Journal of the Korean Ceramic Society
Vol. 43, No. 1, pp. 1~3, 2006.

Synthesis and Morphological Transformation of NaA Zeolite Crystals at High Temperature

Young Mi Kim and Ik Jin Kim†

Institute for Processing and Application of Inorganic Materials (PAIM), Department of Materials Science and Engineering, Hanseo University, Seosan 356-706, Korea
(Received October 21, 2005; Accepted November 8, 2005)

ABSTRACT

Well-shaped NaA zeolite cubic crystals of a large size of 5~7 μm were synthesized by a hydrothermal method in a mother solution having a $3.55Na_2O:Al_2O_3:1.6SiO_2:593\sim2000H_2O$ composition. Thermal treatment of NaA zeolite crystals resulted in the formation of a crystalline phase of $NaAlSiO_4$-Camegeite between 800 and 900°C. Even at 1000°C, $NaAlSiO_4$ phase was found as a major product. Environmental Scanning Electron Microscopy (ESEM), High Resolution Transmission Electron Microscopy (HRTEM), X-Ray powder Diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, and DTA/TGA and BET analyses were used to characterize the initial materials and the obtained products after various heat treatments.

Key words : NaA zeolite, Crystal morphology, Heat treatment, Phase transformation

1. Introduction

Nearly perfect crystalline zeolite structures could be used as proton exchangeable membranes for fuel cells, potentially offering major advantages over current separation and catalytic processes. They could also be employed as host materials for semiconductor clusters from 1 to 20 nm in diameter to create electronic and optical properties specific to the form of nano-crystals.[1,2] However, it is difficult to synthesize uniformly sized NaA zeolites and to grow large zeolite single phase crystals, because crystal nuclei grow rapidly during the growth period. Furthermore, the product may transform into a more stable phase, such as NaP, requiring a longer reaction time once the crystallization period is over.[3,4] For this reason, some scientists contend that it is impossible to grow synthetic zeolite single crystals to an appropriate size to analyze their structure.[5,6] At present, in order to improve existing catalytic and adsorbent processes, a better understanding of the structure of zeolites is required. The aim of the present study is to explain in more detail the structural and morphological transformation of synthetic zeolite as a function of various heat treatments.

2. Experimental Procedure

NaA zeolite crystals of a uniform particle size of 5~7 μm were synthesized by the hydrothermal method in a mother solution having a composition of $3.55Na_2O:Al_2O_3:1.6SiO_2:1000H_2O$ at 90°C for 7 days. The reactant materials were Ludox HS-40 colloidal silica (Aldrich Chem. Co. Inc), NaOH (Junsei Chem. Co.) and $NaAlO_2$ (Junsei Chem. Co.). The autoclave was removed at predetermined times from the oven in order to arrest the reactions. Crystallized samples were obtained by filtration and washed thoroughly with deionized water before being dried at 100°C overnight. A micromeretics accelerated surface area and porosimetry (ASAP 2010) instruments were used to determine the surface area of the synthesized zeolite crystals. A semi-quantitative chemical analysis performed to estimate the SiO_2/Al_2O_3 ratio was carried out via fluorescent X-ray spectrometry (Model 3070, Rigaku Co., Tokyo, Japan). The initial materials and the obtained products after various heat treatments were characterized by XRD (Model RAD-2B, Rigaku Co.) with CuKα radiation, Scanning Electron Microscopy (SEM; Model JXA-840, JEOL Co.), Environmental Scanning Electron Microscopy (ESEM, XL-30, FEG), High Resolution Transmission Electron Microscopy (HRTEM, Tecnai G2, STEM), Fourier Transform Infrared (FT-IR) spectroscopy, and DTA/TGA (Linseis, L81-II) analyses.

3. Results and Discussion

The morphology of NaA crystals from a view image shows that the cubic is comprised of well-shaped crystals between 5 and 7 μm in size in a configuration having six planes. The hexahedron {001} is composed of six perfect square faces that make relative angles of 90°, as shown in Fig. 1(a). The XRD and XTR results of this morphology revealed only NaA crystalline phase, which has an average lattice constant of 24.64 Å with a SiO_2/Al_2O_3 molar ratio of 1.6~2.0. Thermal

†Corresponding author : Ik Jin Kim
E-mail : ijkim@hanseo.ac.kr
Tel : +82-41-660-1441 Fax : +82-41-688-4143

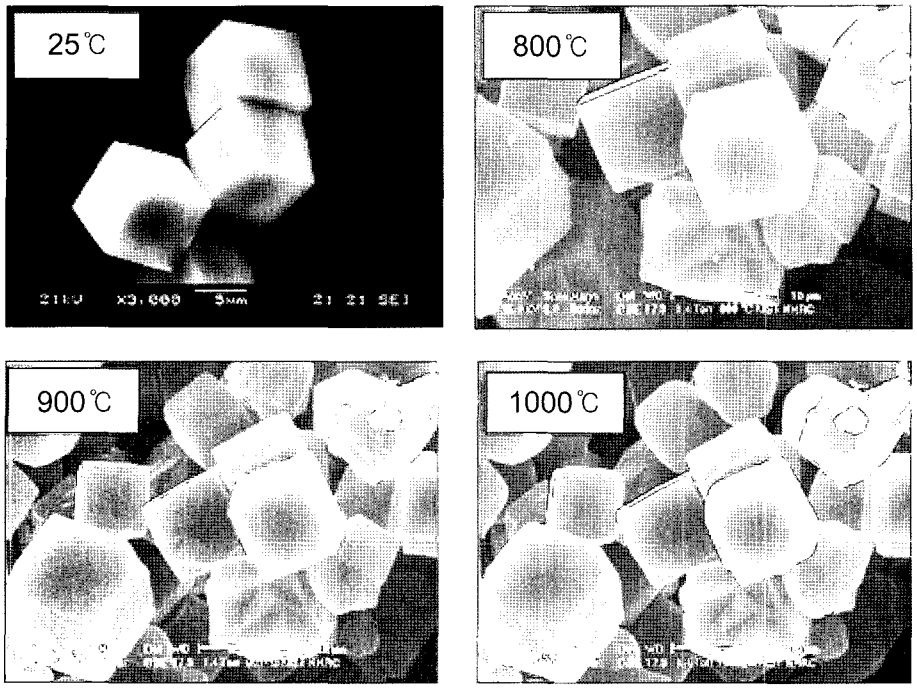

Fig. 1. ESEM images of synthetic NaA zeolite during heat treatment.

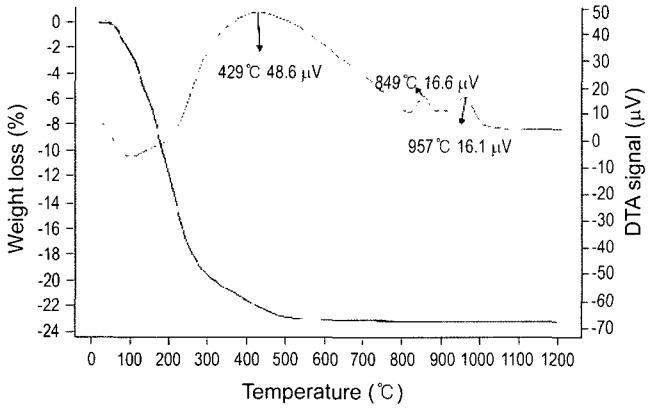

Fig. 2. Thermal analysis of NaA zeolite.

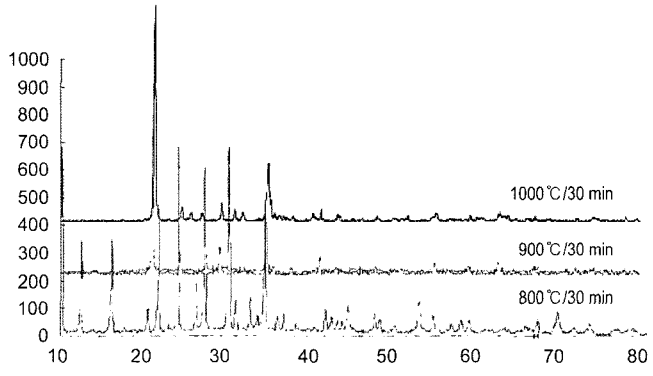

Fig. 3. XRD patterns of NaA zeolite with various heat treatments.

treatment of NaA zeolite resulted in thermal stability of NaA phase up to 800°C for 30 min. This phase transformed to another crystalline phase of Camegeite ($NaAlSiO_4$) at 900°C for 30 min, which transformed to a rounding crystal morphology after heat treatment at 1000°C for 30 min.

DTA/TGA curves of the synthetic NaA zeolite are shown in Fig. 2. The DTA curve of zeolite displays a characteristic endothermic minimum below 120°C, causing thermally induced desorption of physically adsorbed water. The exothermic peak in the temperature range from 300 to 500°C is attributed to the desorption of the remaining zeolite water enclosed in the zeolitic matrix. The exothermic peaks in the DTA curves at 849 and 957°C correspond to high-temperature solid-state transformation, respectively.

The XRD pattern of the calcined sample at 800°C corresponds with the X-ray pattern of the starting synthetic NaA zeolite, $2\theta = 30°(644)$, as shown in Fig. 3. However, thermal treatment of NaA zeolites at a temperature of about 900°C for 30 min yielded a crystalline phase of $NaAlSiO_4$-Camegeite with rounded particles of the final product relative to the original morphologies of NaA zeolite, as indicated by SEM and XRD, and shown in Fig. 1(c) and (d) and Fig. 2, respectively. After prolonged heating at 1000°C for 30 min, the main product was a crystalline phase of $NaAlSiO_4$-Camegeite.

HRTEM imaging of NaA zeolite, which is shown in Fig. 4 (a), reveals a high degree of structural order in the crystal surface formed inside complementary pores between adjacent cylinders. The pore size distribution curve showed two distinct peaks, one centered at 12.389 Å corresponding to the inner diameter of the zeolite structure. Zeolite NaA can be described as an ensemble of sodalite cages joined by dou-

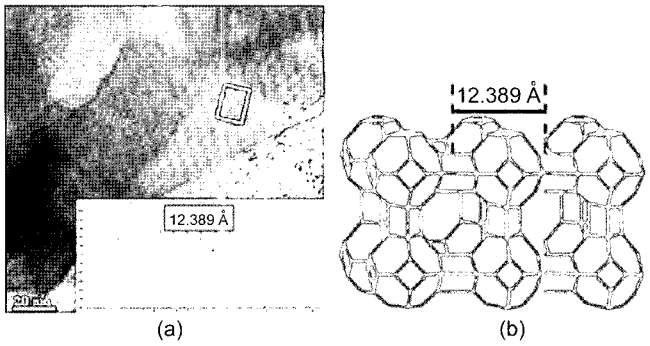

Fig. 4. TEM images of NaA zeolite.

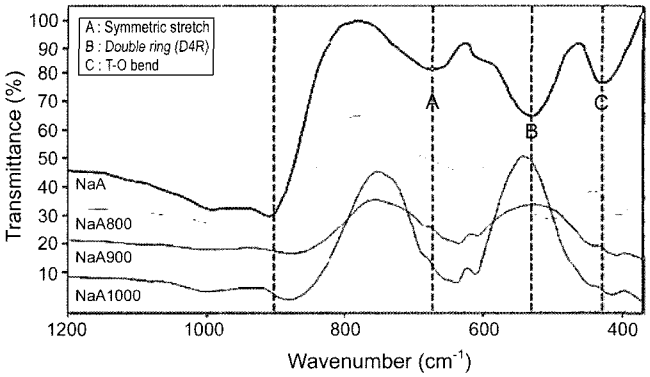

Fig. 5. FT-IR analysis of NaA zeolite with various heat treatments.

ble T4-rings, as shown in the drawing of the unit cell content in Fig. 4(b). In general, the framework of zeolite A can be described in terms of two types of polyhedra: one is a simple cubic arrangement of eight tetrahedrals, the D4R; the other is a truncated octahedron of 24 tetrahedrals or cages, as previously described for sodalite-type minerals. Zeolite A is generated by placing cubic D4R units in the center of the edges of a cube at edge 12.3 Å.[7,8] This nano-structured zeolite material has been applied as host-guest materials for nano-cluster particles.[9]

Fig. 5 shows the FT-IR curves of synthetic heat treated NaA zeolites. The asymmetric vibration at 687 and 548 cm^{-1} (D4R) is assigned to a T-O stretch at 430 cm^{-1}. At high temperature, the symmetric stretching modes involving mainly the tetrahedral atoms are assigned in the region of 748 and 677 cm^{-1}. In general, the stretching modes are sensitive to the Si-Al composition of the framework and may shift to a lower frequency with increasing number of tetrahedral aluminum atoms. The second group of frequencies, which are sensitive to the linkages between tetrahedrals and the topological mode of arrangement of the secondary units of structure in the zeolite, occur in the regions of 600–500 cm^{-1} and 450–400 cm^{-1}, respectively.[10] A band in the 600–500 cm^{-1} region is related to the presence of a double ring in the framework structures and is observed in all the zeolite structures that contain double 4 and double 6-rings. However, the FT-IR curve of the sample obtained at 900°C does not show any peaks between 1000 and 400 cm^{-1}, indicating that the linkages between tetrahedrals and the topological method of arrangement of the secondary units of structure. These results were confirmed by X-ray powder diffraction analysis of heat treated zeolite at 900°C.

4. Conclusion

The crystal morphology of synthetic NaA zeolite shows that the cubic is comprised of well-shaped crystals having six perfect square faces and an average lattice constant of 24.64 Å with a SiO_2/Al_2O_3 molar ratio of 1.6~2.0. Thermally induced transformation of crystalline NaA zeolite takes place through the formation of an intermediate phase of $NaAlSiO_4$-Camegeite from 800 to 900°C and recrystallization to another crystalline material during prolonged heating up to 1000°C.

Acknowledgment

This work was financially supported by the Ministry of Education and Human Resources Development (MOE) and the Ministry of Commerce, Industry and Energy (MOCIE) through a fostering project of the Industrial-Academic Cooperation Centered University.

REFERENCES

1. W. M. Meier, in : Proc. Intern. Symp. "Molecular Sieves," 1st, London, pp. 10-27 (1968).
2. H. J. Lee, H. M. Lim, and I. J. Kim, "Synthesis and Characterization of Large NaX Zeolite Crystal by Continuous Crystallization," *Mater. Sci. Forum.*, **492-493** 731-36 (2005).
3. A. Kosak, D. Makovec, and M. Drofenik, "Engineering High-Temperature Stable Nanocomposite Materials," *Mater. Sci. Forum,* **453-454** 219-24 (2004).
4. D. W. Breck, "Zeolite Molecular Sieves : Structure, Chemistry and Use," Wiley, New York (1974).
5. I. J. Kim and H. J. Lee, "Effects of Seeding on the Formation of Large NaX Zeolite Crystals," *Mater. Sci. Forum,* **492-493** 287-92 (2005).
6. J. C. Lin, J. T. Dipre, and M. Z. Yates, "Novel Aluminium Phosphate-5 Crystal Morphologies Synthesized by Microwave Heating of a Water-in-Oil Microemulsion," *The ACS J. Surface and Colloids*, Langmuir, **20** [4] 1039-42 (2004).
7. Y. Y. Sun, T. Song, S. Qiu, W. Pang, J. Shen, D. Jiang, and Y. Yue, "Cationic Microemulsion-Mediated Synthesis of Silicalite-1," *Zeolites,* **15** 754-53 (1995).
8. N. Chandrasdkharan and P. V. Kamat, "Tuning the Properties of CdSe Nanoparticles in Reverse Micelles," *Res. Chem. Intermed.*, **28**, 847-56 (2002).
9. A. Kameo, A. Suzuki, K. Torigoe, and K. Esumi, "Macromolecular Rapid Communications Colloid," *J. Colloid Interface Sci.*, **241** 298-92 (2001).
10. S. S. Lee, A. M. Rideau, and L. B. McGown, "Advanced Materials : Nanoparticle Synthesis in Engineered Organic Manoscale Reactors," *J. Phys. Chem.*, **100** 5880-87 (1996).