ADSORPTION OF N_2, O_2, CO_2 and H_2 ON HYDROTALCITE-LIKE SYSTEM: Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$

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Abstract—The compound Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$, with a structure similar to hydrotalcite $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, is prepared by a coprecipitation method. Chemical, thermal, and X-ray analysis of the compound lead to the formula:

$$(Mg_{0.741}Al_{0.259}(OH)_2)((Fe^{II}(CN)_6)_{0.067}(CO_3)_{0.002}(H_2O)_{1.05})$$
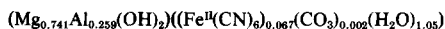
The compound is dehydrated at 100° to 250°C, and the adsorption of N_2, O_2, CO_2, and H_2 on it is measured at −196°C to room temperature by the volumetric method. The water is removed reversibly from 100° to 200°C, and the interstices after dehyration act as sites of adsorption. When dehydration is carried out at 150°C, the adsorptive activity reaches a maximum. Adsorption isotherms of N_2 and O_2 at −196°C and of CO_2 at room temperature are of the Langmuir type, and the saturated amounts of N_2, O_2, and CO_2 adsorbed are 96.3, 65.2, and 91.8 ml (STP)/g, respectively.

Adsorption isotherms of N_2 and O_2 at room temperature are of the Henry type. The amount of O_2 adsorbed is about 67% of that of N_2. The isosteric heats of adsorption at room temperature of N_2, O_2, and CO_2 are 5.1, 4.8, and 11.0 kcal/mol, respectively. A dehydrated product of a Mg^{2+}-Al^{3+}-CO_3^{2-} compound does not permit adsorption of CO_2 at room temperature, but permits the adsorption of H_2O. Hence, it has a molecular sieve effect. No adsorption of H_2 is observed in any of the compounds tested.

Key Words—Adsorption, Hydrotalcite, Isotherm, Surface, Zeolite.

INTRODUCTION

Hydrotalcite-like compounds have the general composition formula: $M_{1-x}^{2+}M_x^{3+}(OH)_2^{x+} A_{x/n}^{n-} \cdot mH_2O$, where M^{3+} is a trivalent cation such as Al^{3+}, Fe^{3+}, or Cr^{3+}, and A^{n-} is an anion having a valence of *n* such as Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, $(CH_2COO)_2^{2-}$, or $(Fe(CN)_6)^{4-}$ (Miyata, 1975). The structure is a repetition of a positively charged brucite-like basic layer: $(M_{1-x}^{2+}M_x^{3+}(OH)_2)^{x+}$ resulting from the substitution of M^{2+} by M^{3+}, and an interlayer: $(A_{x/n}^{n-} \cdot mH_2O)^{x-}$, consisting of an anion and H_2O. Hence, they are non-stoichiometric compounds (Allmann, 1968; Miyata, 1975).

The thickness of the unit layer corresponds to the spacing of the (003) plane: d_{003}. The thickness of the interlayer is obtained by subtracting the thickness of the basic layer from d_{003}, and is nearly equal to the diameter of the anion (Miyata, 1975). The structure of the basic layer in the Mg^{2+}-Al^{3+}-CO_3^{2-} system is analogous to that of brucite, and its thickness is 4.769 Å at 26°C (Wyckoff, 1963).

The water present in the interlayer is removed reversively until the temperature reaches about 300°C, and the structure of the compound does not change until that temperature is reached (Miyata et al., 1971). It is expected, therefore, that interstices in the layer, which result from the removal of water, will become adsorbing sites for molecules by the action of the polarity of the layer surface. Also it is expected that by proper choice of the diameter of the anion, the compound will have a molecular sieve effect like zeolites.

In the present paper, the Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ is expected to have a high adsorptive activity; it was prepared and dehydrated, and the adsorption of N_2, O_2, CO_2, and H_2 were measured at a pressure of 1 to 600 mm Hg and at temperatures from −196°C to room temperature by the volumetric method.

EXPERIMENTAL

Preparation of compound: Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ system

An aqueous solution of magnesium chloride and aluminum chloride (Mg^{2+}: 0.6 mol/liter, Al^{3+}: 0.2 mol/liter), an aqueous solution of sodium hydroxide (2 mol/liter), and an aqueous solution of potassium ferrocyanide (0.1 mol/liter) were mixed continuously into a 2-liter cylindrical vessel with a total flow rate of about 40 ml/min. The temperature and pH of the reaction mixture were 40 ± 1°C and 10 ± 0.2 with a molar ratio, $(Fe(CN)_6)^{4-}$/Al^{3+} maintained at 0.75. The yellowish green precipitate formed was collected by filtration, washed with water, and dried at 80°C for 20 hr.

The compounds Mg^{2+}-Al^{3+}-ClO_4^-, Mg^{2+}-Al^{3+}-SO_4^{2-}, and Mg^{2+}-Al^{3+}-CO_3^{2-} were prepared by the methods described previously (Miyata et al., 1971; Miyata, 1975; Miyata and Okada, 1977).

Chemical analysis

Fe^{3+} and CN^- were analyzed by chelate titrations of the sample dissolved in dilute hydrochloric acid and CHN-analyzer, respectively after decomposing the sample by heat. Analyses of the other components were made in accordance with the previous paper (Miyata, 1975; Miyata and Okada, 1977).
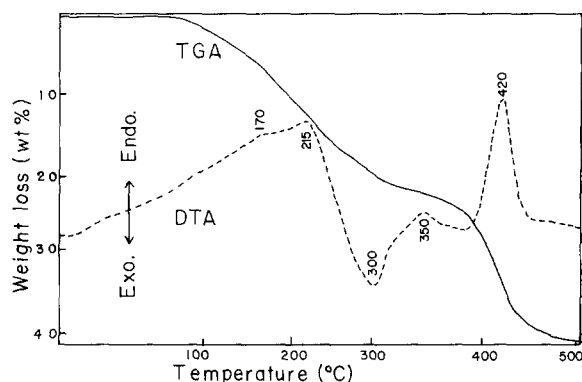
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Fig. 1. DTA and TGA curves for Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$.

Table 2. Chemical analysis of Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$.

MgO	14.1 %
Al_2O_3	31.8
Fe_2O_3	5.72
CO_2	0.62
H_2O	36.5
N	6.05
C	5.16
Total	99.95

X-ray powder diffraction and thermal analysis

X-ray powder diffraction patterns of the samples were chart-recorded on a Phillips X-ray diffractometer using Cu-Kα radiation filtered by Ni. The scanning speed was ½°/min. DTA and TGA diagrams were recorded in air at a heating rate of 5°C/min with a Rigaku Denki DG-CIH unit.

Study of adsorption isotherms

Adsorption isotherms of the samples were determined by the volumetric method at a pressure of 1 to 600 mm Hg after evacuating the samples in vacuo at a given temperature for 1 hr. The dead volume was determined by He. He, N_2, O_2, and H_2 were used after purification by ordinary methods. The CO_2 used was a commercially available bomb-filled gas. Prior to use, it was vacuum-distilled 3 times.

RESULTS AND DISCUSSION

X-ray powder diffraction

The X-ray powder diffraction data of the compound Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ are shown in Table 1. The ob-

Table 1. X-ray powder data for compound, Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$.

(1) $d_{obs.}$ Å	(2) I/I_0	(3) $d_{calc.}$ Å	(4) hkl
11.18	100	11.21	003
5.604	38	5.604	006
3.735	22	3.736	009
2.597	13	2.616	102
2.466	6	2.463	105
2.313	9	2.319	107
2.231	5	2.238	108,00,15
2.009	4	2.002	10,11
1.529	19	1.529	110
1.513	12	1.515	113
1.478	3	1.475	116
1.414	2	1.415	119
1.278	1	1.276	202

(1) Observed reflections. (2) Relative peak height. (3) Calculated spacings. (4) Indices for reflections from cells with $a_0 = 3.06$ Å, $c_0 = 33.62$ Å (hexagonal).

served diffractions can be interpreted in terms of hexagonal cell parameters, $a_0 = 3.06$ Å, $c_0 = 33.62$ Å. It has the same a_0 as hydrotalcite of the same composition (Al/Mg = ⅓) $a_0 = 3.06$ Å, $c_0 = 23.07$ Å (Frondel, 1941), and a larger c_0 than the latter because $(Fe(CN)_6)^{4-}$ has a larger ionic diameter than $CO_3{}^{2-}$. Hence, the thickness of the unit layer in the sample increases by 3.52 Å. Therefore, the compound Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ has a crystal structure similar to hydrotalcite. Since the interlayer of this compound increases by 3.52 Å as compared with hydrotalcite and the diameter of a water molecule is about 3 Å, it is assumed that two layers of water of crystallization are present in the interlayer with a ferrocyanide ion.

Chemical analysis

The results of chemical analysis are shown in Table 2. The chemical composition of this compound, determined in accordance with the previous paper (Miyata, 1975) from the results of chemical analysis and the first-stage weight loss in TGA which corresponds to interlayer water, is given as

$$(Mg_{0.741}Al_{0.259}(OH)_2)((Fe^{II}(CN)_6)_{0.067}(CO_3)_{0.002}(H_2O)_{1.05})$$
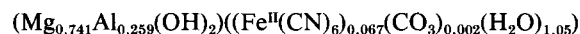
A very small amount of $CO_3{}^{2-}$ comes from the raw material solution and the atmospheric air during sample preparation. The amount of $CO_3{}^{2-}$ in the compound containing a tetravalent anion, $(Fe(CN)_6)^{4-}$, is smaller than in hydrotalcite-like compounds containing a monovalent anion such as Cl^- or NO_3^- because an anion is ion-exchangeable and according to the law of ion exchange, a higher valence ion has stronger reactivity (Miyata and Kumura, 1973).

Thermal analysis

According to TGA and DTA shown in Figure 1, the loss of interlayer water begins at about 100°C, and ends at about 300°C, with two endothermic peaks of dehydration, at 170°C and 215°C. Since one endothermic peak is ascribable to the interlayer water of hydrotalcite, it is believed that two layers of water exist between the layers. The exothermic peak at 300°C is due presumably to the decomposition of $(Fe(CN)_6)^{4-}$, CO_2 and N_2 form, and CO_3 replaces the anion $(Fe(CN)_6)^{4-}$.

For the sample to show adsorption characteristics

Table 3.   Variation of unit layer and interlayer thickness at various pretreatment temperatures.

| Pretreatment temperature	Untreated sample	100°C	150°C	200°C	250°C	300°C
Unit layer thickness	11.18 Å	10.91	10.39	10.80	8.04	Amorphous
Interlayer thickness	6.41 Å	6.14	5.62	6.03	3.27	Amorphous

similar to those of a zeolite, it must be pretreated at 100° to 300°C. Thus, from the X-ray powder diffraction of the sample, evacuated for 1 hr at various temperatures between 100°C and 300°C, changes in the thickness of the unit layer (d_{003}) and the thickness of the interlayer, that is the spacing between layers, are examined, and the results are shown in Table 3. At 100° to 200°C, d_{003} decreases only slightly, but at 250°C it decreases abruptly to 8.0 Å which is almost equal to d_{003} (= 7.8 Å) of hydrotalcite. At 300°C, the compound is nearly amorphous, and at 400°C, the decomposition of the basic layer occurs with the removal of structural water and the anions. Thus, a very broad diffraction pattern in the (200) plane of MgO appears.

Adsorption of N_2

A sample evacuated for 1 hr at room temperature to 700°C was obtained for its adsorption isotherm of N_2 at −196°C. The results, shown in Figure 2, indicate that the adsorption isotherms are of the Langmuir type at 100° to 200°C, and of the BET type at least 300°C. This means that at 100° to 200°C, the surface is heterogeneous and chemical adsorption occurs, and at 300°C or more, physical adsorption occurs. The specific surface areas calculated from the adsorption isotherms are given in Table 4. When the adsorption isotherm is of the Langmuir type, the saturated amount of adsorption (b) in the Langmuir equation

$$V = \frac{ab\sqrt{p}}{1 + a\sqrt{p}}$$

(where V is the amount of adsorption, p is the equilibrium pressure, and a and b are constants) is taken as the amount of adsorption of the monolayer in performing the above calculation. The maximum BET specific surface area is 419 m²/g for the dehydrated state at 150°C, which is about 5 times that of the untreated sample (80 m²/g). At 300°C where dehydration is complete and the structure begins to be destroyed, the specific surface area decreases to 31 m²/g. At 400° to 500°C at which MgO is formed, the specific surface area again increases. It changes little until the temperature rises to 700°C, and is maintained at 260 to 317 m²/g which is extremely high for MgO.
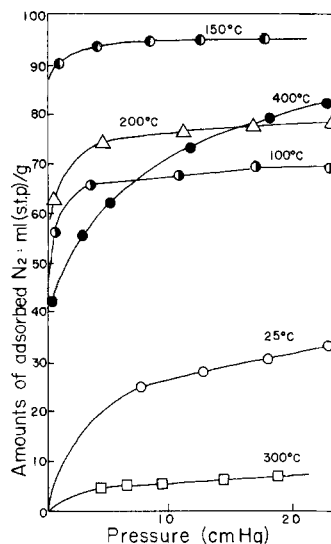
Fig. 2.   Adsorption isotherms of N_2 on Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ pretreated at various temperatures at −196°C.

Since the compound dehydrated at 100° to 200°C shows a Langmuir type adsorption isotherm and has a specific surface area 4 to 5 times as high as that of the untreated compound, it is evident that within this temperature range, N_2 is adsorbed in the interlayer.

The N_2 adsorption isotherm at room temperature was measured with a sample pretreated at 100° to 250°C. Figure 3 shows that all of the N_2 adsorption isotherms are of the Henry type, and the amount of N_2 chemisorbed increases progressively when the pretreating temperature changes as 150° > 200° > 100° > 250°C, and that the amount of adsorption at 250°C is very small.

Since the tendency of the amount of adsorption at room temperature in regard to pretreatment temperature coincides with the result obtained at −196°C, the N_2 adsorbing activity becomes maximum at a pretreatment temperature of 150°C.

Isosteric heats of adsorption, which were determined by using the Clausius-Clapeyron equation from the N_2 adsorption isotherm at room temperature (15° to 35°C) of the Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ compound evacuated in

Table 4.   BET surface area at various pretreatment temperatures.

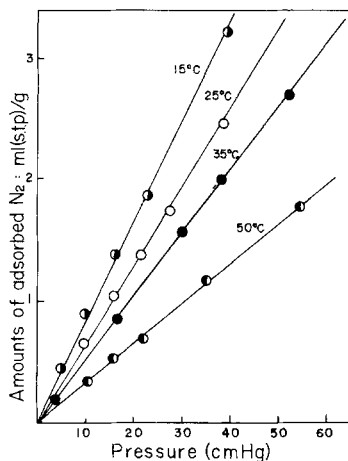| Pretreatment temperature	BET surface area
25°C	80 m²/g
100	314
150	419
200	348
300	31
400	270
500	317
600	265
700	260

Fig. 3. Adsorption isotherms of N_2 on Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ pretreated at $-150°C$ at $15°$, $25°$, $35°$, and $50°C$.

vacuo for 1 hr at 150°C, are 5.1 to 4.8 kcal/mol at an adsorbing amount of 1 to 2 ml (STP)/g. If the saturated amount of N_2 adsorption at $-196°C$ is calculated as the amount of adsorption of the monolayer, the coverage is 0.01 to 0.02. This heat of adsorption is an amount equal to the heat of N_2 adsorption on zeolite 5A which is 4.72 kcal/mol (Takagi, 1959), and is about 4 times as high as the heat of liquefaction of N_2 which is 1.33 kcal/mol (Nipponkagakukai, 1966). The reason for this is probably that since the spacing in the interlayer is close to the diameter of an N_2 molecule as in the case of zeolite 5A, N_2 is strongly adsorbed to the surface of the basic layer charged positively.

Adsorption of O_2

The O_2 adsorption isotherms on the Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ compound evacuated in vacuo at 150°C for 1 hr are determined at $-196°$, $15°$, $25°$, and $35°C$. The
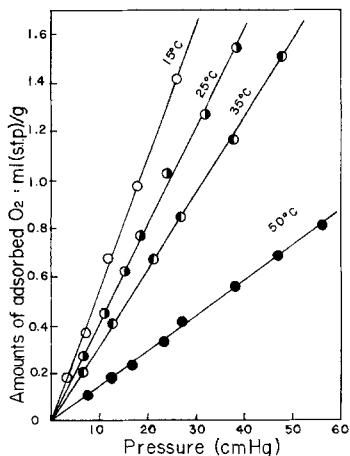

Fig. 4. Adsorption isotherms of O_2 on Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ pretreated at 150°C at $15°$, $25°$, $35°$, and $50°C$.
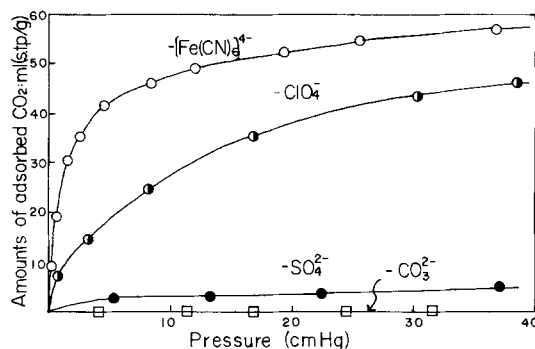

Fig. 5. Adsorption isotherms of CO_2 on Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$,-ClO_4^-,-SO_4^{2-}, and CO_3^{2-} pretreated at 150°C at 25°C.

adsorption isotherm at $-196°C$ is of the Langmuir type, and the saturated amount of adsorption is 65.2 ml (STP)/g. This amount corresponds to about 68% of the saturated amount of adsorption of N_2 at $-196°C$ which is 96.3 ml (STP)/g. It also corresponds to about 37% and 30% respectively of the saturated amount of adsorption of O_2 on zeolite 4A and zeolite 5A (Breck et al., 1956). Figure 4 shows that the adsorption isotherm at room temperature is of the Henry type, the same as in the case of N_2 adsorption. It is seen from Figures 3 and 4 that the amounts of N_2 and O_2 adsorbed at a temperature 25°C and a pressure of 30 cm Hg are 1.91 ml (STP)/g and 1.23 ml (STP)/g, respectively, and the ratio of the amount of O_2 adsorbed to that of N_2 adsorbed is 64%. Since the same ratio at $-196°C$ is 68%, the results are almost the same for both cases. The isosteric heat of adsorption calculated on the basis of Figure 4 is 4.8 kcal/mol when the amount of adsorption is 1.0 ml (STP)/g. The value is slightly smaller than for N_2 adsorption. If the saturated amount of O_2 adsorbed at $-196°C$ is calculated as the amount of monolayer adsorbed, this amount of adsorption corresponds to the coverage of 0.015. This value is higher than the heat of liquefaction of O_2 which is 1.63 kcal/mol, (Nipponkagakukai, 1966) and the isosteric heat of O_2 adsorption on zeolite 5A which is 3.16 kcal/mol (Takagi, 1959). The isosteric heat of adsorption of N_2 is slightly higher than that of O_2 presumably because the diameter of N_2 (3.0 Å) is closer to the thickness of the interlayer than that of O_2 (2.8 Å).

Adsorption of CO_2

In order to ascertain the presence or absence of a molecular sieve effect, adsorption of CO_2 at 25°C is ex-

Table 5. Unit layer and interlayer thickness of the compounds, Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$, -ClO_4^-, -SO_4^{2-}, and CO_3^{2-}.

Compound	-$(Fe(CN)_6)^{4-}$	-ClO_4^-	-SO_4^{2-}	-CO_3^{2-}
Unit layer thickness	11.18 Å	9.15	8.58	7.64
Interlayer thickness	6.41 Å	4.38	3.81	2.87

amined on an Mg^{2+}-Al^{3+}-CO_3^{2-} compound, an Mg^{2+}-Al^{3+}-SO_4^{2-} compound, an Mg^{2+}-Al^{3+}-ClO_4^{-} compound, and an Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ compound having different interlayer thickness. All of these samples are evacuated in vacuo at 150°C for 1 hr prior to testing. The unit layer thickness (d_{003}) and interlayer thickness of the samples are shown in Table 5. Figure 5 and Table 5 show that the CO_3^{2-}-type compound having an interlayer thickness of 2.87 Å does not permit adsorption of CO_2, whereas the SO_4^{2-}, ClO_4^{-}, and $(Fe(CN)_6)^{4-}$-type compounds having an interlayer thickness of at least 3.81 Å all permit adsorption. The amount of CO_2 adsorbed increases in the order of increasing thickness of the interlayer, i.e., $(Fe(CN)_6)^{4-}$ > ClO_4^{-} > SO_4^{2-}-type compound. The critical dimension of a CO_2 molecule is 2.8 Å (Breck et al., 1956). As is clear from the example of the $(Fe(CN)_6)^{4-}$-type compound, the interlayer thickness of the CO_3^{2-}-type compound pretreated at 150°C must slightly decrease over the untreated compound. Hence, the interlayer thickness of the CO_3^{2-}-type compound is actually smaller than 2.8 Å. Accordingly, the CO_3^{2-}-type compound does not permit adsorption of CO_2. However, in the SO_4^{2-}-type compound having an interlayer thickness of 3.81 Å, the real interlayer thickness of this compound after dehydration must be larger than 2.8 Å even when shrinkage by pretreatment is considered. Hence, the SO_4^{2-}-type compound adsorbs CO_2 in the interlayer. The adsorption isotherm of the $(Fe(CN)_6)^{4-}$-type compound is of the Langmuir type, and the saturated amount of adsorption is 72.0 ml (STP)/g. This amount of adsorption corresponds to about 63% of that on zeolite 5A (Breck, 1956). The isosteric heat of adsorption is calculated from the adsorption isotherm of the Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ compound at room temperature when the amount of adsorption is 15 to 40 ml (STP)/g and the coverage is 0.16 to 0.44. Within this range of coverage, the isosteric heat of adsorption is substantially constant at 11.0 kcal/mol. This value represents a relatively weak chemical adsorption.

None of the samples permits adsorption of H_2 at room temperature.

The foregoing results demonstrate that by removing the interlayer water at 100° to 250°C from compounds having structures similar to hydrotalcite, the interstices in the interlayer act as adsorbing sites for molecules. By changing the type of anion, the interlayer thickness of each compound changes accordingly, and the compound exhibits a molecular sieve effect according to the diameter of the anion.
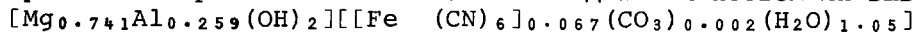
As a specific example, a gas chromatographic column (1 m length), filled with an Mg^{2+}-Al^{3+}-$(Fe(CN)_6)^{4-}$ compound having a size of about 80 mesh, is dehydrated at 150°C for 1 hr in a stream of hydrogen. When a gaseous mixture of air and H_2 is passed through the column using helium as a carrier gas, it is separated into H_2, O_2, and N_2 (Miyata and Kumura, 1973).

Accordingly, the compounds having structures similar to hydrotalcite exhibit properties very similar to those of a zeolite. The only difference is that while the former are of two-dimensional structure and in many cases solid bases, the latter are of three-dimensional structure and solid acids.

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Wykoff, R. W. G. (1963) *Crystal Structure*, Vol. 1: Wiley, New York, p. 268.

Резюме- Соединение Mg^{2+}-Al^{3+}-$[Fe(CN)_6]^{4-}$,со структурой подобной гидроталь-
киту $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ приготавливается методом соосаждения. Химический,
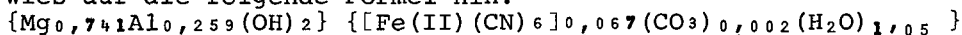термальный и рентгеновский анализы соединения позволили вывести формулу:
$[Mg_{0.741}Al_{0.259}(OH)_2][[Fe (CN)_6]_{0.067}(CO_3)_{0.002}(H_2O)_{1.05}]$
Соединение обезвоживается при температуре от $100^\circ C$ до $250^\circ C$,а адсорбция им
N_2,O_2,CO_2 и H_2 измеряется при температуре от $-196^\circ C$ до комнатной объемным
методом. Вода удаляется реверсивно при температуре от 100° до $200^\circ C$ и про-
межутки после дегидратации ведут себя как места адсорбции. Адсорбционная
активность достигает максимума,когда дегидратация проводится при $150^\circ C$.
Изотермы адсорбции N_2 и O_2 при $-196^\circ C$ и CO_2 при комнатной температуре явля-
ются изотермами типа Лангмуира и адсорбированные количества N_2,O_2 и CO_2
составляют 96,3;65,2 и 91,8мл(С.Т.Д.)/г соответственно.
Изотермы адсорбции N_2 и O_2 при комнатнои температуре являются изотермами
типа Генри. Количество адсорбированного O_2 составляет примерно 67% от ко-
личества адсорбированного N_2.
Изостерическая теплота адсорбции N_2,O_2 и CO_2 при комнатной температуре
соответственно равна 5,1; 4,8 и 11,0 ккал/мол. Продукт дегидратации соеди-
нения Mg^{2+}-Al^{3+}-CO_3^{2} не адсорбирует CO_2 при комнатной температуре,но ад-
сорбирует H_2O. Следовательно,он обладает эффектом молекулярного сита.
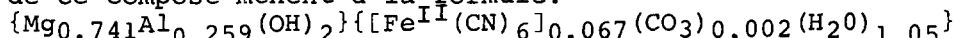Все исследованные соединения не адсорбировали H_2.

Kurzreferat- Die Substanz $Mg(II)$-$Al(III)$-$[Fe(CN)_6]^{4-}$,mit einer Struktur,
die Hydrotalkit $Mg_6Al_2(OH)_{16} CO_3 4H_2O$ ähnelt,wird via einer Mitausfällungs-
methode präpariert.Chemische,thermische und Röntgenanalyse der Substanz
wies auf die folgende Formel hin:
$\{Mg_{0.741}Al_{0.259}(OH)_2\} \{[Fe(II)(CN)_6]_{0.067}(CO_3)_{0.002}(H_2O)_{1.05} \}$
Die Probe wird dehydratisiert bei $100^\circ C$ bis $200^\circ C$ und die Adsorption von
N_2, O_2,CO_2 und H_2 auf der Probe wird bei $-196^\circ C$ bis Zimmertemperatur durch
die volumetrische Methode gemessen.Das Wasser ist umkehrbar entfernt bei
100-$200^\circ C$ und nach der Dehydratisierung wirken die Zwischenräume als Ad-
sorptionsplätze.Wenn die Dehydratisierung bei $150^\circ C$ ausgeführt wird,er-
reicht die adsorptive Aktivität ein Maximun.Adsorptionsisothermen von N_2
und O_2 bei $196^\circ C$ und von CO_2 bei Zimmertemperatur gehören zu dem Langmuir-
typ und die gesättigten Mengen von N_2,O_2 und CO_2 sind in Reihenfolge:96,3
65,2 , 91,8 ml (S.T.P.) /g.Adsorptionsisothermen von N_2 und O_2 bei Zimmer-
temperatur gehören zu dem Henrytyp.Die Menge des adsorbierten O_2 ist un-
gefähr 67 % des N_2 .Die isosterische Hitze der Adsorption bei Zimmertempe-
ratur von N_2 ,O_2 und CO_2 sind 5,1   4,8 und 11,0 kcal/mol.Ein dehydratisier-
tes Produkt einer $Mg(II)Al(III)CO_3^{2-}$Substanz erlaubt keine Adsorption bei
Zimmertemperatur erlaubt jedoch die Adsorption von Wasser. Daher hat es ei-
nen Effekt wie ein Molekularsieb.Adsorption von H_2 wird in keinen der ge-
testeten Proben gefunden.

Résumé-Le composé Mg^{2+}-Al^{3+}-$[Fe(CN)_6]^{4+}$,d'une structure pareille à
l'hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ est préparé par une méthode de
co-précipitation. Des analyses chimiques,thermales et aux rayons-X
de ce composé mènent à la formule:
$\{Mg_{0.741}Al_{0.259}(OH)_2\}\{[Fe^{II}(CN)_6]_{0.067}(CO_3)_{0.002}(H_2O)_{1.05}\}$
Le composé est déshydraté de 100 à $250^\circ C$ et l'adsorption de N_2,O_2,
CO_2 et H_2 est mesurée de $-196^\circ C$ à la température ambiante par la mé-
thode volumétrique.L'eau est retirée réversiblement de 100° à $200^\circ C$,
et les interstices après désydratation agissent comme des sites d'ad-
sorption.Lorsque la déshydratation se fait à $150^\circ C$,l'activité d'adsorp-
tion atteint un maximum.Les isothermes d'adsorption de N_2et de O_2 à
$-196^\circ C$,et de CO_2 à température ambiante sont du type Langmuir,et les
quantités saturées de N_2,O_2 et de CO_2 adsorbées sont respectivement de
96.3,65.2 et91.8 ml (S.T.P.)/g.

Les isothermes d'adsorption de N_2 et O_2 à température ambiante sont du type Henry. La quantité d'O_2 adsorbée est à peu près 67% de celle de N. Les chaleurs isostériques d'adsorption de N_2, O_2 et de CO_2 à température ambiante sont respectivement de 5.1, 4.8, et 11.0 Kcal/mol. Un produit déshydraté d'un composé Mg^{2+}-Al^{3+}-CO_3^{2-} ne permet pas l'adsorption de CO_2 à température ambiante, mais permet l'adsorption d'H_2O. L'effet est donc celui d'un tamis moléculaire. L'adsorption d'H_2 n'a été observé dans aucun des composés testés.