SYNTHESIS AND CO₂ ADSORPTION FEATURES OF A HYDROTALCITE-LIKE COMPOUND OF THE Mg²⁺-Al³⁺-Fe(CN)₆⁴⁻ SYSTEM WITH HIGH LAYER-CHARGE DENSITY

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Abstract—Hydrotalcite-like compounds (HT) with 24%–48% Al³⁺-substitution have been synthesized in the Mg²⁺-Al³⁺-Fe(CN)₆⁴⁻ system. Conditioning of the synthesized and air-dried compound with K₄Fe(CN)₆⁴⁻ solution at 80~ was essential to obtain the 80%–90% pure ionic Fe(CN)₆⁴⁻ form on an equivalent basis. A linear decrease in ao with an increase in the mole ratio of R = Al³⁺/(Mg²⁺+Al³⁺) was extended to R = 0.48. The formation of highly Al³⁺-substituted HTs has been corroborated by the decrease in the hexagonal lattice constant ao down to 3.016 Å. The ao value was independent of the interlayer anions. The CO₂ adsorption profiles were dependent upon both the Al³⁺-substitution and the interlayer distance. The isosteric heat of CO₂ adsorption was 43.3 kJ mol⁻¹ in the range of adsorption of 20 to 40 cm³ g⁻¹ at 298 K and 0.1 MPa.

Key Words—Al³⁺-substitution, CO₂ adsorption, Hydrotalcite-like compound, Ion exchange.

INTRODUCTION

CO₂ 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 CO₂ combined with reduction of consumption, improvement of energy utilization efficiency, and use of solar energy. Recently, magnetite-intercalated mica has been found to show CO₂ 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 H₂O 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., CO₂, SO₃, and NOₓ, were carried out earlier on zeolite and hydrotalcite (Sazarashi et al., 1992; Miyata and Hirose, 1978). The HT general formula is represented by:

\[ [M^{2+} \ldots R M^{3+} (OH)]^{n-} \{R(n)An- \cdot RH₂O\}^{r-} \]

where \( M^{2+} \) and \( M^{3+} \) are divalent and trivalent cations, respectively, \( An^- \) 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 CO₃²⁻ 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 Kieland plot. Adsorption data for CO₂ 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)₆⁴⁻ form with as wide a range of Al³⁺-substitution as possible and 2) to study their CO₂ adsorption behavior.

EXPERIMENTAL METHODS

Synthesis of hydrotalcite-like compound

Appropriate proportions of 0.5 M Mg(NO₃)₂, 0.5 M Al(NO₃)₃, and 0.25 M K₄Fe(CN)₆ solutions were mixed in different glass vessels to give various mole ratios (\( r \)) of Al³⁺/(Mg²⁺ + Al³⁺) and the mole ratio of Fe(CN)₆⁴⁻ to Al³⁺ 1.0. After each mixed solution was degassed with N₂, 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-
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To Vacuum line

Injection of CO2

Sampling to Gas Chromatography

Figure 1. Homemade apparatus for CO2 adsorption.

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 (0.5 g) was immersed in 15 cm³ of 1 M K₄Fe(CN)₆ solution at 80°C to exchange Fe(CN)₆⁴⁻ for NO₃⁻ and CO₃²⁻ 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)₆⁴⁻ ions and air-dried.

Mg²⁺, Al³⁺, and Fe²⁺ 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-Al₂O₃ 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 CuKα radiation. The infrared absorption spectra were recorded by a JASCO FT/IR-8900 equipment with pressed sample disks.

RESULTS AND DISCUSSION

Synthesis of HT in the Fe(CN)₆⁴⁻ 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, v₁ and v₃, and the deformation, v₂, 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 H₂O band. This is because the interlayer distance is expanded by a large Fe(CN)₆⁴⁻ ion, and the OH groups are weakly hydrogen-bonded. The effect may be observed in HTs with
smaller interlayer distance and the larger Al\textsuperscript{3+} substitution. The band at 2040 ± 4 cm\textsuperscript{-1} is the stretching vibration of ν(CN) (Idemura et al., 1989), and bands at 1385 cm\textsuperscript{-1} and 798 cm\textsuperscript{-1} can be assigned to the stretching vibrations, ν\textsubscript{1} and ν\textsubscript{2}, of NO\textsubscript{3}\textsuperscript{-} ion, respectively (Nakamoto, 1986). The former is not shifted to a lower wavenumber. Hence, the hydrogen bond is weak between the interlayer Fe(CN)\textsubscript{6}\textsuperscript{4–} and the OH group of the main layer. The band at 777 cm\textsuperscript{-1} can be assigned to the vibration, ν\textsubscript{5}, of unidentate carbonate–O-CO\textsubscript{2} (Evans and Whateley, 1967). An unidentified absorption band was also observed on both the treated samples as well as the bands for Fe(CN)\textsubscript{6}\textsuperscript{4–} and NO\textsubscript{3}\textsuperscript{-}. An absorption band at 955 cm\textsuperscript{-1} was also observed, which can be assigned to the stretching vibration, ν\textsubscript{2} of bi-carbonate HO-CO\textsubscript{2} (Evans and Whateley, 1967). An unidentified carbonate and bi-carbonate could not completely be removed in the above procedure.

M\textsuperscript{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., \(r_{Al} = 0.535 \text{ Å} < r_{Mg} = 0.720 \text{ Å}\) (Shannon, 1976). The extent of formation of the HT in the Mg\textsuperscript{2+}–Al\textsuperscript{3+}–CO\textsubscript{3}\textsuperscript{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\textsuperscript{2+}–Al\textsuperscript{3+}–Fe(CN)\textsubscript{6}\textsuperscript{4–} system (Kikkawa and Koizumi, 1982). Table 1 represents the lattice parameter \(a_0\) and the layer thickness, \(d_{003}\), of the Fe(CN)\textsubscript{6}\textsuperscript{4–} form as well as the mole ratio of \(\text{Al}^{3+}/(\text{Mg}^{2+} + \text{Al}^{3+})\) 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)\textsubscript{2}, while a product with a large \(R\) value of 0.50 was composed of two HT phases and MgAl\textsubscript{2}(OH)\textsubscript{4}. The Al\textsuperscript{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\textsuperscript{3+}-substitution.

### Table 1. Synthesis conditions and XRD data of the hydrotalcites in the Fe(CN)\textsubscript{6}\textsuperscript{4–} form.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(r)</th>
<th>(R)</th>
<th>(a_0) (Å)</th>
<th>(d_{003}) (Å)</th>
<th>Observed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.05</td>
<td></td>
<td>3.089</td>
<td>8.162</td>
<td>HT + brucite</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
<td>0.124</td>
<td>3.084</td>
<td>8.059</td>
<td>HT</td>
</tr>
<tr>
<td>C</td>
<td>0.15</td>
<td>0.171</td>
<td>3.052</td>
<td>10.64</td>
<td>HT</td>
</tr>
<tr>
<td>D</td>
<td>0.18</td>
<td>0.241</td>
<td>3.048</td>
<td>10.60</td>
<td>HT</td>
</tr>
<tr>
<td>E</td>
<td>0.22</td>
<td>0.251</td>
<td>3.057</td>
<td>10.96</td>
<td>HT</td>
</tr>
<tr>
<td>F</td>
<td>0.25</td>
<td>0.270</td>
<td>3.059</td>
<td>10.91</td>
<td>HT</td>
</tr>
<tr>
<td>G</td>
<td>0.25</td>
<td>0.276</td>
<td>3.052</td>
<td>10.96</td>
<td>HT</td>
</tr>
<tr>
<td>H</td>
<td>0.29</td>
<td>0.299</td>
<td>3.040</td>
<td>10.61</td>
<td>HT</td>
</tr>
<tr>
<td>I</td>
<td>0.33</td>
<td>0.346</td>
<td>3.046</td>
<td>10.96</td>
<td>HT</td>
</tr>
<tr>
<td>J</td>
<td>0.33</td>
<td>0.366</td>
<td>3.042</td>
<td>10.89</td>
<td>HT</td>
</tr>
<tr>
<td>K</td>
<td>0.40</td>
<td>0.334</td>
<td>3.032</td>
<td>10.77</td>
<td>HT</td>
</tr>
<tr>
<td>L</td>
<td>0.42</td>
<td>0.431</td>
<td>3.021</td>
<td>10.71</td>
<td>HT</td>
</tr>
<tr>
<td>M</td>
<td>0.45</td>
<td>0.481</td>
<td>3.016</td>
<td>10.88</td>
<td>HT</td>
</tr>
<tr>
<td>N</td>
<td>0.17</td>
<td></td>
<td>3.046</td>
<td></td>
<td>HT</td>
</tr>
<tr>
<td>O</td>
<td>0.25</td>
<td></td>
<td>3.040</td>
<td></td>
<td>HT</td>
</tr>
</tbody>
</table>

* Mole ratio of Al\textsuperscript{3+}/(Mg\textsuperscript{2+} + Al\textsuperscript{3+}) in the initial solution.
** Mole ratio of Al\textsuperscript{3+}/(Mg\textsuperscript{2+} + Al\textsuperscript{3+}) in the product.
*** HT = hydrotalcite.
(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 and the interlayer. The chemical compositions of synthesized hydrotalcites in the Fe(CN)$_6^{4-}$ form are shown in Table 2.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>[Mg$<em>{0.839}$Al$</em>{0.171}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.0170}$CO$<em>3^{2-}$$\lambda</em>{0.013}$1.15H$_2$O</td>
</tr>
<tr>
<td>D</td>
<td>[Mg$<em>{0.799}$Al$</em>{0.241}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.0235}$0.92H$_2$O</td>
</tr>
<tr>
<td>E</td>
<td>[Mg$<em>{0.789}$Al$</em>{0.251}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.0055}$0.83H$_2$O</td>
</tr>
<tr>
<td>F</td>
<td>[Mg$<em>{0.779}$Al$</em>{0.276}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.022}$1.40H$_2$O</td>
</tr>
<tr>
<td>G</td>
<td>[Mg$<em>{0.777}$Al$</em>{0.273}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.023}$1.26H$_2$O</td>
</tr>
<tr>
<td>H</td>
<td>[Mg$<em>{0.724}$Al$</em>{0.276}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.038}$0.97H$_2$O</td>
</tr>
<tr>
<td>I</td>
<td>[Mg$<em>{0.721}$Al$</em>{0.279}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.057}$1.19H$_2$O</td>
</tr>
<tr>
<td>J</td>
<td>[Mg$<em>{0.652}$Al$</em>{0.356}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.032}$0.83H$_2$O</td>
</tr>
<tr>
<td>K</td>
<td>[Mg$<em>{0.634}$Al$</em>{0.360}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.034}$1.11H$_2$O</td>
</tr>
<tr>
<td>L</td>
<td>[Mg$<em>{0.619}$Al$</em>{0.325}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.036}$1.01H$_2$O</td>
</tr>
<tr>
<td>M</td>
<td>[Mg$<em>{0.604}$Al$</em>{0.334}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.024}$1.46H$_2$O</td>
</tr>
<tr>
<td>N</td>
<td>[Mg$<em>{0.589}$Al$</em>{0.431}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.032}$1.15H$_2$O</td>
</tr>
<tr>
<td>O</td>
<td>[Mg$<em>{0.511}$Al$</em>{0.48}$(OH)$_2$][Fe(CN)$<em>6^{4-}$]$\lambda</em>{0.003}$0.83H$_2$O</td>
</tr>
</tbody>
</table>
and the interlayer based on the pure phase formula. The calculated equivalent fraction of Fe(CN)$_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$_4$Fe(CN)$_6$ solution will be ascribed to the very high ion-exchange selectivity for
CO$_3^{2-}$. The H$_2$O 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$_2$O 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.

**CO$_2$ 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 cm$^3$/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 cm$^3$/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 cm$^3$/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 CO₂ adsorption field could be found on the hydrotalcite with the Al³⁺-substitution of 0.37.

The isosteric heat of CO₂ adsorption, \( -\Delta H_{\text{ad}} \), of sample K was determined by the following equation (Ruthven, 1984) from the adsorption isotherms at 0, 25 and 40°C:

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

where \( \Delta H_{\text{ad}} \) is the enthalpy change on CO₂ 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 CO₂ adsorption was determined to be 43.3 kJ mol⁻¹ at the adsorption amount of 20–40 cm³/g, which indicates the level of chemical adsorption. This is almost the same as the isosteric heat of CO₂ adsorption (40 kJ mol⁻¹) at an infinitesimal coverage on oxygen-deficient magnetite at 150–300°C (Nishizawa et al., 1992). Therefore, CO₂ adsorption on HT is based on the same chemical process as in the latter material. Moreover, HT does not show any adsorption for N₂ gas and is comparable to an activated carbon in the separation performance of CO₂ and N₂ (Ito, 1993).

CONCLUSION

The extent of formation of hydrotalcite in the Mg²⁺–Al³⁺–Fe(CN)₆⁴⁻ system has been determined to range from 0.24 to 0.48. It was evidenced by a linear decrease in the lattice constant \( a_0 \) with an increase in R value. A lower temperature (room temperature) has been demonstrated to be effective for the formation of HTs with high Al³⁺-substitution. Slow polymerization at lower temperature allows an amorphous hydrolysis product to grow in crystals with the high degree of Al³⁺-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)₆⁴⁻ 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. CO₂ can be accommodated more easily in an expanded interlayer space. The amount of CO₂ 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 CO₂ adsorption by hydrotalcite in the Mg²⁺–Al³⁺–Fe(CN)₆⁴⁻ system were found at the Al³⁺-substitution of 0.37. The isosteric heat of CO₂ adsorption on HTs in the Mg²⁺–Al³⁺–Fe(CN)₆⁴⁻ 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 ClO₄⁻ form, which cannot be synthesized directly from aqueous solutions of metal salts.

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