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Organic Template-Free Synthesis of ZSM-34 Zeolite from an Assistance of Zeolite L Seeds Solution

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Zeolites, especially aluminosilicate zeolites, have been widely applied in the petroleum catalysis and refining industry, and most of industrial applications require these zeolites with a low cost and friendly to the environment.[1–3] However, modern synthesis methodologies are generally used by organic templates called structure-directing agents (SDA) for their synthesis,[4–8] which has obvious disadvantages, such as relatively high cost of organic templates and environmentally unfriendly gas formed by the removal of organic templates calcined at high temperature.[9,10] Therefore, organic template free synthesis and even recycling organic template synthesis of zeolites have been paid much attention recently. For examples, organic template-free synthesis of ZSM-5 zeolites is successful;[11–16] partially recycling and fully recycling organic template synthesis of zeolites have been performed from ion-exchange and disassembled−reassembled organic template.[4,17,18] Organic template-free synthesis of ECR-1 zeolite has been carried out by carefully adjusting the Na_2O/SiO_2 in the starting gel.[19]

Aluminosilicate zeolite of ZSM-34 is an intergrowth of offretite and erionite zeolites containing zeolitic building units of cancrinite (CAN) cages,[20] which is known to be a good catalyst for the conversion of methanol to C_2-C_5 olefins.[21]

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ZSM-34 zeolite was first discovered by Rubin et al. using organic template of choline [$(CH_3)_3NCH_2CH_2OH$],[22] and later ZSM-34 samples were successfully synthesized in the presence of different diamines ($NH_2C_nH_{2n}NH_2$, $n = 4, 6, 8, 10$).[23] In these cases, organic templates are necessary. However, these organic templates with relatively high cost in the synthesis severely hinder the practical applications of ZSM-34 zeolite in catalytic reactions. In the present work, we demonstrate a novel and successful route for organic template-free synthesis of ZSM-34 from an assistance of zeolite L seed solution for the first time.

ZSM-34 zeolite was hydrothermally synthesized in a poly-(tetrafluoroethylene)-lined stainless steel autoclave statically at the temperature of 100 °C for 7–17 days with 50:1.0:20:1250–1750 SiO_2:Al_2O_3:Na_2O:H_2O molar ratios of starting gels in the presence of zeolite L seeds solution.[24] As a typical run, zeolite L seed solution was prepared by mixing 29 mL of H_2O, 0.7 g of $NaAlO_2$, 1.4 g of NaOH, 4.4 g of KOH, and 5.4 g of fumed silica under stirring, followed by aging at room temperature for 72 h, giving a clear solution. For the preparation of starting gel, we dissolved 0.8 g of NaOH into 9.2 mL of water, followed by introducing 4.4 mL of colloidal silica (SiO_2:5.72 M). After the solution was stirred for about 5 h, 0.6 mL of $Al_2(SO_4)_3$ (0.88 M) was dropped into the mixture, followed by the addition of a designated amount (1–2 mL) of zeolite L seed solution. After being stirred for 13 h at room temperature, the mixture was transferred into an autoclave to crystallize at 100 °C for 7–17 days. The product was collected by filtration, washed with deionized H_2O, and dried in air. Additionally, the judgment on the quality of zeolite L seed solution is to test the directing effect on crystallization of zeolite L. When a small amount of zeolite L seeds solution with good quality was added into the aluminosilicate gel (28: 1.0:4.4:6.6:440 SiO_2:Al_2O_3:Na_2O:K_2O:H_2O), zeolite L with good crystallinity could be crystallized at 100 °C for 24 h. The zeolite L seed solution appears to serve as seeds for the formation of zeolite L crystals.

The sample morphology was observed with a field-emission scanning electron microscope (JEOS JSM 6700). The X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). The nitrogen adsorption isotherm, surface area, and pore size distribution (HK model) of the sample were measured with a Micromeritics ASAP 2010 M system at 77 K. The ratio of Si/Al was determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV).

Figure 1 shows XRD pattern of the sample synthesized at 100 °C for 7 days from the aluminosilicate gel in the presence of 2.0 mL of zeolite L seed solution. The sample exhibits main peaks at 7.82, 11.86, 13.50, 20.62, 23.82, 25.01, 27.08, 28.48, 31.36, 33.56, and 36.30 in the range of 4–40°, which are typically assigned to those of ZSM-34 structure.[23] Furthermore, SEM image (Figure 2) shows that the sample morphology is rodlike, which is very similar to that of ZSM-34 zeolite reported previously.[25] Additionally, HR SEM image shows that the small partiles on the samples are still crystal-like (Insert in Figure 2). These results indicate that ZSM-34 zeolite could be hydrothermally synthesized at 100 °C for 7 days with the assistance of zeolite L seed solution in the absence of organic templates. In contrast, if zeolite L seed solution is absent in the mixture for crystallization, the solid products obtained are amorphous, although the starting gels have the same composition (runs 1 and 2 in Table 1). Obviously, zeolite L seed solution plays an important role for crystallization of ZSM-34 zeolite. Interestingly, when 1 mL of zeolite L seed solution is added into the mixture, a full crystallization of ZSM-34 zeolite takes 17 days (run 3 in Table 1), which is much longer than that in the presence of 2 mL of zeolite L seed solution (7 days). This phenomenon further confirms the importance of zeolite L seed solution in the crystallization of ZSM-34 zeolite.

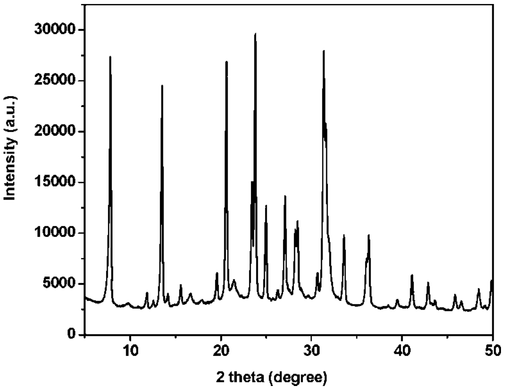

Figure 1. XRD pattern of the sample synthesized at 100 °C for 7 days with a molar ratio of SiO_2:Al_2O_3:Na_2O:H_2O at 50:1.0:20:1250 in starting gel in the presence of 2.0 mL of zeolite L seed solution.

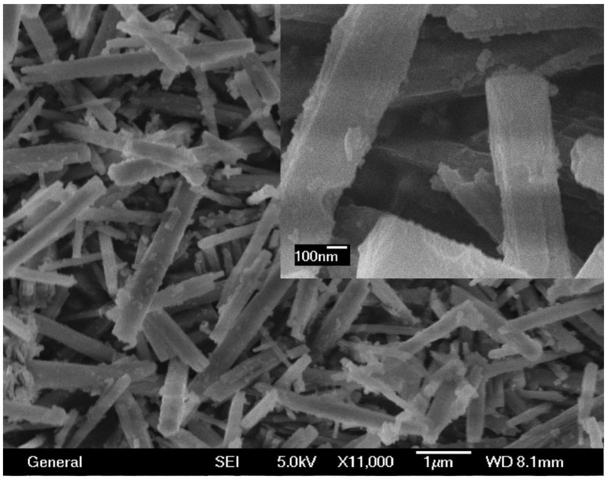

Figure 2. SEM image of the sample synthesized at 100 °C for 7 days with a molar ratio of SiO_2:Al_2O_3:Na_2O:H_2O at 50:1.0:20:1250 in starting gel in the presence of 2.0 mL of zeolite L seed solution. Insert: HR SEM image of the sample.

It is well-known that zeolite seeds solution (zeolite nanoclusters) could effectively direct zeolite crystallization,[26–29] and possibly zeolite building units such as secondary building

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Table 1. Syntheses of Samples in an Aluminosilicate Gel[a] at 100 °C in the Absence or in the Presence of Zeolite L Seed Solution

run	Si/Al ratio in starting gel	volume of zeolite L seed solution in starting gel (mL)	crystallization time (days)	products[b]
1	25	0	7	amorphous
2	25	0	17	amorphous
3	25	1.0	17	ZSM-34
4	25	1.5	12	ZSM-34
5	25	2.0	7	ZSM-34
6	25	3.0	7	ZSM-34+L
7	25	4.0	7	L+ZSM-34
8	25	5.0	14	no product
9	25	6.0	14	no product
10	25	7.0	14	no product
11	20	2.0	7	unidentified
12	30	2.0	7	amorphous

[a] Starting aluminosilicate gel with a molar ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ at 40–60:1.0:25:1250. [b] The phase appearing first is the major phase.

units (SBU) in zeolite seed solution play a key role for the crystallization of zeolite crystals. For example, zeolite β seed solution could be prepared from an aluminosilicate gel with a 60/1.0/22/2.5/800 SiO_2:Al_2O_3:TEAOH:Na_2O:H_2O molar ratio, and addition of a small amount of zeolite β seeds solution (3–5 wt %) into the gel (1:10–40:2.8–12:500–900 Al_2O_3:SiO_2:Na_2O:H_2O) at 140 °C for 2–4 days leads to synthesis of β zeolite with high crystallinity in the absence of organic templates.[28] Zeolite L seed solution has been successfully synthesized for a long time, and this solution could significantly promote crystallization of zeolite L and zeolite T,[24] where both zeolites contain the same zeolitic SBU of CAN cage.[30] In contrast, zeolite L seeds solution does not work for the promotion of synthesis of LTA and FAU zeolites,[24] where the β cage in the two zeolites is the same SBU.[30] These results seem to suggest that CAN cages as zeolite L building units (SBU) could be included in zeolite L seeds solution, which may play an important role for the promotion of zeolite L crystallization.[24] ZSM-34 zeolite is an intergrowth of offretite with erionite, and of course both offretite and erionite contain zeolitic building units of CAN cages. Possibly, when zeolite L seed solution is introduced into aluminosilicate gel, the CAN cages in zeolite L seed solution would direct crystallization of ZSM-34 zeolite, an intergrowth of offretite with erionite, in the absence of organic templates.

It is worth noting that when 3 mL of zeolite L seed solution is introduced into the aluminosilicate gel, the major product is still ZSM-34 zeolite but it contains impurity of zeolite L (run 6 in Table 1); when 4 mL of zeolite L seed solution is introduced into the aluminosilicate gel, the product is zeolite L with a very small amount of ZSM-34 zeolite (run 7 in Table 1). These results strongly demonstrate that zeolite L seed solution plays a key point for crystallization of ZSM-34 zeolite.

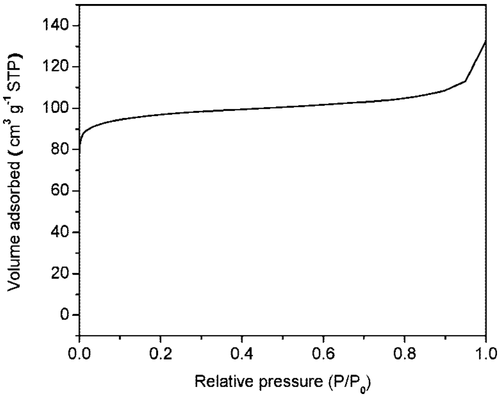

Figure 3. Nitrogen isotherm of the sample synthesized at 100 °C for 7 days with a molar ratio of SiO_2:Al_2O_3:Na_2O:H_2O at 50:1.0:20:1250 in starting gel in the presence of 2.0 mL of zeolite L seed solution.

Furthermore, when the amount of zeolite L seed solution is increased up to 5–7 mL in the aluminosilicate gel, no products could be observed after crystallization at 100 °C for 7–17 days (runs 8–10 in Table 1). These results may be associated with which larger amount of zeolite L seed solution results in an increase of alkalinity, and almost all inorganic species such as silicate and aluminate are dissolved in the gel. Additionally, when the Si:Al ratio in starting aluminosilicate gels is changed from 25 to 20 or 30, we cannot obtain ZSM-34 zeolite (runs 11 and 12 in Table 1). These results indicate that the composition in starting aluminosilicate gels is also important for crystallization of ZSM-34 zeolite.

Figure 3 shows nitrogen isotherm of as-synthesized ZSM-34 zeolite, giving a typical Langmuir adsorption. Correspondingly, surface area, micropore volume, and H-K pore size distribution are estimated at 430 m^2/g, 0.13 cm^3/g, and 5.2 Å, respectively. Interestingly, compared with ZSM-5 (5.6 Å), pore size of ZSM-34 is slightly small, which may be suitable for the conversion of smaller molecules. For example, it has been reported that ZSM-34 zeolite exhibits better ethylene selectivity in methanol to olefins than ZSM-5.[21] Additionally, a ratio of Si:Al for ZSM-34 zeolite is determined by ICP, giving about 4.4. Obviously, compared with ZSM-5, ZSM-34 zeolite exhibits abundant Al species, which offers an opportunity to greatly adjust acidity in ZSM-34 zeolite.

In summary, an aluminosilicate zeolite of ZSM-34 is successfully synthesized at 100 °C for 7–17 days from an assistance of zeolite L seeds solution in the absence of organic templates for the first time, which may provide a novel route for organic template-free synthesis of aluminosilicate zeolites.

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