Structural studies of NH₄-exchanged natrolites at ambient conditions and high temperature

YONGMOON LEE,¹ DONGHOON SEOUNG,¹ YOUNG-NAM JANG,² JIANMING BAI,³ AND YONGJAE LEE¹,*

¹Department of Earth System Sciences, Yonsei University, Seoul 120-749, Korea
²Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Republic of Korea
³National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

ABSTRACT

We report here for the first time that fully and partially NH₄-exchanged natrolites can be prepared in hydrated states using the solution exchange method with potassium-natrolite. The structural models of the as-prepared hydrated phases and their dehydrated forms at elevated temperature were refined in space group Fdd2 using in situ synchrotron X-ray powder diffraction data and Rietveld methods. The unit-cell volumes of the hydrated NH₄-exchanged natrolites at ambient conditions, (NH₄)₁₆₋ₓ₈ₓ[Al₈Si₄O₂⁴]·₄H₂O and (NH₄)₁₂(K)ₓ[Al₈Si₄O₂⁴]·₁₅.₇H₂O, are found to be larger than that of the original sodium-natrolite by ca. 15.6% and 12.8%, respectively. Upon temperature increase, the fully NH₄-exchanged natrolite undergoes dehydration at ca. 150 °C with ca. 16.4% contraction in the unit-cell volume. The dehydrated phase of the fully NH₄-exchanged natrolite exhibits marginal volume expansion up to 425 °C and then becomes amorphized during temperature decrease and exposure to atmospheric condition. In the case of the partially NH₄-exchanged natrolite, the dehydration starts from ca. 175 °C with ~15.1% volume contraction and leads to a partial phase separation to show a phase related to the dehydrated K-natrolite. The degree of the phase separation decreases with temperature increase up to 475 °C, concomitant to the gradual volume contraction occurring in the partially NH₄-exchanged natrolite in the dehydrated state. Upon temperature decrease and exposure to atmospheric condition, only the dehydrated K-natrolite is recovered as a crystalline phase from the partially NH₄-exchanged natrolite. In the hydrated model of the fully NH₄-exchanged natrolite, ammonium cations and water molecules are statistically distributed along the elliptical channels, similar to the disordered pattern observed in natrolites exchanged with larger alkali metal cations such as the K-, Rb-, and Cs-forms. The dehydrated model of the fully NH₄-exchanged natrolite at 400 °C is essentially same as the one reported previously from the sample prepared by direct melt exchange method using sodium-natrolite. Both the hydrated and dehydrated structures of the partially NH₄-exchanged natrolite at RT and at 400 °C, respectively, are characterized by having two separate sites for the ammonium and potassium cations. Comparing the structural models of the monovalent cation forms studied so far, we find that the rotation angle of the natrolite chain is inversely proportional to the cation radius both in the hydrated and dehydrated phases. The distribution pattern of the non-framework species along the natrolite channel also seems to be related to the non-framework cation radius and hence to the chain rotation angle.

Keywords: NH₄-natrolite, dehydration, Rietveld refinement, crystal chemistry

INTRODUCTION

Natrolite is one of the first discovered zeolites (Klaproth 1803) and has been established as a representative member of the fibrous zeolites (Baerlocher et al. 2007). The structure of natrolite is characterized by the well-ordered distribution of both the framework and non-framework cations and water molecules in the ideal composition of Na₆₋ₓCaₓAl₈Si₄O₂⁴·₁₆H₂O (Meier 1960; Pauling 1930; Taylor et al. 1933). In nature, compositional variants of natrolite are found either by framework or non-framework cation substitutions to lead to the Al/Si-disordered phases or Ca-rich forms, respectively. The former is due to the increased Al/Si ratio in the framework sites and includes gonndartite, Na₁₆₋ₓCaₓAl₈Si₄O₂⁴·₉ₓH₂O (0.2 ≤ x ≤ 3.9, 16 ≤ n ≤ 25.2) (Artioli and Galli 1999; Evans et al. 2000; Ross et al. 1992), whereas in the latter, Ca²⁺ cations substitute 2/3 of the Na⁺ cations to form mesolite, NaₓCaₓ₃Ca₃Al₈Si₄O₂⁴·₂₁.₃H₂O (Artioli et al. 1986), or substitute all to form scolecite, Ca₂Al₈Si₄O₂⁴·₂₄H₂O (Kvick et al. 1985). Literature has established these compositional variants as separate phases because direct exchange between the cations is found to be highly limited, i.e., the calcium content does not exceed ca. 0.43 per 80 framework oxygen atoms in naturally occurring natrolites (Baerlocher et al. 2007; Foster 1965; Gunter et al. 1993; Hey 1932).

Attempts to induce direct cation exchange in natrolite to

* E-mail: yongjaeeleeyonsei.ac.kr