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Thermal transformation and ionic conductivity of ammonium ion-exchanger prepared from Na-4-mica

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ABSTRACT

Ammonium ion exchange of Na-4-mica and thermal transformation of the ion-exchanger were investigated and the conductivities of the heated ion-exchangers were estimated. More than 95.4% of Na^+ ions in the interlayer of the Na-4-mica could be substituted by NH_4^+ ions after repeating ion exchange four times. Almost of NH_4^+ ions remained in the interlayer at 700 °C and they were completely decomposed into protons at 900 °C. The conductivities of the ion-exchangers heated at 700–900 °C were 10^{-7}–10^{-6} S/cm at 700 °C. The conduction mechanism of the ion-exchangers heated at 700 and 800 °C was NH_4^+ ion migration in the interlayer and that of the ion-exchanger heated at 900 °C was proton migration. However, the contribution of residual Na^+ ions to the conduction cannot be excluded.

1. Introduction

Na-4-mica is a highly charged sodium fluorophlogopite mica ($Na_4Mg_6Al_4Si_4O_{20}F_4$) of which interlayer contains twice as many Na^+ ions as that of the ordinary Na-type fluorophlogopite ($Na_2Mg_6Al_2Si_6O_{20}F_4$) contains. It has theoretically high ion-exchange capacity and its cation exchange properties have been investigated [1–10].

We synthesized Na-4-mica by novel and simple solid-state reaction and found that the electrical conductivity of Na-4-mica polycrystal (4.3×10^{-4} S/cm at 650 °C) was much higher than that of the ordinary Na-type fluorophlogopite (1.2×10^{-6} S/cm at 650 °C) [11]. The conductivity mechanism was the movement of Na^+ ions in the interlayer, which is the same with that of β-alumina which is well known as Na^+ ion conductor. On the other hand, K-type fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$) is the representative synthetic mica, and its electrical resistance is very high. The reasons may be that the size of K^+ ion in the interlayer is large and the interlayer does not contain as many cations as that of Na-4-mica contains. So if micas have cations with smaller size in the interlayer and/or have many cations in the interlayer like Na-4-mica, they will have a possibility as ionic conductors.

Na^+ ions in the interlayer of Na-4-mica can be exchanged for other kinds of cations [1–10]. So we thought that it would be easy to fabricate proton, lithium ion or other cations conducting micas by the ion exchange of Na-4-mica. In this study, ammonium ion exchange of Na-4-mica and thermal transformation of the ion-exchanger were investigated. And because the obtained ammonium ion-exchanger would be thermally decomposed into proton mica of which the interlayer cation is proton, the conductivities of the heated ion-exchangers were estimated.

2. Experimental procedure

Na-4-mica synthesized by the solid phase reaction method [11] was stirred for 1 h in distilled water, in order to swell the interlayer. And then it was mixed with 1.0 mol/l NH_4Cl solution and stirred for 1 h at 100 °C. In this way, the interlayer cations, Na^+ ions, of the Na-4-mica were exchanged for NH_4^+ ions. The ion-exchanger was separated from the solution using a centrifuge. The ion exchange and separation were repeated two to six times. The separated ion-exchangers were washed with distilled water and dried at 60 °C for 24 h. The phase change, basal spacing ($c \cdot \sin\beta$; c and β are lattice constants) and lattice constant b of the ion-exchangers were estimated using an X-ray diffraction (XRD) analyzer (XRD-6000, Shimadzu, Japan). Sodium content of the ion-exchanger was analyzed in the solid state using an atomic absorption spectrophotometer (ContrAA700, Analytik Jena Japan, Japan).

The ion-exchanger prepared by repeating ion exchange four times was compacted by isostatic pressing at 100 MPa, dried at 150 °C for 24 h and then fired in a sealed platinum container at 200–1000 °C for 1 h. The characters of the heated ion-exchangers were estimated using the XRD analyzer, a thermogravimetric and differential thermal analyzer (TG, DTA: TG8120, Rigaku, Japan),

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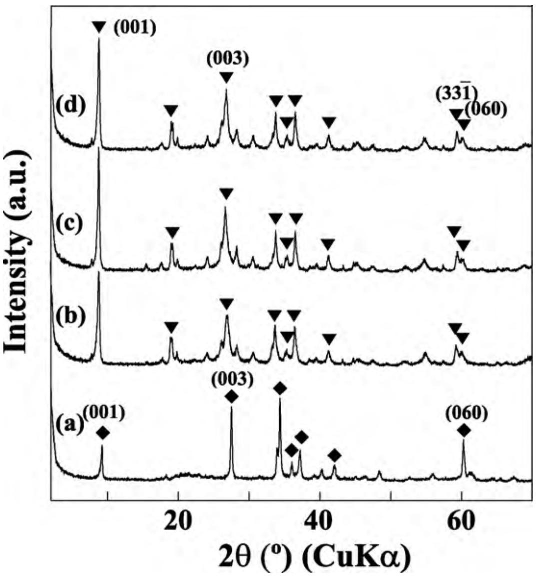

Fig. 1. XRD patterns of (a) the synthesized Na-4-mica, and the ion-exchangers prepared by repeating ion exchange (b) one time, (c) three times and (d) six times. (◆: Na-4-mica, ▼: mica peak, no mark: unknown).

and a Fourier transmission infrared (FT-IR) spectrometer (FT/IR-4200, JASCO, Japan). Specific electrical resistance of the heated ion-exchangers was measured at 500–700 °C by a four-probe method using an impedance analyzer (CHEMICAL IMPEDANCE METER 3532-80, HIOKI, Japan) in a frequency range of 4–10^6 Hz. The samples for electrical measurement were prepared as the size of 3 mm × 4 mm × 25 mm and were sputtered platinum as electrodes. The distance between the electrodes was about 5 mm. The electrodes and the conducting wires made of platinum were contacted and the contacts were held with the silver paste. The samples and conducting wires were shielded from noises by aluminum foil.

3. Results and discussion

3.1. NH_4^+ ion exchange of Na-4-mica

The XRD patterns of the synthesized Na-4-mica and its ion-exchangers are shown in Fig. 1. In the XRD pattern of the synthesized Na-4-mica, dehydrated Na-4-mica and a small amount of unknown materials were observed. The (0 0 1) and (0 0 3) diffraction peaks of the ion-exchangers appeared at lower diffraction angles, compared with those of the dehydrated Na-4-mica, which indicate that Na^+ ions in the interlayer of the Na-4-mica were substituted by larger NH_4^+ ions. While the (0 6 0) diffraction peak observed at about 60.5° was not shifted by the ion exchange, new diffraction peak appeared at 59.5°. The new peak might resulted from the diffraction of (3 3 $\bar{1}$) lattice plane. The (0 6 0) and (3 3 $\bar{1}$) diffraction peaks of the Na-4-mica might appeared at 60.5°, like those of fluorophlogopite ($KMg_3Si_3AlO_{10}F_2$) [12]. By the ion exchange, the interplanar spacing of (0 6 0) lattice plane was not varied, but that of (3 3 $\bar{1}$) lattice plane was widened.

The $c{\cdot}\sin\beta$ and b were determined from the (0 0 3) and (0 6 0) diffraction peaks of the Na-4-mica and the ion-exchangers. The $c{\cdot}\sin\beta$ and b of the Na-4-mica were respectively 9.81 and 9.23 Å. The $c{\cdot}\sin\beta$ was increased by repeating ion exchange and became constant value of about 10.0 Å by repeating ion exchange three or more times, while the b value was not almost changed and was constant value of about 9.24 Å. These results mean that the substitution of NH_4^+ ions for Na^+ ions in the interlayer widened only the interlayer but did not influence the b and the NH_4^+ ion content in the interlayer was almost saturated by repeating ion exchange more than three times.

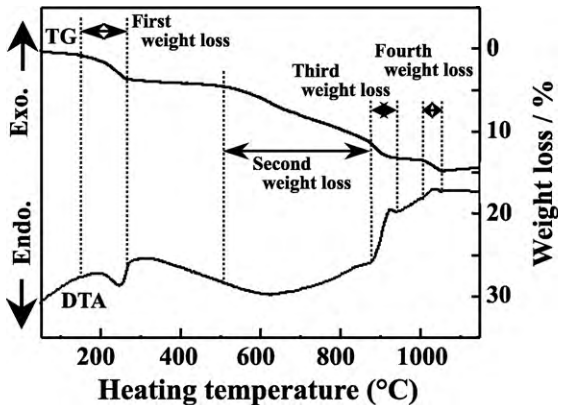

Fig. 2. DTA and TG curves of the ion-exchanger prepared by repeating ion exchange four times.

Sodium content in the ion-exchanger prepared by repeating ion exchange four times was analyzed. It was found that 4.6% of Na element in the synthesized Na-4-mica remained after the ion exchange. The synthesized Na-4-mica contained traces of sodium fluoride and the unknown materials like sodium compounds. This means that more than 95.4% of Na^+ ions in the interlayer of the Na-4-mica were exchanged for NH_4^+ ions.

3.2. Change in characters of NH_4^+ ion-exchanger by heating

The DTA and TG curves of the ion-exchanger prepared by repeating ion exchange four times are shown in Fig. 2. The first weight loss at 150–250 °C and the endothermic peak at 250 °C were caused by the evaporation of water in the interlayer. The weight was not varied at 250–500 °C and was lost gradually at 500–880 °C. The broad endothermic peak was also observed at 350–880 °C. The second weight loss resulted from the decomposition of NH_4^+ ions. The third weight loss at 880–930 °C and the exothermic peak at 920 °C were caused by the decomposition of the Na-4-mica type structure and the fourth weight loss and the exothermic peak at around 1000 °C were also caused by the decomposition of the mica structure. These weight losses resulted from the evaporation of fluorine in the ion-exchanger as fluorides with the decomposition.

The FT-IR spectra of the synthesized Na-4-mica, the ion-exchanger prepared by repeating ion exchange four times and the heated ion-exchangers are shown in Fig. 3. For the non-heated ion-exchanger and the ion-exchangers heated at ≦800 °C, characteristic absorption peaks of NH_4^+ were observed at 3200–3300 and 1400–1450 cm^{-1}. It was reported that the absorption peak at 3200–3300 cm^{-1} was observed for $NH_4^+\beta$-alumina [13] and $(NH_4^+–H_3O^+)\beta''$-alumina [14], and the absorption peak at 1400–1450 cm^{-1} was observed for NH_4^+ ion-exchanged montmorillonite [15]. These results mean that most of NH_4^+ ions remained in interlayer even at 700 °C though the NH_4^+ ions in the interlayer began to be decomposed at 350 °C as shown in Fig. 2. However, a lot of NH_4^+ ions were decomposed at 800 °C and protons might remain in the interlayer, and NH_4^+ ions disappeared at 900 °C. Almost of the absorption peaks at 400–1100 cm^{-1} resulted from tetrahedral sheet of mica [16] and the spectra were varied by the heating, which indicate that the ion-exchanger and the heated ion-exchangers maintained mica structure but the mica structure was modified gradually by heating.

The XRD patterns of the ion-exchanger and the heated ion-exchangers are shown in Fig. 4. The XRD patterns of the ion-exchangers heated at 200–700 °C were almost the same with the XRD pattern of the ion-exchanger, which also indicate that