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Preparation of Nickel(II)-Hydroxide-(Sodium Fluoride Tetrasilicic Mica) Intercalation Complexes and Formation of Ultra Fine Nickel Particles by H_2 Reduction

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Nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) intercalation complexes were prepared by titrating nickel(II) nitrate solutions in the presence of mica with sodium hydroxide. As the degree of interlayering increased, the $I(002)/I(001)$ intensity ratio increased and the specific surface areas decreased. The composition of fully developed nickel(II) hydroxide interlayer, to be exact, hydroxonickel(II) complex was $[Ni_3(OH)_5(H_2O)]^+$ per formula unit. Nickel(II) hydroxide within the interlayers of the silicate was reduced at about 500 °C in H_2 flow and then 5—10 nm ultra fine nickel particles were distributed over the whole surface of mica. With an increase of reducing temperature, the amount of reduced nickel increased and sintering of nickel particles on the surface of mica proceeded.

Intercalation complexes, particularly graphite intercalations, have been one of the most attractive compounds in the study of low dimensional materials. It is well-known that clay minerals have a layered structure like graphite and that intercalation complexes of clay minerals are formed by introduction of organic and inorganic materials within the interlayers of the silicate. In the past several years, extensive studies have been carried out on the formation and properties of aluminium-hydroxide- and magnesium-hydroxide-montmorillonite intercalation complexes in relation to the formation and alteration of clay minerals.[1] The formation of nickel(II)-hydroxide-montmorillonites have been studied as well.[2,3]

The intercalation complexes containing nickel, a typical transition element, must play an important role, particularly on the development of new catalysts and low dimensional magnetic materials. However, the properties and thermal stability of these intercalation complexes have not been fully clarified, especially under reducing conditions.

In the present work, the formation of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) and the thermal stability of the complexes in air and in a H_2 flow were investigated.

Sodium fluoride tetrasilicic mica, $NaMg_{2.5}Si_4O_{10}F_2$, used in this study is an artificial compound, which has swelling properties in water similar to natural montmorillonite and also has a large cation exchange capacity. The layer charge of montmorillonite is -0.33 and that of the silicate is -1.

The thermal stability of sodium fluoride tetrasilicic mica is relatively high compared with that of the natural clay minerals, because the OH ions constituting a part of the crystal lattice in natural clay minerals are substituted by F^- ions in the silicate.[4]

Sodium fluoride tetrasilicic mica has also characteristics of high film forming capability because of its flake-like micro particles. Moreover, the silicate differs from natural montmorillonite in having no acidity at all. Thus it receives much attention as an inert support in the study of catalytic reactions.[5]

Experimental

Materials. A 10 wt% sol of sodium fluoride tetrasilicic mica, (supplied by Topy Ind. Co., under the name of Na-TSM) was used. As the silicate 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 gravimetric sedimentation. Sodium fluoride tetrasilicic mica was finally dried in air at 100 °C.

A diagramatic sketch of the structure of sodium fluoride tetrasilicic mica is shown in Fig. 1.[6] The silicate is

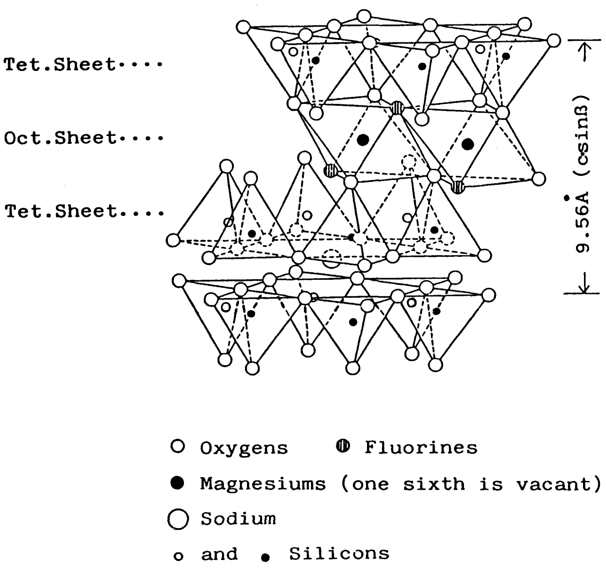


Fig. 1. Diagrammatic sketch of the structure of sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$).

composed of units made up of two silicon (Si–O) tetrahedral sheets with a central magnesium (Mg–O,F) octahedral sheet. The unit layers are stacked one above the other. Na^+ ions are located within the interlayers to balance the negative layer charge derived from the vacancies in the octahedral sheets. These Na^+ ions are exchangeable in water and the theoretical cation exchange capacity is 254 meq/100 g·mica.

The crystal structure of sodium fluoride tetrasilicic mica has not been strictly analyzed, only $b=9.078$ Å and $d(001)=c\cdot\sin\beta=9.562$ Å have been determined.[7] Water molecules can be absorbed within the interlayers. The single water layer hydrated form is stable in air at relative humidities in the range of 40—60% and a double water layer form is stable above that relative humidity.[8] These *d*-spacings are as follows[7];

$d_1(001)=12.34$ Å (single layer form); $d_2(001)=15.17$ Å (double layer form); $d_3(001)=18.36$ Å (three layer form).

The crystal structure of potassium fluoride tetrasilicic mica ($KMg_{2.5}Si_4O_{10}F_2$), isomorphous substituent of sodium fluoride tetrasilicic mica, was also elucidated[9]; $a=5.253$ Å, $b=9.086$ Å, $c=10.159$ Å, $\beta=99.89$.°

Preparation of Nickel(II)-Hydroxide-(Sodium Fluoride Tetrasilicic Mica). Nickel(II)-hydroxide–(sodium fluoride tetrasilicic mica) was prepared by a titration procedure[2] titrating nickel(II) nitrate solution in the presence of the silicate with sodium hydroxide. The preparation procedures are as follows; 10 g samples of the silicate were dispersed in the predetermined amount of 0.1 M (1 M=1 mol dm^{-3}) nickel(II) nitrate solutions. After stirring for 2 d, these suspensions were titrated with a predetermined amount of 0.1 M sodium hydroxide solutions at the rate of 10 ml h^{-1} under vigorous stirring, and stirring was continued for 5 d. Following these treatments, samples were repeatedly washed with distilled water to remove electrolyte and dried at about 100 °C.

Two series of samples were prepared(Table 1); (i) the OH/Ni molar ratio was varied from zero to 1.0 by adding different amounts of 0.1 M sodium hydroxide to 0.1 M nickel(II) nitrate solutions with the sodium fluoride tetrasilicic mica (Ni/mica ratio fixed at 1000 meqNi/100 g·mica). (ii) the Ni/mica ratio was varied from 100 meqNi/100 g·mica to 2000 meqNi/100 g·mica by adding different amounts of 0.1 M nickel (II) nitrate solutions to the silicate (OH/Ni ratio was fixed at 0.5).

Heat Treatment in Air and in H_2 Flow. Since sodium fluoride tetrasilicic mica decomposes at about 800 °C,[10] the thermal stability of the intercalation complexes was studied below 800 °C. The intercalation complexes were heat-treated for 2 h at 100—700 °C in air and at 400—700 °C in H_2 flow (heating rate; 10 °C min^{-1}).

Results and Discussion

Chemical Analyses. Chemical analyses of sodium fluoride tetrasilicic mica and nickel(II)-hydroxide–(sodium fluoride tetrasilicic mica) by atomic absorption analysis are shown in Table 1. The chemical composition of sodium fluoride tetrasilicic mica can be expressed by the formula $Na_{1.00}Mg_{2.63}(Si_{3.98}Al_{0.05}Mg_{0.01}O_{10})O_{0.19}F_{1.81}$,[8] for which the interlayer charge is +1 per formula unit and the interlayer cations are Na^+. Part of interlayer Na^+ cations are displaced by H^+ ions in distilled water when the silicate sol is diluted to eliminate the impurities.

As is shown in Table 1, the amount of nickel taken into the silicate increased with an increase of the OH/Ni ratio or the meqNi/100 g·mica ratio. The highest nickel yields of about 21% were obtained with OH/Ni ratio of 1.0 (No. 8) and meqNi/100 g·mica ratio of 2000 (No. 7). X-Ray diffraction analysis did not detect any free nickel(II) hydroxide in these samples or nickel(II) oxide in the heat-treated ones. Thus, under our experimental conditions, the nickel(II) hydroxide forming reaction took place primarily within the interlayer of the silicate without precipitating free nickel(II) hydroxide.

X-Ray Diffraction. All samples were examined by XRD as thin, oriented films on glass slides. Basal spacings of nickel(II)-hydroxide–(sodium fluoride

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

No.	Conditions of preparation		Chemical analyses (wt%)			Molar ratio ($SiO_2=4$)		
	OH/Ni	meq Ni/ 100 g·mica	SiO_2	Na	Ni	SiO_2	Na	Ni
*			55.74	3.84	—	4.00	0.72	—
1	0	1000	54.13	1.63	2.60	4.00	0.32	0.20
2	0.2	1000	51.15	1.48	7.26	4.00	0.30	0.58
3	0.5	100	53.49	1.72	3.20	4.00	0.34	0.24
4	0.5	250	52.91	1.66	5.40	4.00	0.33	0.42
5	0.5	500	49.90	1.57	8.56	4.00	0.33	0.70
6	0.5	1000	46.84	1.34	13.48	4.00	0.30	1.18
7	0.5	2000	40.35	1.08	21.00	4.00	0.28	2.13
8	1.0	1000	40.23	1.22	20.96	4.00	0.32	2.13

*: Initical sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$)

Interlayer charge is +1; Interlayer cations are Na^+ and H^+ which replaced the part of Na^+ cations in distilled water.

tetrasilicic mica) are listed in Table 2. These basal spacings are almost constant (ca. 14.7 Å) independent of the amount of the nickel taken into the silicate. Therefore, nickel(II) hydroxide developed onto the horizontal plane within the interlayer of the silicate, forming the brucite like layer. The mechanism of formation of nickel(II) hydroxide interlayers must be the same as in montmorillonite.[2)]

X-Ray powder diffraction patterns of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) (1000 meq Ni/100 g·mica) are shown in Fig. 2. With an increase of the OH/Ni ratio, the (001) first order reflection decreased in intensity, on the contrary, the (002)—(004) higher order reflections increased in intensities without any changes in basal spacings. With an increase of the meqNi/100 g·mica ratio, the same XRD changes were observed as for samples prepared with an OH/Ni ratio of 0.5. These indicate that the nickel(II) hydroxide forming reaction took place within the interlayer of the silicate, because it is known that the relative intensities of the first and second order reflections are indicative of interlayering and that generally, the $I(002)/I(001)$ intensity ratio increases with an increase of the degree of interlayering.[11)]

Table 2. Basal Spacings of Nickel(II)-Hydroxide-(Sodium Fluoride Tetrasilicic Mica)

1000 meq Ni/100 g·mica const.	OH/Ni=0.5 const.
initial mica : 9.6 Å	No. 3 (100 meq Ni/100 g·mica) : 14.3 Å
No. 1 (OH/Ni=0) : 14.3 Å	No. 4 (250 meq Ni/100 g·mica) : 14.6 Å
No. 2 (OH/Ni=0.2) : 14.7 Å	No. 5 (500 meq Ni/100 g·mica) : 14.6 Å
No. 6 (OH/Ni=0.5) : 14.7 Å	No. 6 (1000 meq Ni/100 g·mica) : 14.7 Å
No. 8 (OH/Ni=1.0) : 14.7 Å	No. 7 (2000 meq Ni/100 g·mica) : 14.7 Å

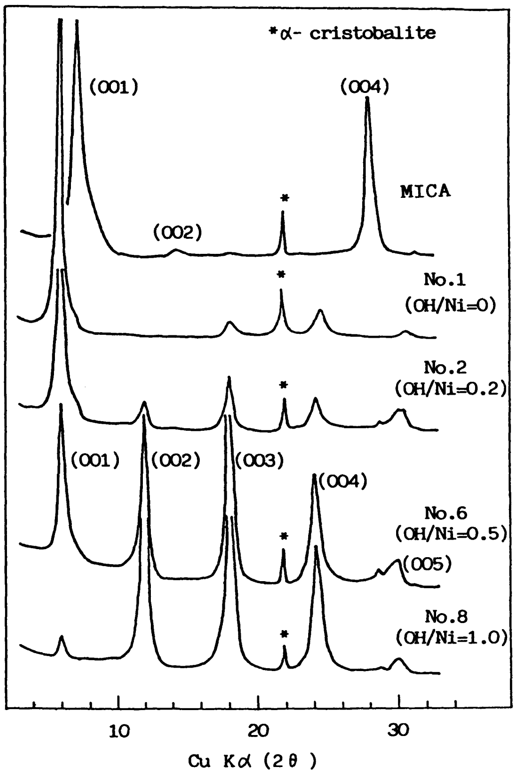


Fig. 2. X-Ray powder diffraction patterns of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) (1000 meqNi/100 g·mica).
: Mica; initial mica; single water layer hydrated form.

Thermal Stability of Nickel(II)-Hydroxide-(Sodium Fluoride Tetrasilicic Mica) in Air. Figure 3 shows the DTA and TGA curves for nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) (No. 2 and No. 8)(the rate of heating was 10 °C min^{-1}). Sample No. 2, which contains a small amount of nickel, showed a single endothermic peak at about 160 °C and a corresponding weight loss. On the other hand, sample No. 8, which contains a large amount of nickel and has a well developed nickel(II) hydroxide interlayer, showed a first endothermic peak at about 120 °C, a second one at about 260 °C, and a third one at about 430 °C with corresponding weight losses. The first endothermic peak corresponds to the loss of absorbed water. The second and the third endothermic peak can be attributed to the dehydration of the nickle(II) hydroxide interlayer, to be exact, hydroxonickel(II) complex $[\mathrm{Ni}_m(\mathrm{OH})_{2m-n}\,x(\mathrm{H_2O})]^{n+}$ i.e.; the second one to the loss of coordinated water and the third one to the loss of hydroxo group.

Changes of basal spacings after heat treatment are shown in Fig. 4. With 2 h heat treatment above 200 °C, sample No. 2 collapsed to under 10 Å, while sample No. 8 retained a basal spacing of 14.7 Å up to 300 °C. These results show that nickel(II) hydroxide within the interlayers of the silicate is stable until the loss of hydroxo begins and that samples with fully developed nickel(II) hydroxide interlayer have higher

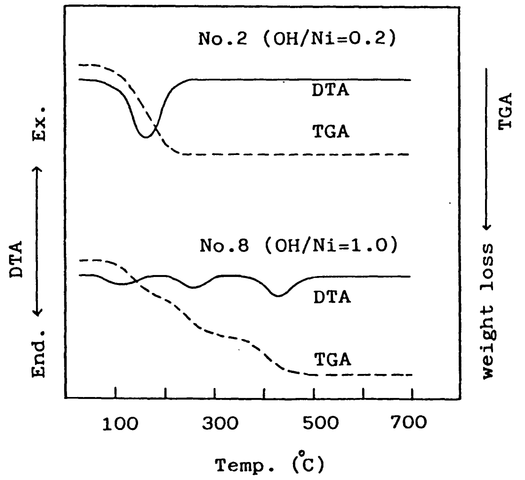


Fig. 3. TGA and DTA curves for nickel(II)-hyroxide-(sodium fluoride tetrasilicic mica) (samles No. 2 and No. 8).

thermal stability. X-Ray diffraction analysis did not detect nickel(II) oxide in these heat-treated samples at 700 °C. Moreover, the (001) mica basal reflection peak of these heat-treated samples broadened with an increase of nickel taken into the interlayer. Therefore, after the nickel(II) hydroxide interlayer has been dehydrated, nickel(II) oxide is present in the interlayers as monomolecules.

The chemical composition of the interlayer material of sample No. 8 was determined by chemical analyses (Table 1) and thermal analyses. From thermal analyses, the amount of coordinated water and hydroxo correspond to the weight loss between 200 and 300 °C, and between 300 and 700 °C respectively. The amounts of dehydration at each temperature are listed in Table 3. Chemical compositions of the interelayer material are calculated to be $Ni_{2.13}(OH)_{3.46}0.61(H_2O)$ per sodium fluoride tetrasilicic mica formula unit. As the ion exchange rate is 68%, this can be rewritten as $[Ni_{3.13}(OH)_{5.09}\text{-}0.90(H_2O)]_{0.68}^{1.17+}$ per formula unit. Therefore, the composition of the fully developed nickel(II) hydroxide interlayer (hydroxonickel(II) complex) must be $[Ni_3(OH)_5(H_2O)]^+$, which balances the negative layer charge of $^-1$, and corresponds to a complete hydroxide interlayer in chlorite. The structure of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica), shown in Fig. 5, is the same as that of chlorite.[12,13]

Table 3. Chemical Compositions of Nickel(II) Hydroxide Interlayer (Hydroxonickel(II) Complex); $[Ni_m(OH)_{2m-n}xH_2O]^{n+}$ (Sample No. 8)

		Chemical analyses (wt%)	Molar ratio ($SiO_2=4$)
SiO_2		40.23	4.00
Ni		20.96	2.13
H_2O	R.T−200 °C (1)	3.22	
	R.T−300 °C (2)	5.05	
	R.T−700 °C (3)	10.26	
xH_2O	(2)-(1)	1.83	0.61
$(OH)_{2m-n}$	(3)-(2)	5.21	3.46

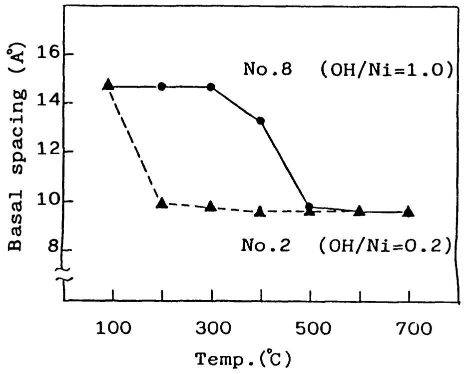


Fig. 4. Changes of basal spacings after heat treatment.

Specific Surface Areas. Specific surface areas of the complexes, measured by the N_2 adsorption method, after heat treatment at 100 and 700 °C are shown in Fig. 6. With an increase of the OH/Ni ratio, the specific surface areas of the complexes heat-treated at

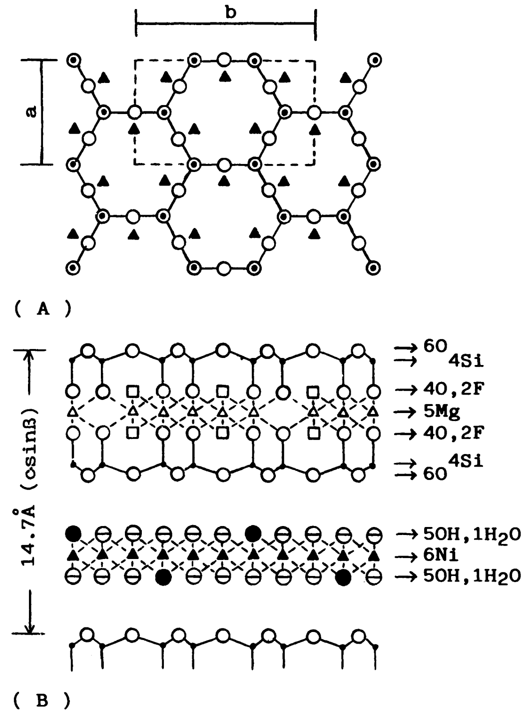


Fig. 5. Structure of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica).

(A) interlayer Ni cations (▲) onto upper tetrahedral sheet of 2 : 1 layer below.

(B) [100] view of structure.

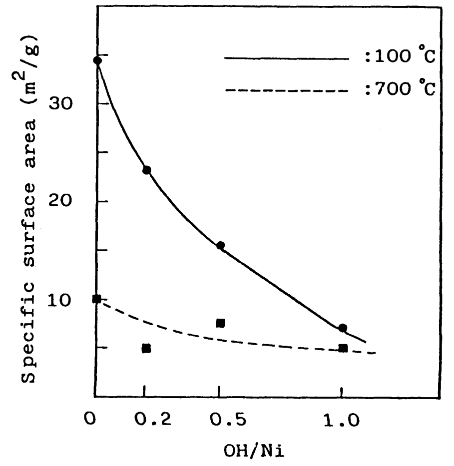


Fig. 6. Specific surface areas of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) (1000 meqNi/100 g·mica) heat-treated at 100 °C and 700 °C.

100 °C decreased rapidly. These results correspond to the fact that, according to the development of nickel(II) hydroxide within the interlayers of the silicate, the interlayer space becomes smaller and that finally the internal surfaces are completely covered with nickel(II) hydroxide.

After heat treatment at 700 °C, the specific surface areas were nearly constant, 5—10 $m^2\,g^{-1}$, independent of the changes of the OH/Ni ratio, because nickel(II) hydroxide within the interlayers completely dehydrated and collapsed at 700 °C.

The specific surface areas of the sample with an OH/Ni ratio of 1.0 heat-treated at 100 °C is also 5—10 $m^2\,g^{-1}$, which is almost equal to that of collapsed sample. This indicates that nickel(II) hydroxide is fully developed within the interlayers of the sample with an OH/Ni ratio of 1.0.

Heat Treatment in H_2 Flow. Nickel(II)-Hydroxide-(sodium fluoride tetrasilicic mica) was heat-treated in H_2 flow at 400, 500, 600, and 700 °C for 2 h. In Fig. 7 are shown the XRD patterns of the H_2 reduced nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica)(sample No. 8). After heat treatment above 500 °C in H_2 flow, sample No. 8 collapsed to a basal spacing of under 10 Å and showed the presence of metallic nickel. With an increase of reducing temperature, the (111) Ni reflection increased in intensity and the (001) mica basal reflection peak became sharper. These results indicate that nickel(II) hydroxide within the interlayer of the silicate decomposed to metallic nickel by H_2 reduction and that reduced nickel atoms migrated from the interlayer of the silicate to its outer surface. This quantity of metallic nickel reduced (shown as relative XRD peak (111) Ni intensity in Fig. 8)increased according to the increase of the OH/Ni ratio, i.e. an increase of nickel(II) hydroxide taken into the silicate interlayer, and an increase of the reducing temperature.

In Fig. 9 are shown the specific surface areas of H_2 reduced nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica). Samples treated above 500 °C in H_2 flow had larger surface areas than those (5—10 $m^2\,g^{-1}$) of collapsed samples in air. These increase of specific surface areas are attributed to the reduced nickel

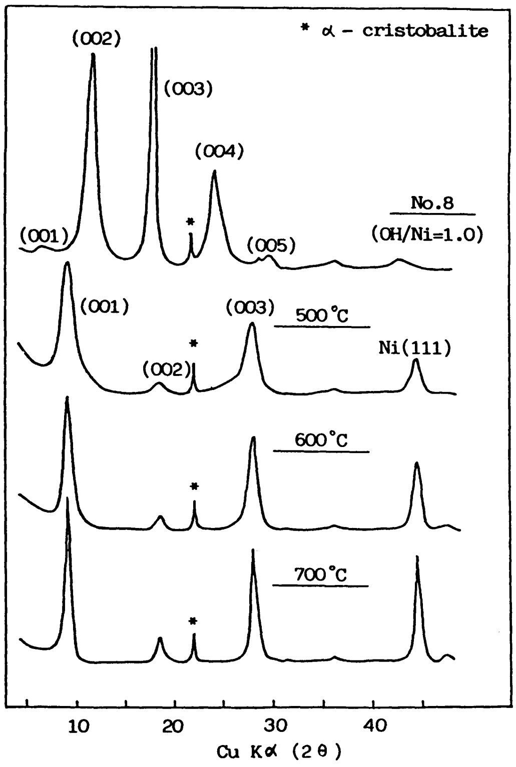


Fig. 7. X-Ray powder diffraction patterns of nickel-(II)-hydroxide-(sodium fluoride tetrasilicic mica) heat-treated in H_2 flow at various temperatures (sample No. 8).

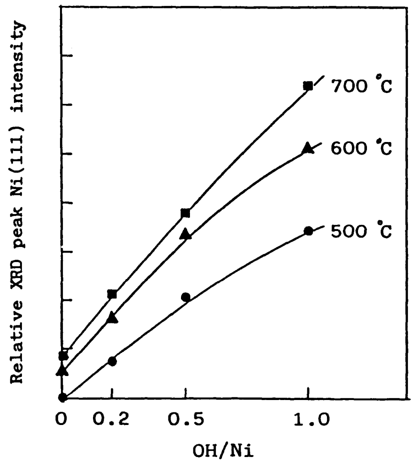


Fig. 8. Quantity of metallic Ni reduced from nickel-(II)-hydroxide-(sodium fluoride tetrasilicic mica)(1000 meqNi/100 g·mica) at various temperatures in H_2 flow.

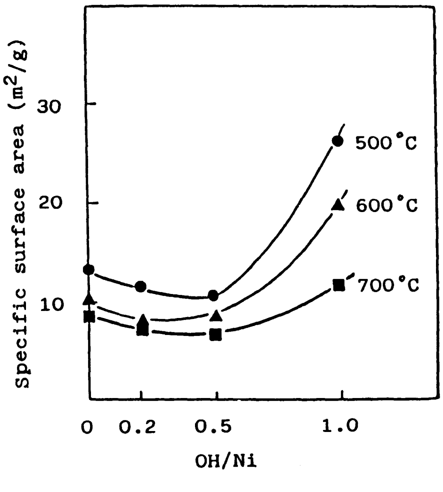
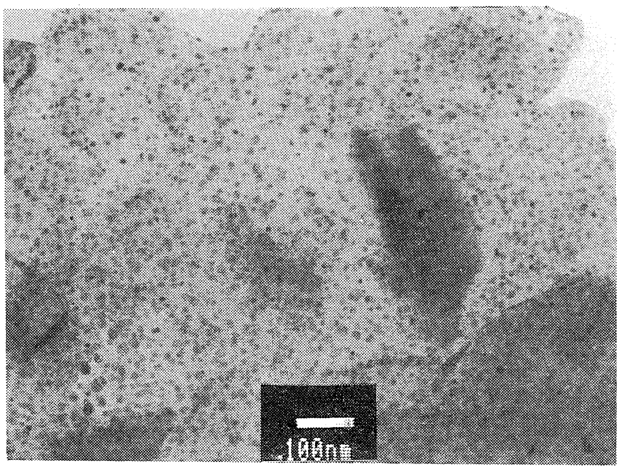


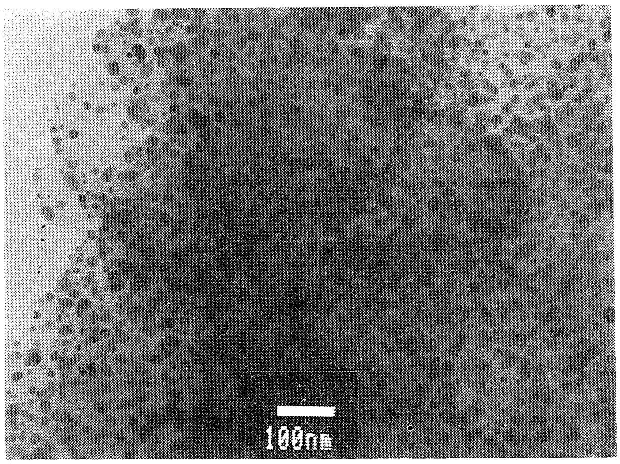
Fig. 9. Specific surface areas of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica)(1000 meqNi/100 g·mica) heat-treated at various temperatures in H_2 flow.

atoms. Specific surface areas decreased with an increase of reducing temperature, which can be explained by the fact that reduction and sintering of nickel particles on the surface of mica simultaneously proceeded with an increace of reducing temperature.

TEM photographs of sample No. 8 heat-treated at 500 °C and at 700 °C in H_2 flow show that ultra-fine metallic nickel particles with almost the same grain diameter are distributed over the whole surface of the mica (Fig. 10). Grain diameter of metallic nickel reduced is about 5—10 nm at 500 °C and 15—25 nm at 700 °C.



(A)



(B)

Fig. 10. Transmission electron micrographs of nickel (II)-hydroxide-(sodium fluoride tetrasilicic mica) heat-treated in H_2 flow.

(A) Nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) (sample No. 8) heat-treated at 500 °C in H_2 flow.

(B) Nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica)(sample No. 8) heat-treated at 700 °C in H_2 flow.

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