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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.

Keyword: NaX zeolite; X-ray methods; Fuel cells; Calcination; Sensors

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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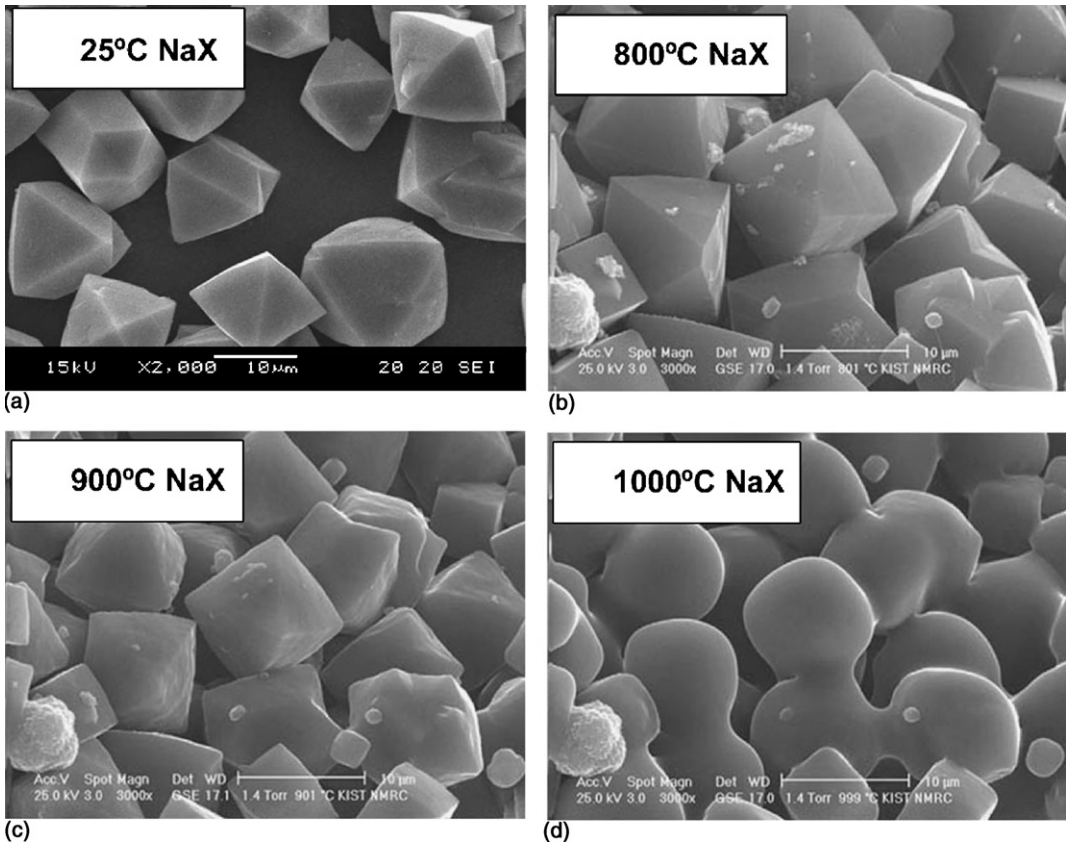

Fig. 1. ESEM images of heat treatment NaX zeolite during heat treatment.

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.

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

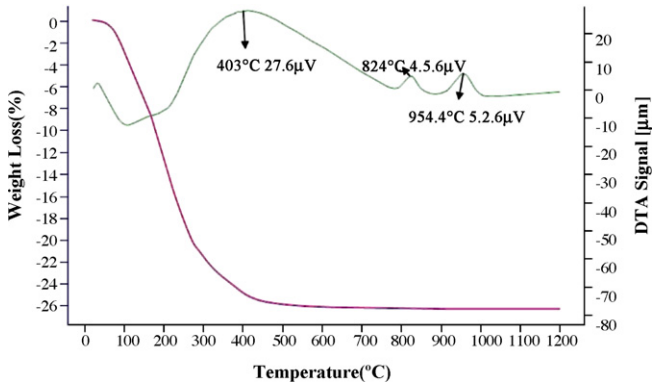

Fig. 2. Thermal analysis of NaX zeolite.

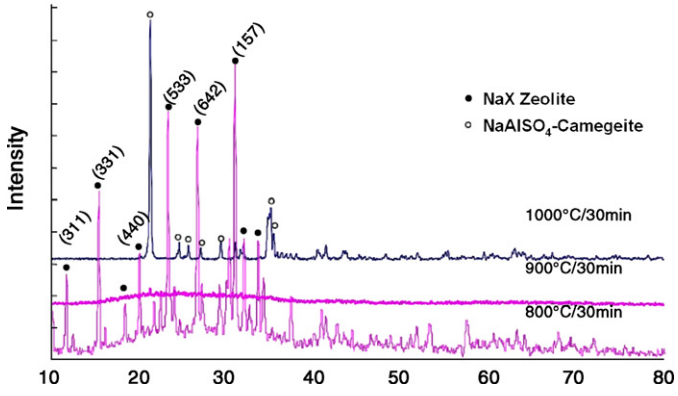

Fig. 3. XRD patterns of NaX zeolite with various heat treatment.