SYNTHESIS OF HYDROTALCITE-LIKE COMPOUNDS AND THEIR PHYSICO-CHEMICAL PROPERTIES— THE SYSTEMS Mg^{2+}–Al^{3+}–SO_4^{2-} AND Mg^{2+}–Al^{3+}–CrO_4^{2-}

SHIGEO MIYATA and AKIRA OKADA

Kyowa Chemical Industry Co. Ltd., Yashimanishi-machi, Takamatsushi, Japan

Abstract—Hydrotalcite-like compounds $[Mg_{1-x}Al_x(OH)_2]^{x+}$ $[A_{x/2}^{2-}.mH_2O]^{x-}$, where A^{2-} is SO_4^{2-} or CrO_4^{2-} and $x \approx 0.25$, were prepared by a coprecipitation method and their physico-chemical properties were studied by X-ray diffraction, thermal analysis, i.r. absorption spectra and acidity–basicity measurement.

The compounds including SO_4^{2-} and CrO_4^{2-} were analogous to an orthorhombic hydrotalcite and the lattice constants, a_0 and c_0 were 3.05 and 25.97 Å, and 3.05 and 26.48 Å, respectively. The crystallite size and strain in the 003 direction were 127 Å and 4.77×10^{-2} for the SO_4^{2-} system or 83 Å and 6.60×10^{-2} for the CrO_4^{2-} system, indicating a largely distorted microcrystallite. Two endothermic peaks observed at 240 and 455°C for the SO_4^{2-} system and at 230 and 460°C for the CrO_4^{2-} system are ascribed to the eliminations of interlayer water (mH_2O) and structural water, respectively. The compound including SO_4^{2-} formed MgO by calcination at 500°C and $MgSO_4$ and $MgAl_2O_4$ by calcination at 800°C, while the compound including CrO_4^{2-} formed MgO at 400°C and $MgAl_{2-x}Cr_xO_4$ at 800°C. I.r. study of the SO_4^{2-} compound indicated that the bonding of SO_4^{2-} was a bridge type. The highest acid and base strengths of the SO_4^{2-} compound were $H_0 \leq 1.5$ and $H_- \geq 12.2$, the acidity and basicity being 0.3 and 0.1 mmol/g, respectively.

INTRODUCTION

Natural minerals expressed by the chemical formula: $Mg_6Al_2(OH)_{16} CO_3.4H_2O$, are known to occur in two dimorphic forms: the hexagonal manasseite has $a_0 \approx 3.1$ and $c_0 \approx 15.5$ Å; The rhombohedral hydrotalcite has the same a_0 value but c_0 is about 23.2 Å (Aminoff and Broome, 1930; Frondel, 1941). The crystal structures of these two minerals have been reported by Allmann and Lohse (1966). They consist of positively charged brucite-like layers $[Mg_6Al_2(OH)_{16}]^{2-}$ and negatively charged interlayers $[CO_3.4H_2O]^{2-}$.

The preparation of hydrotalcite or manasseite has been studied by Gastuche *et al.* (1967) and Miyata *et al.* (Kobo, Miyata *et al.*, 1969; Miyata *et al.*, 1971). In our previous paper, the syntheses and physico-chemical properties of hydrotalcite-like compounds including monovalent anions such as NO_3^-, Cl^- and ClO_4^- were reported (Miyata, 1975). The main interesting results were as follows. (1) The thickness of an intermediate layer consisting of anions and water is substantially governed by the diameter of the anion. (2) The amount of interlayer water decreases with the increase of the amount of an anion. (3) The molar ratio of monovalent anion to aluminium is about 1: (amount of an anion) and increases with the amount of aluminium-substituted divalent cations such as Mg^{2+}, Zn^{2+} and Ni^{2+}. (4) Surface acid strength changes depending on the kinds of anions.

In the present work, hydrotalcite-like compounds containing divalent anions, SO_4^{2-} and CrO_4^{2-}, were

synthesized and the physicochemical properties were studied in detail.

EXPERIMENTAL

Preparation of compounds Mg^{2+}–Al^{3+}–SO_4^{2-}(A) *and* Mg^{2+}–Al^{3+}–CrO_4^{2-}(B)

Compound A was prepared by mixing continuously an aqueous solution of sodium hydroxide (3.5 mol/l) and a mixed aqueous solution of magnesium chloride and aluminium sulphate (Mg^{2+}:0.75 mol/l, Al^{3+}:0.25 mol/l) into a 2 l cylindrical vessel with a total flow rate of about 40 ml/min. The temperature and pH of the reaction mixture were 30 ± 1°C and 10 ± 0.2, respectively. White precipitates formed and were taken out, filtered, washed with water and dried at 80°C for 12 hr.

Compound B was prepared similarly from an aqueous solution of sodium hydroxide (2.0 mol/l), an aqueous solution of sodium chromate (0.25 mol/l), and a mixed aqueous solution of magnesium chloride and aluminium chloride (Mg^{2+}:0.75 mol/l, Al^{3+}:0.25 mol/l).

Chemical analysis

The amounts of Al^{3+} and Mg^{2+} were measured by the chelate titrations of the samples dissolved in dilute hydrochloric acid (Ueno, 1961). The amounts of SO_4^{2-} and CO_3^{2-} were determined by gravimetric analysis of barium sulphate and AGK type measurement of carbonate salt respectively. The amount of

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CrO_4^{2-} was determined by titrating iodine, which is formed by adding potassium iodide to a sample dissolved in hydrochloric acid, with sodium thiosulphate solution.

X-ray powder diffraction, i.r. absorption and thermal analysis

The X-ray powder diffraction pattern of each sample was chart-recorded on a Rigaku Denki diffractometer, using Ni filtered CuK_α radiation. Scanning velocity was 1/4/min in 2θ. The X-ray line broadening was analyzed by the method of Williamson and Hall (1953). A true half-maximum breadth (β) was obtained by Jones' method (1938) after measurement of instrumental broadening from high purity silicon. The crystallite size (ϵ) and strain (η) were calculated by using the following formula:

$$\beta_{(hkl)} = \lambda/\epsilon_{(hkl)}.\cos\theta_{(hkl)} - 2\eta_{(hkl)}.\tan\theta_{(hkl)},$$

where λ is wavelength.

The i.r. absorption spectra of samples in the form of KBr tablets were recorded for 400–4000 cm^{-1} with an Hitachi EPI-G3 i.r. spectrophotometer. The DTA and TGA diagrams were recorded in air for 120–180 mg samples with a Rigaku Denki DG-CIH unit at a heating-rate of 5°C/min.

Surface area and surface acidity and basicity

Surface area was determined by applying the BET method to the adsorption isotherm of nitrogen at -196°C. The samples dried at 70°C were evacuated at room temperature for 1 hr. Other samples were calcined in air at 200°C for 1 hr and then evacuated at 150°C for 1 hr before measurement.

Acidity and basicity were measured by titration with n-butylamine or benzoic acid using a series of Hammett or nitroaniline indicators as previously reported (Miyata et al., 1971). Samples calcined in air at 200°C for 1 hr were calcined again at desired temperatures for 1 hr and stored in glass ampoules until use.

RESULTS AND DISCUSSION

Chemical analysis

The compounds, Mg^{2+}–Al^{3+}–SO_4^{2-} (A) and Mg^{2+}–Al^{3+}–CrO_4^{2-} (B), were white and bright yellow powders. Photo-micrographs showed that both compounds formed aggregates $> 10\,\mu m$ size. The filtrabi-

Table 1. Chemical analyses of samples A and B, wt. percent

	A	B
MgO	34.9	33.6
Al_2O_3	14.7	14.0
A^{2-}(SO_3 or CrO_3)	13.0	11.6
CO_2	1.71	1.70
Mg/Al	3.01	3.04
A^{2-}/2Al	0.939	0.847
$(A^{2-} + CO_3^{2-})$/2Al^{3+}	1.21	1.13

Table 2. Indexing of X-ray powder pattern for sample A, spacing in Å

$d_{obs.}$[1]	I/I_0[2]	$d_{calc.}$[3]	hkl[4]	hkl[5]
17.0	8	17.3		001
8.64	100	8.66	003	002
4.267	32	4.329	006	004
2.583	25	2.590	102	
2.354	14	2.349	105	
2.013	8	2.038	108	
1.527	27	1.527	110	110
1.502	15	1.503	113	112
1.434	3	1.437	116	114
1.317	1	1.315	202	
1.278	1	1.280	205	

[1] Observed reflections.
[2] Relative peak height (Relative intensity).
[3] Calculated spacing.
[4,5] Indices for reflections from cells with $a_0 = 3.05$ Å and $c_0 = 25.97$ and 17.32 Å, respectively.

lity of the compounds was similar to that of synthesized hydrotalcite (Kobo et al., 1969) and higher than that of usual hydroxides.

The results of chemical analysis are shown in Table 1. Both compounds A and B contained about 2% of CO_3^{2-}, which is considered to be supplied from air and aqueous solution in the process of synthesis and drying. This probably is due to high reactivity of CO_3^{2-} whose ion diameter is smaller than those of SO_4^{2-} and CrO_4^{2-}. If the compounds A and B are assumed to have structures analogous to hydrotalcite, the ratio of $(SO_4^{2-} + CO_3^{2-})$/2Al^{3+} or $(CrO_4^{2-} + CO_3^{2-})$/2Al^{3+} should be unity (Miyata, 1975). However, the ratios for the compounds A and B were 1.21 and 1.13, respectively. This result suggests that the excess anions are strongly adsorbed on the positively charged surfaces.

X-ray powder diffraction

X-ray powder diffraction data and indexing are shown in Tables 2 and 3. All of the observed diffractions except weak diffraction (17–18 Å) can be interpreted in rhombohedral cell dimensions: $a_0 = 3.05$ Å, $c_0 = 25.97$ Å for compound A and $a_0 = 3.05$ Å,

Table 3. Indexing of X-ray powder pattern for sample B spacing in Å

$d_{obs.}$	I/I_0	$d_{calc.}$	hkl[1]	hkl[2]
17.8	7	17.7		001
8.94	100	8.83	003	002
4.414	30	4.414	006	004
2.576	29	2.581	102	
2.342	14	2.351	105	
1.984	10	2.060	108	
1.527	33	1.527	110	110
1.502	19	1.502	113	112
1.438	3	1.436	116	114
1.310	1	1.309	202	
1.274	1	1.277	205	

[1,2] Indices for reflections from cells with $a_0 = 3.05$ Å and $c_0 = 26.48$ Å and $c_0 = 17.66$ Å, respectively.

Table 4. Crystallite size (ϵ) and strain (η) in the $\langle 001 \rangle$ direction

	A	B	Synthesized hydrotalcite
(ϵ) Å	127	83	222
(η)	4.77×10^{-2}	6.60×10^{-2}	2.22×10^{-3}

$c_0 = 26.48$ Å for compound B. Thus, a large part of the crystals of both compounds is considered to have a structure analogous to hydrotalcite and a small part a structure analogous to manasseite.

The thickness of unit layer is expressed by d_{003} according to the previous paper (Miyata, 1975). The unit layer consists of a brucite-like basic layer, $[Mg_{1-x}Al_x(OH)_2]^{x+}$, and intermediate layer, $[A_{x/2}^{2-} \cdot mH_2O]^{x-}$ and the thickness of the brucite-like layer is approximately 4.77 Å. Therefore the thickness of the intermediate layer is calculated to be 3.89 Å for compound A and 4.06 Å for compound B. The difference is due to the larger diameter of CrO_4^{2-} than of SO_4^{2-}, bond distances of Cr–O and S–O being 1.63 and 1.49 Å, respectively (Pauling, 1960). In the previous paper, the thickness of the intermediate layer of Mg^{2+}–Al^{3+}–ClO_4^- inclusing ClO_4^- whose ion diameter is 4.72 Å was reported to be 4.38 Å. The thickness of the intermediate layer of compound A and B including SO_4^{2-} and CrO_4^{2-} whose ion diameters are almost the same as that of ClO_4^- is small compared to that of Mg^{2+}–Al^{3+}–ClO_4^-. This difference may be caused by the divalent anions bonding more strongly with the basic layer than the monovalent anions.

Crystallite sizes and strains of compounds A and B are shown in Table 4. Compared with synthesized hydrotalcite, the crystallite sizes are small and the strains are large. One reason for this result may be that the degree of disturbance in the structure with nearly closest packing of oxygen is influenced by ion diameter whose order is $CrO_4^{2-} > SO_4^{2-} > CO_3^{2-} >$ OH^- or H_2O. Another reason would be that crystal growth in the direction of the c axis is more easily hindered, because SO_4^{2-} or CrO_4^{2-} ions adsorb more strongly on positively charged surface (Kobo *et al.*, 1969), in particular, on (001) surface than CO_3^{2-} ions.

Thermal analysis

The DTA and TGA diagrams are shown in Figure 1. The endothermic peak due to elimination of interlayer water was observed at 240°C for compound A and at 230°C for compound B. These temperatures are almost the same as 240°C in the case of synthesized hydrotalcite. An endothermic peak due to decomposition of the brucite-like layer was observed at 455°C for compound A and at 460°C for compound B. These temperatures are a little higher than 440°C in the case of synthesized hydrotalcite. This result suggests that the binding force between anions and the basic layer is stronger in the case of SO_4^{2-}
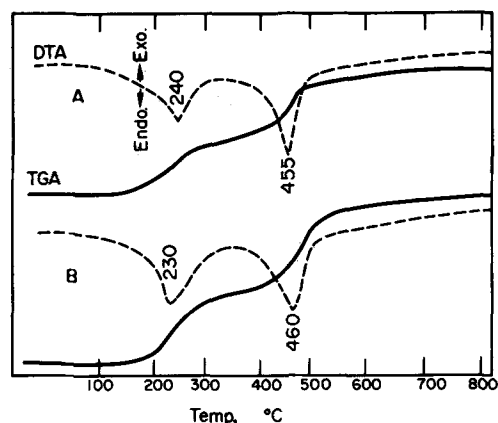

Fig. 1. TGA and DTA curves of compounds A and B.

or CrO_4^{2-} than in the case of CO_3^{2-}. It is easily understood from the comparison of crystallite sizes and strains that the endothermic peaks are broader than in the case of synthesized hydrotalcite.

I.r. absorption spectra

The i.r. spectra in the range of 400–1200 cm^{-1} are shown in Figure 2. For compound A, the absorption bands ν_1 and ν_2 which are inactive to i.r. in the case of the free ion, appeared at 990 and 450 cm^{-1}, respectively, though they were very weak. The ν_3 split bands appeared at 1120, 1150, and 1180 cm^{-1} and the ν_4 split bands at 607, 620, and 650 cm^{-1}. The width of ν_3 splitting was small (60 cm^{-1}).

Comparison of the above results with the results of SO_4^{2-} complexes (Nakamoto, 1957; Eskenazi *et al.*, 1966) reveals that SO_4^{2-} of compound A makes a bridge-type bidentate bond. The width of ν_3 splitting
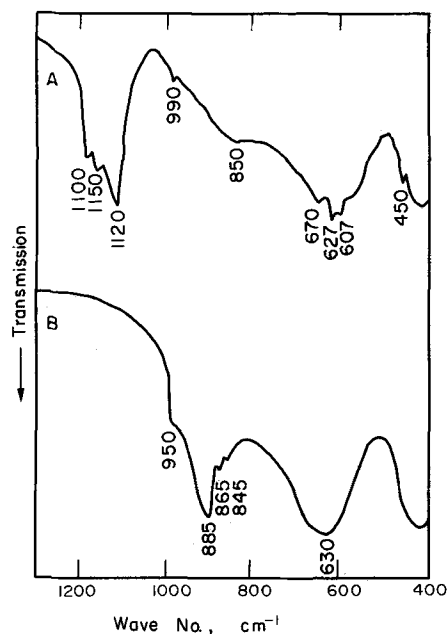
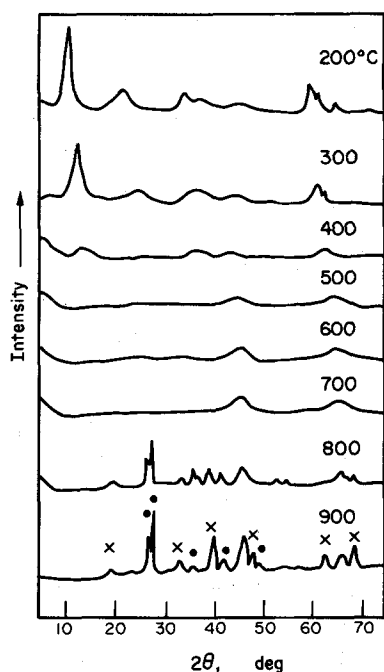Fig. 2. I.r. spectra in the region of 400–1200 cm^{-1} for compounds A and B.

Fig. 3. X-ray powder diffraction patterns for compound A calcined at 200–900°C. ●: $MgSO_4$, x: $MgAl_2O_4$.

for bridge type bond is around $140\,\mathrm{cm}^{-1}$. Since the width is $60\,\mathrm{cm}^{-1}$ in the present case, the bridge-type bidentate bond is considered to be weak. This view is supported by the fact that v_1 and v_2 bands are weak. The weak bridge-type bond corresponds to a model structure of hydrotalcite where SO_4^{2-} coordinates Mg^{2+} or Al^{3+} through OH^- of brucite-like basic layer.

In the case of compound B, a v_1 band appears at $865\,\mathrm{cm}^{-1}$ and split v_3 bands at 845, 885, and $950\,\mathrm{cm}^{-1}$. Since the width of v_3 splitting is $105\,\mathrm{cm}^{-1}$,
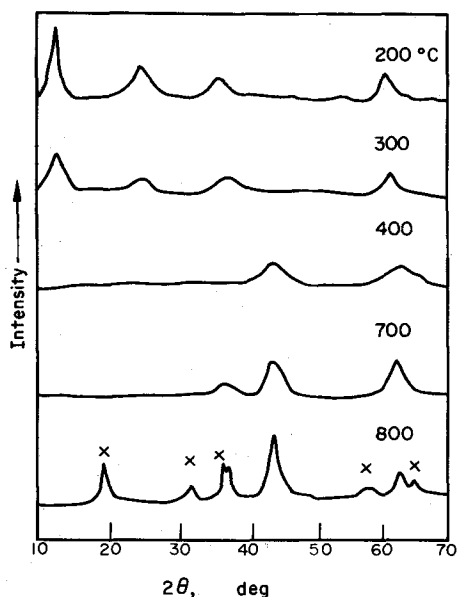

Fig. 4. X-ray powder diffraction patterns for compound B calcined at 200–800°C. x: $MgAl_{2-x}Cr_xO_4$.

CrO_4^{2-} of the compound is also considered to make a weak bridge-type bond.

Change of X-ray powder diffraction pattern and surface area with calcination temperature

The X-ray powder diffraction patterns and surface areas of compounds A and B calcined at various temperatures are shown in Figures 3–5. In the case of compound A, the patterns of samples calcined up to 300°C are the same as that of an untreated sample, though contraction of d_{001} is observed. Change of the patterns to a broad one at 400°C indicates the destruction of the structure. At 500°C, the pattern of an untreated sample disappears and fine crystals of MgO form. The crystal growth is extremely slow up to 700°C. Magnesium sulphate and $MgAl_2O_4$ formed at 800°C rapidly grow at 900°C. Surface area reaches its maximum at 500°C and does not change up to 700°C. This is probably due to the dissolution of aluminium into MgO and the control of crystal growth of MgO by adsorption of SO_4^{2-}.

In the case of compound B, the patterns of samples calcined up to 300°C are the same as that of an untreated sample, though contraction of d_{001} is observed. At 400°C, the pattern of an untreated sample disappears and fine crystals of MgO form. The crystal growth progresses up to 700°C. At 800°C, a spinel of $MgAl_{2-x}Cr_xO_4$ forms. Since the lattice constants of $MgAl_2O_4$ and $MgAl_{2-x}Cr_xO_4$ are $a_0 = 8.08$ and $8.12\,Å$, respectively, Cr^{3+} whose ion radius is larger than that of Al^{3+} is considered to dissolve into $MgAl_2O_4$. Surface area decreases with the progress of crystal growth of MgO.

Acidity and basicity

Acidity and basicity of compound B could not be measured because of its yellow colour. Change of acidity and basicity of compound A calcined at various temperatures are shown in Figure 6. The highest basic strength of compound A was H ≥ 12.2, though that of $Mg^{2+}-Al^{3+}-CO_3^{2-}$ and $Mg^{2+}-Al^{3+}-NO_3^-$ were 1.6–1.7 mmol/g. This is due mainly to the difference in surface area, since the specific surface area of SO_4^{2-} system is about $40\,m^2/g$, while those of CO_3^{2-} and
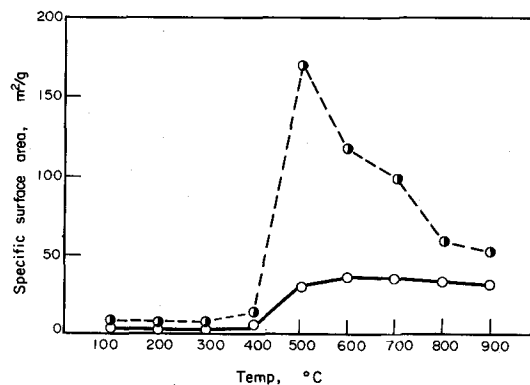

Fig. 5. Specific surface area (BET) vs temperature of heat treatment. ○——○: A; ◑——◑: B.
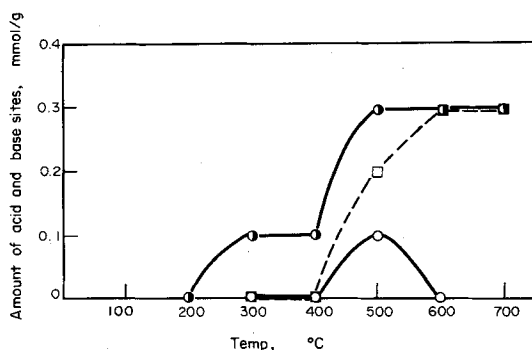
Fig. 6. Amount of acid and base sites vs temperature of heat treatment for compound A. O——O: $H_- \geq 12.2$, O——O: $H_0 \leq 4.8$, □———□: $H_0 \leq 1.5$.

NO_3^- systems are 150–160 m^2/g. On the other hand, acid sites of highest acid strength ($H_0 \leq +1.5$) appear at 400°C, and those of $H_0 \leq +4.8$ at 200°C. In the range of 400–600°C, only acidity at $H_0 \leq +1.5$ increases and above 600°C, only acid sites at $H_0 \leq +1.5$ exist. The appearance of acid sites at $H_0 \leq +1.5$ is considered to be due to the formation of $MgSO_4$.

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