1 g zeolite: 100 g solution). This was repeated for 3 time with the new solution. Then it was calcined in furnace at 450 °C for 8 h. This form is used for characterization of low-temperature N₂-adsorption.

Characterization

This material was characterized by powder X-ray diffraction (XRD, BRUKER AXS model D8 Advance) operated at 40 kV and 30 mA. The measurement ran with angle from 5 to 50 ° of 2θ with a step size of 0.02 ° and the scan speed of 1 °/min. The surface characteristic of the materials was recorded using field emission scanning electron microscopy (FESEM, JEOL model JSM-7610). The elemental composition was measured by the X-Ray fluorescence spectrometer (XRF, Bruker S8 Tiger). The surface properties and pore volume were determined by N₂-adsorption at -196 °C (BELSORP-mini). The sample was pretreated at 200 °C for 12 h (BELPREP-flow) before determination of adsorption isotherm. The specific surface area was calculated by the BET method in the pressure range p/p₀ ≈ 0.035-0.1. The micropore volume was determined by the t-plot analysis. The local environment of aluminium atom in the zeolite framework was determined by solid-state ²⁷Al magic angle spinning nuclear magnetic resonance spectroscopy (²⁷Al MAS NMR, Bruker 400 wide-bore) at the resonance frequency of 104.28 MHz with 4 mm ZrO₂ rotor. The rotor was operated at a spinning rate of 12 kHz with excitation pulses of 5 μs and recycle times of 1 s at 128 scans per spectrum. The ²⁷Al chemical shift is referenced with respect to external solution of AlCl₃ x 6H₂O.

Results and discussion

The synthesis temperature was directly set high at 180 °C instead of 160 °C as reported in conventional synthesis [1, 7]. Type of crystalline material and its crystallization kinetics were observed by the XRD. Without seeding, the material is still amorphous when the synthesis time is for 5 d. This defines by amorphous halo around 2 theta = 16-34 °. The complete crystalline MCM-71 starts at 9 d and transforms to fully crystalline until 11 d as shown in Figure 1. The peak positions and the patterns are similar to those in patent literature [1]. Mordenite was observed as a minor impurity phase (main peaks at 2θ ≈ 6.5, 8.7 and 9.8 °). This crystalline impurity is also found in the XRD patterns reported in the patent. With seeding (0.6 wt.%), it shows crystalline MCM-71 starts to form at shorter time of 5 d as shown in Figure 2. The highest crystallinity was detected at 7 d. Mordenite was found in lesser extent. The synthesis time to obtain the crystalline MCM-71 in case of seed crystal addition (0.3, 0.6 and 0.9 wt.%) is faster than that in case of no seed synthesis.

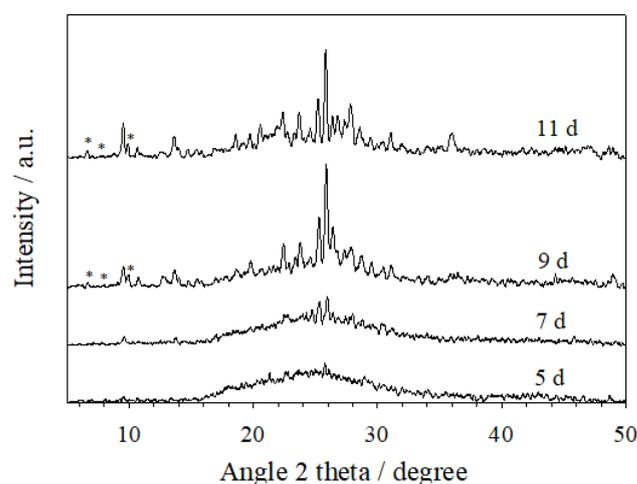


Figure 1 XRD patterns of as-synthesized MCM-71 without seed addition (* denotes mordenite impurity).

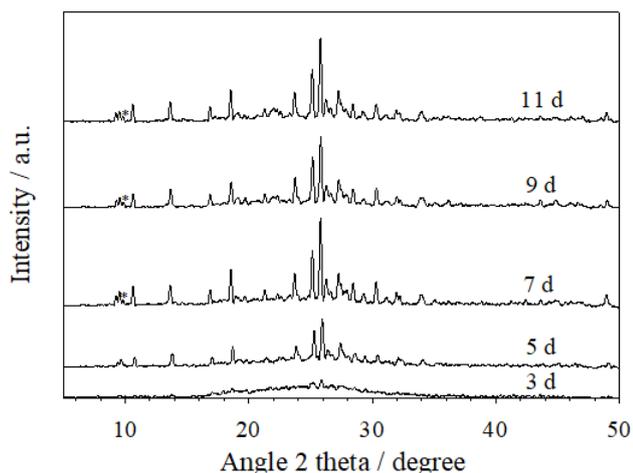


Figure 2 XRD patterns of as-synthesized MCM-71 with seed addition at 0.6 wt.% (* denotes mordenite impurity).

Crystallization kinetics of MCM-71 in all cases are presented in Figure 3. They are referred to the main peaks of MCM-71 at $2\theta = 10.6$ and 25.9° . Without seeding, the crystallization kinetic is at the slowest. With seeding at 0.3 wt.%, the crystallization is slightly faster. By seeding at higher level of 0.6 and 0.9 wt.%, the crystallization kinetics are markedly rapid. They increase linearly from 3 to 7 d and slightly decline from 9 d. The seed levels at 0.6 and 0.9 wt.% do not take much different effect to the crystallinity. This enhancement results by increasing in crystal surface area initially in the synthesis system; consequently, this aids the assimilation of reagents from the synthesis gel and formation of the new crystals.

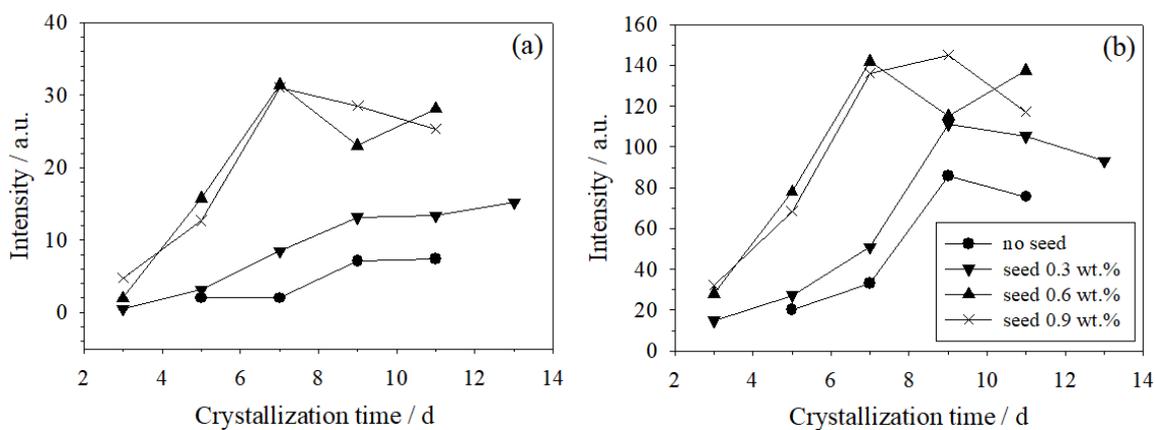


Figure 3 Kinetic curves of crystallization of MCM-71 with different seed amount referring to the peaks at $2\theta =$ (a) 10.6° and (b) 25.9° .

The synthesis with different seed amounts also affects the formation of mordenite impurity. Figure 4 shows the intensity ratio between mordenite peak and MCM-71 peak at $2\theta = 6.5^\circ$ and 10.6° , respectively. Generally, adding seed between 0.3-0.9 wt.% can suppress the impurity formation. It can be obviously seen from 5 d. However, seeding at higher level of 0.6 and 0.9 wt.% will significantly suppress the mordenite impurity, particularly, when synthesis at longer time from 7 d.

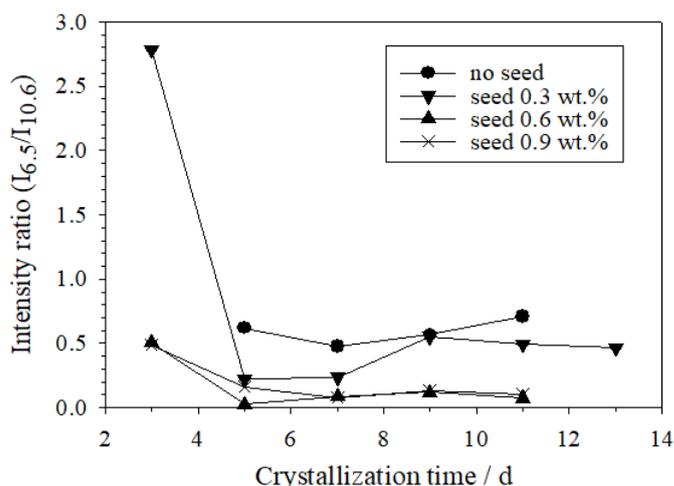


Figure 4 Intensity ratios of the mordenite peak at $2\theta = 6.5^\circ$ and the peak of MCM-71 at $2\theta = 10.6^\circ$ of samples with different seed amount by the crystallization time.

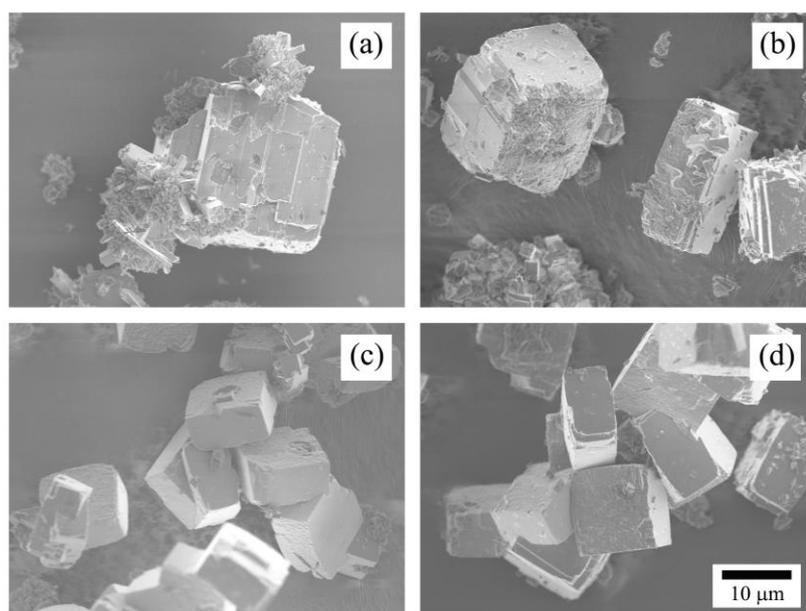


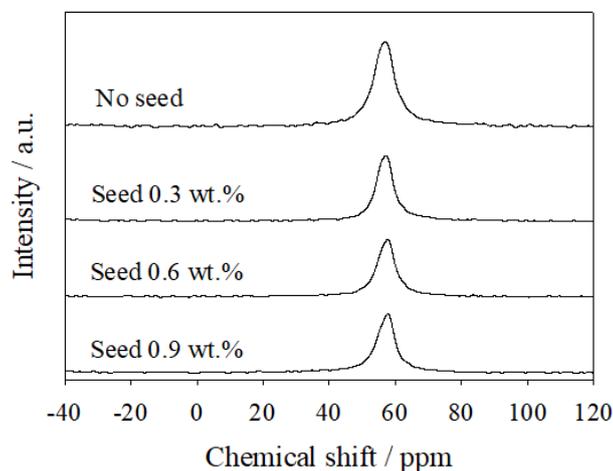
Figure 5 Scanning electron micrograph of as-synthesized MCM-71 (a) no seed (b) seed 0.3 wt.% (c) seed 0.6 wt.% and (d) seed 0.9 wt.% at the crystallization time of 11 d.

The crystal morphology of as-synthesized MCM-71 without seeding and seed addition at the crystallization time of 11 d are shown in Figure 5. MCM-71 without seeding reveals large rectangular shape with size approximately $18 \times 18 \times 15 \mu\text{m}$ with small particles adhering to the crystal surface. Similarly, MCM-71 with small amount of seed at 0.3 wt.% shows the same characteristics. By adding higher amount of seed at 0.6 and 0.9 wt.%, the crystals present well-defined rectangular shape with smaller size of about $14 \times 14 \times 7 \mu\text{m}$. The more uniform crystal size can be observed. This signifies the minimum amount of seed addition to the perfectly well-defined crystal morphology. The obtained crystal size is larger than reported in the literature [7].

MCM-71 is composed of Si, Al, K in the oxide form as shown in Table 1. Potassium is the alkaline positive charge and balances with the negative charge in the aluminosilicate framework. The molar ratio of $n_{\text{K}}/n_{\text{Al}}$ around 1 signifies potassium can balance nearly all the negative charge at the aluminium sites. The molar ratios of $n_{\text{Si}}/n_{\text{Al}}$ of MCM-71 with seeding shows higher values (8.06-8.86) than that of sample without seeding (7.45). This feature leads to higher hydrophobic property and framework stability.

Table 1 Chemical composition of as-synthesized MCM-71 zeolite at the crystallization time of 11 d.

Sample	Si (wt.%)	Al (wt.%)	K (wt.%)	nSi/nAl	nK/nSi	nK/nAl
MCM-71 (no seed)	24.5	3.16	4.65	7.45	0.136	1.013
MCM-71 (seed 0.3 wt.%)	25.2	2.98	4.23	8.12	0.121	0.983
MCM-71 (seed 0.6 wt.%)	23.9	2.85	3.92	8.06	0.118	0.951
MCM-71 (seed 0.9 wt.%)	23.8	2.58	4.02	8.86	0.121	1.072

**Figure 6** ²⁷Al MAS NMR spectrum of as-synthesized MCM-71 at the crystallization time of 11 d.

The ²⁷Al MAS NMR spectra of as-synthesized MCM-71 are shown in Figure 6. The synthesis with seeding does not affect the characteristic of aluminium coordination comparing to the synthesis without seeding. The major line is centered at a chemical shift of ca. 58 ppm with a low-field shoulder at ca. 56 ppm. This reveals pure tetrahedral coordination of aluminium to the framework, Al(OSi)₄, which attributes to relatively less defect crystal structure [8]. There is no sign of octahedrally coordinated non-framework aluminium, which gives rise to a characteristic peak mostly at ca. 0 ppm. The preferred coordination could contribute to the excellent catalytic activity. The amount of tetrahedral coordination aluminium species of the seeded sample is less than that of the sample without seeding (comparing by the peak height). This result is corresponding to the less amount of aluminium by the XRF measurement.

Conclusion

Seed-assisted synthesis is valid for novel MCM-71 zeolite. Synthesis by seed addition at level 0.3, 0.6, and 0.9 wt.% of silica in the synthesis gel contributes to faster crystallization rate at different degree. Sufficient high amount of seed addition at 0.6 and 0.9 wt.% can particularly increase its crystallization rate and suppress the formation of mordenite impurity. This also affects its crystal morphology to a well-defined rectangular shape. The seeded MCM-71 presents improvement of hydrophobicity and framework stability by increase the n_{Si}/n_{Al} ratios. The best sample corresponding to high crystallinity and purity by seeding at 0.6 wt.% can reduce the synthesis time to 7 days (comparing to 11 days with similar synthesis temperature of 180 °C and 14.83 and 20 days from the reported literatures). This MCM-71 (n_{Si}/n_{Al} = 8) shows specific surface area of 355 m²/g, pore volume of 0.15 cm³/g, and crystal morphology of rectangular shape with size 14 x 14 x 7 μm.

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