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Structural and morphological transformation of NaX zeolite crystals at high temperature

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Abstract

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. Well-shaped NaX zeolite octahedral crystals of a large size of 30 μm were synthesized by a hydrothermal method in a mother solution having a $3.5Na_2O:Al_2O_3:2.1SiO_2:593–2000H_2O$ composition. Thermal treatment of NaX zeolite crystals resulted in the formation of an intermediate amorphous phase at temperature above 800 and 900 °C and a crystalline phase of aluminium silicate ($T < 1000$ °C). Environmental scanning electron microscopy (ESEM), high resolution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, DTA/TGA and BET analysis were used to characterize the initial materials and the obtained products after various heat treatments.

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1. Introduction

Large uniform zeolite crystals are highly desired for many uses that range from crystal structure analysis, adsorption and diffusion studies to zeolite functional materials because of their unique crystal structure, the microporous characteristics, and their high chemical as well as thermal stability.[1,2] However, it is difficult to synthesize uniformly sized NaX zeolites and to grow large zeolite single phase crystals because crystal nuclei grow rapidly during the growth period and the product may transform into a more stable phase, such as for example NaP, requiring a longer reaction time once the crystallization period is over.[3,4] For this reason, some scientists mentioned that it is impossible to grow synthetic zeolite single crystals to an appropriate size to analyze their structure.[5,6] In recent years, in order to improve existing catalytic and adsorbent processes, scientists need a better understanding of the structure of zeolites. Additionally, nearly perfect crystalline zeolite structures could be used as proton exchangeable membranes for fuel cells, which could result in major advantages over current separation and catalytic processes,[7,8] or as host materials for semiconductor clusters and optical properties specific to the form of "nano-crystals or quantum dots". The aim of the present study should be explained in more detail the structural and morphological transformation of synthetic zeolite as a function of various heat treatment.

2. Experimental

NaX zeolite crystals of a uniform particle size of 10 μm were synthesized by the hydrothermal method in a mother solution having a composition of $3.5Na_2O:Al_2O_3:2.1SiO_2:1000H_2O$ at 90 °C for 7 days. The reactant materials used 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) instrument were used to determine the surface area of the synthesized zeolite crystals. A semiquantitative chemical analysis performed to estimate the SiO_2/Al_2O_3 ratio was carried out via fluorescent X-ray spec-

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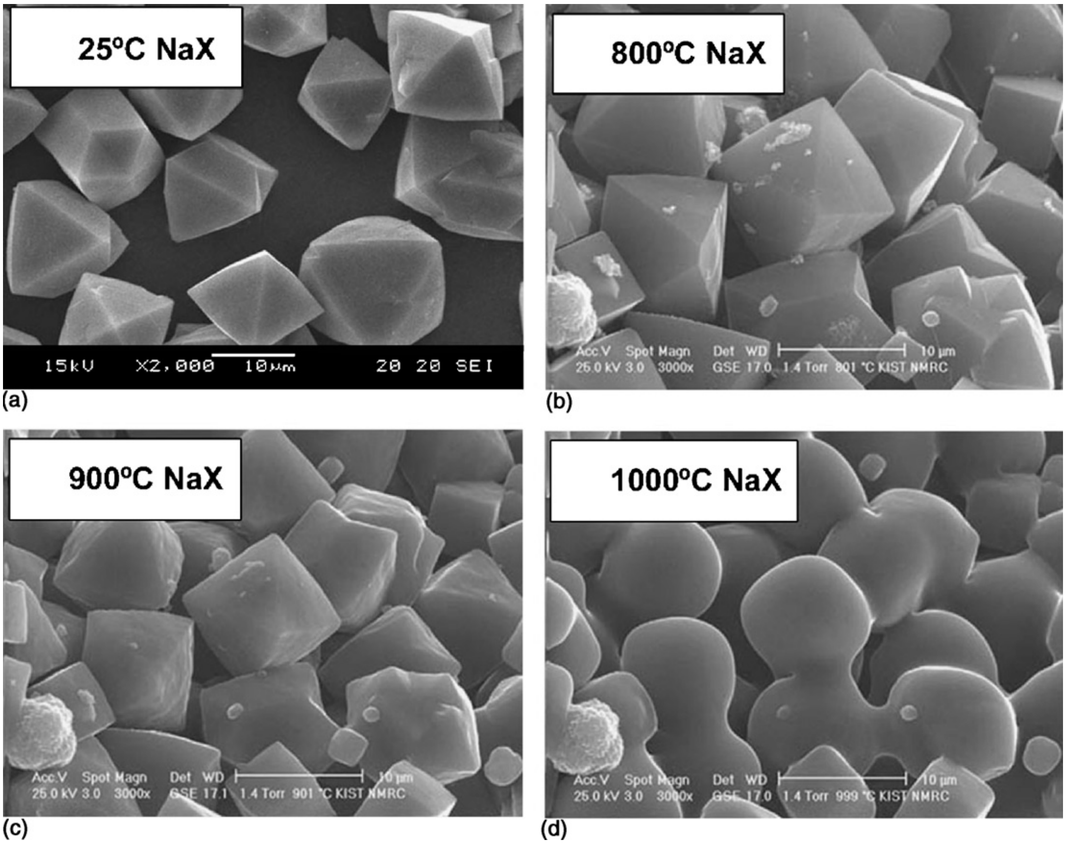

Fig. 1. ESEM images of heat treatment NaX zeolite during heat treatment.

trometry (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 Cu Kα 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.

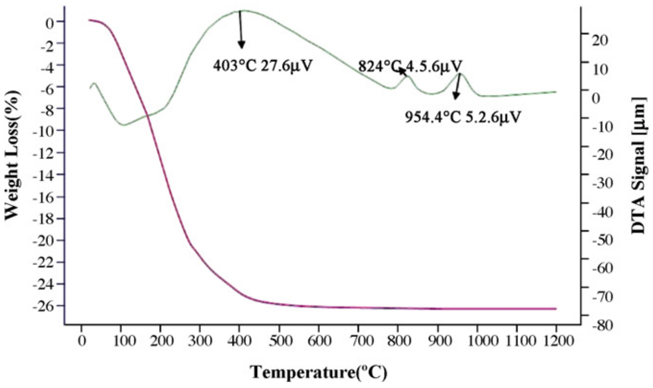

Fig. 2. Thermal analysis of NaX zeolite.

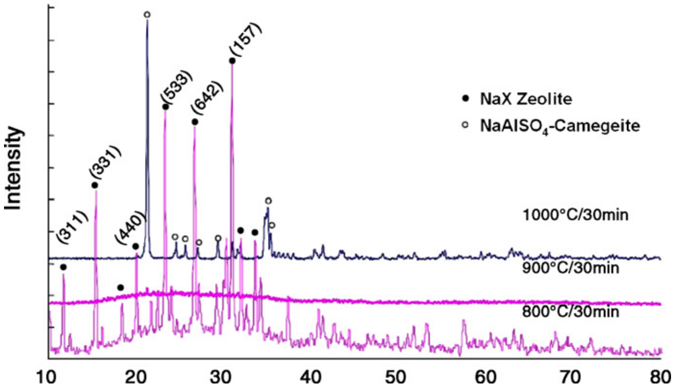

Fig. 3. XRD patterns of NaX zeolite with various heat treatment.

3. Result and discussion

The morphology of NaX crystal from a view image shows that the octahedron is formed composed of eight equilateral triangles. These triangular-shaped faces intersect all three crystallographic axes at the same distance as shown in Fig. 1(a). The XRD results of this morphology revealed only the NaX crystalline phase which has an average lattice constant of 24.9911 Å with a SiO_2/Al_2O_3 molar ratio of 2.1–2.4, as determined by XRD and XRF. Thermal treatment of NaX zeolite resulted in the formation of an amorphous phase at 900 °C for 30 min and a rounding crystalline phase of Camegeite at 1000 °C for 30 min.

The DTA/TGA curves of the synthetic NaX zeolite are shown in Fig. 2. DTA curve of zeolite display a characteristic endothermic minimum below 200 °C, caused by thermally induced desorption of physically adsorbed water. The exothermic peak in the temperature range from 250 to 600 °C is attributed to the

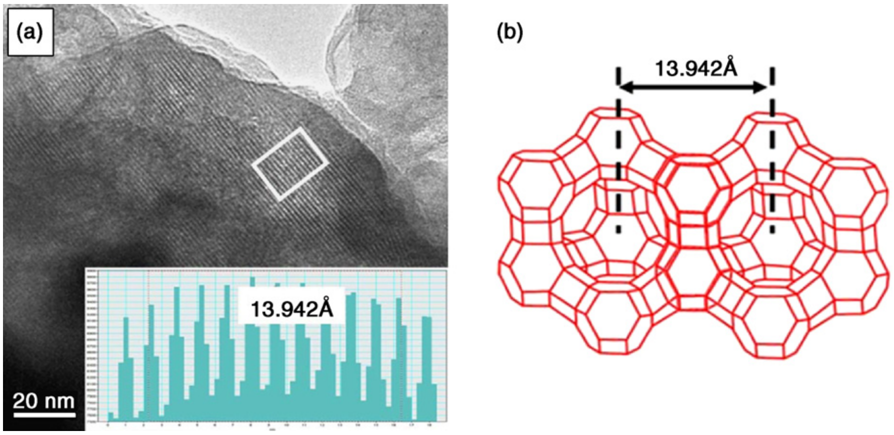

Fig. 4. TEM images of NaX Zeolite.

desorption of the remaining zeolite water of 26% enclosed in the zeolitic matrix. The exothermic peaks in the DTA curves at 824 and 954.4 °C correspond to high-temperature solid-state transformation.

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

HRTEM imaging of NaX zeolite, which is shown in Fig. 4(a), reveals a high degree of structural order in the crystal surface are formed inside the complementary pores between adjacent cylinders. The pores size distribution curve showed two distinct peaks, one centered at 13.942 Å corresponding to the inner diameter of the zeolite structure. Zeolite NaX (FAU) can be described as an ensemble of sodalite cages or β-cages joined by hexagonal prisms, as shown in the drawing of unit cell content in Fig. 4(b). In general, this structure can be envisaged as a stacking layers of sodalite cages joined by double six rings (D6R) in tetrahedral arrangement like carbon atom in diamond, with a center of inversion at the center of the double six rings. The β-cage surround an even large cage, the supercage (cavity with diameter about 13 Å), which forms a three-dimensional network with each cage connected tetrahedrally to four other supercages through the 12-membered ring opening with a crystallographic aperture of 7–8 Å.[9,10] This nano-structured zeolite materials was applied as host–guest materials for nano-cluster particles.[11,12]

Fig. 5 shows the FT-IR curves of synthetic heat treated NaX zeolites. The strongest vibration at 950 cm^{-1} is assigned to a T–O stretch and the stretching modes involving mainly the tetrahedral atoms are assigned in the region of 740 and 620 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 aluminium atoms. The second group of frequencies which are sensitive to the linkages between tetrahedral and the topological mode of arrangement of the secondary units of structure in the zeolite occur in the regions of 600–500 and 430–300 cm^{-1}, respectively.[13] 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 the double 4 and double 6-rings. However, the FT-IR curve obtained at 900 cm^{-1} not show any peaks between 1000 and 400 cm^{-1}, indicating that the linkages between tetrahedral 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.

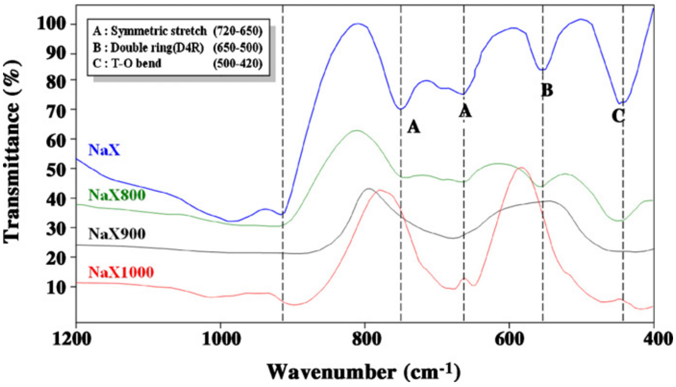

Fig. 5. IR analysis of NaX zeolite with various heat treatment.

4. Conclusions

The crystal morphology of synthetic NaX zeolite shows that the octahedron is comprised of eight equilateral triangles having an average lattice constant of 24.9911 Å with a SiO_2/Al_2O_3 molar ratio of 2.1–2.4. Thermally induced transformation of crystalline NaX zeolite takes place through the formation of an intermediate amorphous phase from 800 to 900 °C and recrystallization to another crystalline material during the prolonged heating above 1000 °C. The obtained intermediate amorphous aluminium silicate and the final product have the other shape as the precursor crystal.

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