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Synthesis of Zeolite EMT with Aid of Sodium Phosphate

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Since the successful synthesis of pure hexagonal faujasite EMT was reported in 1989 by Delprato and co-workers,[1] there has much interest in this potentially useful large-pore zeolite with 12-ring aperture and two-dimensional direct channel systems.[2−12] In the alkylation of isobutane with 2-butene, EMT has been found to perform much better than its cubic analogue—FAU.[13,14] However, a major disadvantage of the EMT zeolite was the high cost of the template—1,4,7,10,13,-16-hexaoxacycleoctadecane. Approaches to reduction of the amount of 18-crown-6 ether include the use of surfactants[15] and auxiliary organic additives[16,17] and the SINTEF method reported by Wendelbo et al.[21,22] The amount of 18-crown-6 ether has been reduced to 0.4−0.5 per Al_2O_3 in recent reports.[15−20] However, it would result in a mixture of EMT and FAU and eventually in pure FAU if the amount of 18-crown-6 ether was reduced further.[15−18,21] Besides that, with the decrease of the amount of 18-crown-6 ether, the crystallization time also increased greatly.[21] Recently, the EMT was synthesized with an 18-crown-6 ether/Al_2O_3 ratio of 0.14 via the SINTEF method.[21,22] Unfortunately, the crystallinity of the product was low, even though it had undergone crystallization for a long period of time and other phases would form while prolonging the crystallization time further. Long crystallization time was also a drawback in acquiring a more cost-effective procedure for synthesis of EMT. Approaches toward resolving this problem such as increasing temperature, raising the pH, and adding fluoride[18] have not been particularly successful because those methods would in some case lead to more defects of structure and mixed phases of crystals.

On the other hand, as was well-known, the evolution of the hydrogel toward the crystalline was a rather complex physico-chemical process. For the crystallization occurred in an aqueous medium upon heating, the water and cation−water complexes were considered to play an important role during crystallization.[23] In the case of EMT, it was synthesized in a dense gel that was highly thixotropic—the viscosity of gel without agitation was 10 times that with agitation.[19,21] It would bring about the slow crystallization rate of EMT and increase the probability of nucleating other phases.[21] So improving the transportation of the water-crowded inorganic species and structural-directing agents was of great help in shortening the crystallization time. Here, we provide an approach to successfully synthesize pure zeolite EMT with high efficiency, that is, the synthetic period is shortened from 30 days to 6 days and the ratio of 18-crown-6 ether/Al_2O_3 decreases to 0.33 by the aid of the auxiliary agent of $Na_3PO_4{\cdot}12H_2O$.

The procedure for synthesizing EMT was based on the Delprato method. The NaOH, auxiliary, and 18-crown-6 ether were dissolved in distilled water first and then colloidal silica (26 wt % SiO_2, 0.5 wt % Na_2O) was added to the mixture dropwise with stirring. Finally, sodium aluminate (43 wt % Al_2O_3) was added to the hydrogel. The resultant gel was continuously stirred for 2 h and aged for 24 h at 25 °C without agitation. The molar composition of the hydrogel was as follows: $10{:}1{:}x{:}y{:}z{:}140$ $SiO_2{:}Al_2O_3{:}Na_2O$:18-crown-6 ether:auxiliary agents:H_2O. Here, $Na_3PO_4{\cdot}12H_2O$, $NaClO_4{\cdot}1H_2O$, and Na_2WO_4 were used as auxiliary agents, respectively. The crystallization was carried out in a PTFE-lined stainless steel autoclave at 100 °C for 6−30 days. The solids obtained were filtered, carefully washed, and dried at 80 °C overnight.

Samples synthesized with a different ratio of Na_2O (x), 18-crown-6 ether (y), and auxiliary (z) are listed in Table 1. From it, one can clearly see that the ratio of ether to Al_2O_3 was decreased from 0.7[14] to 0.33, and the crystallization time was shortened greatly with the aid of sodium phosphate. It was found that the sodium phosphate had a novel effect on the synthesis of EMT. While keeping all other synthetic parameters, the pure

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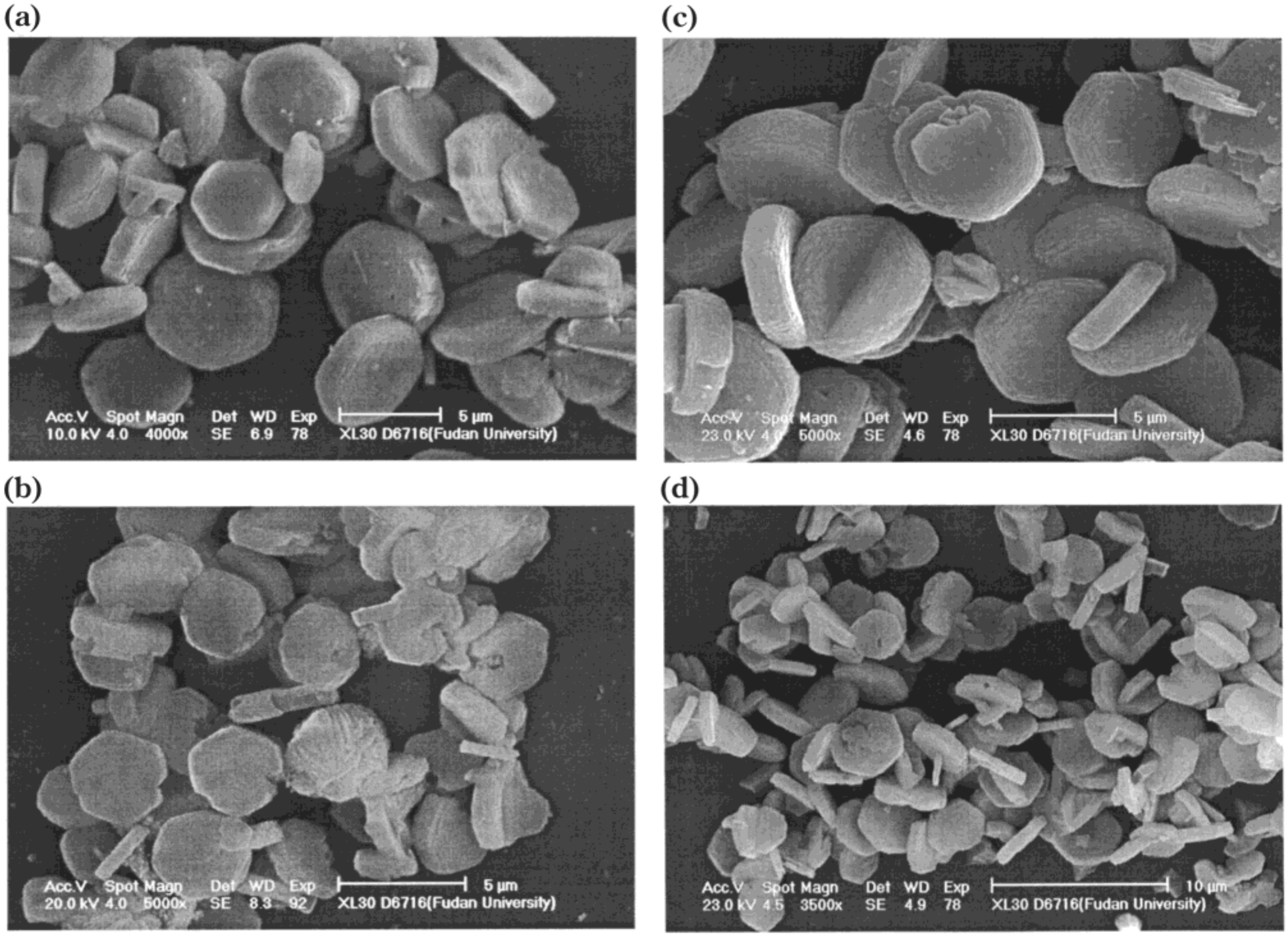

Figure 1. SEM photographs of the samples as-synthesized. (a) and (b) are the SEM photographs of samples 1 and 4 as-synthesized, while (c) and (d) are those calcined, respectively. The SEM images were obtained on a Philips XL-30 microscope.

Table 1. Synthesis of EMT with the Aid of Sodium Phosphate and under Different Ratios[a]

sample no.	x:y:z Na_2O:18-crown-6:P	t (days)	phase	SiO_2/Al_2O_3
1[b]	2.1:0.4:0	30	EMT	7.5
2	2.1:0.33:0.2	25	EMT/FAU	6.7
3	2.1:0.33:0.1	20	EMT	7.0
4	2.1:0.33:0.05	6	EMT	6.1
5	2.1:0.33:0.038	7	EMT	6.8
6	2.1:0.33:0.033	8	EMT	6.8
7	2.1:0.33:0.02	12	EMT	6.6
8	2.1:0.33:0.016	12	EMT	7.0
10	2.1:0.25:0.05	10	EMT/FAU	6.8
11	2.1:0.11:0.05	10	EMT/FAU	6.6

[a] All samples were synthesized via the gel 10:1:x:y:z SiO_2:Al_2O_3:Na_2O:18-crown-6 ether:P. In the recipe the P was the auxiliary agent $Na_3PO_4 \cdot 12H_2O$. The t was the crystallization time. [b] Sample 1 was synthesized without the aid of auxiliary agents. The ratios of SiO_2/Al_2O_3 of various samples were acquired from chemical analysis.

EMT was obtained with a crystallization time of 6−12 days by adding sodium phosphate in an optimal Na_3PO_4/Al_2O_3 ratio range of 0.033−0.05. And the ratio of SiO_2/Al_2O_3 can be adjusted from 6.1 to 7.0 by changing the amount of auxiliary agents. The SEM photographs of samples 1 and 4 and XRD patterns of sample 4 are shown in Figure 1a−d and Figure 2a−b, respectively. The characteristic results clearly illustrate typical hexagonal structures of EMT with high crystallinity.

The result of ^{31}P NMR shows that the PO_4^{3-} ions neither were encaged in the hypo- or hypercages nor were inserted in the framework of EMT. Therefore, the sodium phosphate must play an auxiliary role in the synthesis of EMT like surfactants.[15] Moreover, for the Na^+ has little effect on the synthesis of EMT,[24] the active species must be PO_4^{3-}.

As was known, the phosphate was an emulsifying agent[28] and then it had the function of decentralizing the raw material including silicate and aluminates species into water and producing a homogeneous gel at the initial stage of synthesis. This function of PO_4^{3-} ions would enhance the efficiency of hydrolysis of the inorganic materials, especially that of silicate, and benefit the transportation of various species. As a result, it became more favorable for 18-crown-6 ether molecules to access the framework-forming species directing the formation of the crystal nucleus and the subsequent growth, which would result in shortening the crystallization time and lead to the boost in the efficiency of the ether employed in synthesis—upon that the amount of the ether decreased.

On the other hand, the combination of SDA (structural-directing agent) with inorganic materials was also a

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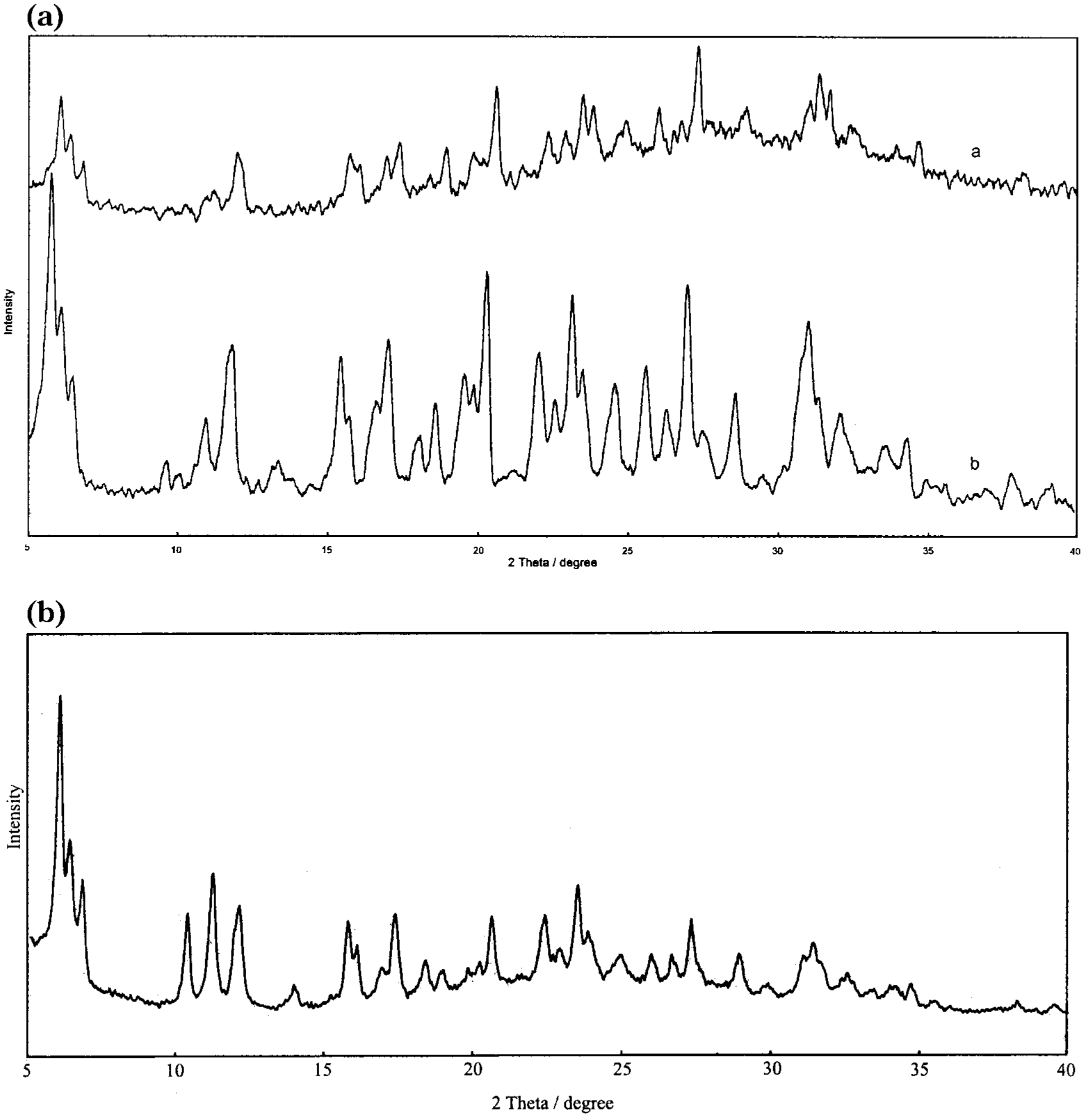

Figure 2. Powder X-ray diffraction patterns of the samples as-synthesized. Part (a) is the XRD pattern of sample 4 as-synthesized. In (a), curve a is the XRD pattern after 4 days of crystallization, while b is that after 6 days of crystallization; part (b) is the XRD pattern of sample 4 calcined (550 °C, 16 h). The XRD patterns were recorded on a Rigaku D/MAX-IIA PADX diffractometer. This diffractometer employed Ni-filtered Cu Kα radiation and was operated at 40 kV and 20 mA.

critical process,[29–31] especially for the synthesis of EMT, which was synthesized in dense gel at low ether/Al_2O_3 under which intergrowth of EMT and FAU occurred generally. After the Na_3PO_4 was introduced into the EMT synthetic system, bseides the dispersion function of PO_4^{3-} ions, the Na_3PO_4 could also act as the auxiliary agent that weakened and broke the water crowding around the SDA and the inorganic species while they were overlapping as Kummar et al. reported.[32,33] So it would enhance the structural-directing ability of the SDA.

Other auxiliary agents of $NaClO_4$ and Na_2WO_4 show, by far, weaker effects of the synthesis of EMT compared with Na_3PO_4. It was illustrated that in the dense synthetic system with high viscosity, adding auxiliary agents with emulsification ability would be of great help in its synthesis.

In conclusion, we provide a method to synthesize pure zeolite EMT at a low ratio of 18-crown-6 ether/Al_2O_3 (0.33) and in short crystallization time with the aid of sodium phosphate with both function of emulsification and weakening of the hydration of 18-crown-6 ether and inorganic materials. The crystal size is in 3−5 μm. The optimal range of the ratio of Na_3PO_4/Al_2O_3 (value of z) is from 0.05 to 0.03, where the crystallization time is concerned.

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Supporting Information Available: Tables and figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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