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SYNTHESIS OF NEW HYDROTALCITE-LIKE COMPOUNDS AND THEIR PHYSICO-CHEMICAL PROPERTIES

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The new hydrotalcite-like compounds which consist of divalent metal, trivalent metal and inorganic or organic anion were synthesized and it was found that they have many characteristic properties such as the formation of solid solutions, anion exchange and molecular sieving. Some of them were capable of separating the mixture of air and hydrogen into N_2, O_2 and H_2.

From our experimental work to establish the optimum synthetic condition of hydrotalcite-like compounds and the study on the physico-chemical properties, we have succeeded in obtaining a possible formula as follows:

$$M^{2+}{}_{x}\, M^{3+}{}_{y}\, (OH)_{2x+3y-nz}\, (A^{n-})_{z} \cdot aH_2O$$

where M^{2+} is a divalent metal; M^{3+} is a trivalent metal; A^{n-} is a n-valent anion; and x, y and z are numbers which satisfy the following:

$$1/2 \leq x/x+y \leq 1, \qquad 1/4 \leq nz/x+y < 1/2$$

(1) Synthesis

Preparations of a series of the compounds were mostly accomplished by the previous method.[1,2] Many experiments were made by varying the kinds of M^{2+}, M^{3+} or anion and the following rules have been found:

(a) $5 \sim 10 \geq pS_1 - pS_2 > 0$, where $pS = -\log S$, and S_1 and S_2 are the solubility products of $M^{2+}(OH)_2$ and $M^{2+}(A^{n-})_{2/n}$ respectively.

(b) $M^{3+}(OH)_3$ is kept as a monomer or almost monomer state.

(c) ion radius of M^{2+} or M^{3+} is close to each other.

The examples that satisfy these rules are given in Tables 1 and 2. As shown in Table 2, $Cr(OH)_3$ polymerizes at pH 10-12 and dissolves above pH 12, for it is an amphoteric hydroxide.

(2) Structure and physico-chemical properties

Experimental data of Zn^{2+} - Al^{3+} - dicarboxylic anions series are given in Fig. 1, which shows the relation between the anion diameter and the thickness of a unit layer that is the spacing of (006) plane. Fig. 1 shows that the spacing of (006) plane is proportional to the carbon number of dicarboxylic anions and that the sum of oxalate ion's diameter, 4.3 Å, and the layer thickness, 4.9 Å, is 9.2 Å, which almost coincides with the value, 9.4 Å, which was measured as the spacing of (006) plane.

Table 1. Relation between stability of $M^{2+}(OH)_2$ and products

Reactants of System M^{2+}, M^{3+}, A^{n-}			Atomic ratio of M^{2+}/M^{3+}	pS_1	pS_2	pS_1-pS_2	Products (X-ray method)
Ni	Al	CO_3	3	14.3	8.2	6.1	Objective product
Zn	Al	CO_3	3	15.3	10.0	5.3	Objective product
Cd	Al	CO_3	3	13.6	13.6	0	Objective product and small amount of $CdCO_3$
Ca	Al	CO_3	3	5.3	7.6	-2.3	$CaCO_3$ and small amount of objective product
Ba	Al	CO_3	3	1.1	8.3	-7.2	$BaCO_3$
Zn		C_2O_4		15.3	10.8	4.5	Objective product
Zn		Cl		15.3		15.3	$Zn(OH)_2$

Table 2. Effect of pH on the system of $Mg^{2+} - Cr^{3+} - CO_3^{2-}$

pH of reaction system	Product (X-ray method)
7	Amorphous
8	Objective product
9	Objective product
10	$Mg(OH)_2$
11	$Mg(OH)_2$
12	$Mg(OH)_2$
13	Objective product

To investigate the properties of aH_2O which we call crystal water, we plotted the ratio, a/x+y, as a function of the amount of water. Fig. 2 shows that the ratio varies from 0.4 to 1.2, depending on the spacing of (006) plane. It is noticed that they can be divided into three groups. We examined another relation between the spacing and the elimination temperature of crystal water which was obtained by D.T.A. In Fig. 3, dehydration temperature goes down with the increase of spacing. We found that the endothermic peak of dehydration is rather broad when the ratio of a/x+y is above 0.5 in the cases of both mono- and divalent anion systems, although the peak is sharp under 0.5.

From these data, we deduced that aH_2O as well as anion would exist in the interlayer sheets, and that these water molecules themselves form layer sheets in parallel with (006) plane. The water molecules in the interlayer make mono-, di- or trilayer, depending on the diameter of anion molecule. Moreover, anion in this series of compounds is exchangeable. For example, in the case of $Mg^{2+} - Al^{3+}$ - anion system, the compound is stable at the range of pH 3 - 12 and its capacity is about 220 meq/100 g and the selectivity coefficients to each anion are expressed as follows:

$$K^{NO_3}_{Cl} = 0.4(3.8),\ K_{Cl} = 2.3(0.1),\ K^{CH_3COO}_{Cl} = 0.2(0.2),\ K^{CO_3}_{2Cl} = \infty,\ K^{CrO_4}_{SO_4} = 1.4$$

$$K^{CO_3}_{SO_4} = 8.4$$

where the values in parentheses are quoted from Doex 1.

Next, we prepared some compounds having different spacing of (006) plane and dehydrated the compounds at different temperatures and then measured the amount of adsorbed CO_2 at room temperature. The compound containing ClO_4^- or $Fe(CN)_6^{3-}$, which has a spacing of the interlayer larger than the diameter of CO_2 molecule, treated at 150°C adsorbed CO_2 gas 2.5 times or 4.5 times as much as that treated at room temperature, respectively. On the other hand, a hydrotalcite containing CO_3^{2-}, which has a spacing less than the CO_2 diameter, treated at 150°C adsorbed CO_2 gas 0.7 times as much as that treated at room temperature. The amount of CO_2 adsorbed on all these compounds was decreased rapidly by the structural decomposition. This seems to indicate that the spacing of interlayer and the polarity becomes suitable for CO_2 adsorption by dehydration.

These compounds have also a molecular-sieve effect depending upon the various anion's diameter. To make certain of this effect, we made the following experiment. One meter long gas chromatgraphic column packed with Mg^{2+} - Al^{3+} - $Fe(CN)_6^{3-}$ system compound was used. After the column was treated at 150°C for 1 hr in a flow of helium gas, a mixture of H_2 and air was injected into the carrier gas of helium keeping the column at 25°C. As shown in Fig. 4, the mixture was separated clearly into H_2, O_2 and N_2, though the system treated at 100°C had no such ability.

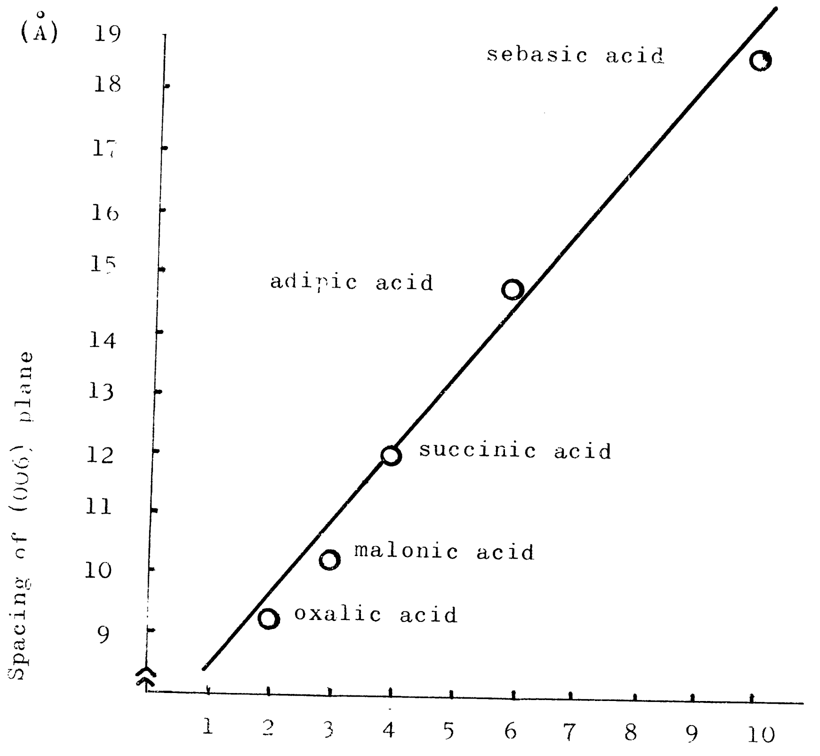

Fig. 1. Relation between carbon number of dicarboxylic acid anions and spacing of (006) plane

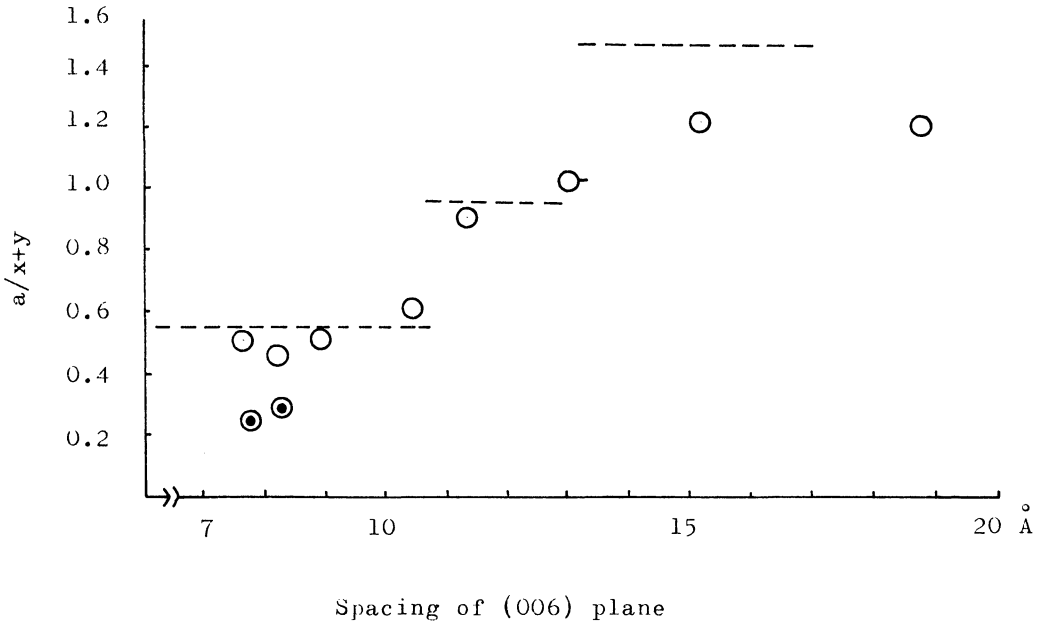

Fig. 2. Relation between spacing of (006) plane and aH_2O

⊙ ; monovalent anion

○ ; divalent anion

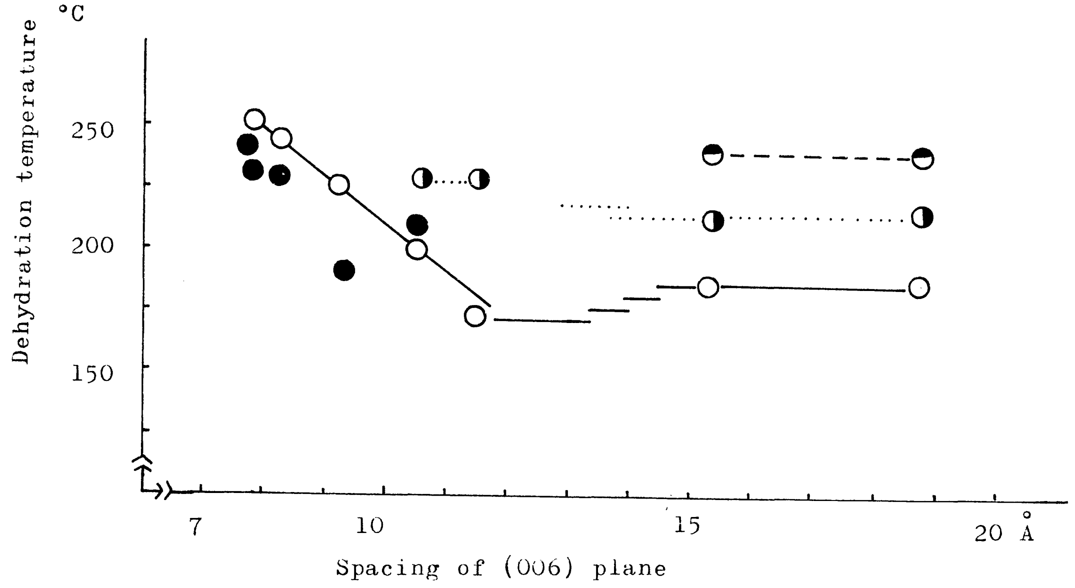

Fig. 3 Relation between spacing of (006) plane and dehydration temperature

○, ◑, ◓ ; The first, the second and the third endothermic peaks of each divalent anion of samples

● ; monovalent anion

Table 3 Adsorption of CO_2 at room temperature

Anions	Distances between layers *	Treated temperatures				
		Room temperature	100°C	150°C	200°C	
CO_3	3.0 Å	6.8 ml/g	-	4.9"	4.8"	4.9" at 290°C
ClO_4	4.5 Å	14.7 ml/g	33.4"	-	37.8"	9.8" at 300°C
$Fe(CN)_6$	6.1 Å	10.4 ml/g	46.5"	48.2"	37.1"	8.4" at 250°C

* These values were obtained by subtracting the thickness (4.8 Å) of brucite layer from the spacing of (006) plane.

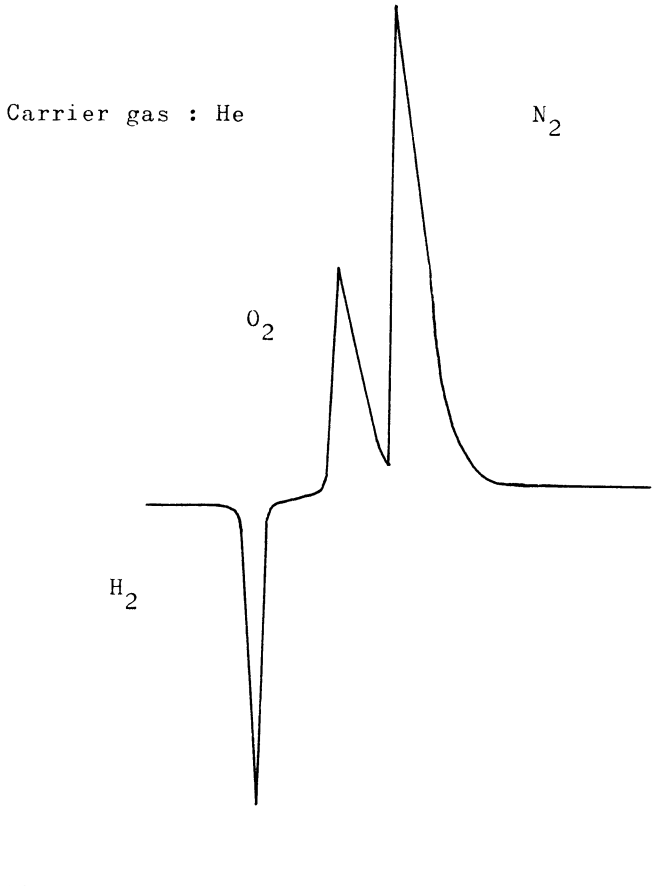

Fig. 4. Separation of N_2, O_2 and H_2 from the mixture of H_2 and air by a column of Mg^{2+} - Al^{3+} - $Fe(CN)_6$.

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