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Preparation and Properties of Iron(II) Hydroxide-(Sodium Fluoride Tetrasilicic Mica) Intercalation Complexes

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Iron(II) hydroxide-(sodium fluoride tetrasilicic mica) intercalation complexes, which have a chlorite-like structure, were prepared by titrating iron(II) sulfate solutions in the presence of mica with sodium hydroxide under oxygen-free conditions. The formation of iron(II) hydroxide sheets between the silicate layers was evaluated by chemical analysis, XRD, DTA-TGA, and surface-area measurement. The presence of water is essential for the oxidizing of these complexes to occur at room temperature by air, because the O_2 attack on the surface of these iron(II) hydroxide sheets is hindered by the silicate layers. Fine highly dispersed iron metal particles (α-Fe) were formed on the external surface of the silicate by the H_2 reduction of the complexes.

We previously reported that ultra-fine, highly dispersed metal (Ni, Co) particles can be prepared on the external surface of silicates by the reduction of metal (Ni, Co) hydroxide-layer silicate complexes.[1,2] This method of preparation, providing isolated metal atoms on the carrier, leads to many applications for catalysts, magnetic materials, electronics, etc. Therefore, it is desired that this technique is applicable to the iron element as well as to the nickel and cobalt elements; the iron element is essential for those applications.

Besides, iron(II) hydroxide-layer silicate complexes, if possible. should be novel reducing agents which are easy to handle, for iron(II) hydroxide has a strong reducing power and this iron(II) hydroxide sheet would be sandwiched between the silicate layers.

Although many attempts have been made to prepare these iron hydroxide-layer silicate complexes,[3-7] no clear evidence for the formation of these complexes has yet been obtained. These attempts to study clay minerals have been connected with the transformation of expansible layer silicate (2:1 layer silicate) to metal hydroxide-layer silicate, which has a chlorite-like structure. Chlorites have a 2:1 layer structure with a metal hydroxide interlayer, and iron(II, III) is considered to exist in both the hydroxide sheet and the 2:1 layer of chlorites.[8-12]

In this work, the preparation and properties of iron hydroxide-layer silicate (sodium fluoride tetrasilicic mica) complexes were investigated. We have attempted to prepare these complexes with the iron(II) ion, not with the iron(III) ion, because we consider that there is an essential difficulty in forming an iron hydroxide interlayer with the iron(III) ion; the iron(III) ion in the metal hydroxide interlayer of chlorites must be introduced by the oxidation of the iron(II) ion or by coprecipitation as a minor constituent with a major constituent (Al, Mg etc.). One of the reasons why the preparation of iron hydroxide-layer silicate complexes has rarely been carried out with the iron(II) ion is evidently that iron(II)-ion solutions are easily oxidized by air. The problems of what kind of cations can give these hydroxide interlayers and of the mechanism of these transformations will be explained in detail in our next paper.

Experimental

Starting Materials. A 10 wt% sol of sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$), obtained from 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 then most of the impurities were separated by centrifugation. Finally sodium fluoride tetrasilicic mica was dried in air at 100 °C.

The characteristics of this mica were described in detail in our previous work.[1] Sodium fluoride tetrasilicic mica is an expansible 2:1 layer silicate. Na^+ ions are located between the silicate layers to balance the negative layer charge of the -1 derived from the vacancies in the silicate layers. These Na^+ ions are exchangeable in water, the theoretical cation-exchange capacity being 254 meq/100 g·mica.

Preparation of Iron(II) Hydroxide–Mica Complexes. Iron(II) hydroxide-(sodium fluoride tetrasilicic mica) complexes were prepared by the titration method: iron(II) sulfate solutions in the presence of mica were titrated with sodium hydroxide under oxygen-free conditions.

The iron(II) ion is thermodynamically unstable with respect to atmospheric oxidation and, especially in alkaline solutions, is rapidly oxidized by the oxygen in the air.[13,14] Hence, great care was taken to prevent it from touching with O_2 during the preparation. The preparation procedures were operated under a N_2 gas atmosphere; N_2 gas was passed through a disoxidation agent in advance. All the solutions were prepared using distilled water free of O_2; dissolved oxygen was expelled by keeping N_2 gas bubbling through the boiling water.

Figure 1 shows the process of preparing the complexes, while Fig. 2 shows the scheme of the preparation system. Oxygen-free water was added to the mica powder, and then this suspension was refluxed in a N_2 flow to expel the oxygen absorbed on the surface of mica. As the iron(II) sulfate reagent has a few iron(III) ions, iron(II) sulfate solutions were aged for 1 day and then passed through glass filters by means of N_2-gas pressure to remove any iron(III) hydroxide. These iron(II) sulfate solutions, thus filtered and transported to the reaction flask, were then mixed with the mica sol to give a 1 mol Fe/100 g·mica, where the concentration of Fe in these mixed suspensions was 0.1 M (1 M=1 mol dm^{-3}). These mixed suspensions were stirred for 1 day to promote ion-exchange between the iron(II) ion and the sodium ion within the mica. Subsequently, in order for the hydrolysis between the silicate layers to proceed, these suspensions were titrated with 0.1 M sodium hydroxide solutions at the rate of 20 ml h^{-1} to yield OH/Fe molar ratios of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 respectively under vigorous stirring. After these additions, stirring was continued for 2 days. The resulting products were washed in oxygen-free water to remove electrolytes, the supernatant being taken out by means of N_2-gas pressure. Finally, these products were centrifuged, dried at 50 °C in a vacuum oven, and stored under nitrogen in a tightly closed desiccator.

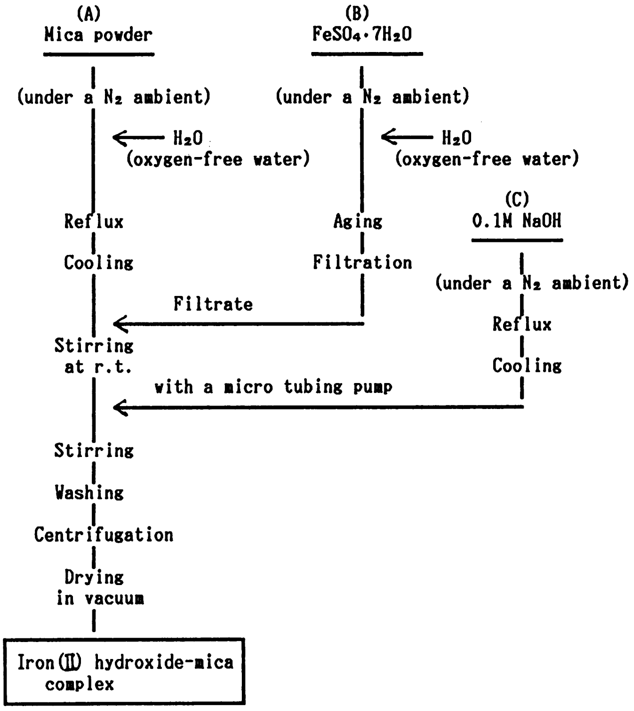

Fig. 1. Process of preparing iron(II) hydroxide-(sodium fluoride tetrasilicic mica).

Techniques of Characterizing the Complexes. Chemical analyses of the complexes were carried out by atomic-absorption analysis. The X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer RU-200, using Cu *Kα* radiation, from specimens basally oriented on glass slides. The surface areas were measured by the nitrogen-adsorption method at the temperature of liquid nitrogen with a Carlo Elba Sorptomatic, Series 1800. The samples were evacuated at 50 °C overnight prior to the measurements. Differential thermal analysis and thermogravimetric analysis (DTA-TGA) were made with a Rigaku Thermoanalyzer M8076 in a N_2 flow at a heating rate of 10 °C min^{-1}. Transmission electron microscopy (TEM) was performed with a JEOL, Model JEM-1200EX. The thermal stability of the complexes in an inert gas and their reduction behavior with H_2 were investigated in a range of 100—700 °C at a heating rate of 10 °C min^{-1}, because this mica is stable below 800 °C.

Measurement of the Room-Temperature Oxidation of the Complexes in Air. In our preliminary experiment, it was found that these complexes were not oxidized only by oxygen, but that the presence of water appeared to be essential for oxidizing to occur at room temperature by air. Therefore, the room-temperature oxidation of these complexes by air was investigated in an air flow with water vapor, the weight change during exposure to air being measured by means of the gravimetric McBain-Bakr balance technique. Samples of about 0.2 g were hung with a quartz spring and evacuated. Subsequently, N_2 gas with a saturated water-vapor pressure (at 30 °C) was passed over the sample (at 31 °C) at a flow rate of 100 ml min^{-1}, the relative humidity being 94%. After a constant weight was achieved, the flow was then switched to air with a saturated water-

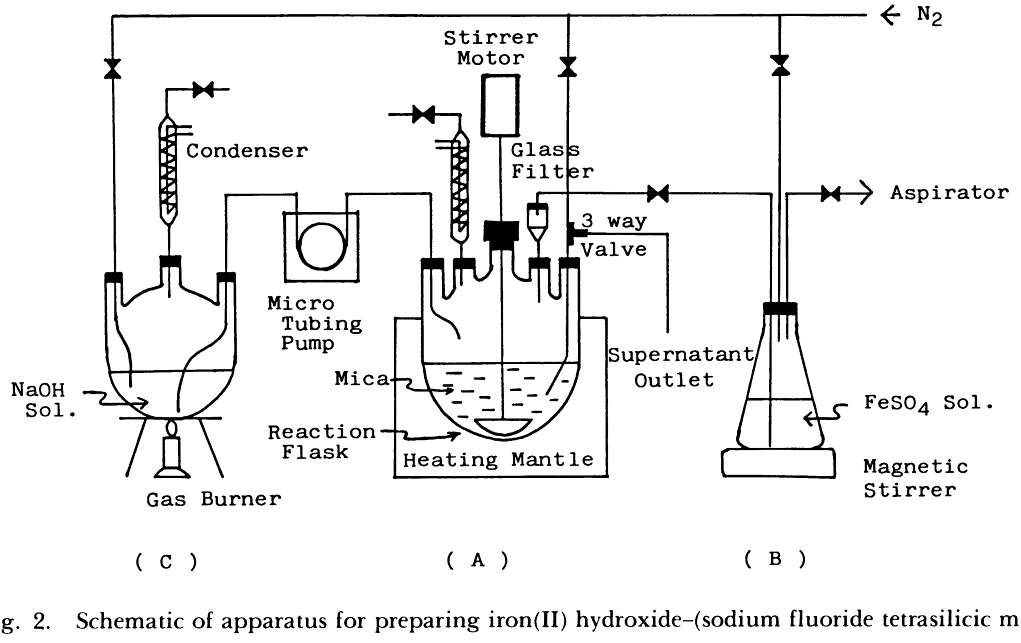

Fig. 2. Schematic of apparatus for preparing iron(II) hydroxide-(sodium fluoride tetrasilicic mica).

vapor pressure (at 30 °C) until the weight gain by oxidation was equilibrated.

Results and Discussion

Chemical Analyses. The results of the chemical analyses of the mica and its intercalation complexes are listed in Table 1. The iron content increased with an increase in the OH/Fe ratio, and the extent of the ion-exchange ratio in the resulting products was almost constant (81—82%). At an OH/Fe ratio of 1.0, the iron content of the complexes was 2.4 mol per formula unit of the mica 82% ion-exchanged, corresponding to 2.9 mol per formula unit of the mica 100% ion-exchanged. The ideal composition of the iron (II) hydroxide-mica complexes, which have a chlorite-like structure, is $[Fe_3(OH)_5(H_2O)](Mg_{2.5}Si_4O_{10}F_2)$;[1,2] the maximum iron content of the complexes is 3 mol per formula unit of the mica 100% ion-exchanged. Therefore, at an OH/Fe ratio of 1.0, the iron(II) hydroxide interlayers in the complex must be well-developed.

XRD Measurement and Specific Surface Area. The X-ray powder diffraction patterns of these complexes are shown in Fig. 3. The basal spacings of these complexes expanded to about 14.3—14.7 Å from the 9.6 Å basal spacing of the mica (Table 2); these basal spacings were almost independent of the iron content. Moreover, with an increase in the OH/Fe

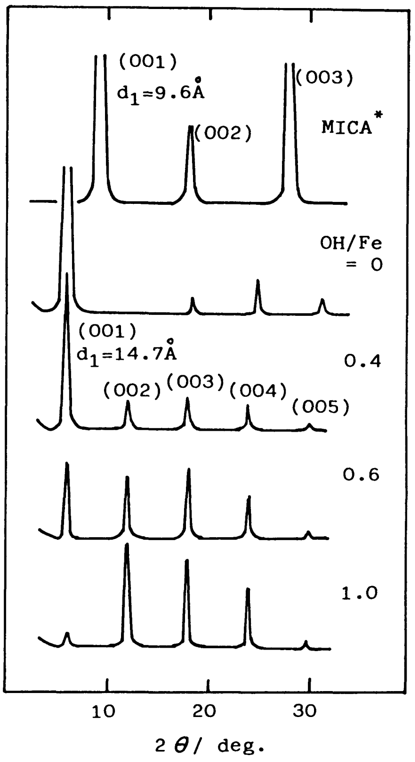

Fig. 3. X-Ray powder diffraction patterns of iron(II) hydroxide-(sodium fluoride tetrasilicic mica). MICA*: anhydrous form.

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

No.	Condition of preparation	Chemical analysis/wt%			Molar ratio (SiO_2=4)			Ion exchange ratio/%[b]
	OH/Fe	SiO_2	Na	Fe	SiO_2	Na	Fe	
MICA[a]		57.34	4.36	—	4.00	0.80	—	—
1	0.0	53.51	0.96	3.29	4.00	0.19	0.26	81
2	0.2	50.43	0.89	8.10	4.00	0.18	0.69	82
3	0.4	47.38	0.82	12.40	4.00	0.18	1.13	82
4	0.6	44.55	0.77	15.98	4.00	0.18	1.54	82
5	0.8	41.94	0.71	19.72	4.00	0.18	2.02	82
6	1.0	39.36	0.67	21.95	4.00	0.18	2.40	82

a) Sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$). Interlayer charge is +1 per formula unit. Initial interlayer cations are Na^+; part of these Na^+ ions are displaced by H^+ ions when the silicate sol is diluted in distilled water to eliminate impurities. b) Ion-exchange ratio is calculated by means of: (1−Na molar ratio)×100.

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

No.	OH/Fe	Basal spacing/Å			
		50 °C[a] in a vacuum	200 °C[b] in Ar	300 °C[b] in Ar	500 °C[b] in Ar
Initial mica		9.6	9.6	9.6	9.6
1	0.0	14.3	9.7	9.6	9.6
2	0.2	14.7	9.7	9.6	9.6
3	0.4	14.7	ML[c]	ML	9.6
4	0.6	14.7	14.6	ML	9.6
5	0.8	14.7	14.7	14.6	9.6
6	1.0	14.7	14.7	14.6	9.6

a) Drying in a vacuum for 24 h. b) Heat-treatment in Ar for 2 h. c) ML=mixed layer (mixtures of 14.7 Å and 9.6 Å layers).

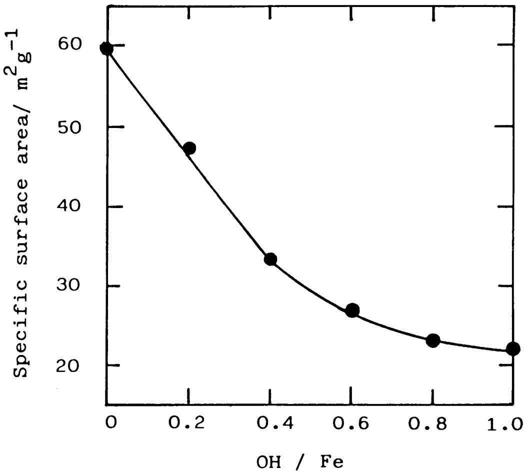

Fig. 4. Specific surface areas of iron(II) hydroxide-(sodium fluoride tetrasilicic mica).

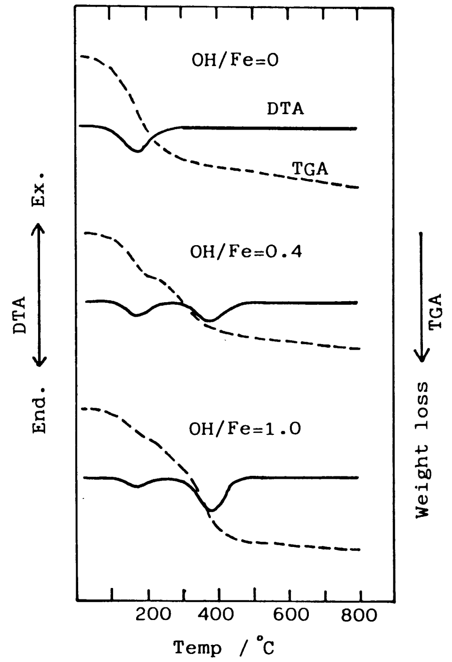

Fig. 5. DTA-TGA curves, obtained using a nitrogen atmosphere, for iron(II) hydroxide-(sodium fluoride tetrasilicic mica).

ratio, the (001) first-order reflection decreased in intensity; on the contrary, the (002)—(004) higher-order reflections increased in intensities. These changes in the relative intensities were the same as those observed in the formation reactions of nickel(II) or cobalt(II) hydroxide-mica complexes, indicating that an iron(II) hydroxide-forming reaction took place between the silicate layers. The XRD patterns of the complexes with OH/Fe ratios of 0.8 and 1.0 showed the essential X-ray characteristics of chlorites. Moreover, XRD analysis revealed the absence of any iron oxide in these heat-treated samples.

The specific surface areas of the complexes are shown in Fig. 4. With an increase in the OH/Fe ratio, the specific surface areas decreased because the development of iron(II) hydroxide between the silicate layers begins at the cation-exchange sites, which are apart from each other, and finally the internal spaces are completely stacked with this iron(II) hydroxide interlayer. These changes are the same as those observed in nickel(II) or cobalt(II) hydroxide-mica complexes.

Thermal Analysis. The DTA-TGA curves for the complexes are shown in Fig. 5. Complexes with an OH/Fe ratio of 0.0 showed a single endothermic peak at about 170 °C. This dehydration is due to the hydration water associated with the iron(II) ions introduced by ion-exchange between the silicate layers. The composition of these iron(II) ions appears to be $[Fe(OH)_{\delta}(H_2O)_{6-\delta}]^{2-\delta}$, because the hydration water of the cation in expansible layer silicates is much more dissociated than in liquid water.[15] However, as the OH/Fe ratio increased, another peak appeared at about 375 °C, while the peak at about 170 °C was diminished. These findings indicate that iron(II) hydroxide $[Fe_x(OH)_y(H_2O)_m]^{2x-y}$ developed between the silicate layers with the progressive hydrolysis and olation of iron(II) cations by the addition of alkali. Therefore, the second peak corresponds to the loss of the hydroxyl group.

Table 2 shows the changes in the basal spacings after heat treatment in an Ar flow. Complexes with OH/Fe ratios of 0.8 and 1.0, which have a well developed iron(II) hydroxide interlayer, did not collapse even upon heat treatment at 300 °C. As iron(II) hydroxide decomposes to FeO at about 200 °C,[16] well-developed iron(II) hydroxide between the silicate layers has a higher thermal stability than iron(II) hydroxide in the bulk state and is strongly fixed to the silicate layers.

Reduction Behavior with H_2. The complexes were heated in a H_2 flow at 400—700 °C for 2 h. The XRD patterns of the reduced complexes with an OH/Fe ratio of 1.0 are shown in Fig. 6. These complexes collapsed to a basal spacing of 9.6 Å, and metallic iron (α-Fe) was detected above 500 °C. As the reducing temperature rose, the reflection intensity of iron increased and the (001) mica basal reflection peak became sharper: reduced iron atoms gradually migrated from the interlayer of the silicate to its external surface.

A TEM photograph of the H_2-reduced complexes with an OH/Fe ratio of 1.0 at 700 °C is shown in Fig. 7. Metallic iron particles with a clear cubic crystal habit are distributed on the external surface of the mica. The grain diameter of these metallic iron particles increased with an increase in the reducing temperature.

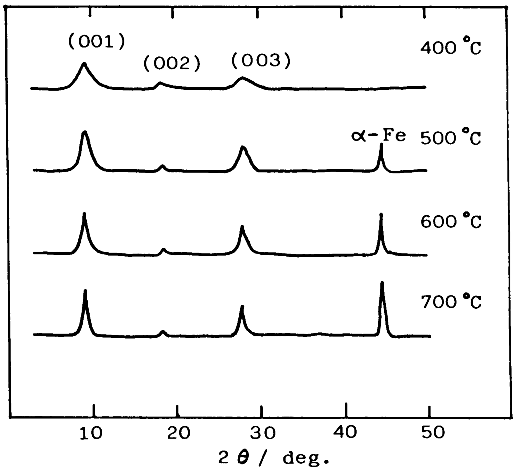

Fig. 6. X-Ray powder diffraction patterns of H_2 reduced iron(II) hydroxide-(sodium fluoride tetrasilicic mica) with a OH/Fe ratio of 1.0 at various temperatures.

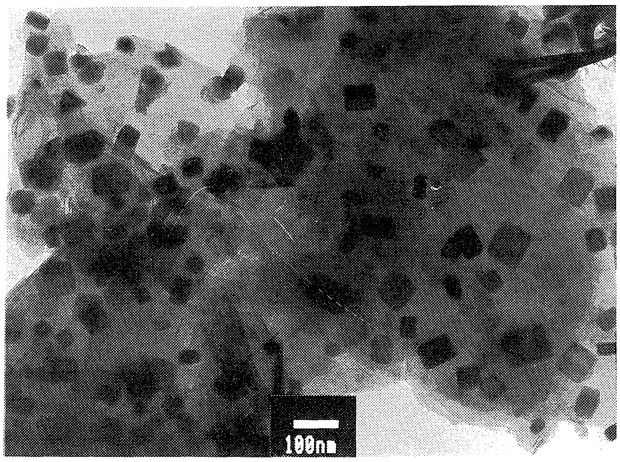

Fig. 7. Transmission electron micrograph of H_2 reduced iron(II) hydroxide-(sodium fluoride tetrasilicic mica) with a OH/Fe ratio of 1.0 at 700 °C.

Room-Temperature Oxidation of the Complexes in Air. Figure 8 shows the room-temperature oxidation of the complexes with time in air with water vapor (P_{H_2O}=4.24 kPa); temp=31 °C, R.H.=94%, air flow rate=100 ml min^{-1}. The weight-gain values are plotted against the time in the logarithmic scale. Oxidation occured gradually, and weight change by oxidation was large in the complexes with high OH/Fe ratios. The final weight-gain of the complexes with an OH/Fe ratio 1.0 was about 5 wt%. With the progress of oxidation, the color of the complexes changed from blue-green to yellow-orange and the chlorite-like structure was destroyed (Fig. 9). The oxidation rate was largely governed by the relative humidity and the reaction temperature, being controlled by the partial isomorphous substitution of

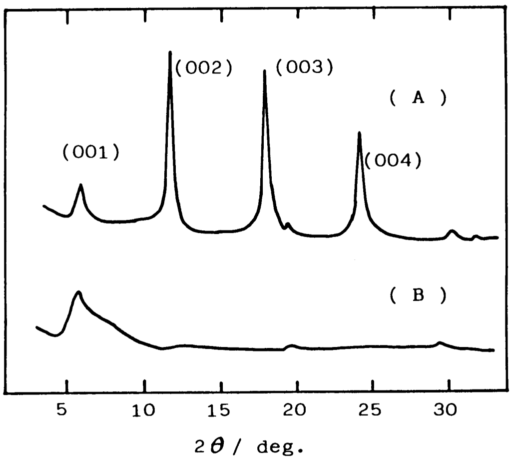

Fig. 9. X-Ray powder diffraction patterns of iron(II) hydroxide-(sodium fluoride tetrasilicic mica) after oxidation in air.
(A): original iron(II) hydroxide-(sodium fluoride tetrasilicic mica) complex with a OH/Fe ratio of 1.0; (B): oxidized complex in air with water vapor (P_{H_2O}=4.24 kPa; R.H.=94%) at 31 °C for 2 d.

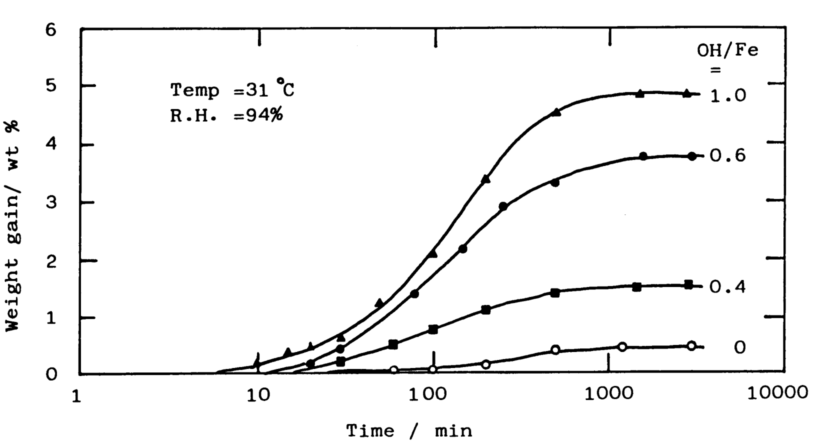

Fig. 8. Weight gain for iron(II) hydroxide-(sodium fluoride tetrasilicic mica) with time in air with water vapor (P_{H_2O}=4.24 kPa; R.H.=94%) at 31 °C. R.H.= relative humidity.

iron(II) ions. The details of this will be given in our next paper.

In contrast, iron(II) hydroxide in the bulk state is rapidly oxidized and ignites spontaneously on exposure to air because of its strong reducing power.

Mechanism of the Room-Temperature Oxidation of the Iron(II) Hydroxide Interlayer in Air. The oxidation of iron(II) hydroxide in air seems to be similar to that in aqueous solutions; the latter has been studied extensively. The oxidation processes in aqueous solutions can be classified into two types.

One consists of solid-phase reactions (surface reactions) which take place rapidly on the surface of iron(II) hydroxide with oxygen. This process is accepted as a topotactic reaction and follows this equation:[16,17]

$$\underset{\text{(hcp)}}{\mathrm{Fe(OH)_2}} + 1/4\,\mathrm{O_2} \rightarrow \underset{\text{(hcp)}}{\delta\text{-}\mathrm{FeOOH}} + 1/2\,\mathrm{H_2O}. \qquad (1)$$

This reaction process can be observed in strong alkaline solutions with a rapid oxidizing agent, because in strong alkaline solutions the concentration of iron(II) ions is extremely small.

The other type consists of liquid-phase reactions (dissolution-precipitation reactions) which take place gradually in the liquid phase.[18,19] When slow oxidation occurs by oxygen dissolved in the solution, iron(II) ions are oxidized in the solution and precipitated as α-FeOOH, γ-FeOOH, Fe_3O_4, or a mixture of them, according to the pH, the reaction temperature, and the kind of anion present.

Therefore, the oxidation process of iron(II) hydroxide in air can be considered to proceed as follows: on exposure to air, rapid oxidation on the surface of iron(II) hydroxide occurs (Eq. 1). However, since this reaction takes place with an evolution of heat, the oxidation and dehydration proceed simultaneously, and result in the formation of γ-Fe_2O_3:

$$\mathrm{Fe(OH)_2} + 1/4\,\mathrm{O_2} \xrightarrow[\text{rapid oxidation}]{\text{in air}} 1/2\ \gamma\text{-}\mathrm{Fe_2O_3} + \mathrm{H_2O}. \qquad (2)$$

In the case of the oxidation of iron(II) hydroxide–mica complexes in air, the solid-phase reaction on the surface of iron(II) hydroxide interlayers does not proceed, bacause these iron(II) hydroxide sheets are sandwiched between the silicate layers; the O_2 attack on the surface of iron(II) hydroxide sheets is hindered by the silicate layers. In fact, iron(II) hydroxide interlayers were not oxidized only by oxygen; the presence of water was indispensable to their oxidation by air at room temperature, as has been mentioned above. Hence, the oxidation of iron(II) hydroxide interlayers occurs in air with water vapor according to the liquid phase reaction: water is absorbed on the edge of the iron(II) hydroxide sheets, and then the dissolved Fe^{2+} ions are oxidized. Consequently, the oxidation rate is slow and depends on the water-vapor pressure. This oxidation process is different from that of iron(II) which is present in the 2:1 silicate layer of clay minerals.[20–23]

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