Phase separation in hydrated LTA zeolite

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Abstract

The coexistence of two distinct phases, $[Li_{0.08}(NH_4)_{0.92}]$- and $[Li_{0.32}(NH_4)_{0.68}]$–A, was observed for a mixed crystal of $[Li_x(NH_4)_{1-x}]$–A of LTA (Linde type A) zeolite in the range of $0.08 < x < 0.32$ at 295 K, where A denotes the aluminosilicate framework of LTA containing water molecules. In contrast, for $x < 0.08$ and $x > 0.32$, a uniform monophase was observed for the mixed crystal. The coexistence of the separated phases was deduced from ion-exchange isotherm measurements at 295 K and thermodynamic analyses. Spinodal and binodal curves were obtained. The monophasic and biphasic states were confirmed by powder X-ray diffraction. The excess Gibbs energy and the excess volume of $[Li_x(NH_4)_{1-x}]$–A were unsymmetrical with respect to $x = 1/2$. The Li ions favored specific ion-exchange sites. The preferential occupation of Li ions in the six-membered oxygen ring of $[Li_x(NH_4)_{1-x}]$–A was proved by Li-isotope measurements, and was demonstrated by ab initio molecular orbital calculations. The separation of two LTA-phases due to ordered Li-occupation within the six-membered oxygen rings is discussed.
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Keywords: Spinodal; Ion-exchange thermodynamics; X-ray diffraction; Isotopic effect; Ab initio molecular orbital calculations

1. Introduction

The LTA (Linde type A) zeolite is a microporous crystal that is formed from aluminosilicate cages and ion-exchangeable cations with volatile water molecules [1]. The chemical formula of LTA is expressed as $M_{12/m}[(AlO_2)_{12}(SiO_2)_{12}] \cdot nH_2O$, where M represents the ion-exchangeable cations of charge m, and n varies from 20 to 30 (hereafter the above formula is abbreviated as M–A). Aluminum and silicon atoms are alternately arranged through an oxygen atom forming oxygen-atom rings and cage structures (Fig. 1). These ring and cage structures of various LTA crystals were originally ascribed to be rigid. The lattice constant of a pseudo-cell

(Pm3m) of LTA (Fig. 1) was nearly constant ($a = 1232 \pm 6$ pm) [2], independent of dehydration and hydration, and was practically unaltered by complete or partial ion-exchange with various cations (Na, K, Cs, Tl, Ag, Mg, Ca, Sr) [2,3]. However, the detailed X-ray studies revealed that LTA framework-angles are not strictly rigid. The appreciable changes in the framework angles (Si–O–Al), corresponding to the rotations of SiO_4 and AlO_4 unites, were observed upon the dehydration of several LTA zeolites (Tl–A [4], Na–A [5], K–A [6], and $Cs_{0.58}Na_{0.42}$–A [7]). The framework-angle flexibility of zeolites is clearly described in a recent literature [8] to account for the mechanism of the structural phase transformation of Li–LSX (Li–faujasite with Si/Al = 1) at low temperature.

Significant short length of the cubic LTA pseudo-cell was observed for hydrated $[Li_{0.67}Na_{0.33}]$–A ($a = 1204$ pm) [9], dehydrated Li–A ($a = 1210.5$ pm) [2],

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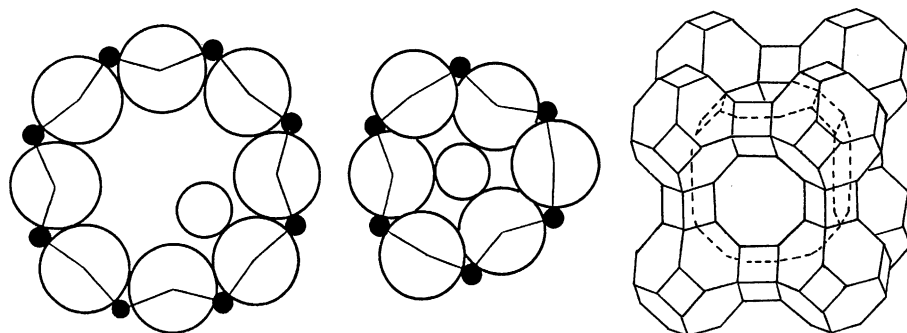*E-mail address:* ishikaw@shinshu-u.ac.jp (A. Ishikawa).

Fig. 1. LTA zeolite: structure and rings. The three-dimensional framework is a pseudo-cell. A framework corner indicates the position of the Si or Al atom. Oxygen atoms lie on the edges, and form four-, six-, and eight-membered rings, which form the faces of cages. The truncated octahedron cages and the rhombitruncated cuboctahedron cage (which is formed inside the eight truncated octahedrons connected by twelve cubes), contain water molecules. Cations are located in the center of the six-membered oxygen rings and on the side of the eight-membered oxygen rings with hydrating water. Water molecules are not shown in the Figure.

and a molten salt contained $Li_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 9.8$-$LiNO_3 \cdot 9.3H_2O$ ($a = 1207.5$ pm) [10]. The internal molecules in the large cage did not resist the cell length to shrink from the normal size ($a = 1232 \pm 6$ pm). In the case of the hydrated LTA zeolites (Tl–A, Na–A, K–A, and $Cs_{0.58}Na_{0.42}$–A), the water molecules sustain the normal Si–O–Al angles and cell length [7]. The above hydrated $[Li_{0.67}Na_{0.33}]$–A showed the appreciable size reduction (the lattice constant: ca. −2%; the volume: ca. −8%). This suggests that the small size of Li ion strongly attracts the oxygen atoms with the rotations of AlO_4 and SiO_4 tetrahedra, and causes the shrinkage over the framework. A wide variation of Si–O–Al angles of the framework was confirmed in dehydrated $[Li_{0.75}Na_{0.25}]$- and dehydrated $[Li_{0.81}Na_{0.19}]$–A by X-ray and neutron diffraction [11]. The strong interaction between a Li ion and the oxygen atoms of the six-membered oxygen ring of hydrated Li–A was evident in infrared and Raman spectroscopy [12]. The rotation behavior of AlO_4 and SiO_4 tetrahedra of the six-membered oxygen ring of Li–X (faujasite) was clearly illustrated in a recent neutron diffraction study [8].

Recently, a study using chromatography has suggested the coexistence of two distinct solid phases in $[Li_x(NH_4)_{1-x}]$–A [13]. The biphasic behavior were qualitatively deduced form the phase rule and the pseudo-selectivity-coefficient. In addition to this thermodynamic analysis, structural evaluation for the two phases will be important. In the phase separation of (Na_xSr_{1-x})–X, the distinct two solid-phases of $(Na_{0.29}Sr_{0.71})$- and $(Na_{0.13}Sr_{0.87})$–X were proved by X-ray diffraction [14]. Relocation of Na and Sr cations in the crystal sites was suggested for the phase separation mechanism.

For the mechanism of the phase separation of $[Li_x(NH_4)_{1-x}]$–A, the cooperative distortion of the six-membered oxygen rings caused by Li occupation may be an origin. The zeolite framework shows flexibility in a certain extent; however phase-separation phenomena have been unusual in almost all zeolites. Therefore the definite confirmation of the phase separation of $[Li_x(NH_4)_{1-x}]$–A and the corresponding framework flexibility are the subjects of the present investigation.

The phase-separation thermodynamics of $[Li_x(NH_4)_{1-x}]$–A was studied using ion-exchange equilibrium experiments. The separated phases and the lattice-flexibility were directly clarified through powder X-ray diffraction measurements. The positions of the Li^+ and NH_4^+ ions within the zeolite were hypothesized by thermodynamics and by Li isotopic measurements. Ab initio molecular orbital calculations were also carried out to interpret the experimental isotopic results and to support the hypothetical Li-sites.

2. Experimental

2.1. Ion-exchange

Experiments utilized homogeneous fine powder (ca. 10 μm) of NH_4–A, which was prepared from Na–A (Tosoh) by ion-exchange [13]. At the final process of the ion-exchange, to remove the excess amount of NH_3 within the column voids, a dilute solution (ca. 40 mM) of NH_4NO_3 at pH 8 prepared by mixing acid (HNO_3) and base (NH_3) was fed onto a $[Na_x(NH_4)_{1-x}]$–A column until every Na ion was replaced with NH_4^+ ions.

The prepared NH_4–A hydrated powder and a solution of $LiNO_3$ at pH 8 made from LiOH and HNO_3 were mixed at room temperature (295 ± 1 K). Ion-exchange equilibrium between $[Li_x(NH_4)_{1-x}]$–A and $LiNO_3$ or NH_4NO_3 solutions was attained by the procedures listed in Table 1.

In the case of Entry 3, a mixed crystal of $[Li_x(NH_4)_{1-x}]$–A was obtained by the single ion-exchange between certain amounts of NH_4–A and of $LiNO_3$ solution. To reach different points of equilibrium