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Organic Template Free Synthesis of Aluminosilicate Zeolite ECR-1

Jiangwei Song, Lei Dai, Yanyan Ji, and Feng-Shou Xiao*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, People's Republic of China

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Zeolites, especially large pore zeolites, have been widely applied in many industrial technologies, including gas adsorption, ion exchange, separation, and catalysis, for their unique porosity and high surface area,[1,2] which attract extensive studies on the influence of composition, temperature, and environment on the synthetic process of zeolites.[3] Aluminosilicate zeolites are the most important for many applications used commercially in the petroleum catalysis and refining industry, and most of the applications require that the zeolites are of low cost and friendly to the environment. Notably, modern synthesis methodologies for preparing zeolites or zeolite-like materials typically involve the use of organic molecules that direct the assembly pathway and ultimately fill the pore space.[4−6] The use of the organic template has obvious disadvantages such as the relatively high cost and the harmful gas produced during the removal of the template normally carried out by high-temperature combustion.[4,7,8]

Interestingly, there are a couple of successful approaches for recycling organic templates in the syntheses of zeolites.[9−16] For example, Takewaki et al. report that partial tetraethylammonium cations (TEA^+) in the synthesis of zeolite Beta can be recycled by an ion-exchange procedure, but the organic cations interacted strongly with the zeoltie framework still cannot be removed.[9] Recently, Lee et al. reported a novel route for complete recycle of the organic template in the synthesis of ZSM-5. They create an organic structure-directing agent that can be disassembled within the zeolite pore space to allow removal of their fragments for possible use again by reassembly.[4]

Large-pore aluminosilicate zeolite of ECR-1 is an intimate twin of the mordenite-like sheets between layers of mazzite-like cages, which was first discovered by Leonowicz and Vaughan using the organic template of bis(2-hydroxyethyl)-dimethylammonium chloride.[17−19] Later, ECR-1 is success-

* To whom correspondence should be addressed. Fax: +86-431-5168624. Tel.: +86-431-5168590. E-mail: fsxiao@mail.jlu.edu.cn.

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fully synthesized in the presence of adamantine-containing diquaternary alkylammonium iodides[20] or in the presence of tetramethylammonium (TMA^+).[21] In these cases, organic templates in the synthesis of ECR-1 are necessary. However, these organic templates with relatively high cost in the synthesis severely hinder the practical applications of ECR-1 in catalytic reactions for the petroleum industry.

More recently, gallosilicate zeolite (TNU-7), an analogue of aluminosilicate ECR-1, is hydrothermally synthesized in the absence of organic template, while the synthesis system is not suitable for the synthesis of ECR-1.[22] Notably, compared with the synthesis of ECR-1,[17−21] the ratio of Na_2O/SiO_2 in the synthesis of TNU-7 is relatively low, which suggests that the ratio of Na_2O/SiO_2 plays an important role for the synthesis of ECR-1. We demonstrate here a successful organic template free synthesis of the large-pore aluminosilicate zeolite of ECR-1 by carefully adjusting the molar ratio of Na_2O/SiO_2 in the synthesis for the first time.

The samples were hydrothermally synthesized with poly(tetrafluoroethylene)-lined stainless steel autoclaves statically at the temperatures of 100−160 °C for 1−14 days with molar ratios of starting gels at $SiO_2/Al_2O_3/Na_2O/H_2O$ = 10:1.0:2.0−3.3:200. In addition, the filling rate of the autoclave was near 40%, and the pH value of the starting gel was about 12.5. As a typical organic template free synthesis of zeolite ECR-1, a precursor solution ($SiO_2/Al_2O_3/Na_2O/H_2O$ = 15:1.0:16:320) was prepared by mixing NaOH, $NaAlO_2$, and water glass under stirring, followed by aging at room temperature for 20 h, giving a clear solution. Then, 1.4 mL of the clear solution was mixed with 1.2 mL of H_2O, 10 mL of water glass, 2.3 mL of $Al_2(SO_4)_3$ (0.88 M), 2.4 mL of $NaAlO_2$ (2 M), and 0.4 mL of HCl (10 M), giving the ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ for the final mixture at 10:1.0:2.5:200. After stirring, the gel mixture was transferred into an autoclave to crystallize at 100 °C for 2 weeks. The product was collected by filtration, washed with deionized H_2O, and dried in air. The morphology of the samples 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 step size was 0.02°, and the scanning speed was 1.5°/min. The ratio of Si/Al was determined by ^{29}Si NMR spectra which were recorded on a Varian Infinity plus 400 spectrometer (fitting the sample in a 7 mm ZrO_2 rotor, spinning at 4 kHz with the number of scans being 308 and a collection time of 25.6 min) and by the result of inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV).

Figure 1 shows XRD pattern of the sample synthesized at 100 °C for 2 weeks with a molar ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ at 10:1.0:2.5:200 in starting gel. The sample exhibits

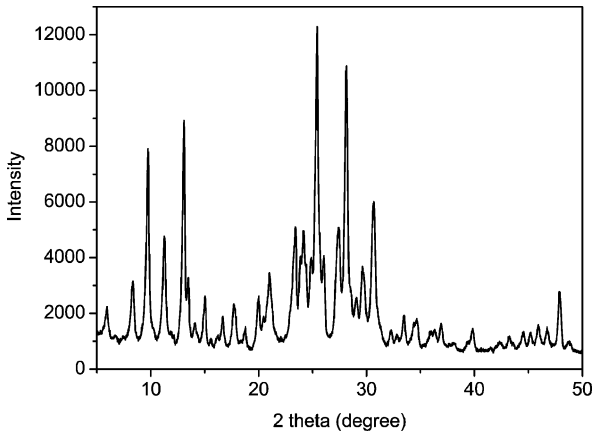

Figure 1. XRD pattern of as-synthesized zeolite ECR-1 synthesized at 100 °C for 14 days with a molar ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ at 10:1.0:2.5:200 in the starting gel.

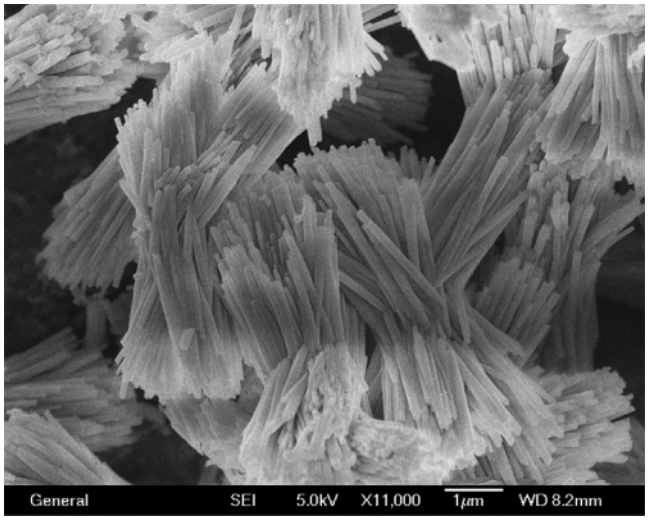

Figure 2. SEM image of the as-synthesized zeolite ECR-1 synthesized at 100 °C for 14 days with a molar ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ at 10:1.0:2.5:200 in the starting gel.

obvious peaks at 5.9, 6.7, 8.3, 9.7, 11.2, 13.0° and so on, which are typically assigned to those of ECR-1 structure. Furthermore, the scanning electron microscopy (SEM) image of the sample synthesized at 100 °C for 2 weeks (Figure 2) shows that a pure phase is obtained, and its morphology is the same as that of ECR-1.[18−20] All of these results indicate that a pure phase of ECR-1 could be hydrothermally synthesized at 100 °C for 2 weeks in the absence of organic templates. Possibly, hydrated alkali-metal cations in the synthesis may organize ECR-1 structural subunits and solution-mediated crystallization of the amorphous gel.[23] More importantly, the successful organic template free synthesis of zeolite ECR-1 may offer a novel route for the syntheses of other zeolites normally templated from organic templates.

As observed in Table 1, the molar ratio of Na_2O/SiO_2 in the synthesis significantly influences the final products of zeolites. When the ratio is 0.33, a pure phase of zeolite Y is formed; when the ratio is 0.28, a mixture of zeolite Y and ECR-1 is crystallized; when the ratio is 0.25, a pure phase of ECR-1 is successfully synthesized; when the ratio is 0.20,

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Table 1. Syntheses from Starting Gels with Molar Ratios of SiO_2/Al_2O_3/Na_2O/H_2O at 10:1.0:2.0−3.3:200[a]

	reaction conditions		
Na_2O/SiO_2	temp (°C)	days	product[b]
0.33	100	1	Y
0.28	100	14	Y + ECR-1
0.25	100	14	ECR-1
0.20	100	14	amorphous
0.25	140	5	ECR-1 + P
0.25	160	1	ECR-1 + P[c]

[a] Ratios of Na_2O/SiO_2 are varied between 0.20 and 0.33. [b] The phase appearing first is the major phase. [c] With other peaks unidentified (Figure S1, Supporting Information).

the product is amorphous silica. Furthermore, it is found that the crystallization rate of ECR-1 increases obviously with temperature in the synthesis. For example, when the temperature in the synthesis is 160 °C, ECR-1 with an impurity is crystallized for 1 day (Figure S2, Supporting Information). In contrast, crystallization of ECR-1 at 100 °C takes 14 days. Notably, although the synthesis at 100 °C takes a longer time, it is a pure phase of ECR-1.

Figure 3 shows the ^{29}Si magic-angle spinning (MAS) NMR spectrum of the calcined sample of ECR-1, which is synthesized at 100 °C for 2 weeks with the molar ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ at 10:1.0:2.5:200 in the starting gel. The resulting spectrum exhibits peaks at about −95, −100, −106, and −112 ppm with reference to tetramethylsilane, which are reasonably assigned to $Si(OSi)_x(OAl)_{4-x}$ units where $x = 1$ (Q^1), $x = 2$ (Q^2), $x = 3$ (Q^3), and $x = 4$ (Q^4), respectively. The ratio of SiO_2/Al_2O_3 in our sample estimated from Figure 3 is near 7.0, which is similar to the ICP result of 7.2, in agreement with those 7.0−9.0 in ECR-1 templated from organic cations.[18−21]

In summary, an aluminosilicate zeolite of ECR-1 is successfully synthesized at 100−160 °C for 1−14 days in the absence of organic templates for the first time. The

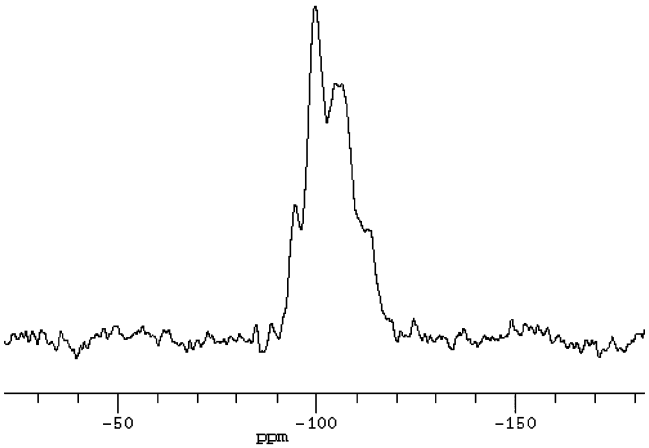

Figure 3. ^{29}Si MAS NMR spectrum of calcined ECR-1 synthesized at 100 °C for 14 days with molar ratio of $SiO_2/Al_2O_3/Na_2O/H_2O$ at 10:1.0:2.5:200 in the starting gel.

organic template free synthesis could be important for potentially industrial applications of zeolite ECR-1 in catalytic reactions.

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Supporting Information Available: SEM image of zeolite ECR-1 synthesized at a temperature of 160 °C; XRD patterns of the samples synthesized at 140 and 160 °C; simulated XRD and experimental XRD patterns of zeolite ECR-1; and XRD tabulation of *d* values and relative intensities for ECR-1 synthesized at 100 °C for 14 days (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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