PROPERTIES OF HEXACYANOCOBALTATE(III)-EXCHANGED HYDROTALCITE-LIKE MINERALS

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Abstract—Hydrotalcite-like minerals, containing Mg^{2+}-Al^{3+}-X^{n-} (X^{n-} = NO_3^-, Cl^-, SO_4^{2-}, or CrO_4^{2-}), Zn^{2+}-Al^{3+}-NO_3^-, or Zn^{2+}-Cr^{3+}-NO_3^- ions, were intercalated with $Co(CN)_6^{3-}$ by an anion exchange method. For most of the minerals examined, the degree of anion exchange was 79–90%. X-ray powder diffraction patterns of the ion-exchanged samples revealed two peaks at about 8° and 11°2θ (CuKα radiation) attributable to reflections from expanded and non-expanded interlayers, respectively. The intensity of the peak at about 8°2θ was a linear function of the degree of anion exchange. The amount of hexane adsorbed onto the anion-exchanged sample increased linearly with the increase in degree of anion exchange. From these results, anions near the edge of the interlayers appear to have been preferentially replaced by $Co(CN)_6^{3-}$ at a low degree of anion exchange, whereas those at some distance from the edge were replaced only at a high degree of anion exchange. The adsorption capacity of the $Co(CN)_6^{3-}$-exchanged sample for hydrocarbons was: hexane $\simeq$ 2-methylpentane $\gg$ cyclohexane > methylcyclohexane. The adsorption of chain hydrocarbons and cyclic hydrocarbons was different.

Key Words—Adsorption, Anion exchange, Hexacyanocobaltate, Hydrocarbons, Hydrotalcite, Intercalation.

INTRODUCTION

Hydrotalcite is one of the few naturally occurring minerals capable of anion exchange (Frondel, 1941). It has the composition of $Mg_6Al_2(OH)_{16}CO_3\cdot4H_2O$, where Mg and Al are randomly distributed in the octahedral layer. The layers are positively charged and stacked on top of each other. Carbonate ions and water molecules occupy interlayer sites (Allmann, 1970). Miyata (1980) prepared hydrotalcite from aqueous solutions of $MgCl_2$, $AlCl_3$, NaOH, and Na_2CO_3.

Synthetic hydrotalcite-like minerals can be prepared by the substitution of cations in the layer and/or anions in the interlayer sites of the structure. Thus, the formula for the hydrotalcite-like minerals can be expressed as follows:

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot m\ H_2O]^{x-},$$
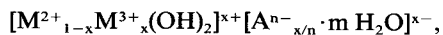
where M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}, etc.; M^{3+} = Al^{3+}, Cr^{3+}, Fe^{3+}, etc.; A^{n-} = NO_3^-, Cl^-, CO_3^{2-}, etc.; and x = 0.2–0.33. The interlayer anion, A^{n-}, is anion-exchangeable (Miyata and Kumura, 1973). Thus, the interlayer spacing varies depending on the size of anions intercalated into the interlayer by anion exchange (Miyata, 1983).

Expanding the interlayer spacing of layered minerals is of great utility, because for adsorption and, ultimately, catalytic purposes, it is advantageous to utilize an interlayer space that possesses a large internal surface area. Indeed, swelling phyllosilicates, such as montmorillonite and hectorite, have been pillared with hydroxy-Al polymers to produce acidic catalysts or catalyst supports having specific surface areas of 300

m^2/g, far greater than their external surface area (Pinnavaia *et al.,* 1985; Plee *et al.,* 1985). Several reactions catalyzed by interlayer transition metal complexes have also been reported (Pinnavaia, 1983).

Interlayer spacings of hydrotalcite-like minerals containing NO_3^-, Cl^-, SO_4^{2-}, or CrO_4^{2-} range from 3.0 to 4.0 Å (Miyata and Okada, 1977; Miyata, 1983). Miyata and Kumura (1973), Kikkawa and Koizumi (1982), and Cavalcanti *et al.* (1987) reported the synthesis of $Fe(CN)_6^{3-}$- or $Fe(CN)_6^{4-}$-intercalated hydrotalcite-like minerals, the interlayer spacings of which were 6.1 Å. Naphthol Yellow S^{2-} anion was also used as an intercalating anion and formed a hydrotalcite-like mineral having an interlayer spacing of 8.1 Å.

Intercalation of the hydrotalcite-like minerals has not been examined to the extent it has been in phyllosilicates. The present work concerns the intercalation of hexacyanocobaltate(III) anion, $Co(CN)_6^{3-}$, into the interlayer space of several hydrotalcite-like minerals by an anion-exchange method. The aim of this work was to advance the knowledge of the intercalation process and to examine the adsorption properties of the resulting $Co(CN)_6^{3-}$-intercalated mineral.

EXPERIMENTAL

Synthesis of hydrotalcite-like minerals

Anion-substituted hydrotalcites containing NO_3^-, Cl^-, SO_4^{2-}, or CrO_4^{2-} interlayer ions were prepared according to the method reported by Miyata (1975) and Miyata and Okada (1977). Thus, for example, a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^-
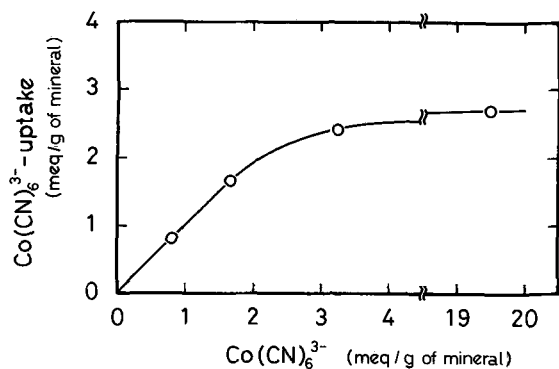
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Figure 1.   Uptake of $Co(CN)_6^{3-}$ at 60°C by a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^- ions as a function of $Co(CN)_6^{3-}$ added in solution.

ions was synthesized at 65°C using aqueous solutions of $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and NaOH, under a nitrogen atmosphere and at a constant pH of 10. The precipitate was filtered, washed with fresh decarbonated water, and dried in vacuo at 110°C for 12 hr. The composition of the mineral thus prepared was determined by chemical analysis. The amount of Mg^{2+} and Al^{3+} was determined by the chelate titration of the sample dissolved in dilute hydrochloric acid. The amount of Cl^- was determined by back-titrating the sample solution obtained by dissolving the sample into nitrous acid, adding an excess of silver nitrate and dilute nitric acid (Miyata and Okada, 1977; Miyata, 1975). The anion-exchange capacity and the molar ratio of Cl^- to Al^{3+} were determined to be 3.25 meq/g of mineral and 0.960, respectively.

Both cation- and anion-substituted minerals, containing Zn^{2+}-Al^{3+}-NO_3^- or Zn^{2+}-Cr^{3+}-NO_3^- ions, were prepared using $Zn(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (Miyata, 1975; Reichle, 1985). The X-ray powder diffraction (XRD) patterns of the materials thus synthesized were identical to those previously reported (Miyata, 1975; Miyata and Okada, 1977). All the reagents were obtained from Kanto Chemical Co., Inc.

Anion-exchange reaction

A sufficient quantity of a hydrotalcite-like mineral to possess a 9.75 meq of anion-exchange capacity (e.g., 3.00 g of a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^- ions) was suspended with stirring in 300 cm³ of decarbonated water containing a given amount of $K_3Co(CN)_6$ under a nitrogen atmosphere at 60°C for 2 hr. The solid was then filtered, washed with fresh decarbonated water, and dried in vacuo at 110°C for 12 hr. The degree of anion exchange was determined from the decrease in the concentration of $Co(CN)_6^{3-}$ in the solution, which was determined from the absorbance at 312 nm recorded on a Shimadzu UV-265 spectrophotometer. For hydrotalcite-like minerals containing

NO_3^-, SO_4^{2-}, or CrO_4^{2-} as interlayer anions, the degree of anion exchange with $Co(CN)_6^{3-}$ ion was determined also from the decrease in an infrared absorption band characteristic of the respective interlayer ions, recorded on a Shimadzu IR-460 spectrophotometer by the KBr-pellet method. The degree of anion exchange obtained by the two methods were in good agreement.

X-ray powder diffraction measurement

X-ray powder diffraction (XRD) patterns of samples were recorded on a Philips PW1700 diffractometer using monochromatic $CuK\alpha$ radiation, operating at 40 kV and 30 mA.

Hydrocarbon adsorption measurement

Adsorption measurements were carried out at 20°C in a conventional static adsorption apparatus equipped with a hydrocarbon reservoir and a vacuum system. A 0.1-g portion of a mineral was evacuated at 150°C for 2 hr before starting the measurements.

RESULTS AND DISCUSSION

Ion-exchange of interlayer anions with $Co(CN)_6^{3-}$

Figure 1 illustrates the uptake of $Co(CN)_6^{3-}$ by a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^- ions as a function of the amount of the $Co(CN)_6^{3-}$ salt initially present in the anion-exchange solution. At low levels of $Co(CN)_6^{3-}$, the slope of the isotherm is unity, which indicates that practically all the $Co(CN)_6^{3-}$ ion in the solution was taken up by the mineral, suggesting a great affinity of the mineral for $Co(CN)_6^{3-}$. At levels of $Co(CN)_6^{3-}$ exceeding 1.63 meq/g of the mineral, the uptake of $Co(CN)_6^{3-}$ deviates from a straight line. At 3.25 meq/g of the mineral, the level at which the amount of $Co(CN)_6^{3-}$ equals the amount of interlayer Cl^- initially present in the mineral, $Co(CN)_6^{3-}$ uptake was 2.40 meq/g of the mineral, 74% of Cl^- in the interlayer of the starting mineral having been exchanged. At 19.5 meq of $Co(CN)_6^{3-}$ added, the degree of anion exchange was 83%.

The degrees of $Co(CN)_6^{3-}$-anion exchange for various hydrotalcite-like minerals reacted with 19.5 meq of $Co(CN)_6^{3-}$/g of the mineral in the starting anion-exchange solution are listed in Table 1. For all the hydrotalcite-like minerals examined, interlayer anions were exchanged with $Co(CN)_6^{3-}$. The degree of exchange fell in the range 79–90%, except for a mineral containing Zn^{2+}-Cr^{3+}-NO_3^- ions, in which the degree of anion exchange was only 21%.

For hydrotalcite-like minerals containing NO_3^-, SO_4^{2-}, or CrO_4^{2-} interlayer anions, infrared absorption bands characteristic of the anions at 1380 and 825 cm⁻¹, 1113 and 616 cm⁻¹, or 884 cm⁻¹, respectively, were observed. These observations are in accord with those of Miyata (1975) and Miyata and Okada (1977).

Table 1. Degree of anion exchange and basal spacing of hydrotalcite-like minerals exchanged with $Co(CN)_6^{3-}$.

Cations in layer	Interlayer anion	Degree of anion exchange (%)	d(003) value before anion exchange (Å)		d(003) value after anion exchange (Å)
Mg^{2+}-Al^{3+}	NO_3^-	79	8.2	8.2	10.7
Mg^{2+}-Al^{3+}	Cl^-	83	7.8	7.8	10.8
Mg^{2+}-Al^{3+}	SO_4^{2-}	89	8.7	—	10.8
Mg^{2+}-Al^{3+}	CrO_4^{2-}	83	8.0	—	10.8
Zn^{2+}-Al^{3+}	NO_3^-	90	8.7	—	11.3
Zn^{2+}-Cr^{3+}	NO_3^-	21	8.8	8.8	10.9

Figure 2. X-ray powder diffraction patterns in 003, 006, and 009 reflection region for (a) hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^- ions and (b) for the mineral anion exchanged (83%) with $Co(CN)_6^{3-}$.

For the minerals subjected to the anion exchange with $Co(CN)_6^{3-}$, the intensity of these absorption bands decreased, e.g., to 21%, 11%, and 17% of that for the starting mineral containing Mg^{2+}-Al^{3+}-NO_3^-, Mg^{2+}-Al^{3+}-SO_4^{2-}, and Mg^{2+}-Al^{3+}-CrO_4^{2-} ions, respectively. Simultaneously, a new absorption band at 2124 cm^{-1} appeared, attributable to a $C \equiv N$ stretching band in the $Co(CN)_6^{3-}$ ion (Jones, 1964). These results show that a replacement of the interlayer anion with $Co(CN)_6^{3-}$ ion occurred during the anion-exchange experiment.

Expansion of interlayer space by anion exchange

XRD patterns were made of samples before and after anion exchange with $Co(CN)_6^{3-}$ to assess the change in interlayer spacing upon anion exchange (Table 1). All the hydrotalcite-like minerals before the anion exchange gave 003 reflections at 10.1–11.3°2θ, from which basal spacings, d(003), were determined to be 7.8–8.8 Å. Because the layer thickness of hydrotalcite-like minerals is 4.8 Å (Miyata, 1975), the interlayer spacing was therefore 3.0–4.0 Å.

For hydrotalcite-like minerals containing Mg^{2+}-Al^{3+}-SO_4^{2-}, Mg^{2+}-Al^{3+}-CrO_4^{2-}, and Zn^{2+}-Al^{3+}-NO_3^- ions, the 003 reflection shifted to a lower angle, 7.8–8.1°2θ, after the sample was anion exchanged with $Co(CN)_6^{3-}$. The basal spacings ranged from 10.8 to 11.3 Å, giving interlayer spacings of 6.0–6.5 Å. Thus, interlayer spacings were expanded from 3.0–4.0 Å to 6.0–6.5 Å by anion exchange with $Co(CN)_6^{3-}$, which is in accord with results reported for $Fe(CN)_6^{3-}$- or $Fe(CN)_6^{4-}$-intercalated hydrotalcite-like minerals (Miyata, 1975; Kikkawa and Koizumi, 1982; Cavalcanti et al., 1987). In hexacyanocobaltate(III) anion, Co^{3+} is octahedrally coordinated with CN^- ions. By assuming Co–C and C–N bond lengths of 1.89 and 1.15 Å, respectively, and an ionic radius of 1.40 Å for N^{3-} (Curry and Runciman, 1959), the dimensions of the octahedra can be estimated to be 8.88, 6.00, and 7.10 Å along the four-,three-, and two-fold symmetry axis, respectively. Inasmuch as the observed interlayer spacing was 6.0–6.5 Å, $Co(CN)_6^{3-}$ was most probably oriented in the interlayer with its threefold symmetry axis perpendicular to the host layer, in agreement with results re-
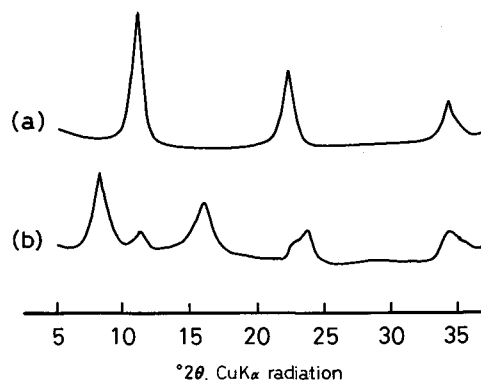
ported for $Fe(CN)_6^{4-}$-intercalated hydrotalcite-like minerals (Kikkawa and Koizumi, 1982; Cavalcanti et al., 1987).

For hydrotalcite-like minerals containing Mg^{2+}-Al^{3+}-NO_3^-, Mg^{2+}-Al^{3+}-Cl^-, and Zn^{2+}-Cr^{3+}-NO_3^- ions, an XRD reflection peak at 10.0–11.3°2θ was observed in addition to the reflection at 8.1–8.3°2θ after anion exchange with $Co(CN)_6^{3-}$. For example, XRD patterns in the 5–37.5°2θ region, obtained for hydrotalcite-like minerals containing Mg^{2+}-Al^{3+}-Cl^- ions before and after the anion exchange with $Co(CN)_6^{3-}$, are compared in Figure 2. In accord with the observation of Miyata (1975), the mineral before anion exchange (Figure 2a) gave 003, 006, and 009 reflections at 11.3, 22.4, and 34.5°2θ, respectively, from which interlayer spacings of 7.8, 3.9, and 2.6 Å can be calculated. After the anion exchange (Figure 2b), the three peaks at 11.3, 22.4, and 34.5°2θ became diffuse, and simultaneously three new peaks at 8.1, 16.0, and 24.1°2θ appeared, giving rise to calculated interlayer spacings of 10.8, 5.5, and 3.7 Å, respectively. The ratios of interlayer spacings, 10.8/7.8, 5.5/3.9, and 3.7/2.6, were essentially identical. Thus, the three new peaks at 8.1, 16.0, and 24.1°2θ can be assigned to 003, 006, and 009 reflections shifted from 11.3, 22.4, and 34.5°2θ, respectively, on anion exchange of the mineral with $Co(CN)_6^{3-}$.

Expansion of interlayer space on anion exchange with $Co(CN)_6^{3-}$ was confirmed also by a change in specific surface area of the minerals, as determined by a nitrogen adsorption method. Thus, the specific surface area of Mg^{2+}-Al^{3+}-NO_3^--hydrotalcite-like mineral evacuated at 150°C for 2 hr was 13 m^2/g, whereas for the mineral anion exchanged (79%) with $Co(CN)_6^{3-}$ and evacuated at 150°C for 2 hr, the specific surface area was 330 m^2/g. The increase in specific surface area observed here is in good agreement with that reported by Cavalcanti et al. (1987), who obtained 14 m^2/g and 355 m^2/g for the areas for the hydrotalcite-like mineral
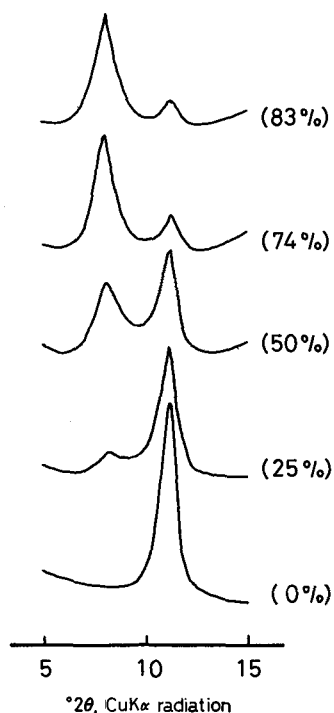
Figure 3.   X-ray powder diffraction patterns in 003 reflection region for $Co(CN)_6^{3-}$-intercalated hydrotalcite-like minerals containing Mg^{2+}-Al^{3+}-Cl^- ions. Values in parenthesis denote degree of anion exchange by $Co(CN)_6^{3-}$.

Figure 4.   Fraction of intensity of 003 reflection at $8.1°2\theta$ in X-ray powder diffraction as a function of degree of anion exchange.

containing Mg^{2+}-Al^{3+}-NO_3^- ions and for the mineral intercalated with $Fe(CN)_6^{3-}$, respectively.

Change in 003 reflection vs. degree of anion exchange

The XRD patterns in the 003 reflection region of a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^- ions, anion exchanged with $Co(CN)_6^{3-}$ ion at various degrees of anion exchange are shown in Figure 3. With the increase in the degree of anion exchange, the intensity of the peak at $11.3°2\theta$ decreased monotonously; simultaneously, the intensity of a new peak at $8.1°2\theta$ increased. As mentioned above, the two peaks at $11.3°$ and $8.1°2\theta$ are attributed to reflections from the non-expanded and expanded interlayers, respectively.

The fraction of the integrated intensity of peaks at $8.1°2\theta$, $I^8/(I^8 + I^{11})$, depended on the degree of anion exchange, as shown in Figure 4. Here, I^8 and I^{11} represent the integrated intensities for the peaks at $8.1°$ and $11.3°2\theta$, respectively. The fraction is proportional to the degree of anion exchange, and the slope of the line is unity. The linear dependence suggests that the material consisted of two distinct regions; one containing expanded interlayers and the other containing non-expanded interlayers. The former region proportionally increased with the degree of anion exchange at the expense of the latter. This relationship clearly
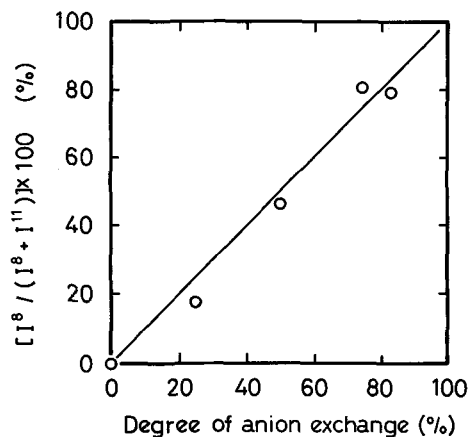
indicates that Cl^- near the edge of interlayer was preferentially replaced by $Co(CN)_6^{3-}$ and that those far from the edge were replaced only at high levels of anion exchange. It also suggests no free interchanges of positions between the two kinds of anions.

Hydrocarbon adsorption

To evaluate the accessibility of the $Co(CN)_6^{3-}$-intercalated interlayer space to large molecules, the adsorption of different hydrocarbons onto the samples was examined. Adsorption isotherms for several hydrocarbons at 20°C obtained on a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-NO_3^- ions anion exchanged (79%) with $Co(CN)_6^{3-}$ are shown in Figure 5. For each hydrocarbon, the adsorbed amount increased with an increase in the relative pressure of the hydro-
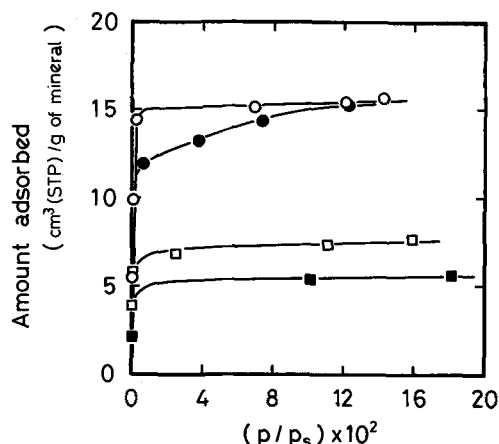

Figure 5.   Hydrocarbon adsorption isotherms at 20°C for $Co(CN)_6^{3-}$-exchanged hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-NO_3^- ions. Adsorbates are hexane (O), 2-methylpentane (●), cyclohexane (□), and methylcyclohexane (■).
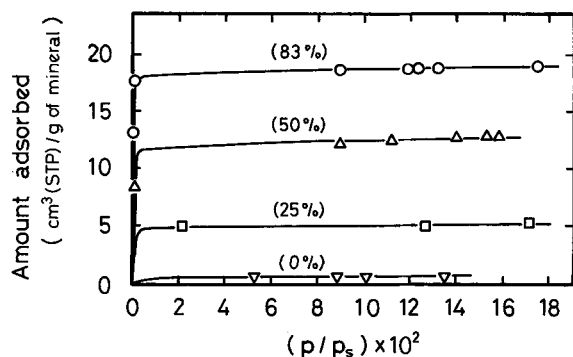
Figure 6. Hexane adsorption isotherms at 20°C for $Co(CN)_6^{3-}$-exchanged hydrotalcite-like minerals containing Mg^{2+}-Al^{3+}-Cl^- ions. Values in parenthesis denote degree of anion exchange by $Co(CN)_6^{3-}$.

Figure 7. Dependence of ceiling value for the adsorption amount, V_m, on the degree of anion exchange.

carbons and approached a ceiling value. The mineral sorbed essentially identical amount of hexane and 2-methylpentane, indicating that the difference in structure of the two hydrocarbons is not large enough to have caused a preferential adsorption of one over the other. The cyclic hydrocarbons, cyclohexane and methylcyclohexane, however, adsorbed to lesser amounts on the mineral than hexane or 2-methylpentane, attributable to the larger dimensions of the cyclic hydrocarbons. Adsorption capacities for hydrocarbons were, in decreasing order: hexane $\simeq$ 2-methylpentane $\gg$ cyclohexane > methylcyclohexane.

The isotherms of hexane on a hydrotalcite-like mineral containing Mg^{2+}-Al^{3+}-Cl^- ions anion exchanged to different degrees by $Co(CN)_6^{3-}$ are shown in Figure 6. With an increase in the relative pressure of hexane, the adsorption amount increased and approached a ceiling value, V_m. The adsorption obeyed a Langmuir adsorption for all the samples examined. Thus, a straight line was obtained in a plot of $p/(p_s)/V$ vs. p/p_s. From the slope in the plot, the value of V_m can be estimated.

As illustrated in Figure 7, a linear dependence of V_m on the degree of anion exchange is apparent. In the preceding section, we concluded that interlayers near the edge were preferentially expanded at low degrees of anion exchange, whereas those far from the edge were expanded only at high degree of anion exchange. The linear dependence shown in Figure 7 indicates that hexane adsorbed onto the expanded interlayers near the edge at low degrees of anion exchange and that it adsorbed onto those far from the edge only at high degrees of anion exchange.

SUMMARY AND CONCLUSION

The hexacyanocobaltate(III) anion, $Co(CN)_6^{3-}$, was intercalated into the interlayer space of several hydrotalcite-like minerals by an anion exchange method. For most of the minerals examined, the maximum degree of anion exchange was 79–90%. Specific surface areas
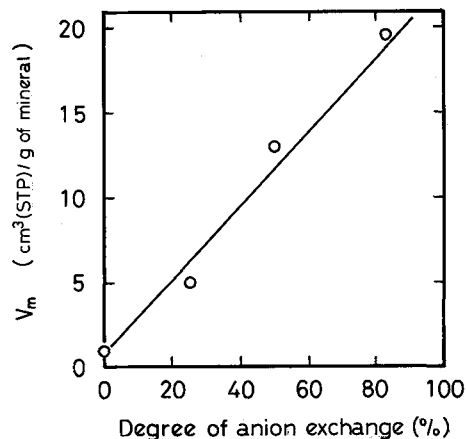
of hydrotalcite-like minerals containing Mg^{2+}-NO_3^- ions increased from 13 to 330 m²/g on anion exchange.

On intercalation of $Co(CN)_6^{3-}$, the interlayer spacing partly expanded. Thus, anions near the edge of interlayer were preferentially replaced by $Co(CN)_6^{3-}$ at a low degree of anion exchange, whereas those far from the edge were replaced only at a high degree of anion exchange.

Accessibility of $Co(CN)_6^{3-}$-intercalated interlayer space to hydrocarbons decreased in the order; hexane $\simeq$ 2-methylpentane $\gg$ cyclohexane > methylcyclohexane. A preference for chain hydrocarbons over cyclic hydrocarbons by the adsorbent was evident.

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