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Synthesis of Novel Ni-Hectorite Inorganic Complexes

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Novel Ni-hectorite inorganic complexes were synthesized hydrothermally from homogeneous Ni-Si hydrous oxide gel at 200 °C for 2 h. Dispersed slurries of these complexes showed rheological properties similar to those of natural smectites and, on heating, formed porous materials characterized by large specific surface areas and high thermal stability.

Smectite minerals, which consist of two-dimensional silicate layers separated by hydrated exchangeable cations, swell with a variety of molecules and form intercalated complexes. Metal-oxide pillared clays, prepared from smectites and polynuclear metal complex cations, have attracted considerable attention as new types of molecular sieves, which are structurally different from zeolites. These materials offer new possibilities as catalysts and adsorbents.$^{1)}$ Recently a new hydrothermal method of producing hectorite-inorganic complexes was proposed.$^{2)}$ Dispersed slurries of these complexes showed attractive rheological properties similar to those of natural smectites. On dehydration, they transformed to porous materials characterized by large specific surface areas and high thermal stability. The present paper is concerned with the hydrothermal synthesis of Ni-hectorite inorganic (NHI) complexes having attractive properties for industrial applications.

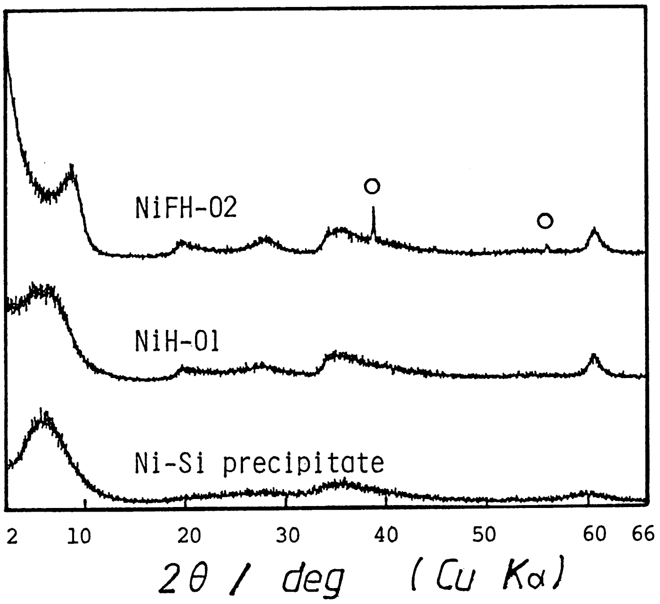

Fig. 1. X-Ray powder diffraction patterns of Ni-hectorite inorganic complexes and the initial Ni-Si precipitate. O:NaF

The hydrothermal synthesis procedure was as follows: (1) A Ni-Si solution was prepared having a Ni/Si atomic ratio of 5.4/8.0 by dissolving nickel(II) chloride hexahydrate in 1 mol•dm^{-3} acidic solution containing sodium silicate No 3 (SiO_2/Na_2O = 3.22) (2) A Ni-Si hydrous oxide gel (NSH) was formed by mixing the above Ni-Si homogeneous solution with 2 mol•dm^{-3} NaOH solution (3) The NSH was washed and filtered to remove secondary products (4) A slurry is prepared from the NSH, LiOH, and HF (5) NHI complexes were formed hydrothermally by heating the NSH in an autoclave at 200 °C under autogenous water vapor pressure for 2 h (6) The products were dried at 80 °C and powdered.

X-Ray powder diffraction patterns of the products and the NSH are shown in Fig. 1. The NSH produced at room temperature has a poorly crystalline smectite-like structure. NHI complexes of good quality therefore appear to have formed in a short time under the relatively mild hydrothermal condition of this study. Presumably the Ni-hectorite materials that compose the complexes have crystal structures in which Ni substitutes for Mg in the octahedral sheets of hectorite.

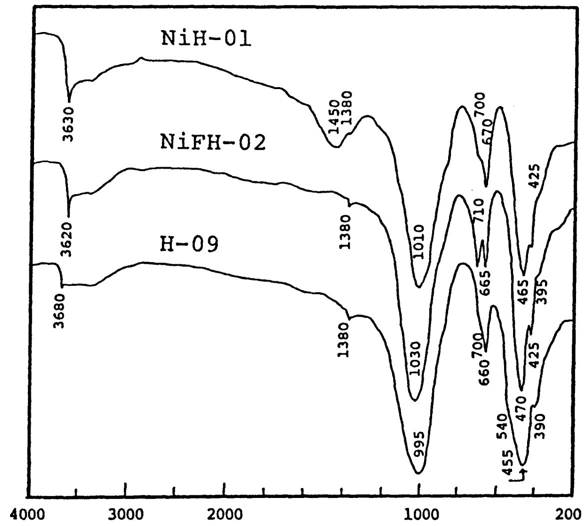

Fig. 2. IR spectra of Ni-hectorite inorganic complexes, and a hectorite inorganic complex H-09.[2)]

Table 1. Colour of synthetic Ni-hectorite inorganic complexes according to the CIE 1976(L*a*b*)

	L*	a*	b*
NiH-01	77.5	-20.0	7.2
NiFH-01	83.8	-19.8	6.5
NiFH-02	81.2	-16.9	8.4

Figure 2 shows infrared (IR) spectra of NHI complexes measured on KBr discs heated at 130 °C. The band near 3630 cm^{-1} is attributable to structural OH and is coincident with the OH vibration frequency close to 3 Ni ions in octahedral site of synthetic Ni-talc.[3)] The 1200-300 cm^{-1} region in the pattern of the NHI complexes is similar to that in the pattern of hectorite inorganic complexes.[4)] The Si-O bands in the NHI patterns, however, are at higher frequencies than those of hectorite inorganic complexes.

The colour specification of three products according to the CIE 1976 (L*a*b*) space[5)] is shown in Table 1. The a* values, which are highly negative are due to the green color derived from Ni^{2+} in the octahedral sheets of the products. The magnetic susceptibility values of specimens NiH-01 and NiFH-02, measured with a magnetic balance, are 25.9 × 10^{-6} and 27.3 × 10^{-6} emu•g^{-1}, respectively. Using an effective Bohr magneton number for Ni^{2+} of about 3.2, the magnetic susceptibility of NiH-01 calculated from the Langevin expression[5)] is 26.3 × 10^{-6} emu•g^{-1}, close to the measured value. This also implies that nickel exists as Ni^{2+} in the structure.

Table 2 shows the effect of the addition of fluorine on the properties of the

Table 2. Properties of hydrothermal synthetic Ni-hectorite inorganic complexes[a)] compapred with those of a synthetic Laponite product RD, a synthetic sodium fluoro tetrasilicic mica and a natural hectorite

Specimens	Amount	MB adsorbed	SSA[c)]	Rheological properties[d)] AV/mPa·s		PV	YV	GS/Pa	
	of F[b)]	mequiv. g^{-1}	m^2 g^{-1}	1022 s^{-1}	10.2 s^{-1}	mPa·s	Pa	10 s	600 s
NSH[e)]	0	0	14.8	--	--	--	---	---	--[f)]
NiH-01	0	0.72	150.6	9	75	6	2.4	0.7	7.2
NiFH-01	1	0.72	193.3	8	150	4	3.4	1.9	15.3
NiFH-02	3	0.24	293.9	--	--	--	---	---	--[f)]
NTSM	4	0	21.7	6	--	5	0.5	0.2	0.2
DPI-AW		0.88	36.5	8	150	6	1.9	1.4	1.7

a) Preparation composition : Si:Ni:Li=8:5.4:0.7 ; hydrothermal condition : 200 °C, 2 h.
b) Atomic ratio versus Si=8.
c) Specific surface area measured on the specimens activated at 300 °C for 20 min.
d) Measured 2.5% gel solution at 25 °C with Fann VG meter. AV:Apparent viscosity; PV:Plastic viscosity; YV:Yield value; GS:Gel strength.
e) Ni-Si hydrous oxide gel.
f) Not dispersed in the water.

Table 3. Effect of treatment on basal spacings in Ni-hectorite inorganic complex and natural hectorite (DPI-AW)

Treatment	Basal specing / Å NiH-01	DPI-AW
Untreatment	14.5	14.7
Wet	Free swelling	20.5
Ethylene glycol	18.0	17.1
Glycerol	20.5	18.0

NHI complexes, along with those of (1) a synthetic sodium fluor-tetrasilicic mica NTSM (Topy Ind. Ltd.) and (2) a natural hectorite DPI-AW (American Colloid Co.). Fluorine-free specimen NiH-01 easily dispersed in water to form a gel. A water dispersion of NiH-01 showed almost equal or better rheological properties, compared with those of the two commercial products. The rheological properties of synthetic hectorite[4)] and trioctahedral Mg-smectite[7)] were reported to be improved by the addition of fluorine. For the NHI complexes at fluorine addition value of 1 on the basis of Si = 8, the methylene blue (MB) adsorption and rheological properties were as almost the same as those the fluorine-free specimen but increasing fluorine addition (F = 3) gave rise to a decrease in MB adsorption and poorer rheological properties.

Moreover, these specimens showed large specific surface areas (SSA). The NSH, a starting material for the synthesis, had small SSA of 14.8 m^2 g^{-1}, however after hydrothermal treatment of the SNH at 200 °C for 2 h, had a SSA of 151-294 m^2 g^{-1}. In contrast to MB adsorption and the rheological properties, the SSA increased with increasing fluorine addition. Presumably these NHI complexes contain some material, between the silicate layers of the Ni-hectorites, similar to the hectorite inorganic complexes.[2)] The abnormal large XRD d-valus of ethylene glycol- and glycerol-treated specimens of sample NiH-01 also support the existence of extraneous substances in the interlayer region (Table 3).

The effect of heating temperature on the SSA for two NHI complexes is shown in Fig. 3. Specimen NiFH-02 showed a higher SSA value and excellent thermal stability, compared with the Al-pillared synthetic fluoro-hectorite (AL-PFH).[8] These novel porous materials, containg inorganic matter between silicate layers of Ni-hectorites, may be of considerable interest as catalysts and adsorbents, due to their higher SSA, high thermal stability, and their ability to include some nickel component in the structure.

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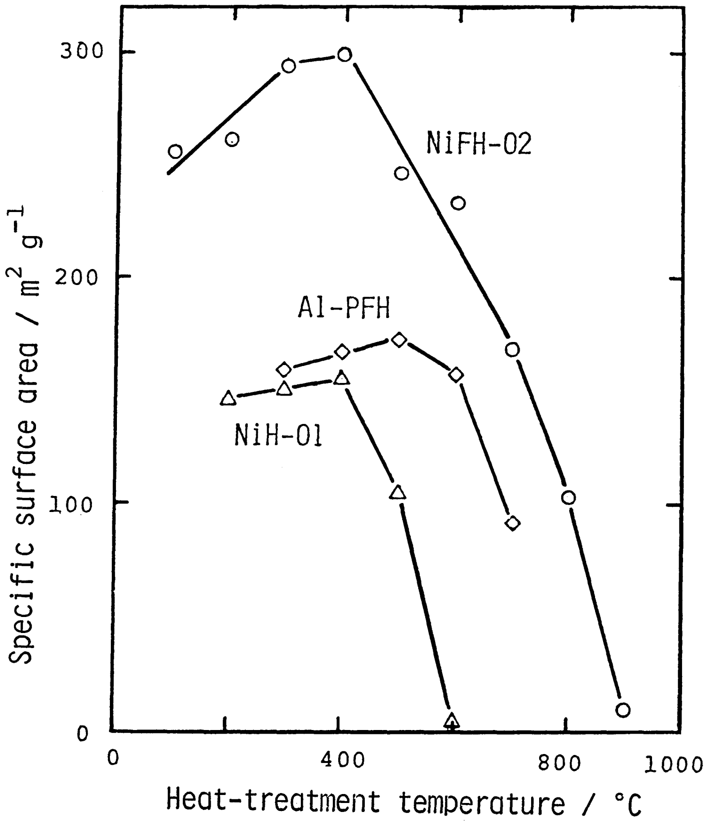

Fig. 3. BET surface areas of Ni-hectorite inorganic complexes as a function of heat-treatment temperature.

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