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A novel, organic-additive-free synthesis of nanometer-sized NaX crystals

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Ultra-fine NaX zeolite crystals of dimensions *ca*. 20–100 nm have been synthesized with a novel, efficient, organic-additive-free hydrothermal approach.

The synthesis of nanometer-sized zeolites has received much attention recently owing to their utility in fundamental studies of zeolite crystal growth, in the preparation of ultra-thin zeolite films and nano-composites, and as supports for catalytic and photochemical reactions.[1–10] Reduction of the particle size from the micrometer to the nanometer scale can improve the mass- and heat-transfer in catalytic and sorption processes, thereby enhancing their catalytic selectivity and reducing coke formation in some petroleum reactions.[11] Furthermore, zeolite nano-crystals can be used to fabricate ordered porous structures.[12] Zeolite nano-crystals are usually synthesized *via* hydrothermal procedures using clear aluminosilicate solutions, most commonly in the presence of organic additives as templates. Nano-crystalline faujasite (FAU) zeolites have been synthesized using tetramethylammonium (TMA) as a template.[1–3,6] However, the conditions have to be critically controlled in order to get pure FAU crystals, as TMA is also a template for growth of zeolite A; furthermore, removal of the templates can lead to an irreversible aggregation of nano-crystals into larger solid particles.[13] Moreover, organic additive template routes are not suited for nano-scale synthesis, whereas the ‘build-the-bottle-around-the-ship’ method (or one-step approach) can directly synthesize the zeolite host matrix around guest molecules, as very pure and homogeneous nano-composites.[14,15] We are interested in developing novel organic-additive-free routes to ultra-fine FAU zeolites. These materials could have very different physical properties from microcrystalline zeolites, and could provide insights into nucleation and crystal growth during the hydrothermal process. Here we report an efficient, organic-additive-free synthesis of NaX zeolite with particle sizes in the range 20–100 nm.

The hydrothermal synthesis was conducted in a shaker with a temperature controller. Aluminosilicate gel was prepared by mixing freshly prepared aluminate and silicate solutions together in the molar ratio 5.5 Na_2O : 1.0 Al_2O_3 : 4.0 SiO_2 : 190 H_2O. Typically, an aluminosilicate gel containing 5.34 g NaOH, 2.42 g $NaAlO_2$, 3.43 g SiO_2 and 50.0 g H_2O was used. $NaAlO_2$ was freshly prepared from $Al(OH)_3$ and NaOH. SM-30 colloidal silica (Aldrich), silica fume (Sigma), and TEOS (tetraethyl orthosilicate, Aldrich) were chosen as the silicate sources, with no significant difference observed in the final particle size-distribution. For TEOS, the hydrolysis was controlled at 0 °C in order to obtain nanometer-sized aluminosilicate gel. Hydrothermal crystallization was conducted at 60 °C for 2–4 days in a shaker with a rotation rate of 250 rpm. The powder product, henceforth referred to as NaX-*nano*, was recovered *via* centrifugation, washed with DI water until pH < 8, and then dried at room temperature for 24 h. In a control experiment, larger particle sizes of FAU zeolite, here denoted NaX-μ, were synthesized with exactly the same aluminosilicate gel composition, but the hydrothermal crystallization was performed at 90 °C for 2 days with no shaking.

Powder X-ray diffraction (XRD) diagrams of as-synthesized zeolite samples and commercial micron-sized FAU zeolite (from Aldrich) are shown in Fig. 1. The XRD patterns of the two synthesized samples and the commercial FAU powder match very well, demonstrating that our approach can indeed be used to synthesize pure FAU crystals. The XRD peaks for the NaX-μ sample are almost the same as for the commercial sample, in both intensity and width. However, the diffraction lines of the NaX-*nano* sample are significantly less intense and much broader, indicating that the crystals are much smaller. From the diffraction peaks (2θ) at 6° [111], 16° [331], and 27° [642] and Scherrer’s equation, we calculate an average crystal dimension of 23 ± 4 nm.[2,16] XRD patterns taken after different hydrothermal synthesis periods reveal that NaX-*nano* is more than 95% crystalline after two days of shaking at 60 °C. Longer crystallization times might slightly increase the particle size. The Si/Al ratio was found to be 1.25 ± 0.05 for NaX-*nano* (by X-ray fluorescence) and 1.3 ± 0.1 for NaX-μ (from ^{29}Si solid state NMR). These values fall in the Si/Al range of 1–1.5 for NaX zeolites. Therefore, both synthesized samples are NaX. The as-synthesized samples have slightly lower 2θ values than the commercial sample, as would be expected for reduced Si/Al ratios.

Uncoated NaX-*nano* and NaX-μ samples were imaged with a Hitachi S-4700 cold-field emission scanning electron microscope (SEM) operated at 1 kV. A typical micrograph of NaX-*nano* (Fig. 2) clearly shows that most particle sizes of NaX-*nano* are in the range 20–100 nm. This is one of the smallest faujasite particle sizes reported.[1–4,6] This size distribution is consistent with the results calculated from the XRD patterns, proving that our method does indeed successfully synthesize ultra-fine NaX

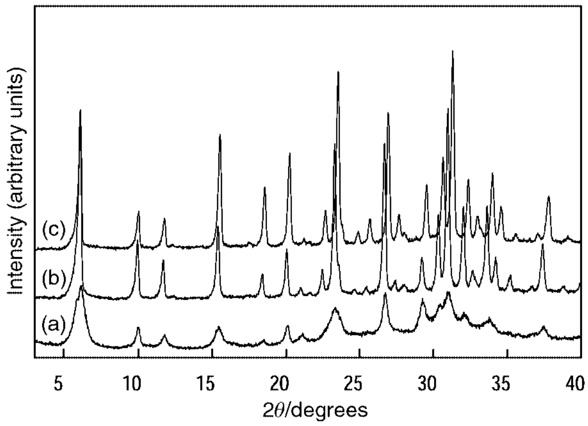

Fig. 1 XRD powder patterns for (a) NaX-*nano*, (b) NaX-μ and (c) a commercial NaX sample (Aldrich). The XRD data were recorded on a Rigaku Miniflex System using Cu-Kα radiation, 30 kV, 15 mA with a scanning speed of 1° (2θ) min^{-1}, T = 20 °C.

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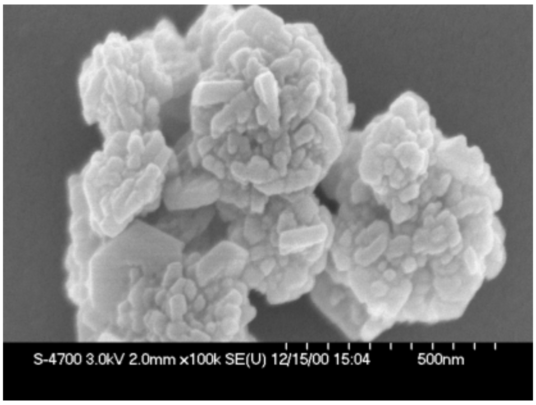

Fig. 2 SEM images of NaX-*nano* (HITACHI S-4700 cold-field emission SEM, 1 kV).

crystals without the assistance of any organic additives. The micrographs of NaX-μ show the particles to be in the micron range (*ca*. 0.8 μm). The significant decrease in particle size from NaX-μ to NaX-*nano* indicates that lower crystallization temperatures and strong shaking conditions, which would together accelerate the nucleation process and lower the crystal growth rates, are key factors in controlling the size of zeolite crystals obtained. By controlling the crystallization temperature, shaking time and silicate source (and its particle size), we successfully synthesized several NaX zeolite samples with average particle sizes ranging from 20 nm to 1 μm.

Both NaX-*nano* and NaX-μ were further characterized by FT-IR and ^{29}Si solid-state NMR. In the FT-IR spectra, three features were noted. First, a symmetric stretching band at 744 cm^{-1} was observed in NaX-*nano*,[17,18] with a corresponding peak at 750 cm^{-1} in the NaX-μ sample. Secondly, the double-ring vibration at 566 cm^{-1}, characteristic of faujasite zeolites, appears as two bands at 608 and 566 cm^{-1} in NaX-*nano*. Thirdly, a new broad band at 860 cm^{-1} was observed in the ultra-fine sample, and it can reasonably be assigned to the silanol (Si–OH) bending mode associated with the Q^3 silicon species (Si connected to three O that have connections to Si or Al),[17] detected with ^{29}Si solid-state NMR. The existence of an abundance of silanol groups in NaX-*nano* is attributed to the large total particle surface area, associated with the reduction to the ultra-fine particle size. From a simple calculation assuming cubic particles, one would expect about 12% Q^3 from the external surface in an NaX zeolite with a 50 nm particle size. Q^3 species could also be formed at internal defects. It was reported that about 20% of Si was in the silanol form in an 18–100 nm particle-size silicalite-1 zeolite studied by solid-state NMR.[5] With both single-pulse and cross-polarization ^{29}Si solid-state NMR techniques, we found all four Q^3 bands and five Q^4 bands in the NaX-*nano* sample. To our knowledge, this is the first time that Q^3 bands have been observed in a nanometer-sized NaX sample. This finding agrees well with the observation of silanol bending modes in the vibrational spectroscopy experiment. On the other hand, only the five Q^4 bands, located at −84.8, −89.5, −94.2, −99.3 and −103 ppm, were detected in the larger-particle NaX-μ sample, as expected.

In conclusion, a novel organic-additive-free approach has been developed to synthesize nanometer-sized faujasite NaX. The XRD pattern of the as-synthesized NaX-*nano* sample matches very well with the commercial micron-sized FAU, but it is broader and less intense. The average crystal size of 23 nm calculated from XRD is in accord with SEM images. The crystal size depends critically on the synthetic conditions, *e.g.* temperature and shaking. In comparison with the micron-sized zeolite, ultra-fine NaX shows a broad silanol vibration peak at 860 cm^{-1}, associated with the Q^3 silicon detected in ^{29}Si solid-state NMR.

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