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Ion-Exchange Reaction of n-Pentylamine-Intercalated Layered Perovskite with Alkali and Alkaline Earth Metal Ions in Aqueous Solution

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A layered perovskite type oxide, $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, can incorporate mono- and divalent metal ions from aqueous solution. n-Pentylamine intercalates into the interlayer of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ and the resulting oxide had an excellent reactivity for metal ions such as Cs^+ , Ca^{2+} or Sr^{2+} . The mechanism of the intercalation of the metal ions into the hydrophobic interlayer in aqueous medium was studied.

1 Introduction

$\text{KCa}_2\text{Nb}_3\text{O}_{10}$ has a structure comprised of perovskite-like layers of NbO_6 octahedra with Ca^{2+} occupying twelve coordinate sites and K^+ in the interlayer.[1-2] The area of unit layer charge is 0.147nm^2 , which is narrower than those of clays such as the smectites, therefore, this compound has the potential to become a high capacity ion-exchanger. The ion-exchange reaction of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ with alkali metal ions in the molten state of alkali metal chlorides or nitrates[1], and that of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, in which potassium ion was substituted by proton, with alkali metal ions in aqueous medium[3] were performed. In the aqueous medium, the ion-exchange reaction of the interlayer cation incompletely proceeded, in 30-70%, because of the difficulty for hydrated ions to enter or move into the interlayer. Ion-exchange reactions will be promoted by delamination of the layered $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. Delamination of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ is more difficult[4] than that of $[\text{Zr}(\text{PO}_4)_2]\text{H}_2\cdot\text{H}_2\text{O}$ [5] and HTiNbO_5 [6] because of its higher charge, and it is necessary to investigate another approach to promote the ion exchange.

In the present study, we investigated the ion-exchange reactions of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ and an amine-intercalate of this oxide with alkali and alkaline earth metal ions in aqueous solutions. Our purpose is to develop these layer compounds into ion exchangers, which can incorporate metal ions from aqueous solutions under mild conditions. The role of amines in the acceleration of the ion-exchange reactions is discussed.

2 Experimental

2.1 Materials

A mixture of CaCO_3 , K_2CO_3 , and Nb_2O_5 in stoichiometric amounts was ground and fired at 1023 K for 12 h. After the addition of more K_2CO_3 in 20%, the mixture was ground and fired again at 1473 K for 24 h to obtain $\text{KCa}_2\text{Nb}_3\text{O}_{10}$. $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ was obtained by the treatment of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ with 6 mol dm^{-3} HCl at 333 K for 24 h, filtered off, and dried at 383 K for 24 h. Alkali and alkaline earth metal solutions were prepared by dissolving the

metal chlorides in double deionized water except for cesium sulfate. All reagents used were commercially available.

2.2 Apparatus

Powder X-ray diffraction patterns were measured with a Rigaku RINT 2000V diffractometer using CuK α radiation. Determination of the metal concentration was carried out with a Shimadzu AA-625 atomic absorption spectrophotometer or Varian Liberty Series II ICP-AES. The amounts of water and organic amine in the solids were analyzed with a Mac Science TG-DTA 2010T-R by heating in air to 1073 K at 10 K min⁻¹.

2.3 Ion exchange of HCa₂Nb₃O₁₀ with the metal ions

A 0.1 g sample of HCa₂Nb₃O₁₀ was equilibrated in a plastic bottle with 20 cm³ of metal solution at 333 K for 24 h. After centrifugation at 14500 rpm for 10 min, the solid was washed with water and followed by the treatment with 20 cm³ of 6 mol dm⁻³ HCl at 333 K for 24 h. The metal concentration in the supernatant after each centrifugation was measured.

2.4 Ion exchange of the amine-intercalated HCa₂Nb₃O₁₀ with the metal ions

In order to avoid the precipitation of carbonate salts, a series of experiments for the alkaline earth metal ions were carried out under an N₂ atmosphere in a glovebox. A 0.1 g sample of HCa₂Nb₃O₁₀ and appropriate amounts of an amine were added to a plastic bottle. After sealing, the mixture was allowed to stand at room temperature for 2 h. A 20 cm³ of 5 mmol dm⁻³ of the metal solution was then added and left for 24 h at 333 K with occasional shaking. In a similar manner as described above, preparation of the solutions for measurement was performed.

3 Results and Discussion

The XRD patterns of KCa₂Nb₃O₁₀ and HCa₂Nb₃O₁₀ dried at 383 K were in good agreement with those reported in the literature [1-3]. Although the wet HCa₂Nb₃O₁₀ contained 1.5 molecules of H₂O, conversion to the anhydrate at 363 K was confirmed by the TG-DTA measurements.

3.1 Ion-exchange of HCa₂Nb₃O₁₀ by the metal ions

The ion-exchange reaction is expressed as follows.

The percentages of ion-exchange, E , by Li⁺, Na⁺ and K⁺ were ca. 50% as shown in Fig. 1, but that by Cs⁺ was 30%. E for Ba²⁺ attained ca. 100 %, and the equilibrium concentrations of the ions remaining in solution were less than sub- μ mol dm⁻³.

In general, the order of the ion-exchange affinity of the alkali metal ions is Cs > K > Na > Li. This means that a significant hydration of the metal ion reduces their reactivity. But our experiment showed the order of Na = K > Li > Cs, and the affinity with Cs⁺ was the lowest. Any of alkali metal ions could not be substituted for protons completely. The use of alkali hydroxide solutions also did not enhance E . The incomplete ion-exchange of K⁺, Rb⁺ and Cs⁺ and a low reactivity of Cs⁺ were also pointed out by Jacobson et al.[3] As the high charge density of HCa₂Nb₃O₁₀ did not permit the delamination of the sheet, the metal ions would have difficulty in entering or diffusing in the rigid interlayer of HCa₂Nb₃O₁₀, particularly for Cs⁺ having the largest crystal ionic radius.

3.2 Intercalation of various amines into HCa₂Nb₃O₁₀

Fig.1 Ion-exchange of HCa₂Nb₃O₁₀ by the alkali and alkaline earth metal ions.

n-Propyl-, n-butyl-, n-pentyl-, n-hexyl-, n-octyl-, and n-decylamine intercalated into $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ with basal spacings increasing in this order. The basal spacing (h/nm) of the amine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ was related to the carbon number of the amine (n) in a linear fashion, i.e., $h = 0.243n + 1.45$. The coefficient 0.243 is greater than the C-C bond length (0.154 nm), but smaller than twice the bond length. If the amines are oriented at an angle to the layer, being parallel to each other, and form a bilayer in the interlayer, then the tilting angle can calculate as 53° .

With increasing mole ratio of the n-pentylamine to $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, the basal spacing had a constant value of 2.69 nm at mole ratios above 1.0 (Fig.2). From the TG-DTA measurement of the sample obtained at a mole ratio of 2, it was found that $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ incorporated 0.7 molecule of n-pentylamine after volatilization of the excess amine at room temperature.

The interlayer amine is fixed by the layer proton. The cross section of the amine (0.20 nm^2) is greater than the area of unit layer charge, and amines are likely to form a bilayer in the interlayer at the stoichiometric ratio. If the amines are oriented perpendicular to the sheet, there would be many vacancies in the interlayer. However, it is too narrow to accommodate another amine molecules. Therefore, excess amine did not intercalate and the interlayer amines were oriented at an angle to the sheet to form the bilayer.

The bilayer structure of the amine in the interlayer was confirmed by the XRD patterns of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, which was pre-intercalated with 3-fold n-pentylamine and treated with 20 cm^3 aqueous solutions of pH 3.4 – 11.3 for 24 h at 333 K.(Fig. 3)

3.3 Ion exchange of the amine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ with Sr^{2+}

We consider the ion-exchange reaction as follows.

Fig. 4 shows the effect of the n-alkylamine to $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ mole ratio on the percentage E of Sr^{2+} taken up by the oxide. The reactivity of Sr^{2+} was low in the case of the n-propylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, particularly at low amine ratios. The E values of n-pentyl-, n-hexyl-, and n-octylamine became constant at ratio above 2. On the other hand, the E value of n-decylamine showed the lowest value equal to that achieved with $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. A complete ion exchange of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ with Sr^{2+} was not achieved using any n-alkylamines. Jacobson et al. also tried the exchange of the n-butylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ by K^+ , but the result was an incomplete exchange.[3]

n-Alkylamines are more or less soluble in aqueous solution. n-Propylamine having a hydrophilic property can easily dissolve, as given by eq.3,

Therefore most part of Sr^{2+} reacted with not the amine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ but $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. Because the amount of n-propylamine that remained in the interlayer increased with the increasing amount of amine added in the solution, then, the percent E increased.

Fig.2 Basal spacings and percentage E of Sr^{2+} against the amine/ $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ mole ratio.

Fig.3 XRD patterns of the pentylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ after reaction with the solutions of various pH.

Fig.4 Effect of the molar ratio of n-alkylamines to $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ on E

The n-decylammonium ion in the interlayer was not exchanged with Sr^{2+} because the n-decylamine is highly stable. The release of n-decylamine from the interlayer into the solution was inhibited by the addition of excess amine to the solution.

The ion-exchange reaction in Eq. 2 progressed in the case of the n-pentyl-, n-hexyl-, and n-octylamines. In spite of the low solubility of these amines, they were exchanged with Sr^{2+} . The close stacking of the layers, namely a reduced interlayer distance, causes the layered compounds to become more stable. For hydrophobic amines, their transfer into the interlayer decreases their chemical potentials, but it causes an increase in the chemical potential of the interlayer due to an increased interlayer distance. An ion-exchange reaction will occur when the total chemical potential difference is negative. The total chemical potential difference is given by the changes in the chemical states of the reaction components: for the amines, solution species as monomers and aggregates or interlayer species as bilayer associates; for the interlayer, small or large interlayer distances, and for the metal ions, hydrated or dehydrated states.

3.4 Ion exchange of the n-pentylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ with Sr^{2+}

Fig. 2 shows that the increase in the n-pentylamine above 3 lead to a constant E higher than 70 %. As the intercalation of more than 1 molecule of amine did not occur, more than 2-fold n-pentylamine in aqueous solution needs to attain a higher E for the exchange of Sr^{2+} . The reaction of the n-pentylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ was faster than that of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ at 333 K (Fig. 5). The peak at 1.62 nm in the XRD pattern, which corresponds to $\text{Sr}_{1/2}\text{Ca}_2\text{Nb}_3\text{O}_{10}$, appeared within 1 h for the pre-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, and became higher with time and was accompanied by the decrease in the peak height at 2.69 nm. Moreover, the peak at 2.69 nm remained at least for 72 h.

3.5 Ion exchange of the n-pentylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ with metal ions

Fig. 6 shows the reactivity of the n-pentylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ with alkali and alkaline earth metal ions. The intercalation of n-pentylamine produced an increase in E for Cs^+ to the level of the other alkali metal ions. Moreover, Ca^{2+} could exchange on $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. More precise experiments for the bivalent metal cation with small ionic radius are now in progress.

Fig.5 Effect of the reaction time on E .

Fig.6 Ion-exchange of the n-pentylamine-intercalated $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ by the alkali and alkaline earth metal ions.

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