SYNTHESIS AND CO_2 ADSORPTION FEATURES OF A HYDROTALCITE-LIKE COMPOUND OF THE Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ SYSTEM WITH HIGH LAYER-CHARGE DENSITY

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Abstract—Hydrotalcite-like compounds (HT) with 24%–48% Al^{3+}-substitution have been synthesized in the Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ system. Conditioning of the synthesized and air-dried compound with $K_4Fe(CN)_6^{4-}$ solution at 80°C was essential to obtain the 80%–90% pure ionic $Fe(CN)_6^{4-}$ form on an equivalent basis. A linear decrease in a_0 with an increase in the mole ratio of $R = Al^{3+}/(Mg^{2+}+Al^{3+})$ was extended to $R = 0.48$. The formation of highly Al^{3+}-substituted HTs has been corroborated by the decrease in the hexagonal lattice constant a_0 down to 3.016 Å. The a_0 value was independent of the interlayer anions. The CO_2 adsorption profiles were dependent upon both the Al^{3+}-substitution and the interlayer distance. The isosteric heat of CO_2 adsorption was 43.3 kJ mol^{-1} in the range of adsorption of 20 to 40 cm^3 g^{-1} at 298 K and 0.1 MPa.

Key Words—Al^{3+}-substitution, CO_2 adsorption, Hydrotalcite-like compound, Ion exchange.

INTRODUCTION

CO_2 emits from power, ceramic, and steel plants as well as automobiles, contributing to the "green-house," or global warming, effect. Reduction of emission rates may be possible, however, through chemical processes that involve separation, recovery, and chemical transformation of recovered CO_2 combined with reduction of consumption, improvement of energy utilization efficiency, and use of solar energy. Recently, magnetite-intercalated mica has been found to show CO_2 decomposition reactivity (Tsuji *et al.*, 1993b). There exist a large number of layered compounds such as phosphates and tobermorite that are well known as cation exchangers or H_2O adsorbers (Clearfield, 1988; Komarneni and Tsuji, 1989; Tsuji and Komarneni, 1989, 1991). Other layered compounds belonging to solid bases, such as hydrotalcite-like compounds(HT) and $Al(OH)_3$-derived compounds, exhibit an anion-exchange property (Miyata, 1983; Sissoko *et al.*, 1985).

Studies on the adsorption of acidic gases, e.g., CO_2, SO_x, and NO_x, were carried out earlier on zeolite and hydrotalcite (Sazarashi *et al.*, 1992; Miyata and Hirose, 1978). The HT general formula is represented by:

$$[M^{2+}_{1-R}M^{3+}_R(OH)_2]^{R+}[(R/n)A^{n-}\cdot m\ H_2O]^{R-}$$
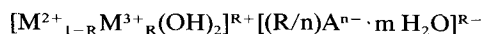
where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, A^{n-} is an anion, and R is M^{3+}-substitution defined by the mole ratio: $R = M^{3+}/(M^{2+}+M^{3+})$ (Allmann, 1968; Bish and Brindley, 1977; Brindley and Kikkawa, 1979; Gastuche *et al.*, 1967; Miyata, 1975, 1980; Taylor, 1973). A large layer-charge is desirable if HT is to be a significant adsorbent for the above gases.

There have been reported Al-rich hydrotalcite-like compounds in the CO_3^{2-} form with the maximum substitution of $R = 0.44$ (Pausch *et al.*, 1986; Thevenot *et al.*, 1989; Tsuji *et al.*, 1993a; Yamaoka *et al.*, 1989). Moreover, contradictions and confusions have been recently pointed out on the thermodynamic treatment of the anion exchange on this type of material (Tsuji *et al.*, 1992). The standard state for the solid is not clearly defined in the ion-exchange treatment, and the ion-exchange isotherm is not consistent with the Kielland plot. Adsorption data for CO_2 on the HT are randomly scattered among HTs with the same layer charge synthesized by different authors (Miyata and Hirose, 1978; Kikkawa and Koizumi, 1982). Therefore, the objectives of the present study were 1) to synthesize HTs in the $Fe(CN)_6^{4-}$ form with as wide a range of Al^{3+}-substitution as possible and 2) to study their CO_2 adsorption behavior.

EXPERIMENTAL METHODS

Synthesis of hydrotalcite-like compound

Appropriate proportions of 0.5 M $Mg(NO_3)_2$, 0.5 M $Al(NO_3)_3$, and 0.25 M $K_4Fe(CN)_6$ solutions were mixed in different glass vessels to give various mole ratios (r) of $Al^{3+}/(Mg^{2+}+Al^{3+})$ and the mole ratio of $Fe(CN)_6^{4-}$ to Al^{3+} 1.0. After each mixed solution was degassed with N_2, 2 M NaOH was added slowly until pH 10.0 was reached while stirring. The precipitated amorphous hydrolysis produce was aged in the mother solution at room temperature overnight, washed with water, filtered under suction, and air-dried at room temperature for several days to allow slow polymer-
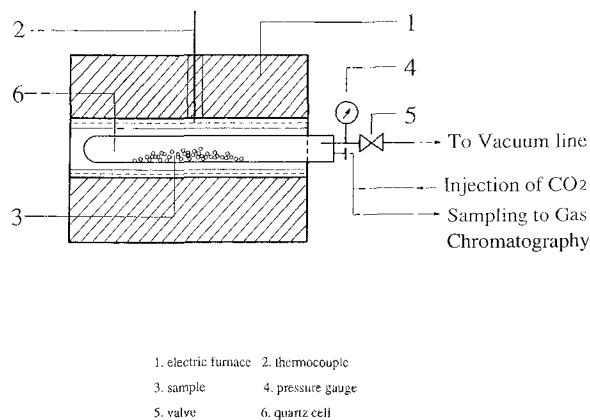
Figure 1. Homemade apparatus for CO_2 adsorption.

ization. Drying at higher temperature (55°–80°C) adopted by other authors prevented the growth of hydolysis products in crystals with a high degree of Al^{3+}-substitution.

Conditioning of air-dried products and chemical analyses

The air-dried products were mixed ionic forms, as will be discussed later, and were conditioned as follows to obtain a well-defined ionic form. They were ground and sieved to obtain a fraction of 100–200 mesh size (37–74 μm in diameter). A portion of the sieved material (0.50 g) was immersed in 15 cm^3 of 1 M $K_4Fe(CN)_6$ solution at 80°C to exchange $Fe(CN)_6^{4-}$ for NO_3^- and CO_3^{2-} in the interlayer. The solution was replaced every 90 minutes for 4 cycles. The process is based on the ion exchange. However, the ion exchange selectivity for these ions has not been investigated, and the experimental conditions cannot be decided to obtain each ionic form. The present procedures were taken from our conventional method (Tsuji and Komarneni, 1989). Then the samples were washed with water to remove the excess $Fe(CN)_6^{4-}$ ions and air-dried.

Mg^{2+}, Al^{3+}, and Fe^{2+} were determined by inductively coupled atomic emission spectrometry (ICP-AES) with a Seiko Instrument Spectrometer Model SPS 7000 after dissolving the compounds in hydrochloric acid. Thermal analyses (TG and DTA) were undertaken with a Rigaku Thermoflex-type thermal analyzer model 8001 at a heating rate of 10°C min^{-1} by using α-Al_2O_3 as the reference material. The content of water in the interlayer of the samples was determined from the TG weight loss curve. Powder X-ray diffraction was carried out with a Rigaku X-ray diffractometer RINT 1100 at a scanning speed of 2°(2θ) min^{-1} with Ni-filtered $CuK\alpha$ radiation. The infrared absorption spectra were recorded by a JASCO FT/IR-8900 equipment with pressed sample disks.
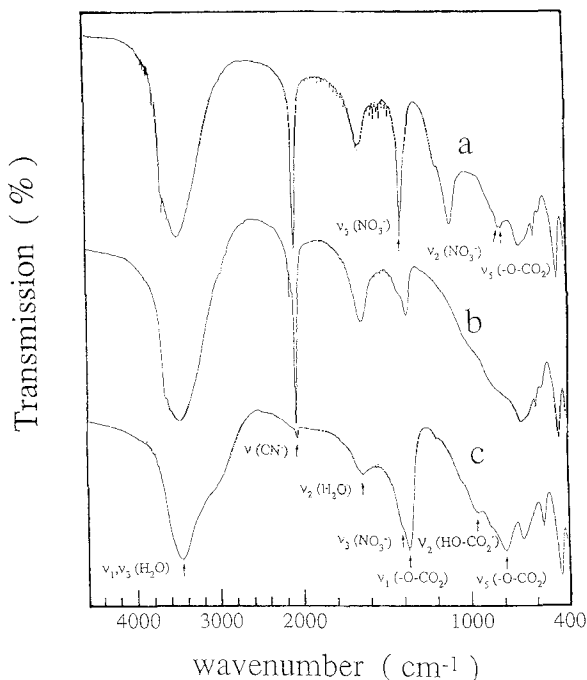

Figure 2. The infrared absorption spectra of sample K (R = 0.366): a) unconditioned, b) $Fe(CN)_6^{4-}$-conditioned, and c) NO_3^--conditioned.

CO_2 adsorption

CO_2 adsorption experiments were carried out with a homemade apparatus (Figure 1). Prior to the adsorption experiment, the samples were heated at 150°C for 10 min while evacuating to expel the interlayer water molecules. The layer structure was not collapsed upon heating at 150°C, but degraded at >200°C. After cooling to a required temperature, a given amount of CO_2 gas was injected into the quartz cell (20 cm long × 3 cm diameter) and the equilibrium CO_2 content in the cell was determined with gas chromatography (Shimadzu GC-8A).

RESULTS AND DISCUSSION

Synthesis of HT in the $Fe(CN)_6^{4-}$ form

A typical IR spectrum of air-dried or unconditioned HT is shown for sample K in Figure 2a. Broad absorption bands with peak tops at 3448 ± 3 cm^{-1} and 1635 ± 5 cm^{-1} can be assigned to the stretching vibrations, ν_1 and ν_3, and the deformation, ν_2, of the interlayer water, respectively. They are the same as those for liquid water irrespective of the R value. Although these absorption bands should also stem from the OH groups of the main layer, the contribution is hidden by the large interlayer H_2O band. This is because the interlayer distance is expanded by a large $Fe(CN)_6^{4-}$ ion, and the OH groups are weakly hydrogen-bonded. The effect may be observed in HTs with
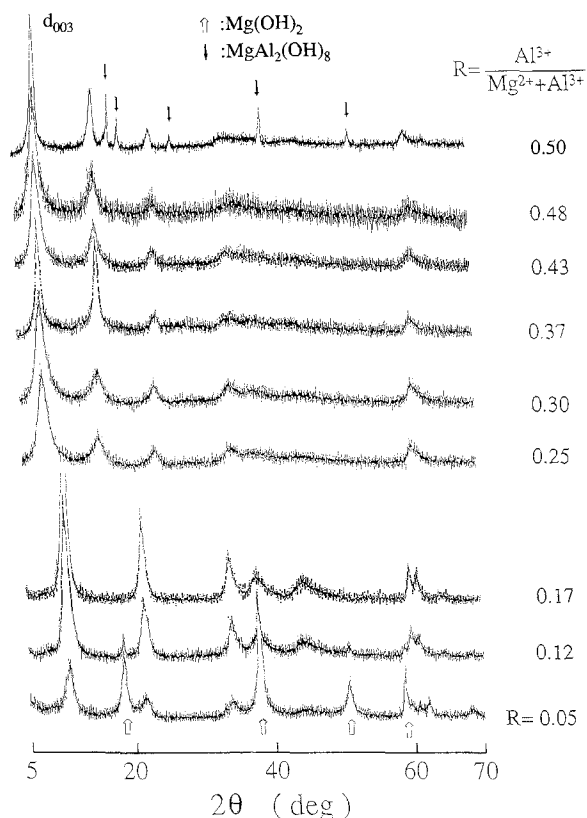
Figure 3. X-ray diffraction patterns of products.

Table 1. Synthesis conditions and XRD data of the hydrotalcites in the Fe(CN)$_6^{4-}$ form.

Sample	r*	R**	a$_0$ (Å)	d$_{003}$ (Å)	Observed phase
A	0.05				HT*** + brucite
B	0.10	0.124	3.089	8.162	HT + brucite
C	0.15	0.171	3.084	8.059	HT
D	0.18	0.241	3.048	10.64	HT
E	0.22	0.251	3.052	10.63	HT
F	0.25	0.270	3.057	10.96	HT
G	0.25	0.273	3.059	10.91	HT
H	0.25	0.276	3.052	10.96	HT
I	0.29	0.299	3.040	10.61	HT
J	0.33	0.346	3.046	10.96	HT
K	0.33	0.366	3.042	10.89	HT
L	0.33	0.325	3.053	10.91	HT
M	0.40	0.334	3.032	10.77	HT
N	0.42	0.431	3.021	10.71	HT
O	0.45	0.481	3.016	10.88	HT

* Mole ratio of Al^{3+}/(Mg^{2+} + Al^{3+}) in the initial solution.
** Mole ratio fo Al^{3+}/(Mg^{2+} + Al^{3+}) in the product.
*** HT = hydrotalcite.

The absorption band, ν_1, assigned to unidentate carbonate –O–CO$_2$ at 1364 cm^{-1} was also observed on both the treated samples as well as the bands for Fe(CN)$_6^{4-}$ and NO$_3^-$. An absorption band at 955 cm^{-1} was also observed, which can be assigned to the stretching vibration, ν_2 of bi-carbonate HO–CO$_2^-$ (Evans and Whateley, 1967). The unidentate carbonate and bicarbonate could not completely be removed in the above procedure.

M^{3+}-substitution in the brucite layer can be evidenced by the decrease in a$_0$ with an increase in the R value because the crystal ionic radius of a trivalent metal ion is normally smaller than that of a divalent metal ion, e.g., r$_{Al^{3+}}$ = 0.535 Å < r$_{Mg^{2+}}$ = 0.720 Å (Shannon, 1976). The extent of formation of the HT in the Mg^{2+}–Al^{3+}–CO$_3^{2-}$ system has been believed to range from R = 0.20 to 0.33 (Brindley and Kikkawa, 1979; Miyata, 1980). The R value of HT is known to be limited to 0.26 to 0.32 in the Mg^{2+}–Al^{3+}–Fe(CN)$_6^{4-}$ system (Kikkawa and Koizumi, 1982). Table 1 represents the lattice parameter a$_0$ and the layer thickness, d$_{003}$, of the Fe(CN)$_6^{4-}$ form as well as the mole ratio of Al^{3+}/(Mg^{2+}+Al^{3+}) in the starting solution for preparation, r, and that of the conditioned product, R. The R values are basically the same as the r values. The whole mass of precipitate was crystallized to form a single HT phase in the hexagonal system from R = 0.171 to 0.481 (Figure 3). A product with a small R value of 0.05 showed two HT phases and Mg(OH)$_2$, while a product with a large R value of 0.50 was composed of two HT phases and MgAl$_2$(OH)$_8$. The Al^{3+}-substitution is evidenced by the linear decrease in a$_0$ with an increase in the R value (Figure 4). The smallest a$_0$ value of 3.016 Å was observed on the sample O with R = 0.481. These results corroborate the formation of the HT in the wide range of Al^{3+}-substitution
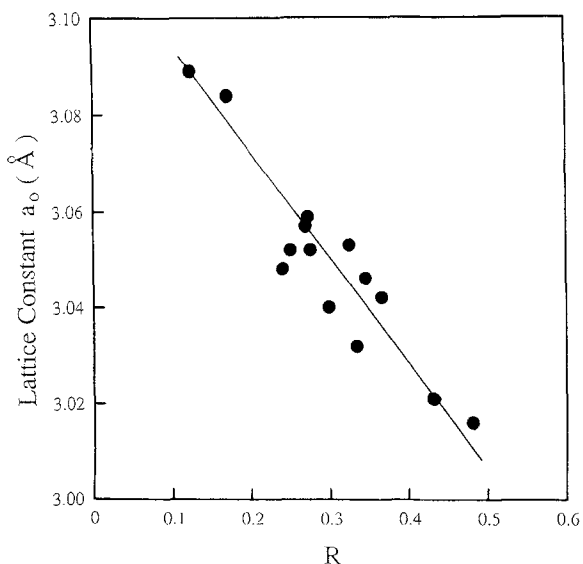
smaller interlayer distance and the larger Al^{3+}-substitution. The band at 2040 ± 4 cm^{-1} is the stretching vibration of ν(CN) (Idemura et al., 1989), and bands at 1385 cm^{-1} and 798 cm^{-1} can be assigned to the stretching vibrations, ν_3 and ν_2, of NO$_3^-$ ion, respectively (Nakamoto, 1986). The former is not shifted to a lower wavenumber. Hence, the hydrogen bond is weak between the interlayer Fe(CN)$_6^{4-}$ and the OH group of the main layer. The band at 777 cm^{-1} can be assigned to the vibration, ν_5, of unidentate carbonate–O–CO$_2$ (Evans and Whateley, 1967). An unidentified absorption band was also observed at 1085 cm^{-1} on the air-dried HT. Thus, air-dried materials are mixed ionic forms containing Fe(CN)$_6^{4-}$, NO$_3^-$ and CO$_3^{2-}$ in the interlayer.

Air-dried samples were conditioned with 1 M K$_4$Fe(CN)$_6$ or NaNO$_3$ solutions to obtain each ionic form (Figures 2b and 2c). Fe(CN)$_6^{4-}$ could be exchanged for NO$_3^-$, but a small amount of CO$_3^{2-}$ still remained in the interlayer. NO$_3^-$-conditioned HT showed an additional absorption band at 3000 cm^{-1}. It is ascribed to the hydrogen bonds between the M–OH group and the interlayer anion, O–H...N, and between the M–OH groups of the main layer. However, the hydrogen bond is not so strong, and the dependence of the wave number on the R value was not observed.

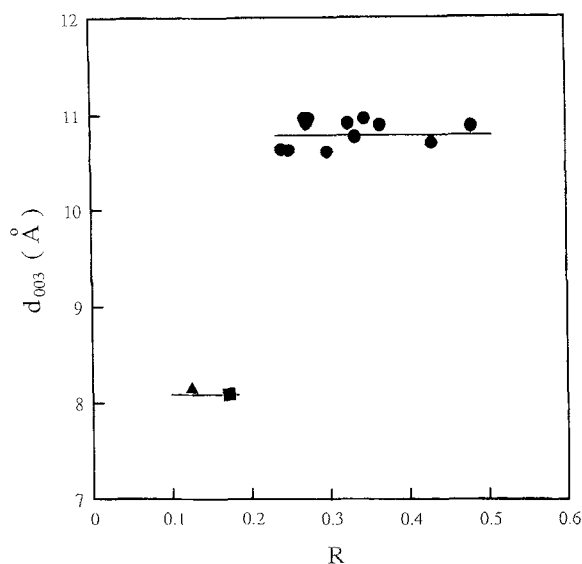Figure 4. Plot of the lattice constant (a_o) *vs.* Al^{3+}-substitution (R).

Figure 5. Plot of the d_{003} spacing of hydrotalcites in the $Fe(CN)_6^{4-}$ form *vs.* Al^{3+}-substitution (R).

(0.24–0.48 as the R value) in the Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ system.

Figure 5 shows the change in the d_{003} spacing with the R value. The samples with R > 0.24 exhibited an expanded layer thickness of about 10.6–10.9 Å. It is equal to the sum of the thickness of the brucite layer (4.77 Å) and the dimension of $Fe(CN)_6^{4-}$ (5.94 Å) (Wilson, 1951). HTs with R < 0.17 showed a smaller layer thickness of about 8.1 Å. In another words, HTs with high charge density can easily incorporate $Fe(CN)_6^{4-}$ within the interlayer, but the compounds with lower R values cannot accommodate the large tetravalent ion $Fe(CN)_6^{4-}$ as an interlayer anion. A sufficient charge in the brucite layer is necessary to take up the large and highly charged $Fe(CN)_6^{4-}$ ion within the interlayer. When the R value is lower, the locations of charge in

the brucite layer are distant from each other and not close enough to form the ionic bond with the $Fe(CN)_6^{4-}$. In such case, the main layer of HTs will be able to form the ionic bond with small anions such as CO_3^{2-} or NO_3^{-}. HT between R = 0.17 and R = 0.24 could not be obtained, though various r values were used for HT preparation. The r values of 0.15 and 0.18 gave the R values of 0.171 and 0.241 in the product, respectively. The reason is not clear. Thus, the extent of Al^{3+}-substitution in the brucite layer has been demonstrated to range from R = 0.24 to 0.48 in the Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ system. It is much wider than that reported previously.

The chemical compositions of conditioned HTs are shown in Table 2. The contents of CO_3^{2-} were calculated by balancing the charges between the brucite layer

Table 2. Chemical composition of synthesized hydrotalcites in the $Fe(CN)_6^{4-}$ form.

| Sample	Chemical composition
C	$[Mg_{0.829}Al_{0.171}(OH)_2][(Fe(CN)_6^{4-})_{0.0170}(CO_3^{2-})_{0.0513} \cdot 1.15H_2O]$
D	$[Mg_{0.759}Al_{0.241}(OH)_2][(Fe(CN)_6^{4-})_{0.0590}(CO_3^{2-})_{0.0025} \cdot 0.920H_2O]$
E	$[Mg_{0.749}Al_{0.251}(OH)_2][(Fe(CN)_6^{4-})_{0.0600}(CO_3^{2-})_{0.0055} \cdot 0.835H_2O]$
F	$[Mg_{0.730}Al_{0.270}(OH)_2][(Fe(CN)_6^{4-})_{0.0562}(CO_3^{2-})_{0.0226} \cdot 1.40H_2O]$
G	$[Mg_{0.727}Al_{0.273}(OH)_2][(Fe(CN)_6^{4-})_{0.0651}(CO_3^{2-})_{0.0063} \cdot 1.26H_2O]$
H	$[Mg_{0.724}Al_{0.276}(OH)_2][(Fe(CN)_6^{4-})_{0.0619}(CO_3^{2-})_{0.0142} \cdot 0.977H_2O]$
I	$[Mg_{0.701}Al_{0.299}(OH)_2][(Fe(CN)_6^{4-})_{0.0675}(CO_3^{2-})_{0.0145} \cdot 1.19H_2O]$
J	$[Mg_{0.654}Al_{0.346}(OH)_2][(Fe(CN)_6^{4-})_{0.0742}(CO_3^{2-})_{0.0246} \cdot 0.803H_2O]$
K	$[Mg_{0.634}Al_{0.366}(OH)_2][(Fe(CN)_6^{4-})_{0.0756}(CO_3^{2-})_{0.0318} \cdot 1.11H_2O]$
L	$[Mg_{0.675}Al_{0.325}(OH)_2][(Fe(CN)_6^{4-})_{0.0618}(CO_3^{2-})_{0.0389} \cdot 1.01H_2O]$
M	$[Mg_{0.666}Al_{0.334}(OH)_2][(Fe(CN)_6^{4-})_{0.0711}(CO_3^{2-})_{0.0248} \cdot 1.46H_2O]$
N	$[Mg_{0.569}Al_{0.431}(OH)_2][(Fe(CN)_6^{4-})_{0.0917}(CO_3^{2-})_{0.0321} \cdot 1.15H_2O]$
O	$[Mg_{0.519}Al_{0.481}(OH)_2][(Fe(CN)_6^{4-})_{0.0802}(CO_3^{2-})_{0.0801} \cdot 0.893H_2O]$
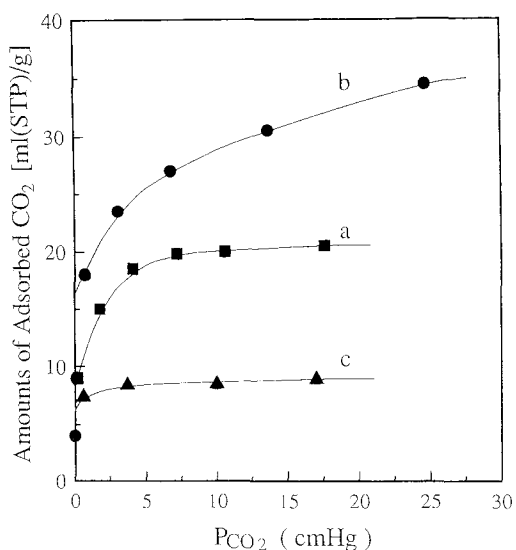
Figure 6. Effect of the ionic form on isotherms for CO_2 adsorption. Sample K (R = 0.366): a) unconditioned (d_{003} = 10.67 Å), b) $Fe(CN)_6^{4-}$-conditioned (d_{003} = 10.89 Å), and c) NO_3^--conditioned (d_{003} = 8.01 Å).

Figure 7. Variation of amounts of adsorbed CO_2 on HTs in the $Fe(CN)_6^{4-}$ form with different Al^{3+}-substitution. Adsorption temperature = 25°C.

and the interlayer based on the pure phase formula. The calculated equivalent fraction of $Fe(CN)_6^{4-}$/ $(CO_3^{2-} + Fe(CN)_6^{4-})$ was 0.8–0.9. These samples will be referred to as the "$Fe(CN)_6^{4-}$ form". Incompleteness of conditioning with $K_4Fe(CN)_6$ solution will be ascribed to the very high ion-exchange selectivity for CO_3^{2-}. The H_2O content was determined from TG weight loss subtracted by the contribution of CN^- and CO_2. The chemical composition shows that approximately one mole of water is contained per chemical formula of hydrotalcite in the $Fe(CN)_6^{4-}$ form. The amount of H_2O is approximately two times of that of the CO_3^{2-} form reported (Tsuji *et al.*, 1993a). The expanded interlayer can accommodate more water than the CO_3^{2-} form with the close packing.

CO₂ adsorption behavior

The CO_2 adsorption isotherms were determined on the mixed ionic form, $Fe(CN)_6^{4-}$- and NO_3^--conditioned product of sample K to study the effect of the ionic form on the adsorption behavior (Figure 6). The smallest amount of CO_2 adsorption (about 10 cm³/g at 20 cmHg) was observed on the NO_3^--conditioned form with a layer spacing of d_{003} = 8.01 Å. The amount of adsorption is given on a STP basis or at 298 K and 0.1 MPa. The air-dried product or mixed ionic form with d_{003} = 10.67 Å exhibited the saturated amount of adsorbed CO_2 of about 21 cm³/g at 20 cmHg. The $Fe(CN)_6^{4-}$ form with d_{003} = 10.89 Å showed a larger adsorption for CO_2, about 33 cm³/g at 20 cmHg. The adsorption did not reach saturation in the present experiments. In comparison with the mixed ionic form, the "d_{003}" of the $Fe(CN)_6^{4-}$ is larger by only 2%, but
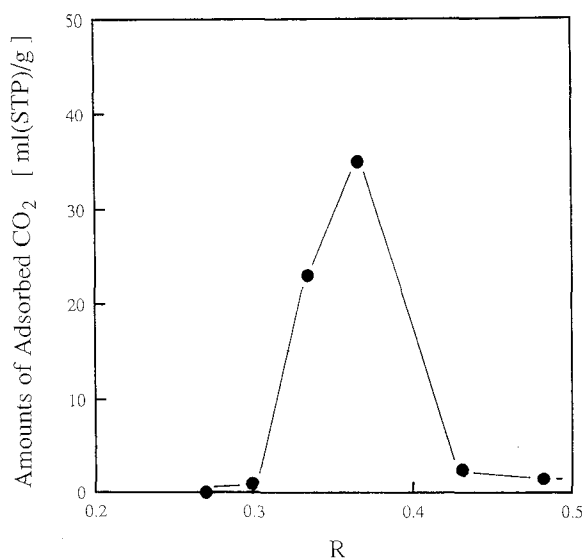
the amount of CO_2 adsorption increased by 65%. It is clear that the NO_3^- ions in the interlayer clogged the adsorption spaces for CO_2 in the interlayer of hydrotalcite in the mixed ionic form. The expanded space with the large anion $Fe(CN)_6^{4-}$ can accommodate more CO_2 gas. The interlayer space may be designed for the adsorption field of CO_2 and other gas molecules if it could be tuned by suitable guest anions. Thus, the ionic form of HT is an important factor for the CO_2 adsorption characteristics as well as the interlayer spacing. In the present research, *in situ* infrared adsorption spectra of CO_2-adsorbed material were not recorded. The technique is critical for probing the state of CO_2 adsorption on these materials, but the equipment was not available.

CO_2 adsorption isotherms were determined on other samples with R = 0.24–0.48 and the amount of CO_2 adsorption at 25 cmHg was plotted as a function of the R value (Figure 7). The sample with R = 0.37 exhibited the maximum amount of CO_2 adsorption and others showed a smaller amount of adsorption. They possess nearly the same d_{003} (10.6 Å–10.9 Å). If the amount of CO_2 adsorption was only determined by the interlayer thickness, almost the same amount of CO_2 adsorption should be observed for these samples. Therefore, besides d_{003}, the effect of the second factor, the layer charge, will have to be taken into account for interpretation of the maximum adsorption. It also affects the amount of CO_2 adsorption because the void space in the interlayer is determined by the density and sizes of the incorporated ions. In this study, the largest amount of adsorbed CO_2 was observed in the sample with R = 0.366. Thus, the optimum space

and the charge density in the interlayer as a CO_2 adsorption field could be found on the hydrotalcite with the Al^{3+}-substitution of 0.37.

The isosteric heat of CO_2 adsorption, $-\Delta H_{ad}$, of sample K was determined by the following equation (Ruthven, 1984) from the adsorption isotherms at 0, 25 and 40°C:

$$\log \frac{P_2}{P_1} = -\frac{\Delta H_{ad}}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where ΔH_{ad} is the enthalpy change on CO_2 adsorption, R is the gas constant, and P_1 and P_2 are the equilibrium pressures at the corresponding temperatures (T_1 and T_2) for the same amount of adsorption. The isosteric heat of CO_2 adsorption was determined to be 43.3 kJ mol^{-1} at the adsorption amount of 20–40 cm^3/g, which indicates the level of chemical adsorption. This is almost the same as the isosteric heat of CO_2 adsorption (40 kJ mol^{-1}) at an infinitesimal coverage on oxygen-deficient magnetite at 150–300°C (Nishizawa et al., 1992). Therefore, CO_2 adsorption on HT is based on the same chemical process as in the latter material. Moreover, HT does not show any adsorption for N_2 gas and is comparable to an activated carbon in the separation performance of CO_2 and N_2 (Ito, 1993).

CONCLUSION

The extent of formation of hydrotalcite in the Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ system has been determined to range from 0.24 to 0.48. It was evidenced by a linear decrease in the lattice constant a_o with an increase in R value. A lower temperature (room temperature) has been demonstrated to be effective for the formation of HTs with high Al^{3+}-substitution. Slow polymerization at lower temperature allows an amorphous hydrolysis product to grow in crystals with the high degree of Al^{3+}-substitution. Several anions coming from the starting materials or atmosphere usually coexist in the interlayer. When the R value is lower than 0.17, the HTs containing highly charged $Fe(CN)_6^{4-}$ ions were not formed because the charge density of the brucite layer was not high enough to accommodate the large ion. Anions in the interlayer could be mostly replaced by other anions by ion-exchange treatment for obtaining a required anion form. CO_2 can be accommodated more easily in an expanded interlayer space. The amount of CO_2 adsorption is affected not only by the interlayer spacing (d_{003}) but also by the layer charge and the ionic form. The optimum space and the charge density for CO_2 adsorption by hydrotalcite in the Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ system were found at the Al^{3+}-substitution of 0.37. The isosteric heat of CO_2 adsorption on HTs in the Mg^{2+}–Al^{3+}–$Fe(CN)_6^{4-}$ system indicated a level of chemical adsorption. The above HT compound with the expanded interlayer will be taken advantage of for obtaining, for instance, the ClO_4^- form, which cannot be synthesized directly from aqueous solutions of metal salts.

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