

## Synthesis and characterization of TMA-A zeolite nanocrystals

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Well-controlled cubic nanocrystals of TMA-A zeolite with a size of 60~100 nm were synthesized by a hydrothermal method in a solution with a Al(i-pro)<sub>3</sub>: 2.2 TEOS: 2.4 TMAOH: 0.3 NaOH: 200H<sub>2</sub>O composition. The single TMA-A nanocrystals has an average lattice constant of 24.61 Å and a surface area of 742.36 m<sup>2</sup>/g. A thermal treatment of the TMA zeolite crystals resulted in their becoming amorphous above 900°C. Environmental scanning electron microscopy (ESEM), high resolution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and a DTA/TGA and BET analysis were used to characterize the initial materials and the products obtained after various heat treatments.

**Key words:** TMA-A zeolite, nanocrystal, morphology, heat treatment, phase transformation.

### Introduction

Nearly perfect crystalline zeolite structures are very important for a variety of studies. They aid in the fundamental understanding of the crystal structure, for use as such as a micro-reactor for model reaction, a chemical sensor and host materials for semiconductor clusters. At sizes from 1 to 20 nm in diameter, they can create electronic and optical properties specific to the form of nanocrystals [1, 2]. In addition, the well-shaped zeolite nanocrystals behave as organizing media for various semiconductor quantum dots in a highly ordered and oriented arrangement [3, 4]. Therefore, the synthesizing of zeolite single nanocrystals is of great interest [5]. Despite the great applicability of zeolite nanocrystals, the crystal morphologies were only characterized in detail at room temperature; in particular, the issue of whether the as-synthesized nano crystals were or were not single crystals remained to be determined at high temperatures. In this study, the focus was on a synthesis of a well-controlled single phase nanocrystal TMA-A zeolite. It sought to explain in more detail the structural and morphological transformation of synthetic zeolite nanocrystals as a function of various heat treatments.

### Experimental Procedure

TMA-A zeolite nanocrystals of a uniform particle size between 60-150 nm were synthesized by a hydro-

thermal method in a mother solution having a composition of Al(i-pro)<sub>3</sub>: 2.2 TEOS: 2.4 TMAOH: 0.3 NaOH: 200H<sub>2</sub>O at 100 for three days. The reactant materials used were aluminum isopropoxide Al(i-pro)<sub>3</sub> (Aldrich, 98 wt%), tetraethylorthosilicate (TEOS, Aldrich, 98 wt%), tetramethylammonium hydroxide (TMAOH, Aldrich, 25 wt% in water), and sodium hydroxide (NaOH, Aldrich, 99.99 wt%). The autoclave was removed at predetermined times from the oven to arrest the reactions. The crystallized samples were collected and separated by centrifugation. The products were repeatedly dispersed in distilled water using ultra sonication and centrifugation as above to remove the remaining mother solution until the pH of the dispersion was close to 7. The samples were obtained by drying at 80°C for 4 h. A micromeritics accelerated surface area and porosimetry (ASAP 2010) instrument was used to determine the surface area of the nanocrystals. A semiquantitative chemical analysis performed to estimate the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was carried out by fluorescent X-ray spectrometry (Model 3070, Rigaku Co., Tokyo, Japan). The initial materials and the products obtained after various heat treatments were characterized by XRD (Model RAD-2B, Rigaku Co.) with CuK $\alpha$  radiation, environmental scanning electron microscopy (ESEM, XL-30, FEG), high resolution transmission electron microscopy (HRTEM, Tecnai G2, STEM), Fourier transform infrared(FT-IR) spectroscopy and differential thermal analysis (DTA)/thermogravimetry analysis (TGA, Linseis, L81-II).

### Results and Discussion

The morphology of a TMA-A zeolite crystal as seen in an image shows that a cube is comprised of well-controlled crystals between 60 and 100 nm in size in a

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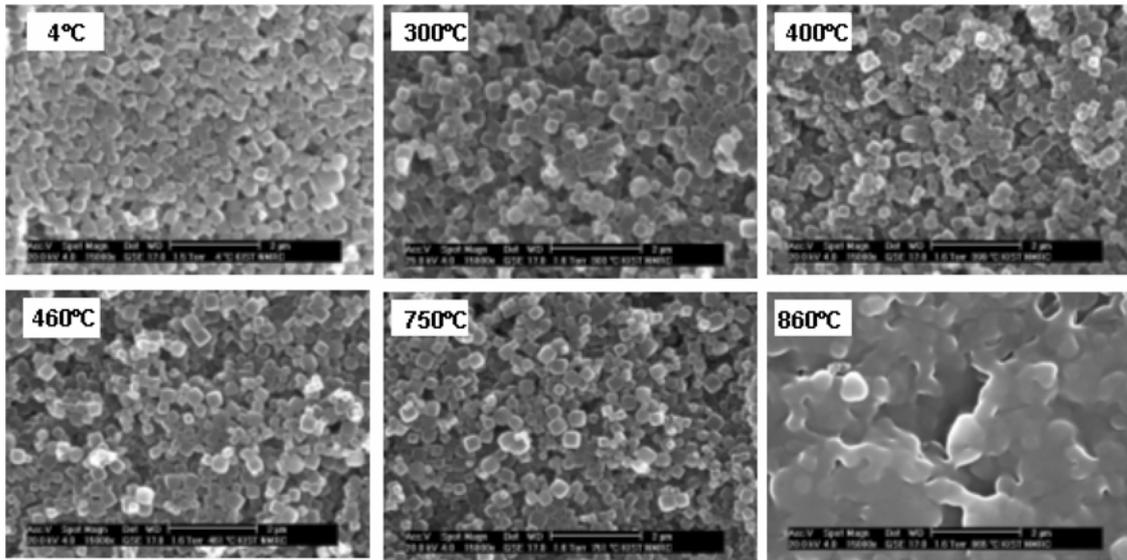


Fig. 1. ESEM image of the TMA-A Zeolite as a function of heat treatment.

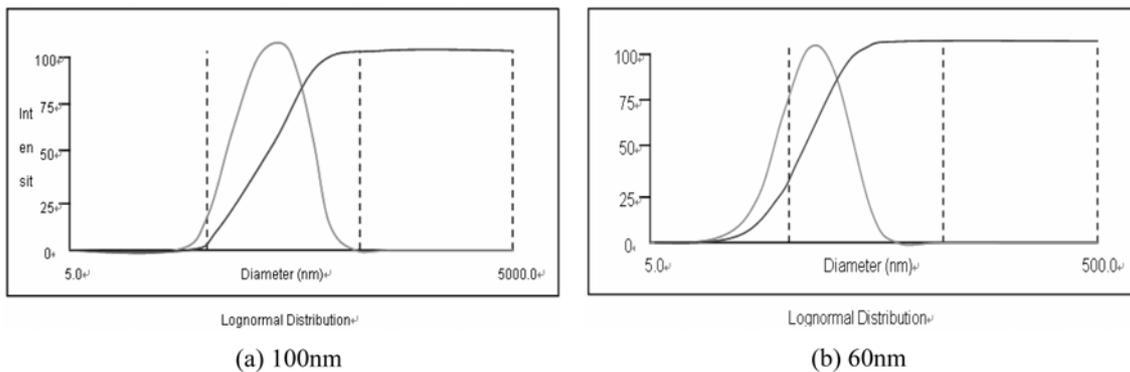


Fig. 2. Particle size distribution of the TMA-A Zeolite.

configuration having six planes, as shown in Fig. 1. The cube or hexahedron {001} is composed of six perfect square faces that have  $90^\circ$  angles. A thermal treatment of the TMA-A zeolite results in the thermally-stable phase of zeolite up to  $800^\circ\text{C}$  for 30 minutes. This phase transformed to an amorphous phase when treated at  $860^\circ\text{C}$  for 30 minutes, and transformed to a round crystal morphology after heat treatment at  $900^\circ\text{C}$  for 30 minutes, as shown in Fig. 1.

The particle size distribution can be estimated from a low-magnification image and is further characterized by DLS, as shown in Figs. 2(a) and (b). The resulting solids of (a) and (b) were collected and separated by centrifugation with a relative centrifugal speed (rpm) of 3,000 and a maximum speed above 5,000. A DLS measurement of the zeolite TMA-A shows two maxima at 100 and 60 nm in the size distribution, which is in agreement with the HRTEM observation. These two different particle size distributions in the same mother solution reflect different nucleation processes [6].

The XRD results of this morphology showed only the TMA-A zeolite. For the TMA-A zeolite,  $2\theta=7^\circ$

(200),  $10^\circ$  (220), and  $24^\circ$  (600), of a single phase with an average lattice constant of 24.61 Å and with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 1.6~2.0, as determined by XRD and XRF. The XRD pattern of the sample calcined at  $900^\circ\text{C}$  for 30 minutes indicated an amorphous phase, as shown in Fig. 3.

Figure 4 shows HRTEM images of the nano crystals of the TMA-A zeolite. The images show a high degree

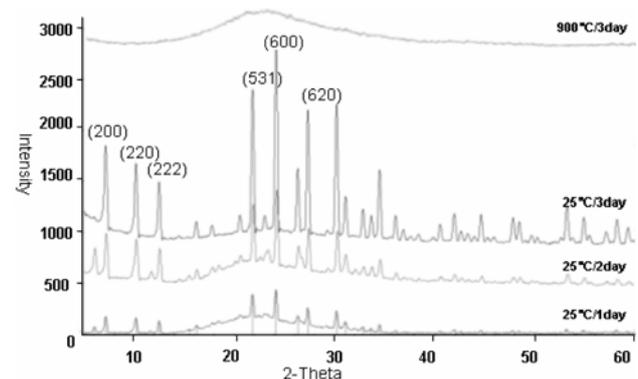


Fig. 3. XRD-pattern of the TMA-A as a function of reaction time.

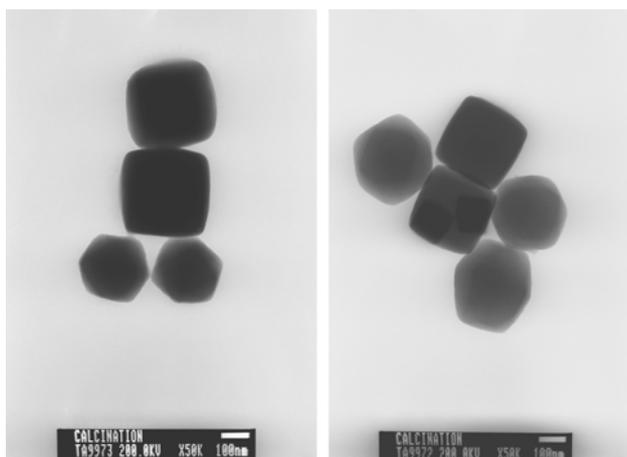


Fig. 4. HRTEM imaging of nano crystal of the TMA-A zeolite.

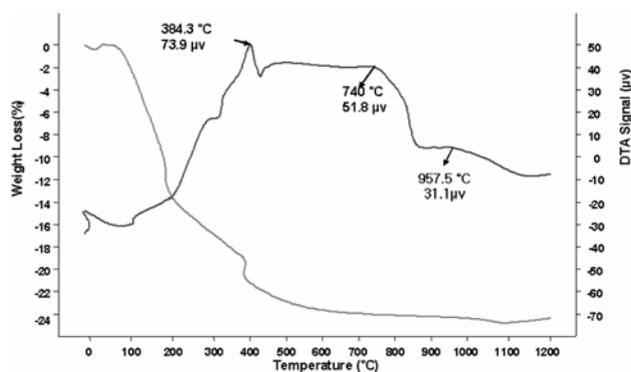


Fig. 5. Thermal analysis of the TMA-A Zeolite.

of structural order and a perfect crystalline morphology. It is clear from the low-magnification image that the crystals have a typical cubic form with a difference in edge size of approximately 60 or 130 nm. In general, the framework of TMA-A zeolite can be described in terms of two types of polyhedra; one has a simple cubic arrangement of eight tetrahedral and is termed D4R, and the other is a truncated octahedron of 24 tetrahedra or cages as previously described for the sodalite-type minerals. The TMA-A zeolite is generated by placing the cubic D4R units in the center of the edges of a cube with an edge of 12.3 Å [7]. This nano-structured zeolite material was applied as host-guest material for nano-cluster particles [8, 9].

DTA/TGA curves of the synthetic NaA zeolite are shown in Fig. 5. The DTA curves of the zeolite have a characteristic endothermic minimum below 120°C, caused by the thermally-induced desorption of physically absorbed water. An exothermic peak in a temperature range from 370 to 440°C results from the desorption of the remaining zeolite water (21.5%) enclosed in the

zeolitic matrix. The wide endothermic peaks in the DTA curves between 740 and 957.5°C correspond to a high-temperature solid-state transformation.

## Conclusions

The crystal morphology of TMA-A zeolite shows that a cube is comprised of well-controlled crystals between 60 and 100 nm in size in a configuration having six perfect square planes and an average lattice constant of 24.61 Å with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.6~2.0. A thermally-induced transformation of the crystalline TMA-A zeolite takes place through the formation of an amorphous state at 860°C for 30 minutes. The mono-distributed average crystal size was determined to be between 60 and 100 nm, which is an agreement with the TEM observations.

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## References

1. W.M. Meier, in : Proc. Intern. Symp. "Molecular Sieves" (London, 1968) p. 10.
2. D.W. Breck, in "Zeolite Molecular Sieves: Structure, Chemistry and Use" (John Wiley and Sons, New York, 1974).
3. K. Byrappa and M. Yoshimura, in "Handbook of Hydrothermal Technology" (William Andrew Publishing, LLC, Norwich, New York, U.S.A, 2000).
4. A. Kosak, D. Makovec, and M. Drogenik, Mater. Sci. Forum. (2004) 219 453-454.
5. G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu, and O. Terasaki, Am. Chem. Soc. 10 (1998) 1483-1486.
6. N.Y. Chen, T.F.J. Degan, and C.M. Smith, in "Molecular Transport and Reaction in Zeolites: Design and Application of Shape Selective Catalysts" (New York, 1994).
7. J.-C. Lin, J.T. Dipre, and M.Z. Yates, Chem. Mater. 15 (2003) 2764-2770.
8. H.G. Karge, J. Weitkamp (Eds.), in "Zeolite Synthesis" (Springer Verlag, Berlin, 1998).
9. Y.Y. Sun, T. Song, S. Qiu, W. Pang, J. Shen, D. Jiang and Y. Yue, in "Zeolites 15" (1995) p. 754.
10. N. Chandrasdkharan, and P.V. Kamat, Res. Chem. Intermed. 28 (2002) 847-856.
11. A. Kameo, A. Suzuki, K. Torigoe, and K. Esumi, J. Colloid Interface Sci. 241 (2001) 298-292.
12. S.S. Lee, A.M. Rideau, and L.B. McGown, J. Phys. Chem. 100 (1996) 5880-5887.