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Synthesis of MTW-type Zeolites in the Absence of Organic Structure-directing Agent

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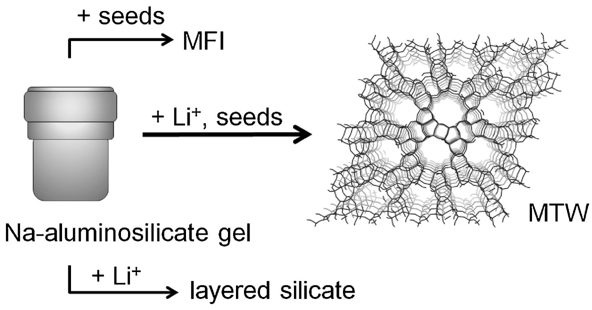
The synthesis of MTW-type aluminosilicate zeolites in the absence of organic structure-directing agents (OSDAs) was successfully attained by the addition of calcined ZSM-12 seeds to (Li, Na)-aluminosilicate gels. In this system, Li cation plays a crucial role in the growth of the MTW crystals.

Zeolites are crystalline microporous aluminosilicates useful as adsorbents, ion-exchangers, and catalysts due to their well-defined micropores, large ion exchange capabilities, and high acidity.[1] Since the first zeolite synthesis by Barrer and Milton in 1940s, various zeolites have been synthesized under hydrothermal conditions. In the state-of-the-art synthesis, organic structure-directing agents (OSDAs) are often used, and many new zeolites with novel framework structures have been synthesized by using specially designed OSDAs. However, the use of OSDAs is undesirable from a practical point of view because of its high cost as well as high environmental burdens when OSDAs occluded in the zeolite channel are removed by calcination.

Currently, among many types of zeolites that are commercially available, those produced without using OSDAs are very limited. Therefore, a versatile route for OSDA-free synthesis has been strongly desired. The syntheses of ECR-1,[2] ZSM-34,[3] beta,[4] and RUB-13[5] have recently been realized by adding calcined zeolite seeds to the initial reactant gels and hydrothermal treatment. However, the crystallization mechanisms have not been clarified yet, and the possible zeolites obtained by OSDA-free seed-assisted route are still limited.

In the conventional OSDA-free synthesis of zeolites, alkali metal cations such as Na^+ and K^+ act as SDAs. The type of cation strongly affects the nucleation and crystallization process. For example, it is known that a potassium aluminosilicate zeolite, zeolite L, is formed when K^+ is used instead of Na^+ for the synthesis of zeolite Y.[6] Moreover, we have reported the cooperative effect of Na^+ and K^+ on the crystallization of ferrierite.[7] The structure-directing effect of other alkali metal cations such as Li^+ and Cs^+ have not been well-studied. It is expected that effective use of these cations independently or in combination with Na^+ and K^+ would expand possibilities of OSDA-free synthesis with the addition of seed crystals.

In this letter, we focus on ZSM-12, a high silica aluminosilicate zeolite with framework code MTW, which has a one-dimensional 12-membered-ring channel along the *b* axis[8] and has been expected to be a useful catalyst in cracking of hydrocarbons or in other petrochemical processes.[9] In addition, Kaliaguine et al. have recently found that ZSM-12 can be a superior candidate as adsorbents for hydrocarbon trap to reduce cold-start emissions of automotive exhaust due to its high trapping capacity and elevated desorption temperature.[10] For the synthesis of MTW-type zeolites, OSDAs such as tetraethylammonium (TEA)[11] have been essential and there are no previous reports of the OSDA-free synthesis. Here, we report the first OSDA-free synthesis of MTW-type aluminosilicate zeolite, in which calcined seeds of ZSM-12 and lithium cation are cooperatively used (Scheme 1).



Scheme 1. OSDA-free synthesis of MTW-type zeolites.

ZSM-12 for seed crystals was prepared using TEAOH as OSDA following a reported procedure.[12] The initial gel composition was $0.79Na_2O{:}6.4(TEA)_2O{:}80SiO_2{:}1.0Al_2O_3{:}1040H_2O$. Sodium aluminate was dissolved in 35% aqueous TEAOH solution. Colloidal silica (LUDOX HS-40, DuPont) was then added to the solution, and the mixture was stirred until homogeneous gel was obtained. The gel was heated at 160 °C for 5 days in a Teflon-lined autoclave under static conditions. The product was collected by filtration, washed with distilled water, dried at 60 °C, and calcined at 550 °C for 10 h.

For the OSDA-free synthesis of MTW zeolites, aluminum hydroxide (Aldrich) was added to an aqueous solution containing sodium hydroxide (Wako) and lithium bromide (Wako). Then calcined ZSM-12 seeds ($Si/Al = 50.6$, 10 wt% of SiO_2) and fumed silica (Cab-O-Sil M5, Cabot) were added to the solution. The gel compositions were $NaOH/Si = 0.375$, $Li/(Li + Na) = 0.29$, $H_2O/Si = 16$, and $Si/Al = 5$–30. Hydrothermal treatment was carried out at 140 °C for 7 days under static conditions. The obtained products were washed and dried.

X-ray diffraction (XRD) patterns of the calcined seeds and the products synthesized at different Si/Al ratios (5.0, 7.5, 10, 20, and 30) are shown in Figure 1a. The products synthesized at $Si/Al = 7.5$, 10, and 20 are identified as MTW zeolite. However, at $Si/Al = 5$, MOR zeolite (mordenite) was formed in place of MTW. At higher Si/Al ratio (≥ 30), a layered silicate magadiite appeared along with MTW. Thus, MTW zeolites are successfully crystallized in the OSDA-free, (Li, Na)-aluminosilicate system within a certain range of the Si/Al ratios. On the other hand, the products obtained from the Na–aluminosilicate gels without seeds and lithium cation were completely amorphous.

The solid-state ^{27}Al magic-angle spinning (MAS) NMR spectrum of the product synthesized at $Si/Al = 10$ (Supporting Information, Figure S1a)[13] showed a peak at ca. 56 ppm, corresponding to the tetrahedrally coordinated framework Al,

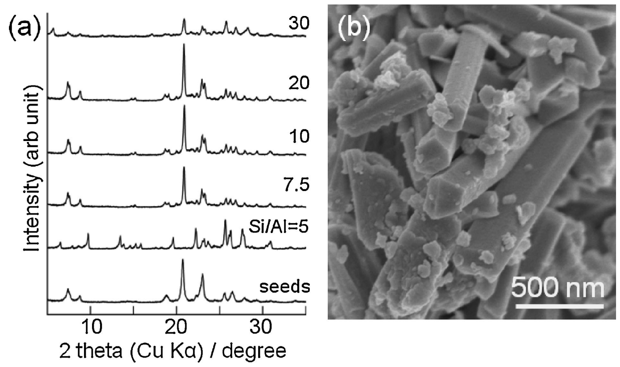


Figure 1. (a) XRD patterns of the calcined seeds and the products synthesized with different Si/Al ratios in the initial gel. (b) Typical SEM image of the product synthesized at Si/Al = 10 (before acid treatment).

along with a peak at ca. 0 ppm corresponding to the octahedrally coordinated Al. This fact, together with the XRD data, suggests that amorphous extra-framework Al species coexisted in the as-synthesized MTW zeolites. This impurity phase (ca. 5%) was almost completely removed by treating with 2 M hydrochloric acid at 60 °C under static conditions for 2 days (Figure S1b).[13] Although a small amount of granular matter attached to the rod-like crystals of MTW was observed before acid treatment, they were removed after treatment, as confirmed by SEM (Figure 1b and S2).[13] Even after the treatment, no change was observed in the XRD patterns (Figure S3).[13]

The solid-state ^{29}Si MAS NMR spectrum of the acid-treated product synthesized at Si/Al = 10 (Figure S4)[13] showed a peaks at −101, −108, and −111 ppm, and these peaks were assigned to the Si(1Al) and two Si(0Al) of MTW zeolite, respectively.[14] By deconvolution of the spectrum, the Si/Al ratio was calculated to be 23.2, which agreed well with the value of 27.0 obtained by chemical analysis. This is one of the lowest values among the previously reported ZSM-12.[15] Similar results were obtained for other products synthesized at Si/Al = 7.5 and 20 in the initial gel composition, and the Si/Al ratios of the acid-treated products were 34.1 and 34.3 (by chemical analysis), respectively.

Unfortunately, the BET surface areas of obtained MTW zeolites were around half of reported values.[12,15] It might be due to a small amount of aluminum species that remained even after the acid treatment. Thus, optimization of the acid treatment conditions is needed.

As shown in Scheme 1, both calcined seed crystals and lithium cation are indispensable for the OSDA-free synthesis of MTW in the present system. In the absence of the seeds, only a layered silicate magadiite was obtained and no zeolite phase was detected by XRD. A crucial role of the seeds in nucleation of MTW is suggested by this. On the other hand, in the absence of lithium cation, MFI zeolite (ZSM-5) was a main product, and only a small amount of MTW coexisted. This suggests that lithium cation plays a key role in crystal growth of MTW zeolites. We found that the optimum lithium content, i.e., Li/(Li + Na) ratio in the initial gel, to obtain pure MTW was limited in a narrow range. When Li/(Li + Na) ratio was changed from 0.29 to 0.44, the crystallinity of MTW decreased and lithium silicate ($Li_2Si_2O_5$) appeared. Lithium alminosilicate zeolites are rare,[16] and there are few previous reports on the use of lithium cation as SDA. More details on the role of lithium cation in the present system are under investigation and will be reported in near future.

In conclusion, MTW-type zeolites with relatively low Si/Al ratios were successfully synthesized in the absence of OSDAs by the addition of both calcined seeds and lithium cation. This finding should expand the possibility of MTW-type zeolites especially for practical applications.

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