Nitrate Ion-sieve Properties of Layered Double Hydroxides

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Layered double hydroxides (LDHs) with different kinds of metals in the brucite layer were prepared and their anion exchange properties were studied batchwise. A nitrate ion-sieve property was observed for LDHs depending on the basal spacing of the brucite layer. The distribution coefficient of nitrate ion was a maximum on the Ni–Fe type LDHs having a basal spacing of 0.81 nm.

Layered double hydroxides (LDHs) consist of stacked mixed-valence brucite layers, $(M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2)^{x+}$, where M^{2+} and M^{3+} are divalent and trivalent metals, respectively, separated by anionic species and water molecules, $(A^{q-}{}_{x/q}\ nH_2O)$, where A is the interlayer anion. The interlayer anions are exchangeable with other different kinds of anions, halide ions, oxoanions, or organic anions. LDHs are attractive in the field of green sustainable chemistry, since they are useful for the removal of harmful oxoanions (phosphate, nitrate ions, etc.) from aqueous solutions. There have been many studies on the adsorptive properties of LDHs for various anions,[1,2] but there have been relatively few studies on the anion selectivity mechanism of LDHs. Ookubo et al. have reported a high selectivity for phosphate ions on Mg–Al type LDHs. Zhang et al. have reported a high selectivity for NO_3^- on Mg–Fe type LDHs.[3] However, it is not clear why LDHs show different selectivity sequences depending on the skeletal metal species.

In the present paper, we prepared LDHs with different kinds of metals; Li^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, and Fe^{3+} in the brucite layer, and their anion exchange properties were studied by measurements of distribution coefficients (K_ds) and exchange capacities. The NO_3^- ion-sieve property was observed depending on the basal spacing of the brucite layer. To the best of our knowledge, this is the first report that shows the anion-sieve property although there have been many reports on the ion-sieve property for alkali metal cations.[4]

LDHs with different metals (Mg–Al, Mg–Fe, Ni–Fe, Co–Fe, and Li–Al) were prepared by a coprecipitation method using metal chlorides as the starting materials.[5] The precipitates were washed with water and dried at 323 K. The metal contents of each LDHs were determined by atomic absorption spectrometry or ACP–AES after it was dissolved in a HCl solution. The water content was determined from the weight loss by heating at 473 K in the TG–DTA curve.

Distribution coefficients (K_ds) of NO_3^-, CO_3^{2-}, HPO_4^{2-}, and SO_4^{2-} were determined batchwise using a mixed solution of $NaNO_3$, Na_2CO_3, NaH_2PO_4, and Na_2SO_4 (1 mM each). LDHs (0.10 g) were added to the mixed solution (10 cm^3) and shaken for 3 days at 298 K. After adsorption, the concentration of each anion in the supernatant solution was determined by ion chromatography (Shimazu, LC-10Ai). Anion uptakes were calculated by the decrease of each anion concentration relative to its initial concentration. The K_d values were calculated using the following equation; K_d (cm^3/g) = anion uptake (mg/g)/equilibrium anion concentration (mg/cm^3). The NO_3^- exchanged LDHs were obtained by treating them with a 0.1 M $NaNO_3$ solution (100 cm^3) for 3 days at 298 K. The solids were separated by filtration and their NO_3^- contents were determined by ion chromatography after the solids were dissolved in a 18 M H_2SO_4 solution. The XRD analyses were carried out for the starting LDHs and the NO_3^--exchanged samples.

The chemical compositions of LDHs obtained are given in Table 1, where only Cl^- ions are assumed to exist as interlayer anions. The theoretical exchange capacities could be calculated from the chemical compositions as 3.7, 2.2, 1.9, 2.2, and 5.4 mmol/g for Mg–Al, Mg–Fe, Ni–Fe, Co–Fe and Li–Al types, respectively. The Li–Al type has a relatively large exchange capacity compared to the other four samples. XRD patterns showed a typical LDHs structure with reflections of basal planes (003), (006), and (009), as is shown in Figure 1. The basal spacing varies with the metal species in the brucite layer (Table 1).

The K_d values of anions on LDHs are summarized in Table 1. Markedly high $K_d(CO_3^{2-})$ values are observed for all the samples, while the $K_d(NO_3^-)$, $K_d(HPO_4^{2-})$, and $K_d(SO_4^{2-})$ values vary with the metal species in the brucite lay-

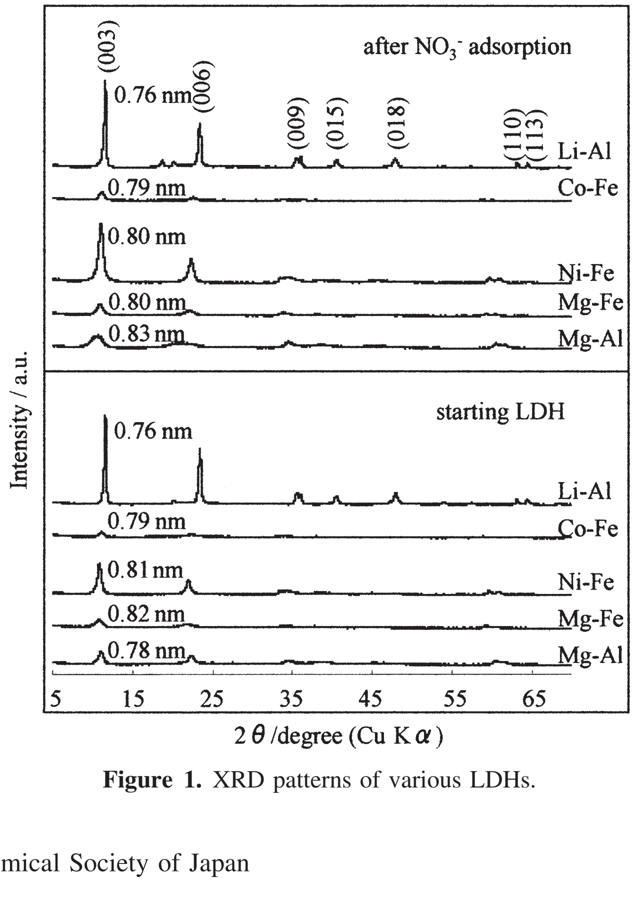

Figure 1. XRD patterns of various LDHs.

Table 1. Chemical composition, basal spacing and K_d of various LDHs

Sample	Chemical composition	Basal spacing /nm	NO_3^- exchange capacity/mmol·g^{-1}	Distribution coefficient/cm^3·g^{-1}				
				pH	CO_3^{2-}	NO_3^-	HPO_4^{2-}	SO_4^{2-}
Mg–Al	$(Mg_{0.71}Al_{0.29}(OH)_2)(Cl_{0.29}\cdot 0.59H_2O)$	0.78	1.5	6.43	$>10^4$	16	$>10^4$	$>10^4$
Mg–Fe	$(Mg_{0.84}Fe_{0.16}(OH)_2)(Cl_{0.16}\cdot 0.68H_2O)$	0.82	1.4	9.93	$>10^4$	462	$>10^4$	192
Ni–Fe	$(Ni_{0.79}Fe_{0.21}(OH)_2)(Cl_{0.21}\cdot 0.63H_2O)$	0.81	1.3	7.32	$>10^4$	$>10^4$	318	146
Co–Fe	$(Co_{0.74}Fe_{0.26}(OH)_2)(Cl_{0.26}\cdot 0.80H_2O)$	0.79	0.7	7.62	$>10^4$	10	287	5
Li–Al	$(Li_{0.31}Al_{0.69}(OH)_2)(Cl_{0.38}\cdot 0.12H_2O)$	0.76	0.3	7.33	$>10^4$	20	792	40

er. The LDHs (Mg–Al and Mg–Fe types) with Mg atoms show a markedly high selectivity for HPO_4^{2-} ions. This suggests a strong interaction between the skeletal Mg atoms and HPO_4^{2-} ions. Since Mg^{2+} and phosphate ions form a stable and slightly soluble magnesium phosphate, we can expect a strong chemical bonding between skeletal Mg and HPO_4^{2-}. The $K_d(NO_3^-)$ value is maximal for the Ni–Fe type LDHs. Unlike HPO_4^{2-}, NO_3^- ions cannot form slightly soluble compounds with the skeletal metal atoms. Therefore, it is reasonable to think that the selectivity of NO_3^- is controlled mainly by physical, but not chemical parameters. The $K_d(NO_3^-)$ is plotted as a function of basal spacing in Figure 2. It is maximal around the basal spacing of 0.81 nm, which corresponds to an interlayer distance of 0.33 nm, assuming the thickness of the brucite layer to be 0.48 nm, as in the literature.[6] The interlayer distance is close to the ionic size (0.33 nm)[7] of NO_3^- ions, suggesting that the basal spacing (0.81 nm) of the Ni–Fe type is advantageous for fixing NO_3^- ions in the interlayer from a steric standpoint. This suggests that the selectivity of NO_3^- on LDHs is largely influenced by the ion-sieve produced by the spatial limits between the brucite layer.

XRD studies of NO_3^--exchanged LDHs were performed in order to study the nitrate ion-sieve property in more detail. The NO_3^- exchange capacities were 1.5, 1.4, 1.3, 0.7, and 0.3 mmol/g, for Mg–Al, Mg–Fe, Ni–Fe, Co–Fe, and Li–Al types, respectively. The exchange reaction progresses topotactically maintaining the layered structure; the XRD patterns of LDHs after the NO_3^- exchange are the same as those of the starting LDHs (Figure 1, top). Some of the LDHs change the basal spacings by NO_3^- loading. The basal spacing of Mg–Fe and Ni–Fe type LDHs decrease slightly to 0.80 nm by the overall NO_3^- exchange. Since the NO_3^- ion has a triangular form, the decrease of basal spacing suggests that the NO_3^- ions in the interlayer are arranged parallel to the brucite layer, as was proposed by Cavani et al. for NO_3^- type LDHs.[8] The basal spacing of Mg–Al type increases from 0.78 to 0.83 nm by NO_3^- loading. Mg–Al type characteristically has low selectivity but a large exchange capacity for NO_3^- ions. These results suggest that the brucite layer of the Mg–Al type can expand more easily than the other LDHs; therefore, it may be able to exchange a large amount of guest anions although less selectively. On the other hand, since Ni–Fe and Mg–Fe types have a less expansive character, they may have a strong ion-sieve effect for anions, especially for NO_3^-. The preliminary adsorptive study has shown that Ni–Fe type has an effective NO_3^- uptake from seawater.

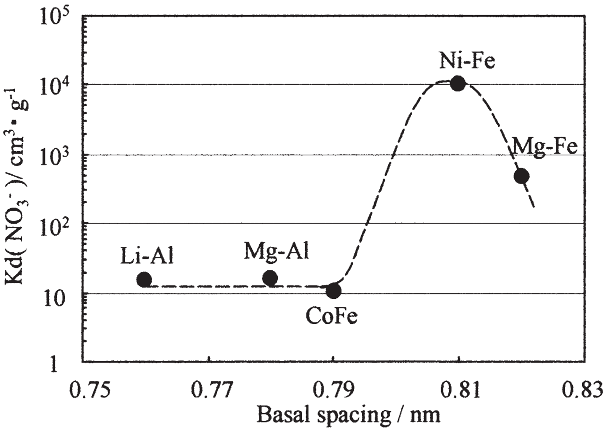

Figure 2. Relationship between distribution coefficient (K_d) of NO_3^- and basal spacing for various LDHs.

In conclusion, Ni–Fe-type LDH shows a nitrate ion-sieve property owing to its suitable interlayer spacing and suitable charge density for fixing NO_3^- ions. The "ion-sieve effect" is beneficial to the development of a novel adsorbent for selective removal of harmful oxoanions including nitrate ions.

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