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Preparation and Properties of Cobalt(II) Hydroxide-(Sodium Fluoride Tetrasilicic Mica) Intercalation Complexes and of Highly Dispersed Cobalt on Mica

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Cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica) intercalation complexes were prepared by titrating cobalt(II) nitrate solutions in the presence of mica with sodium hydroxide under oxygen-free conditions. These complexes were characterized by chemical analysis, XRD, DTA-TGA, IR, and surface area measurements. These confirmed that the brucite-like cobalt(II) hydroxide sheet developed within the interlayer of the silicate. Cobalt atoms reduced at 400—700 °C by H_2 migrated from the interlayer of the silicate to the external surface of these where highly dispersed cobalt particles were formed. Ultra-fine cobalt metals (50—200 Å) with a hexagonal close-packed form were prepared at 400 °C by H_2. The degree of reduction and the grain diameter of cobalt increased with an increase of the reducing temperature and/or the reducing time.

The preparation and properties of metal hydroxide-expansible layer silicates (montmorillonite, vermiculite, etc.) intercalation complexes are important subjects concerning the research of clay minerals. Much work has been done on this topic: especially, on aluminium hydroxide-,[1] magnesium hydroxide-,[1] and nickel(II) hydroxide-[2,3] expansible layer silicate intercalation complexes in relation to the formation and alternation of clay minerals.

On the other hand, only a few studies have been carried out on the reduction behavior of metal hydroxide interlayers of these complexes.[3,4] We found that highly dispersed nickel particles can be formed on the external surface, not in the interlayer space of the silicates, by the reduction of the nickel hydroxide interlayer of the complex.[3] Therefore, metal (especially transition elements) hydroxide-layer silicate complexes appear to be unique materials as catalysts and magnetic materials etc, since the reduction of these complexes may provide isolated metal atoms on the external surface of the silicates.

Cobalt is a typical transition element that is widely used in catalysts and magnetic materials etc. However, no attempt has been made to study the preparation of cobalt(II) hydroxide-layer silicate complexes. In this work, the preparation of cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica) intercalation complexes, the thermal stability of these complexes, and the reduction behavior with H_2 were investigated. Sodium fluoride tetrasilicic mica, $NaMg_{2.5}Si_4O_{10}F_2$, has very important characteristics: first, it has no acidity at all; second, it has a high thermal stability; and third, it has a sheet-forming capability owing to its flake-like particles.

Experimental

Materials. A 10 wt% sol of sodium fluoride tetrasilicic mica, synthesized silicate material, (supplied by Topy Ind. Co., under the name of Na-TSM) was used. Since this mica sol contains a little α-cristobalite and magnesium fluoride richiterite, $Na_2Mg_6F_2(Si_4O_{11})_2$, as impurities, the sol was diluted with distilled water and most of the impurities were separated by centrifugation. Sodium fluoride tetrasilicic mica was finally dried in air at 100 °C. The characteristics of this mica were described in detail in our previous work.[3] Na^+ ions are located within the interlayer of the silicate and balance the negative layer charge of −1 derived from vacancies in the octahedral sheets. These Na^+ ions are exchangeable in water and the theoretical cation-exchange capacity is 254 meq/100 g·mica.

Preparation and Examination of Intercalation Complexes. Cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica) complexes were prepared by titrating cobalt(II) nitrate solutions in the presence of the mica with sodium hydroxide under oxygen-free conditions. In general, the addition of alkali metal hydroxide to a solution of cobalt(II) salts results in the precipitation of cobalt(II) hydroxide. However, suspensions of cobalt(II) hydroxide are gradually oxidized by air to cobalt(III) oxide hydrate and/or cobalt(III) oxide hydroxide.[5] Therefore, the preparation procedures were operated under a N_2 gas atmosphere. All solutions were prepared using distilled water free of O_2; dissolved oxygen was expelled by keeping N_2 gas bubbling through the boiling water for 2 h.

The preparation procedures were as follows: 1.5 g samples of the mica were dispersed in 150 ml of 0.1 M (1 M=1 mol dm^{-3}) cobalt(II) nitrate solutions to give a 1 mol Co/100 g·mica. After stirring for 1 d, these suspensions were titrated with an appropriate volume of 0.1 M sodium hydroxide solutions to yield OH/Co molar ratios of 0, 0.2, 0.5, 0.8, and 1.0, respectively, at a rate of 5 ml h^{-1} under vigorous stirring, and kept stirring for 3 d. Following these treatment, samples were repeatedly washed in order to remove any electrolyte with the distilled water free of O_2 and dried at 50 °C in a vacuum oven. These samples were stored under nitrogen in a tightly closed desiccator.

Cobalt(II) hydroxide were also prepared by titrating a 2 M cobalt(II) nitrate solution with an equivalent volume of a 2 M sodium hydroxide solution under similar conditions.

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Table 1. Conditions of Preparation and Chemical Analyses of Sodium Fluoride Tetrasilicic Mica and Cobalt(II) Hydroxide-(Sodium Fluoride Tetrasilicic Mica)

No.	Condition of preparation	Chemical analysis/wt%			Molar ratio (SiO_2=4)		
	OH/Co (1 mol Co/100 g·mica)	SiO_2	Na	Co	SiO_2	Na	Co
a)		57.34	4.36	—	4.00	0.80	—
1	0.0	50.89	0.65	3.37	4.00	0.13	0.27
2	0.2	46.51	0.59	7.45	4.00	0.13	0.65
3	0.5	43.88	0.55	14.41	4.00	0.13	1.34
4	0.8	41.83	0.52	18.57	4.00	0.13	1.81
5	1.0	39.61	0.49	22.36	4.00	0.13	2.30

a) Initial sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$). Interlayer charge is +1; interlayer cations are Na^+ and H^+ that replaced the part of Na^+ cations in distilled water.

Table 2. Basal Spacings (Å) of Cobalt(II) Hydroxide-(Sodium Fluoride Tetrasilicic Mica) after Heat Treatment

No.	OH/Co	Heat treatment/°C[a]				
		105	200	250	300	350
Initial mica[b]		9.6	9.6	9.6	9.6	9.6
1	0.0	15.0[c]	9.6	9.6	9.6	9.6
2	0.2	14.5	9.6	9.6	9.6	9.6
3	0.5	14.5	9.6	9.6	9.6	9.6
4	0.8	14.5	14.5	14.5	ML[d]	9.6
5	1.0	14.6	14.5	14.5	ML	9.6

a) Heat treatment for 2 h. b) Basal spacing of sodium fluoride tetrasilicic mica is 9.6 Å (anhydrous form); 12.3 Å (single water layer hydrated form); 15.2 Å (double water layer hydrated form). c) Rehydrated form on exposure to air at room temperature. d) ML=mixed layer (mixtures of 14.5 and 9.6 Å layers).

The resulting precipitate was cobalt(II) hydroxide in pink form (β-$Co(OH)_2$) determined by XRD analysis. The pink cobalt(II) hydroxide has a brucite ($Mg(OH)_2$) structure.

The chemical analyses of the complexes were performed by atomic absorption analyses. Surface areas were measured by the nitrogen-adsorption method with a Carlo Elba Sorptomatic Series 1800. All samples were examined by XRD as thin, oriented films on glass slides. IR spectra were obtained from KBr disks. The thermal stability of the complexes in air and the reduction behavior with H_2 were investigated at 100—700 °C (the mica is stable below 800 °C); the heating rate was 10 °C min^{-1} and slowly cooled after holding for a set time.

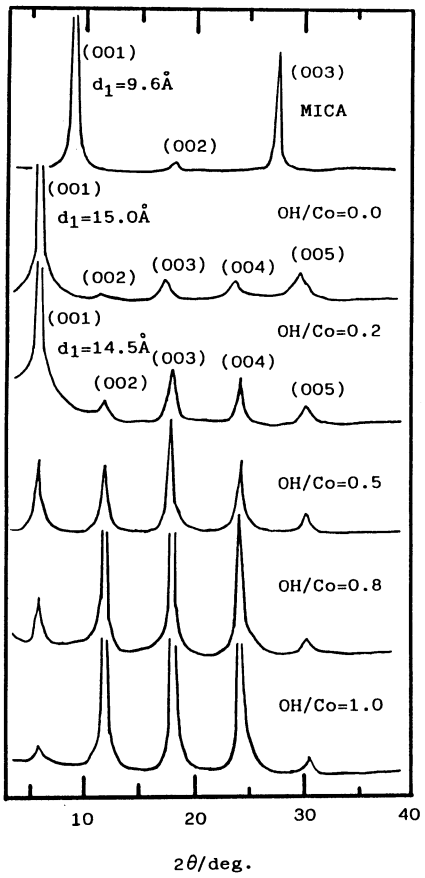

Fig. 1. X-Ray powder diffraction patterns (Cu $K\alpha$ radiation) of cobalt (II) hydroxide-(sodium fluoride tetrasilicic mica). MICA: Anhydrous form.

Results and Discussion

Chemical Analysis and XRD Measurements. Chemical analyses of the mica and its intercalation complexes are listed in Table 1. The amount of Co taken into the mica increased with an increase of the OH/Co ratio. The highest Co yield of about 2.3 mol Co per formula unit of the mica was obtained with a OH/Co ratio of 1.0. As the ion-exchange rate is 87%, this value corresponds to 2.6 mol Co per formula unit of the mica being 100% ion exchanged. In the case a complete cobalt(II) hydroxide developed between the silicate layers, as a nickel(II) hydroxide interlayer,[3] for instance, the limiting composition would be $[Co_3(OH)_5(H_2O)](Mg_{2.5}Si_4O_{10}F_2)$. This composition corresponds to 3 mol Co per formula unit of the mica 100% ion exchanged. Therefore, at a OH/Co ratio of 1.0, the cobalt(II) hydroxide interlayer would be well developed, but not completely.

The basal spacings of these complexes are expanded by about 14.5 Å from the 9.6 Å basal spacing of the mica; these basal spacings are almost constant and independent of the amount of cobalt taken into the mica (Table 2). Moreover, X-ray diffraction analyses did not show any free cobalt(II) hydroxide in these

complexes or cobalt oxide in the heat-treated sample. Therefore, a brucite-like cobalt(II) interlayer must have developed between the silicate layers without free cobalt(II) hydroxide. The X-ray powder diffraction patterns of these complexes are shown in Fig. 1. With an increase in the OH/Co ratio, the (001) first-order reflection decreased in intensity; on the contrary, the (002)—(004) higher-order reflections increased in intensities. These changes of the relative intensities also indicate that a cobalt(II) hydroxide-forming reaction took place in the interlayer of the silicate.[6]

Changes of the basal spacings after heat treatments are shown in Table 2. Basal spacings of the samples with OH/Co=0.8, 1.0 retained 14.5 Å up to 250 °C and reduced to about 9.6 Å with further heating. The XRD patterns of these collapsed samples are almost similar to that of the original mica; the (001) reflection of these collapsed samples increased in intensity. β-Cobalt(II) hydroxide changed to cobalt (II, III) oxide after a heat treatment at 150 °C for 2 h; therefore, well-developed cobalt(II) hydroxide within the interlayer of the silicate has a higher thermal stability than β-cobalt(II) hydroxide.

Thermal Analysis. Figure 2 shows the DTA and TGA curves for the complexes; the heating rate was 10 °C min^{-1}. Sample No. 1 (prepared at OH/Co=0.0) showed a single endothermic peak at about 164 °C with a corresponding weight loss. This dehydration is due to the water of hydration associated with the exchanged cobalt(II) ions within the interlayer of the silicate; this water is much more dissociated than water in the bulk state.[7] Therefore, the composition of these interlayer cobalt(II) ions is $[Co(OH)_\delta(H_2O)_{6-\delta}]^{2-\delta}$.

On the other hand, samples prepared with the addition of sodium hydroxide, OH/Co=0.2—1.0, showed a first endothermic peak at about 140—160 °C and a second one at about 380—400 °C, with corresponding weight losses. With an increase in the OH/Co ratio, the endothermic peak area at about 380—400 °C increased; on the contrary, the endothermic peak area at about 140—160 °C decreased. These correspond to the fact that cobalt(II) hydroxide, to be exact, hydroxocobalt(II) complex $[Co_x(OH)_y(H_2O)_m]^{2x-y}$ developed within the interlayer of the silicate with the progressive hydrolysis and olation of cobalt(II) cations by addition of alkali. Therefore, the first endothermic peak (140—160 °C) corresponds to the loss of absorbed water and coordinated water and the second one (380—400 °C) to the loss of hydroxo. The mechanism of formation of cobalt(II) hydroxide interlayers must be the same as that discussed in the study of the formation of a nickel(II) hydroxide interlayer.[2] The endothermic peaks at about 820 and 884 °C are due to the reactions between cobalt oxide and the mica; cobalt silicate (Co_2SiO_4) was detected by XRD after the measurement of DTA-TGA.

The DTA-TGA curves for β-cobalt(II) hydroxide showed an endothermic peak corresponding to the dehydration of hydroxyl at about 295 °C; this temperature is considerably lower than the dehydration temperature (380—400 °C) of the hydroxo of cobalt(II) hydroxide interlayer. These correspond to the fact that a well developed cobalt(II) hydroxide interlayer has a higher thermal stability than β-cobalt(II) hydroxide; that cobalt(II) hydroxide interlayer is strongly fixed by electrostatic force and hydrogen bond to the silicate layer like as brucite interlayer in chlorite.[8]

Specific Surface Areas. The specific surface areas of the complexes are shown in Fig. 3. With an increase

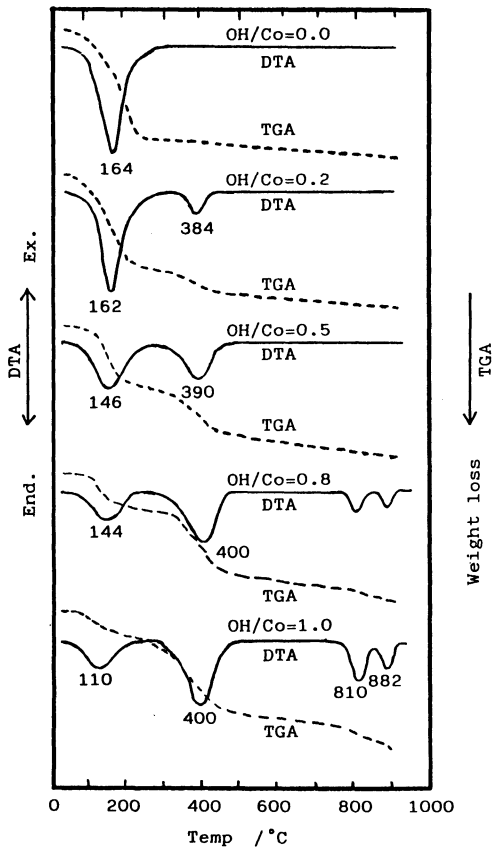

Fig. 2. DTA and TGA curves for cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica).

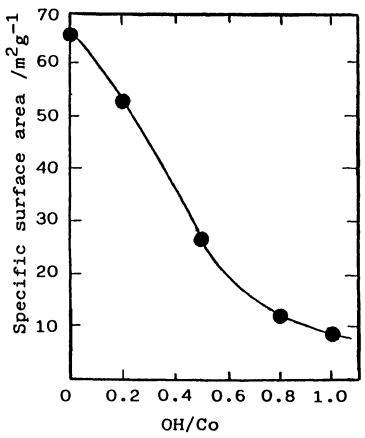

Fig. 3. Specific surface areas of cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica).

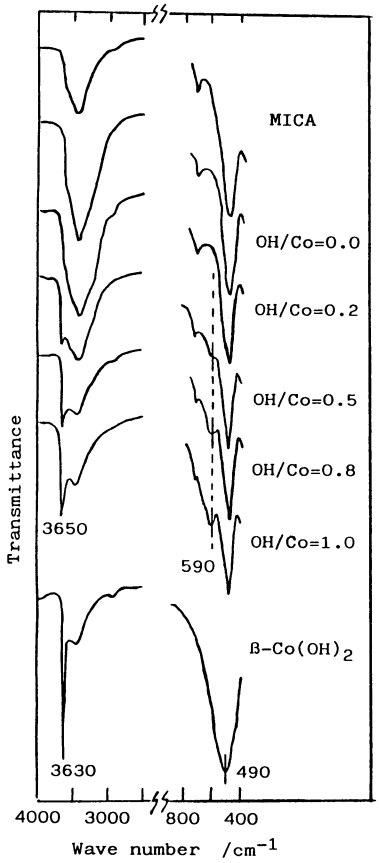

Fig. 4. IR absorption spectra of β-cobalt(II) hydroxide and cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica).

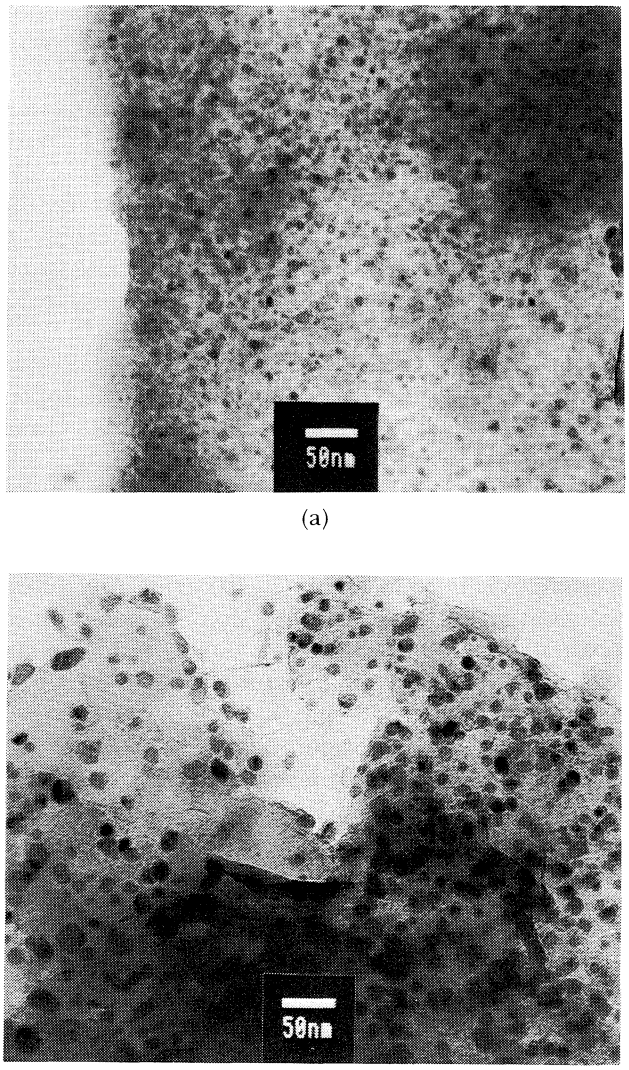

Fig. 5. Transmission electron micrographs of cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica) (OH/Co=1.0) heat treated at 400°C for 24 h (a) and 48 h (b) in H_2 flow.

in the OH/Co ratio, the specific surface areas decreased since the interlayer space becomes smaller with the development of a cobalt(II) hydroxide interlayer; finally, the internal surfaces become completely covered.

IR Analysis. The IR absorption spectra of the complexes and β-cobalt(II) hydroxide are shown in Fig. 4. Characteristic absorption bands appeared at about 3650 and 590 cm^{-1} in the complexes with an increase of the OH/Co ratio. The 3650 cm^{-1} band is due to the OH stretching vibration of cobalt(II) hydroxide interlayer. The 590 cm^{-1} band is also from the cobalt(II) hydroxide interlayer and appears to be shifted from 490 cm^{-1} band shown in absorption spectrum of β-cobalt(II) hydroxide.

Reduction Behavior with H_2. Complexes with OH/Co=1.0 were heat treated in flowing H_2 at 400, 500, 600, and 700 °C for 2 h. All samples collapsed to a basal spacing of 9.6 Å and metallic cobalt was detected by XRD above 500 °C. These metallic cobalt structures were mixtures of the face centered cubic and hexagonal close-packing phases. In general, cobalt exists as a h.c.p phase (α-Co) at ordinary temperatures; above 417 °C, it has a f.c.c phase (β-Co). However, mixtures normally coexist because of the very low free energy change associated with the α-β transformation.[9] On the other hand, those complexes with OH/Co=1.0 were also heat treated in flowing H_2 at 400 °C for 2, 4, 6, 24, and 48 h and cobalt with h.c.p form was identified by XRD after over a 4 h heat treatment.

With an increase in the reducing temperature and/or the reducing time, the reflection intensity of cobalt increased and the (001) mica basal reflection peak became sharper. These results indicate that reduced cobalt atoms gradually migrate from the interlayer of the silicates to its external surface. Patel[10] reported that finely divided metal particles (15—100 Å) can be formed in interlayer spaces of clay minerals with an H_2 reduction of transition metal (Ni^{2+}, Cu^{2+}) interlayer cations. However, our results have shown that reduced cobalt metals exist mainly not in the interlayer of the silicates but on the external surface of the silicate, owing to the fact that the basal spacings of the silicate are always 9.6 Å after H_2 reduction. TEM

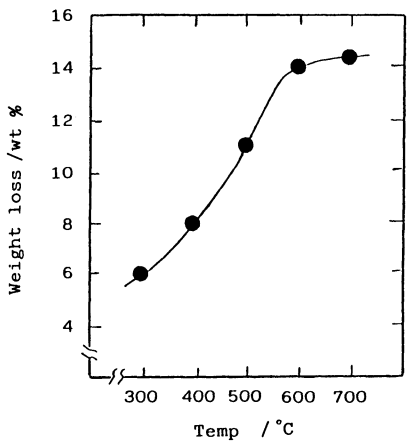

Fig. 6. Weight loss for cobalt(II) hydroxide-(sodium fluoride tetrasilicic mica) after various temperatures of reduction for 2 h.

photographs (heat treated complexes at 400 °C for 24 and 48 h in H_2 flow) show that ultra-fine metallic cobalt particles (50—200 Å) are distributed on the whole surface of the mica and that the grain diameter of this cobalt increases with an increase of the reducing time (Fig. 5). Furthermore, particles with a crystal habit of hexagonal plates can be observed.

Only a few studies have hitherto been made on the reduction behavior of transition metal cations and/or transition metal (=nickel) hydroxide within the interlayer of the expansible layer silicate. However, many studies have been performed on the reduction behavior of metal cations in zeolite. It is generally accepted that the metal ions in a zeolite are reduced to zero valent metal particles by H_2 as follows:[11]

$$Me^{x+}(ZO^-)_x + x/2H_2 \rightarrow M\overset{0}{e} + x(ZOH).$$

Here, $(ZO^-)_x$ represents the zeolite lattice and ZOH represents surface hydroxyl groups. Moreover, a similar reaction mechanism was proposed in the case of metal ions in montmorillonite.[10]

The following reduction mechanism is likely in the case of metal hydroxide-layer silicate complexes as well:

$$[Me_x(OH)_y(H_2O)_m]^{1+} \text{ (O-MICA)}^- + H_2 \rightarrow H^+\text{(O-MICA)}^- + xM\overset{0}{e} + (m+y)\,H_2O, \quad (1)$$

where $[Me_x(OH)_y(H_2O)_m]^{1+}$ represents the metal hydroxide interlayer and $(O\text{-MICA})^-$ represents a mica layer sheet. The weight loss during H_2 reduction was determined on sample No. 5 (OH/Co=1.0); it was first heat treated at 100 °C for 2 h and then heated in flowing H_2 (i) at 300, 400, 500, 600, and 700 °C for 2 h (Fig. 6), and (ii) at 400 °C for 2, 4, 6, 24, and 48 h. From chemical analyses of sample No. 5, the chemical composition of the complex were evaluated to be

$$\{[Co_{2.64}(OH)_{4.28}(H_2O)]^{+1}\}_{0.87}\,Na_{0.13}\,(Mg_{2.5}Si_4O_{10}F_2) = \{Co_{2.3}(OH)_{3.72}(H_2O)_{0.87}\}Na_{0.13}\,(Mg_{2.5}Si_4O_{10}F_2),$$

assuming that the cobalt(II) hydroxide interlayer has a composition of $[Co_x(OH)_y(H_2O)_m]^{+1}$, $(y+m)/x=2$ with a charge of +1.0 to balance the negative layer charge. The theoretical weight loss of the sample after a complete reduction was calculated to be 13.3 wt% (according to the Eq. 1). As shown in Fig. 6, the cobalt(II) hydroxide interlayer was almost reduced to cobalt metal upon being heat treated at about 600 °C for 2 h; the theoretical and experimental values agreed well. On the other hand, the weight losses after heat treatments at 400 °C for 2, 4, 6, 24, and 48 h were 8.0, 8.8, 9.3, and 10.5 wt%, respectively. Therefore, the reduction reaction was not completed, even after a 48 h treatment.

References

1) G. W. Brindley and Chih-chun Kao, *Clays Clay Miner.*, **28**, 435 (1980).

2) S. Yamanaka and G. W. Brindley, *Clays Clay Miner.*, **26**, 21 (1978).

3) K. Ohtsuka, M. Suda, M. Ono, M. Takahashi, M. Sato, and S. Ishio, *Bull. Chem. Soc. Jpn.*, **60**, 871 (1987).

4) C. Ghesquiere, J. Lemaitre, and A. J. Herbillon, *Clay Miner.*, **17**, 217 (1982).

5) M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, Oxford (1966), p. 325.; D. Nicholls, "Comprehensive Inorganic Chemistry," ed by J. C. Bailar, H. J. Emeleus, Sir Ronald Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford (1973), Vol. 3, pp. 1071, 1094.

6) C. I. Rich, *Clays Clay Miner.*, **16**, 15 (1968).

7) D. M. C. MacEvan and M. J. Wilson, "Crystal Structures of Clay Minerals and Their X-ray Identification," ed by G. W. Brindley and G. Brown, Mineralogical Society, London (1980), p. 219.

8) S. W. Baily, "Crystal Structures of Clay Minerals and Their X-ray Identification," ed by G. W. Brindley and G. Brown, Mineralogical Society, London (1980), p. 86.

9) D. Nicholls, "Comprehensive Inorganic Chemistry," ed by J. C. Bailar, H. J. Emeleus, Sir Ronald Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford (1973), Vol. 3, p. 1054.; A. Taylor, *J. Inst. Metals*, **77**, 585 (1950).; M. Hansen and K. Anderko, "Constitution of Binary Alloys 2nd ed," McGraw-Hill, New York (1958), p. 485.

10) M. Patel, *Clays Clay Miner.*, **30**, 397 (1982).; M. Patel, *Trans. Indian Ceram. Soc.*, **42**, 1 (1983).

11) P. A. Jacobs, "Carboniogenic Activity of Zeolite," Elsevier, Amsterdam (1977), p. 183.