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Na-4-mica: Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} ion exchange

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Selective cation exchange for divalent transition metals of Cd, Ni, Co, Mn and Zn has been investigated with the high-charge-density sodium fluorophlogopite mica, Na-4-mica. The Na-4-mica was easily and economically prepared by the crystallization from a mixture of NaF, MgO and metakaolin, the latter serves as an inexpensive aluminosilicate source. Ion exchange isotherms for Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} were obtained at room temperature and the thermodynamic functions of the ion exchange equilibria were calculated. The $2Na^+ \rightarrow M^{2+}$ exchange with the Na-4-mica showed the following selectivity: $Zn^{2+} > Ni^{2+} \approx Co^{2+} \approx Cd^{2+} > Mn^{2+}$. The interlayer structure of the hydrated Na-4-mica with the open interlayer space in the range 12.1–13.9 Å was retained during the ion-exchange reaction, indicating the possibility of the reversible $2Na^+ \rightleftarrows M^{2+}$ exchange. The basic selective cation exchange studies of the high-charge-density ion exchanger are of relevance in recovery of metals from waste solution, and waste water treatment and disposal.

Introduction

Clay minerals and zeolites form two large families of natural cation exchangers. Zeolites have been used extensively by the industry for hydrocarbon separation, the intensive drying of liquids, industrial gases, air and natural gas, removal of sulfur compounds from petroleum, air separation, catalysis and cation separations by exchange.[1–3] Synthetic and naturally occurring clays have numerous applications including their extensive use in the decontamination and disposal of nuclear and other wastes.[4–6]

Studies on the ion exchange and adsorption of clay minerals had for many years been restricted to low-charge-density materials, such as the semectite and kaolinite types.[7] The ion exchange capacities are generally less than 100 milliequivalents (mequiv) per 100 g of dry clay. In recent years, synthetic clays with the ion exchange capacities on the order of 200–250 mequiv $(100\ g)^{-1}$ have been prepared and are now the subject of considerable interest.[8,9] However, in the last few years, a very highly charged sodium fluorophlogopite mica of the theoretical chemical composition $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$, informally named Na-4-mica, has extended the range of interesting clay minerals further.[10–14] The Na-4-mica has theoretical ion-exchange capacity of 468 mequiv $(100\ g)^{-1}$ on anhydrous basis. This synthetic clay was first discovered or synthesized by Gregorkiewitz *et al.* in 1974.[10] This mica contains an unusually large number of 4 interlayer cations per unit cell, which has never been observed before for micas. The Na-4-mica has the unique advantage among micas of becoming hydrated on contact with water or even in moist air at ambient conditions. This behavior arises from its unusually large number of interlayer cations with an offset layer stacking mode to accommodate them and this offset stacking allows the structure to expand from a dehydrated 9.81 Å to a hydrated 12.18 Å *c*-axis spacing to achieve a more thermodynamically stable interlayer structure. The open interlayer space with hydration enables cation exchange in the interlayers.

Preliminary cation exchange experiments were reported on millimeter-sized flakes which were synthesized by heating a mixture of ground augite, sodium fluoride and magnesium fluoride at 1080 °C.[10] One of the present authors and others, however, previously showed that a very fine and pure phase of the Na-4-mica could be prepared by a solution sol–gel processing using tetraethoxysilane, aluminum nitrate and magnesium nitrate.[14] They further showed that the materials thus produced had high ion-exchange selectivities for many divalent transition-metal ions and for strontium and barium, but not for other alkali-metal ions, magnesium and calcium.[12] A somewhat simplified procedure was later reported for the synthesis of this mineral using fumed silica as the silica source.[13] For large scale use of Na-4-mica in cation exchange separations for waste disposal or metal recovery, however, it is useful to have a more cost-effective synthetic process.

Recently, we have succeeded in the synthesis of Na-4-mica using calcined kaolinite (metakaolin) as a very cheap aluminosilicate source with the desired 1 : 1 Si to Al molar ratio.[14] Highly crystalline Na-4-mica can be easily and economically synthesized by the crystallization from the mixture of NaF, MgO and metakaolin at 850–890 °C for 24 h. The present work provides basic information on ion exchange for divalent transition metals of Cd, Ni, Co, Mn and Zn on the cost-effectively synthesized and highly charged ion exchanger, Na-4-mica.

Experimental

Preparation of Na-4-micas from metakaolin

Naturally occurring kaolinite has the desired 1 : 1 Si to Al molar ratio in its chemical composition $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ and serves as a good aluminosilicate source for the synthesis of a Na-4-mica. A poorly crystallized kaolinite (supplied by Georgia Kaolin Company), ultrafine MgO (supplied by Ube Industries, Ube, Japan) and NaF were the starting materials for the synthesis of Na-4-mica in the present work. The poorly crystallized kaolinite $[Al_2Si_2O_5(OH)_4 \cdot 0.08H_2O]$ was first calcined at 700 °C for 18 h to transform it to amorphous product (on heating to around 600 °C, kaolinite is completely dehydrated and loses its crystalline character) which is the so-called metakaolin $(Al_2Si_2O_7)$. The product of the metakaolin was cooled and stored in a desiccator over silica gel at room temperature. The water contents of metakaolin and ultrafine MgO were determined by thermal analysis using TG DTA 2010, Mac Science. Appropriate proportions of the ultrafine MgO and the metakaolin were mixed to obtain a stoichiometric composition of the mixture, which when reduced to pure

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oxides was exactly $3MgO–Al_2O_3–2SiO_2$. The mixture was mixed with an equal mass of NaF and transferred to a platinum vessel. It was heated for 6, 12 and 24 h at 890 °C in an air-atmosphere furnace. The resulting solid was ground up and washed in deionized water several times to remove the remaining NaF. The remaining low percentage of impurity phases that are not water soluble, which may include insoluble fluoride salts, were then removed with repeated washings with a saturated boric acid solution. Then, the solid was washed with 1 M NaCl solution three times to completely saturate all the exchange sites with Na^+. The product was again washed with deionized water and dried at 60 °C in an oven for 2–3 days. The Na-4-mica thus prepared was finally stored in a desiccator over silica gel at room temperature. Although as-synthesized Na-4-mica was anhydrous, the washed sample hydrated readily.

Powder X-ray diffraction (XRD) was carried out to check for phase purity, to determine the basal spacings of the Na-4-mica, and to monitor crystallinity using a Rigaku RAD-rA diffractometer with Cu-Kα radiation. Scanning electron microscopy (SEM) was used to determine particle size and shape. An ISI-DS 130 instrument was used for SEM. Water contents of the hydrated Na-4-mica were determined by thermal analysis to be $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot 2.6H_2O$.

Cation exchange isotherm determination

A 25 mg portion of the Na-4-mica (anhydrous basis) was equilibrated with 25 cm^3 of the mixed solution having different mole ratios of Na^+/M^{2+} (M = Cd, Ni, Co, Mn and Zn) with shaking at 25 °C for 4 weeks (in the previous study[11] of Na^+/Sr^{2+} exchange in the sol–gel processed Na-4-mica, it took almost 4 weeks to reach the equilibrium. This is because the Na-4-mica has a high layer charge and narrow interlayer basal spacing of about 12 Å). The total normality of the solutions was kept constant at 0.00468 N (Na^+/M^{2+} = 0.0–0.9) except for two solutions containing only M^{2+} without Na^+ in which the total normalities of 0.00585 and 0.00702 N were used. To avoid the hydrolysis of cations in the solution and the precipitation of metal hydroxides and oxides, the pH of the solutions was previously set to 3.0 by adding an HCl solution before the ion exchange reaction. The pH of the solution increased quickly to about 4–5 in a few minutes upon equilibration with mica. In the previous report,[14] ^{27}Al and ^{29}Si MAS NMR spectroscopy showed that the Na-4-mica synthesized from metakaolin is very close to ideal nearest neighbor distribution of Al and Si, indicating that the Na-4-mica phase did not contain a significant amount of amorphous phase. And the mica was previously washed with a saturated boric acid solution of about pH = 3.6 as mentioned before. Therefore, there is no possibility that these acidic conditions dissolve amorphous phase in the Na-4-mica sample and nullify the thermodynamic treatment. After equilibration, the supernatant solution was analyzed for the divalent metal ions by atomic emission spectroscopy (SpectraSpan III instrument). The amounts of metal ions exchanged or released by Na-4-mica were determined from the difference in the concentration between the sample solution and the reference. All these equilibria experiments were conducted in triplicate to check for reproducibility. The errors in the triplicates were about ± 5%. The theoretical cation-exchange capacity [468 mequiv (100 g)$^{-1}$ of anhydrous form] was used for representing the ion exchange isotherm.

Results and discussion

Synthesis of Na-4-micas from metakaolin

Fig. 1 shows XRD pattern of the resultant Na-4-mica prepared through the crystallization at 890 °C for 6 h from the mixture of NaF, ultrafine MgO, and metakaolin as the aluminosilicate source. That a Na-4-mica was synthesized was evident from the presence of the first order (001) reflection in the XRD pattern. A very strong peak observed at $d = 12.1$ Å corresponded to a basal spacing for hydrated form of Na-4-mica with single sheet of interlayer water. A peak observed at $d = 9.8$ Å was due to a basal spacing of the anhydrous form. Strong peaks observed at $d = 6.06$, 4.05 and 3.03 Å could be assigned to (002), (003) and (004) reflections of *c*-axis spacing of the hydrated form with single sheet of interlayer water. Specific characteristic peaks observed at $d = 4.21$, 3.26, and 2.63 were almost consistent with the limited powder XRD data reported previously for the hydrated Na-4-mica.[13] Similar XRD patterns were observed on the Na-4-mica prepared by the crystallization at the same temperature for 12 and 24 h.

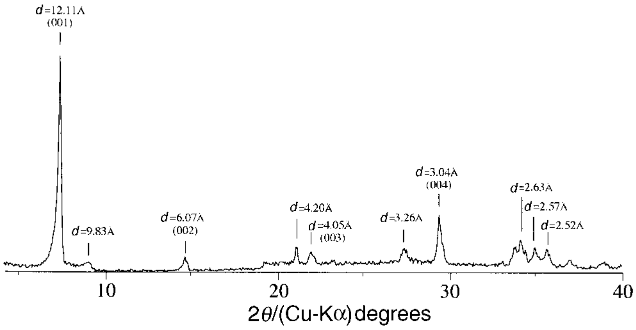

Fig. 1 XRD pattern of the Na-4-mica prepared by the crystallization at 890 °C for 6 h from the precursors of the mixture of NaF, MgO and metakaolin.

The change in crystal shape and size by the prolonged crystallization period was not clearly evident in Fig. 2. The SEM micrographs showed pseudo hexagonal crystallites. All of the Na-4-micas had large distribution in size, ranging from 0.5 to 5 µm. The average crystallite size of the Na-4-mica for the crystallization period = 24 h was *ca.* 2.5 µm.

These results indicate that the fine particles of highly crystallized Na-4-micas smaller than 5 µm were easily and economically synthesized by the crystallization from the mixture of NaF, MgO and metakaolin at 890 °C for 6–24 h.

Theory of cation exchange study

The mono–divalent ion exchange process in the Na-4-mica is represented by,

$$2\,\overline{Na}^+ + M^{2+} \rightleftarrows 2Na^+ + \overline{M}^{2+} \tag{1}$$

where the bar above the symbols represents the ion exchanger phase. The thermodynamic equilibrium constant, *K*, of the reversible ion-exchange reaction is defined by,

$$K = \frac{[Na^+]^2 \overline{X}_M \gamma_{Na}{}^2 f_M}{[M^{2+}] \overline{X}_{Na}{}^2 \gamma_M f_{Na}{}^2} \tag{2}$$

where $[Na^+]$ and $[M^{n+}]$ are molalities of the ions in solution, γ_i and f_i are activity coefficients in the solution phase and in the ion-exchanger phase, respectively. The standard states are taken for the ion-exchanger phase as the exchanger is in its pure Na^+ form and pure M^{2+} form, and the activity coefficients, f_{Na} and f_M, are chosen as unity when the exchanger is at the standard state of the Na^+ form and the M^{2+} form, respectively. $\overline{X}_i$ is an equivalent fraction of ion *i* in the ion-exchanger phase, defined by

$$\overline{X}_{Na} = \frac{[\overline{Na}^+]}{2[\overline{M}^{2+}] + [\overline{Na}^+]}, \quad \overline{X}_M = \frac{2[\overline{M}^{2+}]}{2[\overline{M}^{2+}] + [\overline{Na}^+]} \tag{3}$$

The molarities $[Na^+]$ and $[M^{2+}]$ can be replaced by the

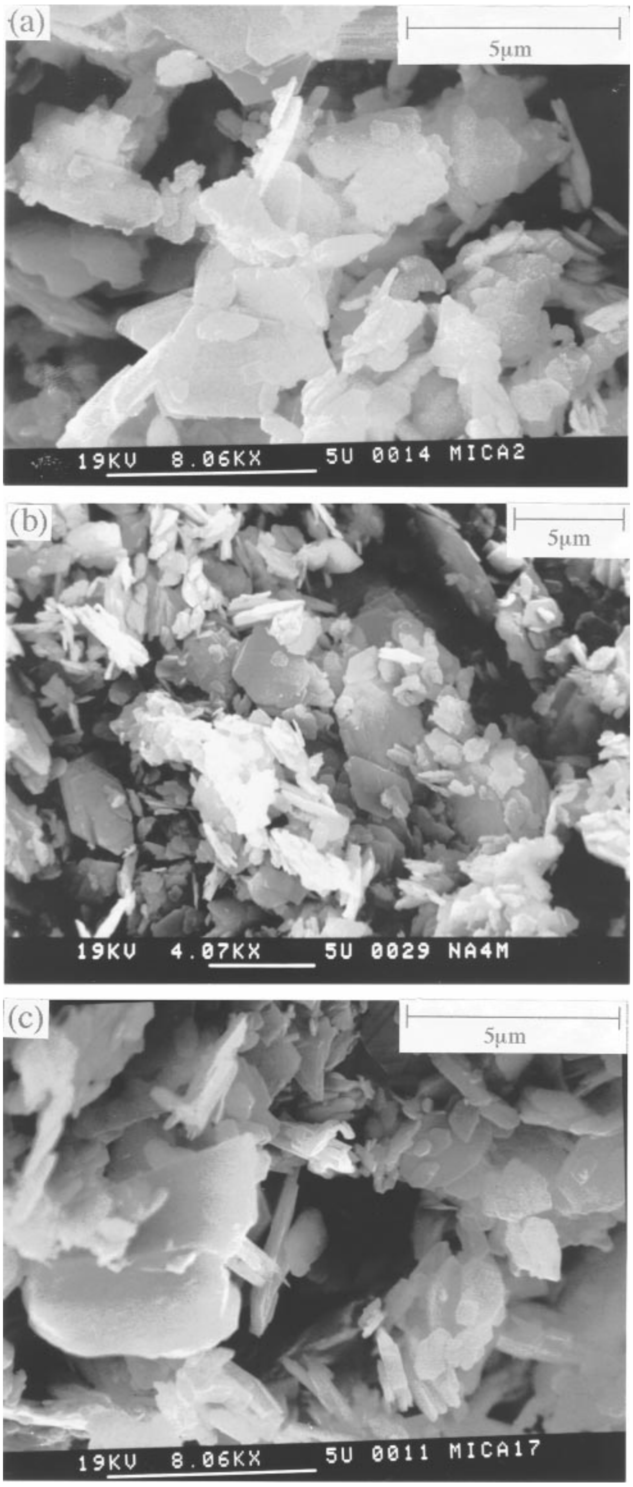

Fig. 2 SEM micrographs of the Na-4-micas prepared by different crystallization periods of (a) 24 h, (b) 12 h and (c) 6 h at 890 °C from the precursors of the mixture of NaF, MgO and metakaolin.

equivalent fractions of the ions in the solution (X_i):

$$X_{\mathrm{Na}}=\frac{[\mathrm{Na}^+]}{2[\mathrm{M}^{2+}]+[\mathrm{Na}^+]},\ X_{\mathrm{M}}=\frac{2[\mathrm{M}^{2+}]}{2[\mathrm{M}^{2+}]+[\mathrm{Na}^+]} \qquad (4)$$

$$[\mathrm{Na}^+]+2[\mathrm{M}^{2+}]=\mathrm{TN} \qquad (5)$$

where TN represents the total normality of the solution. Using a corrected selectivity coefficient, $K^{\mathrm{M}}_{\mathrm{Na}}$, the thermodynamic equilibrium constant is rewritten as,[15]

$$K^{\mathrm{M}}_{\mathrm{Na}}=\frac{X_{\mathrm{Na}}{}^2\overline{X}_{\mathrm{M}}\gamma_{\mathrm{Na}}{}^2}{X_{\mathrm{M}}\overline{X}_{\mathrm{Na}}{}^2\gamma_{\mathrm{M}}}[2(\mathrm{TN})] \qquad (6)$$

where

$$K=K^{\mathrm{M}}_{\mathrm{Na}}\frac{f_{\mathrm{M}}}{f_{\mathrm{Na}}{}^2} \qquad (7)$$

When the total normality, $\mathrm{TN}=[\mathrm{Na}^+]+2[\mathrm{M}^{2+}]$, is lower than 0.01 N, $\gamma^2_{\mathrm{Na}}/\gamma_{\mathrm{M}}$ will be close to unity. As shown by eqn. (7), the corrected selectivity coefficient is dependent on the total normality.

The corrected selectivity coefficient larger than unity ($\ln K^{\mathrm{M}}_{\mathrm{Na}}>0$) indicates selectivity for the ion M^{2+}.[16] Na^+ ions are more preferred if $K^{\mathrm{M}}_{\mathrm{Na}}$ is smaller than unity ($\ln K^{\mathrm{M}}_{\mathrm{Na}}<0$). When $K^{\mathrm{M}}_{\mathrm{Na}}$ is equal to unity ($\ln K^{\mathrm{M}}_{\mathrm{Na}}=0$), no preference between these ions is indicated.

The corrected selectivity coefficient, $K^{\mathrm{M}}_{\mathrm{Na}}$, is related to the Kielland coefficient as given below. Kielland plots show the details of the ion exchange selectivity as a function of the equivalent fraction, $\overline{X}_{\mathrm{M}}$.[17]

$$\log K^{\mathrm{M}}_{\mathrm{Na}}=\sum_{m=1}(m+1)C_m\overline{X}_{\mathrm{M}}{}^m+\log(K^{\mathrm{M}}_{\mathrm{Na}})_{\overline{X}_{\mathrm{M}}\to 0} \qquad (8)$$

where the coefficient, C_m, is called generalized Kielland coefficient. These plots often give linear relationships with a slope $2C_1$, in which case eqn. (8) can become

$$\log K^{\mathrm{M}}_{\mathrm{Na}}=2C_1\ \overline{X}_{\mathrm{M}}+\ \log(K^{\mathrm{M}}_{\mathrm{Na}})_{\overline{X}_{\mathrm{M}}\to 0} \qquad (9)$$

If the Gibbs–Duhem equation is applied to the ion-exchange reaction, the thermodynamic equilibrium constant, K, is given by the integration of Kielland plot from $\overline{X}_{\mathrm{M}}=0$ to $\overline{X}_{\mathrm{M}}=1$.[18,19]

$$\ln K=(Z_{\mathrm{Na}}-Z_{\mathrm{M}})+\int_0^1\ln K^{\mathrm{M}}_{\mathrm{Na}}\mathrm{d}\overline{\mathrm{X}}_{\mathrm{M}}+\Delta \qquad (10)$$

Here, Z_{Na} and Z_{M} are the number of charges on the Na^+ and M^{2+}. The third term on the right, Δ, is negligible when compared with experimental accuracy in measuring the equilibrium.[15] Eqn. (9) and (10) are combined to give the thermodynamic constant K:

$$\ln K=(Z_{\mathrm{Na}}-Z_{\mathrm{M}})+2.303C_1+\ln(K^{\mathrm{M}}_{\mathrm{Na}})_{\overline{X}_{\mathrm{M}}\to 0} \qquad (11)$$

Thus, the thermodynamic equilibrium constant is determined by the valences of the exchanged and exchanging cations, the generalized Kielland coefficient C_1 and the intercept of Kielland plot, $(K^{\mathrm{M}}_{\mathrm{Na}})_{\overline{X}_{\mathrm{M}}\to 0}$.

The Gibbs standard free energy change ΔG° can be calculated by,

$$\Delta G^\circ=-RT\ln K \qquad (12)$$

The corrected selectivity coefficient when C_1 value is zero can be used as an index of the ion-exchange selectivity for ‘ideal’ exchange with no steric hindrance.[20,21]

$$\ln K_{\mathrm{ideal}}=(Z_{\mathrm{Na}}-Z_{\mathrm{M}})+\ln(K^{\mathrm{M}}_{\mathrm{Na}})_{\overline{X}_{\mathrm{M}}\to 0} \qquad (13)$$

The Gibbs standard free energy change for ‘ideal exchange’ is given by,

$$\Delta G^0{}_{\mathrm{ideal}}=-RT\ln K_{\mathrm{ideal}} \qquad (14)$$

$2\mathrm{Na}^+\to\mathrm{Cd}^{2+}$ exchange with the Na-4-micas

The $2\mathrm{Na}^+\to\mathrm{Cd}^{2+}$ exchange reaction was performed with two different Na-4-micas prepared by different crystallization periods = 6 and 24 h at 890 °C. The isotherms are shown in Fig. 3 as the equivalent fraction of the divalent metal in the Na-4-mica phase against the equivalent cation fraction in the solution. Almost the same isotherms were obtained for the two different Na-4-micas. The cadmium-exchange isotherm steeply increased in the initial stage of $X_{\mathrm{Cd}}<0.07$, and then increased with a very gentle slope. It seemed to be a sigmoid-type isotherm which is often observed in the ion-exchange isotherm of inorganic ion-exchange materials.[16] From the isotherm, its cadmium exchange capacity was determined to

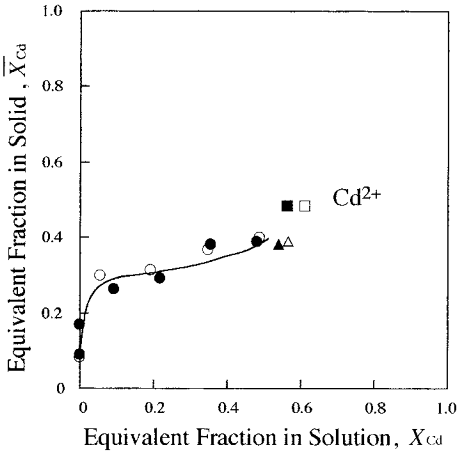

Fig. 3 Cation exchange isotherm for $2Na^+ \rightarrow Cd^{2+}$ exchange on the Na-4-mica. Open symbols are for the Na-4-mica sample prepared by the crystallization period of 6 h and solid symbols for that by the crystallization period of 24 h. Total normalities of 0.00468 N (circles), 0.00585 N (triangles), and 0.00702 N (squares) were used.

be 229 mequiv $(100\ g)^{-1}$ which is 49% of the theoretical exchange capacity of Na-4-mica. Fig. 4 shows the Kielland plots for the $2Na^+ \rightarrow Cd^{2+}$ exchange. The Kielland plots gave a linear relation, indicating that the cadmium-exchange reaction proceeds on one kind of exchangeable site of Na-4-mica, which is interlayer Na^+ site. The plots for the different Na-4-micas were almost distributed closely to the same straight line (solid line in Fig. 4), indicating that there is not much difference in the thermodynamic properties of the Na-4-mica for cation exchange caused by the difference in the crystallization period of 6 and 24 h. The dotted line indicates that the corrected selectivity coefficient is equal to unity. At $\overline{X}_{Cd} < 0.13$, the Kielland plots fall above the dotted line, indicating selectivity for Cd^{2+}. In the very initial stage of the $2Na^+ \rightarrow Cd^{2+}$ exchange reaction, Cd^{2+} ions are preferred over Na^+. At $\overline{X}_{Cd} > 0.13$, however, Na^+ ions are more preferred over Cd^{2+}.

One of the present authors previously reported the $2Na^+ \rightarrow Sr^{2+}$ exchange with the Na-4-mica prepared by a solution sol–gel processing using tetraethoxysilane, aluminium nitrate and magnesium nitrate.[11] The strontium-exchange isotherm flattened out at $\overline{X}_{Sr} > 0.4$. The strontium-exchange capacity was 47% of the theoretical exchange capacity of Na-4-mica. In the strontium exchange, the interlayer spacing collapsed considerably when about half of the exchange sites were occupied by strontium, as confirmed by powder X-ray diffraction which showed that *c*-axis decreased from 12.2 to 10.2 Å and that the peak for the (001) reflection became very weak and broadened. Since interlayer spacing collapsed, the reversible exchange $2Na^+ \rightleftarrows Sr^{2+}$ can not occur with the Na-4-mica. For the cadmium exchange, however, the interlayer spacing was retained as shown in Fig. 5. The XRD peak for (001) reflection remained strong for the cadmium exchanged Na-4-mica with $\overline{X}_{Cd} \leq 0.48$. The basal spacings in the range 12.1–13.8 Å indicate that the interlayer structure of the hydrated Na-4-mica was retained during the cadmium exchange as discussed later. Thus, a reversible $2Na^+ \rightleftarrows Cd^{2+}$ exchange will be possible in the open interlayer space of the hydrated Na-4-mica. The basal spacings of the cadmium-exchanged Na-4-micas with $\overline{X}_{Cd} = 0.39$ and 0.49 were $d = 12.2$ and 12.1 Å which correspond to a structure of single sheet of interlayer water. For the cadmium-exchanged Na-4-mica with $\overline{X}_{Cd} = 0.19$, however, the basal spacing increased to 13.5 Å, which may be due to the formation of a structure containing double sheets of interlayer water. The layer spacing of 13.82 Å is reported on vermiculite prepared by progressive removal of interlayer water from the normal vermiculite with double sheets of interlayer water.[7] On the dehydration of the normal 14.36 Å phase, a 13.82 Å phase is first formed corresponding to a structure containing double sheets of interlayer water with an arrangement different from that in the 14.36 Å phase. A similar structure of double sheets of interlayer was apparently formed in the Na-4-mica when a small amount of interlayer Na^+ was exchanged by Cd^{2+}. The dehydration of interlayer water was caused when the $2Na^+ \rightarrow Cd^{2+}$ exchange

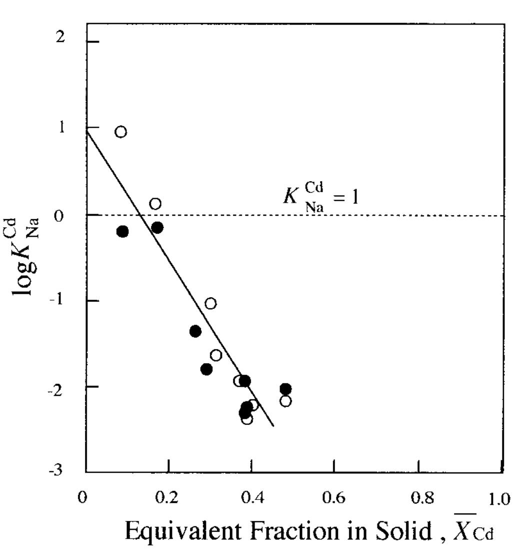

Fig. 4 Kielland plot for $2Na^+ \rightarrow Cd^{2+}$ exchange on the Na-4-mica. Open circles are for the Na-4-mica sample prepared by the crystallization period of 6 h and solid circles that by the crystallization period of 24 h.

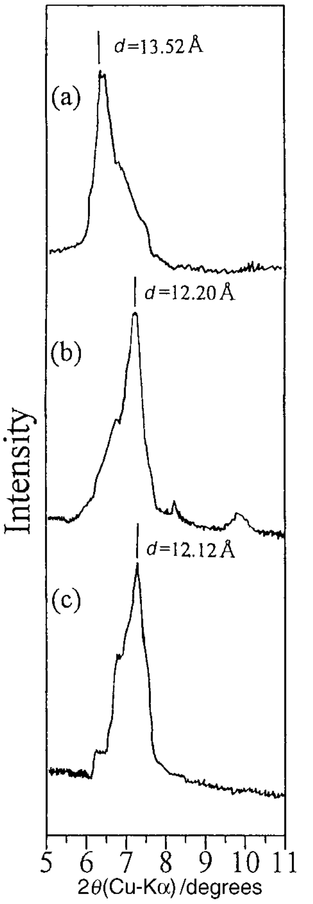

Fig. 5 Change in XRD peak for (001) reflection of cadmium-exchanged Na-4-mica. The equivalent fractions of cadmium in the Na-4-micas were $\overline{X}_{Cd}$ = (a) 0.19, (b) 0.39 and (c) 0.49.

proceeded to some extent and the double sheets of interlayer water reverted to single sheet.

$2Na^+ \rightarrow Ni^{2+}$, Co^{2+}, Mn^{2+} and Zn^{2+} exchange with the Na-4-mica

The $2Na^+ \rightarrow M^{2+}$ exchange reactions were performed with the Na-4-mica prepared by the crystallization period = 12 h at 890 °C for Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+}. The isotherms are shown in Fig. 6. The isotherms all appeared to be sigmoid-type isotherms like the cadmium exchange isotherm. Especially, the $2Na^+ \rightarrow Zn^{2+}$ exchange reaction very readily proceeded up to *ca.* $\overline{X}_{Zn} = 0.4$, indicating much higher selectivity for Zn^{2+} ion than for others. From the isotherm, its zinc exchange capacity was determined to be 295 mequiv $(100\ g)^{-1}$ which is 63% of the theoretical exchange capacity of Na-4-mica. The ion exchange capacities for Ni^{2+}, Co^{2+} and Mn^{2+} are 42, 47 and 39% of the theoretical exchange capacity of Na-4-mica, respectively (Table 1). Fig. 7 shows the Kielland plots for the zinc, cobalt, nickel and manganese exchange. These Kielland plots gave straight lines, indicating that the $2Na^+ \rightarrow M^{2+}$ exchange reactions proceeded on one kind of exchangeable site of Na-4-mica, which is interlayer Na^+ site. From these Kielland plots, Zn^{2+} and Co^{2+} ions can be deduced to be more preferred over Na^+ ions at $\overline{X}_{Zn} < 0.32$ and $\overline{X}_{Co} < 0.14$, respectively. For Mn^{2+} and Ni^{2+}, Na^+ ions are more preferred almost throughout the $2Na^+ \rightarrow M^{2+}$ exchange reaction.

The XRD peak for (001) reflection remained strong for the divalent metal exchanged Na-4-micas and the basal spacings ranged from 12.1 to 13.9 Å (Fig. 8), indicating that the interlayer structure of the hydrated Na-4-mica was retained for the $2Na^+ \rightarrow Ni^{2+}$, Co^{2+}, Mn^{2+} and Zn^{2+} exchange. The reversible $2Na^+ \rightleftarrows M^{2+}$ exchange will be possible in the open interlayer structure of the hydrated Na-4-mica for Ni^{2+}, Co^{2+} Mn^{2+} and Zn^{2+}. In manganese and zinc exchanged Na-4-micas, the (001) peak was broadened. For the zinc exchanged Na-4-mica, the peak broadening may be due to the coexistence of structures of single sheet and double sheets of interlayer water in the divalent metal exchanged mica. The structures of double interlayer water sheets with different arrangements may coexist in the manganese exchanged Na-4-mica in which the basal spacings of 13.9 and 13.5 Å were both observed.

Thermodynamic functions and the selectivities for $2Na^+ \rightarrow M^{2+}$ exchange with the Na-4-mica

The Kielland coefficient C_1 and $\log(K^M_{Na})_{\overline{X}_M \rightarrow 0}$ are obtained from the Kielland plots of Fig. 4 and 7 (Table 1). From the eqn. (11)–(14) using C_1 and $\log(K^M_{Na})_{\overline{X}_M \rightarrow 0}$, ΔG°_{ideal}, and ΔG° for the $2Na^+ \rightarrow M^{2+}$ exchange reactions were estimated and listed in Table 1. The ΔG° for Zn^{2+} was the smallest and those for Ni^{2+}, Co^{2+} and Cd^{2+} were almost the same. The order of the selectivity is $Zn^{2+} > Cd^{2+} \simeq Ni^{2+} \simeq Co^{2+} > Mn^{2+}$. From the values of ΔG°_{ideal}, the order of the ion-exchange selectivity for 'ideal' exchange with no steric hindrance can be

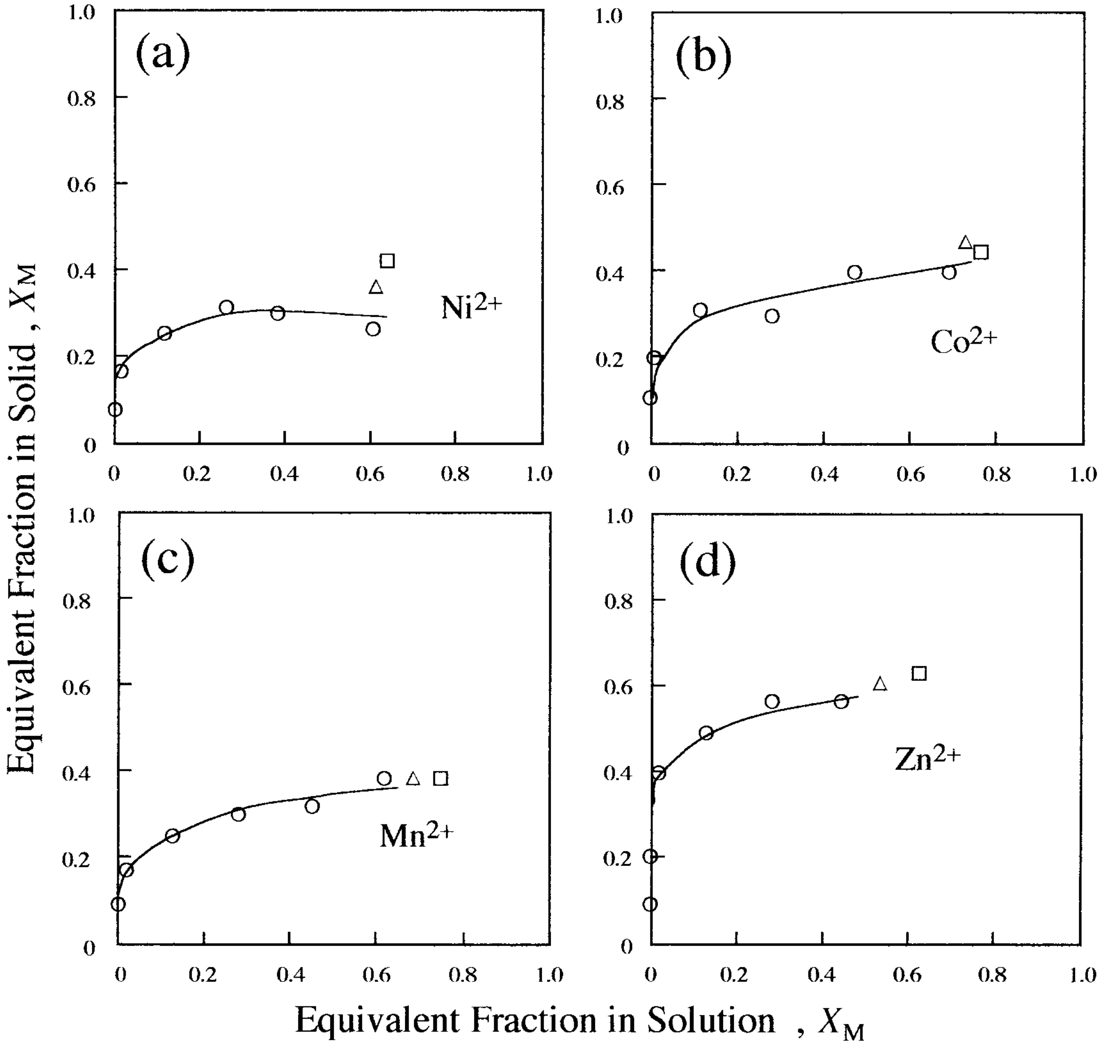

Fig. 6 Cation exchange isotherm for $2Na^+ \rightarrow M^{2+}$ (M = Ni, Co, Mn, and Zn) exchange on the Na-4-mica. The Na-4-mica sample prepared by the crystallization period of 12 h at 890 °C was used. Total normalities used were 0.00468 N (circles), 0.00585 N (triangles), and 0.00702 N (squares).

Table 1 Cation exchange capacities (CECs) and thermodynamic data for $2Na^+ \rightarrow M^{2+}$ exchange on Na-4-mica at room temperature

Cation	CEC for M^{2+} mequiv $(100\ g)^{-1}$	$\log (K^M_{Na})_{\bar{X}_M \rightarrow 0}$	C_1	$\Delta G°_{ideal}$/ kJ $(equiv)^{-1}$	$\Delta G°$/ kJ $(equiv)^{-1}$
Cd^{2+}	229	0.955	−3.77	−1.48	9.26
Zn^{2+}	295	1.75	−2.81	−3.76	4.26
Ni^{2+}	197	−0.152	−2.93	1.67	10.0
Co^{2+}	220	1.24	−4.54	−2.29	10.7
Mn^{2+}	183	0.225	−3.82	0.60	11.5

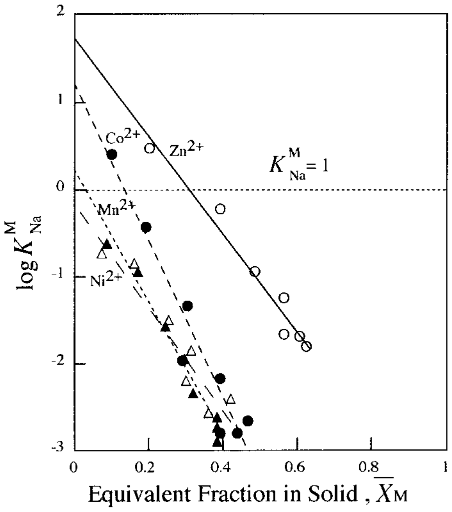

Fig. 7 Kielland plots for $2Na^+ \rightarrow M^{2+}$ (M = Ni, Co, Mn, and Zn) exchange on the Na-4-mica. The Na-4-mica sample prepared by the crystallization period of 12 h at 890 °C was used.

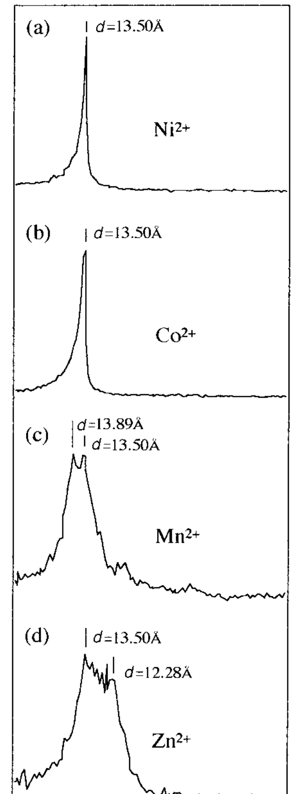

Fig. 8 XRD peak for (001) reflection of the divalent metal exchanged Na-4-mica for $2Na^+ \rightarrow M^{2+}$ (M = Ni, Co, Mn, and Zn) exchange. The equivalent fractions of divalent metal ion in the Na-4-micas were (a) $\bar{X}_{Ni} = 0.27$, (b) $\bar{X}_{Co} = 0.40$, (c) $\bar{X}_{Mn} = 0.39$ and (d) $\bar{X}_{Zn} = 0.57$.

determined to be $Zn^{2+} > Co^{2+} > Cd^{2+} > Mn^{2+} > Ni^{2+}$. With no steric hindrance for the exchanging cation, the selectivity for Co^{2+} is higher than that for Ni^{2+} or Cd^{2+}. The generalized Kielland and coefficient, C_1, is related to the energy term for the steric limitation or jumping barrier for the exchanging ions in the interlayer.[22,23] Generally, the C_1 value is negative, and the energy term for the steric limitation is larger as the $|C_1|$ value is larger. From the values of $|C_1|$, the energy term for the steric limitation increases in the order of $Co^{2+} > Cd^{2+} \approx Mn^{2+} > Ni^{2+} \approx Zn^{2+}$. We could not clearly explain the reasons for the orders of the selectivities for cations, for example, from the hydrated radii or effective ionic radii of the cations in the present work. Further experimental data for many other divalent cations with different ionic radii are required to find the relation between its selectivity and the radii of cations.

Conclusions

Highly crystalline Na-4-mica could be easily and economically synthesized by the crystallization from the mixture of NaF, MgO and metakaolin and the ion exchange reaction with the Na-4-mica was demonstrated for divalent transition metals of Cd, Ni, Co, Mn and Zn at room temperature. Zn^{2+} was found to be the most selective among these five cations on Na-4-mica. From the Kielland plots, Zn^{2+}, Co^{2+} and Cd^{2+} ions were found to be more selective than Na^+ ions at $\bar{X}_{Zn} < 0.32$, $\bar{X}_{Co} < 0.14$ and $\bar{X}_{Cd} < 13$, respectively, while Na^+ ions were selective almost throughout the $2Na^+ \rightarrow Mn^{2+}$ or Ni^{2+} exchange reaction. The ion-exchange selectivity for 'ideal' exchange with no steric hindrance increased in the order of $Zn^{2+} > Co^{2+} > Cd^{2+} > Mn^{2+} > Ni^{2+}$. The selectivity for 'ideal' exchange with no steric hindrance is the highest and the energy term for steric limitation is the smallest for Zn^{2+}, resulting in the highly selective $2Na^+ \rightarrow Zn^{2+}$ exchange. From $\Delta G°$ for the ion exchange reactions, estimated using Gibbs–Duhem equation, the order of the selectivity for $2Na^+ \rightarrow M^{2+}$ exchange is determined to be $Zn^{2+} > Ni^{2+} \approx Co^{2+} \approx Cd^{2+} > Mn^{2+}$. The interlayer structure of the hydrated Na-4-mica was retained during the ion-exchange reaction, indicating that the reversible $2Na^+ \rightleftarrows M^{2+}$ exchange will be possible in the open interlayer space of 12.1–13.9 Å. These studies are of relevance in metals recovery by separation from solubilized ores and waste solution and waste water treatment.

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