HYDROTHERMAL SYNTHESIS AND PHYSIOCHEMICAL PROPERTIES OF Ni-HECTORITE

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ABSTRACT

Hectorite containing Ni$^{2+}$ instead of Mg$^{2+}$ in the trioctahedral sheets has been synthesized at 300°C for 12 h under autogenous water vapor pressure by hydrothermal reaction of four kinds of starting slurry with the initial molar ratios Na: Ni: Li: Si = 0.7: 5.4: 0.6: 8.0, 1.4: 5.4: 1.2: 8.0, 1.4: 4.8: 1.2: 8.0 and 1.4: 4.8: 1.2: 7.5 made from Ni-Si homogeneous precipitates, lithium fluoride and sodium hydroxide. The resulting Ni-hectorite has been characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectrophotometry (FT-IR), thermogravimetry and differential thermal analysis (TG-DTA), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. The Ni-hectorite is relatively large massive plate-like particles with a characteristic tint of green and has similar structure to other hectorites, a smaller cation exchange capacity (CEC) and lower adsorptive ability of methylene blue (MB) compared to a commercial Mg-hectorite and a synthetic Zn-hectorite as reference. It has also been clarified that the Ni-hectorite modified electrode shows a redox reaction Ni$^{2+}$ to Ni$^{3+}$ and Ni$^{3+}$ to Ni$^{2+}$ in cyclic voltammetry.

Key words: Ni-hectorite, Smectite, Hydrothermal reaction, Cation exchange, Adsorption, Cyclic voltammetry

INTRODUCTION

Hectorite is typical cationic clay family and a trioctahedral member of smectite group. It has layered silicate structure composed of one Mg$_3$(OH)$_6$ trioctahedral sheet sandwiched between two SiO$_4$ tetrahedral sheets, and then has exchangeable cations and water on the surface and within interlayer space. An ideal chemical formula is represented as Na$_{0.6}$(Mg$_{5.4}$Li$_{0.6}$)Si$_8$O$_{20}$(OH)$_4$·nH$_2$O. In several decades, smectite becomes important industrial materials, and is now widely used as adsorbent, ink, cosmetics, catalyst, soil conditioner and so on because of its abilities in cation exchange, adsorption, catalysis, viscosity and swelling.

Until now some investigations on synthesis, characterization and physicochemical properties of hectorite, saponite and sauconite containing Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ instead of Mg$^{2+}$ in the trioctahedral sheets were performed (Tiller et al., 1974; Bruce et al., 1986; Kawi et al., 1999; Shirai et al., 1999; Higashi et al., 2002; Nakakuki et al., 2004). Electrochemical property of clay-modified electrodes (CME) prepared by depositing thin film of Co-clay and Cu-clay onto conductive substrates was studied (Xiang et al., 1996; Xiao et al., 1998). Ni-saponite and Zn-hectorite were also recognized to have catalysis in some organic reactions (Kawi et al., 1999; Shirai et al., 1999). However, very few attempts have been made to clarify the details in experimental conditions for synthesis and characterization of hectorite and saponite containing such heavy metals.

In this study, we have investigated the synthetic conditions of a Ni equivalent of hectorite with an ideal composition of Na$_{0.6}$(Ni$_{5.4}$Li$_{0.6}$)Si$_8$O$_{20}$(OH)$_4$·nH$_2$O referred to as Ni-hectorite here under autogenous water vapor pressure as well as its physicochemical properties: swelling property, thermal stability, CEC, MB adsorptive ability and electrochemical property.

MATERIALS AND METHODS

Materials

Water glass (JIS No. 3) was offered by Fuji Chemical Co., Ltd. All other chemicals were purchased from Wako...
Pure Chemical Ind. Co., Ltd. and used without further purification.

A procedure for preparation of starting materials is as follows (Torii et al., 1987): A Ni-Si aqueous suspension (the initial molar ratios Ni:Si = 5.4:8.0, 4.8:8.0 and 4.8:7.5) was obtained by adding NiCl₂ aqueous solution in an acid silicate gel made from water glass (29 wt% SiO₂) and HCl solution. A Ni-Si homogenous precipitate was prepared by mixing the Ni-Si aqueous suspension with NaOH aqueous solution at pH 8-9 and washed with distilled water. Four kinds of the starting Na-Ni-Li-Si slurry with the different initial molar ratios Na:Ni:Li:Si = 0.7:5.4:0.6:8.0, 1.4:5.4:1.2:8.0, 1.4:4.8:1.2:8.0 and 1.4:4.8:1.2:7.5 (Si concentration 0.2 mol/l) were prepared from the Ni-Si homogenous precipitates, NaOH and LiF aqueous solutions.

**Hydrothermal synthesis of Ni- Hectorite**

The starting slurry (7 ml) was put into a Teflon tube (10 ml) set in a stainless steel autoclave, and then treated hydrothermally at 200-300°C for 3-24 h under autogenous water vapor pressure. The solid products were separated by centrifugation, washed with distilled water and then dried at 80°C for 24 h.

**Characterization of Ni-hectorite**

XRD patterns of solid product randomly oriented on glass slide were obtained by a Rigaku RINT-2200 powder X-ray diffractometer using Cu Kα radiation with Ni filtered at 20 mA, 40 kV and scanning speed of 2°/min in the range 2-70° (2θ). FT-IR spectra were recorded on a JASCO W/S/IR-7300 spectrophotometer with the standard KBr pressed disk method in the spectral region 4600-400 cm⁻¹. TG-DTA were carried out with a Rigaku THERMFLEX TAS200 by heating of sample (10 mg) from 25°C to 1000°C at heating rate of 10°C/min under air atmosphere. XPS spectra were obtained by an ULVAC-PHI ESCA 5600CIS using Al Kα X-ray source at power of 150 W, pass energy of 187.85 eV, step ratio of 1.6 eV for survey scans, take off angle of 45° and the X-ray spot size of 800 μm for analysis. The particle shape and size of the solid product were observed by a Hitachi S-2250 scanning electron microscope. Chemical composition was determined from chemical analysis data obtained by a Shimadzu AA-6650 atomic absorption spectrophotometer (AAS) after the solid product was decomposed by hydrothermal treatment in HF, HNO₃ and H₂O₂ mixed solutions at 130°C for 3 h under autogenous water vapor pressure.

**Fig. 1.** XRD patterns of the solid products with the initial molar ratio Na:Ni:Li:Si = 0.7:5.4:0.6:8.0 synthesized at different temperatures for various durations and commercial Mg-hectorite as reference.
Physicochemical properties of Ni-hectorite

Swelling property of Ni-hectorite was confirmed by the treatment with ethylene glycol. Measurement of CEC was as follows: All the exchangeable cations of the solid product (0.2 g) were exchanged with Ca\(^{2+}\) ion by shaking and centrifugation cycles with 1 mol/l CaCl\(_2\) aqueous solution. After washing with 80 wt% ethanol aqueous solution to remove extra Ca\(^{2+}\) ion, all the exchangeable Ca\(^{2+}\) ion was exchanged with Ba\(^{2+}\) ion by shaking and centrifugation cycles with 10 mmol/l BaCl\(_2\) aqueous solution. The amount of Ca\(^{2+}\) ion released was measured by AAS.

Evaluation method of adsorptive ability of MB was as follows: The solid product (0.1 g) was added into MB aqueous solution (35 ml) with the various initial concentrations in the range 1.5–6.5 mmol/l. The mixed suspension was horizontally shaken at 25°C for 24 h. After the mixed suspension was separated into the solid phase and liquid phase by centrifugation, the MB concentration in the equilibrium liquid phase was measured by a JASCO UV-VIS spectrophotometer V-570 on a wavelength of 664 nm.

The Ni-hectorite modified electrode of approximately 300 nm thick film (2 cm\(^2\) area) was deposited onto 1 cm × 6 cm pieces of In-doped SnO\(_2\) coated glass by evaporation of 1 wt% Ni-hectorite aqueous suspension. Cyclic voltammogram was recorded by a Hokutodenko HZ-3000 polarization system with an undivided three-electrode cell at potential scanning speed of 25 mV/s. The counter electrode was a Pt screen and the reference electrode was a saturated calomel electrode (SCE). The electrolyte solution was 0.1 mol/l Na\(_2\)HPO\(_4\) aqueous solution at pH 9.4 and 25°C.

RESULTS AND DISCUSSION

Hydrothermal synthesis of Ni-hectorite

In this section, the hydrothermal synthetic condition of Ni-hectorite has been examined in detail. The XRD patterns of the green solid products obtained at 200–300°C for 3–24 h with the initial molar ratio Na:Ni:Li:Si = 0.7:5.4:0.6:8.0 are shown in Fig. 1. Although the solid products obtained at under 220°C for 3 h have an obscure 001 reflection, the solid products obtained at 250–300°C indicate more clear 001 reflection, and then show the similar XRD patterns to that of a commercial Mg-hectorite as reference (CO-OP Chemical Co., Ltd.). This indicates that these synthetic products are Ni-hectorite. Only the solid product formed at 300°C for 24 h is accompanied with quartz (PDF No. 46-1045) as a by-product. However, all the green products have a smaller basal spacing (d\(_{001}\)) of about 10 Å in comparison with the Mg-hectorite. It suggests that these synthetic products are no water Ni-hectorite. Next, the synthesis of Ni-hectorite with the different initial molar ratios Na:Ni:Li:Si = 0.7:5.4:0.6:8.0, 1.4:5.4:1.2:8.0, 1.4:4.8:1.2:8.0 and 1.4:4.8:1.2:7.5 has been attempted at 300°C for 12 h. The result is shown in Fig. 2. All the green solid products have also similar XRD patterns to the Mg-hectorite, as for the initial molar ratio Na:Ni:Li:Si = 1.4:4.8:1.2:8.0, though quartz is formed as a by-product. In the cases of the initial molar ratios Na:Ni:Li:Si = 1.4:4.8:1.2:8.0 and 1.4:4.8:1.2:7.5, the each basal spacing of the resulting Ni-hectorites is 12.1–12.7 Å, although each 001 reflection of the Ni-hectorites is relatively smaller than that of the Ni-hectorite with initial molar ratios Na:Ni:Li:Si = 0.7:5.4:0.6:8.0 and 1.4:5.4:1.2:8.0. It suggests that these synthetic products are one water layer Ni-hectorite. These Ni-hectorites are trioctahedral because the d\(_{006}\) values are 1.52 Å. From
these above results, it has been found that no waterlayer Ni-hectorites (10 Å) and one waterlayer Ni-hectorites (12 Å) can be synthesized at 300°C for 12 h. One of the reasons for two kinds of Ni-hectorites is due to the amount of exchangeable cations. Since the molecules of water are arranged around the exchangeable cations, the interlayer water is thought to be increased with an increase in the amount of exchangeable cations. The hydrothermal synthesis of Mg-hectorite was studied at

150–300°C for 2–24 h, and it was found that the lower temperature (at 150°C) was, the longer duration (for 24 h) was needed for formation of Mg-hectorite (Torii et al., 1987). It was also recognized that Zn-hectorite could be synthesized by the hydrothermal reaction at lower temperature for shorter duration in comparison with Mg-hectorite (Higashi et al., 2002; Nakakuki et al., 2004). In consideration of these earlier studies, it has been also found that the Ni-hectorite can be synthesized at the severer condition (300°C for 12 h) compared to the cases of Mg-hectorite and Zn-hectorite.

### Characterization and physicochemical properties of Ni-hectorite

Swelling property of smectite is generally confirmed by the treatment with ethylene glycol. The basal spacing of smectite expands from 12–15 Å into about 18 Å by the intercalation of ethylene glycol molecules. Table 1 summarizes the changes in the d₀₀₁ values of the representative Ni-hectorites treated with ethylene glycol. Although Ni-hectorite 1 synthesized at 250°C for 12 h shows no diffraction pattern, Ni-hectorites 2 and 3 synthesized at 300°C for 12 h show the obscure 001 and 002 reflections and then their each basal spacing expands into about 18 Å like Mg-hectorite and Zn-hectorite. The reason for no diffraction pattern of Ni-hectorite 1 after the treatment with ethylene glycol is still unclarified. Ni-hectorites 2 and 3 were vouched to have the intrinsic swelling property of smectite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Air dried d₀₀₁ (Å)</th>
<th>Ethylene glycol treatment d₀₀₁ (Å)</th>
<th>d₀₀₂ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-hectorite 1</td>
<td>10.25</td>
<td>No diffraction</td>
<td>No diffraction</td>
</tr>
<tr>
<td>Ni-hectorite 2</td>
<td>9.86</td>
<td>17.45</td>
<td>9.07</td>
</tr>
<tr>
<td>Ni-hectorite 3</td>
<td>12.69</td>
<td>17.87</td>
<td>8.82</td>
</tr>
<tr>
<td>Mg-hectorite</td>
<td>13.84</td>
<td>17.94</td>
<td>9.07</td>
</tr>
<tr>
<td>Zn-hectorite</td>
<td>12.54</td>
<td>18.17</td>
<td>9.07</td>
</tr>
</tbody>
</table>

1: Synthetic condition is at 250°C for 12 h with initial molar ratio Na: Ni: Li: Si = 0.7: 5.4: 0.6: 8.0.
2: Synthetic condition is at 300°C for 12 h with initial molar ratio Na: Ni: Li: Si = 0.7: 5.4: 0.6: 8.0.
3: Synthetic condition is at 300°C for 12 h with initial molar ratio Na: Ni: Li: Si = 1.4: 4.8: 1.2: 7.5.

Zn-hectorite: Synthetic condition is at 200°C for 3 h with initial molar ratio Na: Zn: Li: Si = 0.7: 5.4: 0.6: 8.0 (Nakakuki et al., 2004).

![SEM photographs of Ni-hectorites and Mg-hectorite](image-url)
Next, the representative Ni-hectorite samples have been characterized by various analyses. First, the particle shape and size have been observed by SEM. The results are shown in Fig. 3. The Ni-hectorite 1 is fine particles, while the Ni-hectorites 2 and 3 are massive plate-like particles as similar to the Mg-hectorite. From this result, it can be said that the synthetic condition at 300°C makes the crystalline particles of Ni-hectorite well developed.

The FT-IR spectra of the Ni-hectorites and Mg-hectorite are shown in Fig. 4. The small bands around 3630 cm⁻¹ of the Ni-hectorites 2 and 3 and Mg-hectorite are assigned to O-H stretching and bending vibration in the trioctahedral sheets. Each broad and sharp bands around 3400 cm⁻¹ and 1600 cm⁻¹ are assigned to interlayer water. The broad bands around 1000 cm⁻¹ are also assigned to Si-O stretching vibration in the tetrahedral sheets. The Ni-hectorites 2 and 3 are marked by the band around 670 cm⁻¹ against for the band around 655 cm⁻¹ of the Mg-hectorite. In the earlier studies, the band around 670 cm⁻¹ was assigned to Zn-O vibration in the trioctahedral sheets (Higashi et al., 2002; Nakakuki et al., 2004). Therefore, the Ni-hectorite is quite similar to the Zn-hectorite in FT-IR spectra. This similarity can be explained by the nearness in cation radius.

The XPS measurement was applied to synthetic Ni-hectorite hitherto (Seyama et al., 2002; Korakianiti et al., 2004). The XPS spectra of the Ni-hectorites 2 and 3 and Mg-hectorite are indicated in Fig. 6. The XPS results indicate that the Ni-hectorites are decomposed at higher temperature. Incidentally, there are no data in Figs. 4 and 5, the FT-IR spectrum and TG-DTA curve of Ni-hectorite 1 are similar to those of Ni-hectorite 2.

The TG-DTA curves of the Ni-hectorites and Mg-hectorite are shown in Fig. 5. The endothermic reaction at 50–70°C is due to the release of interlayer and adsorbed water. Moreover, the endothermic reaction is observed at 770°C (Ni-hectorite 2) and 730°C (Ni-hectorite 3), which are due to the dehydroxylation of the trioctahedral sheets. This result is caused by the difference that the Ni-hectorite 3 is a solid solution containing a double amount of Li compared to the Ni-hectorite 2. Zn-hectorite was characterized by the thermal decomposition at lower temperature compared to Mg-hectorite (Higashi et al., 2002; Nakakuki et al., 2004). These results indicate that the Ni-hectorites are decomposed at higher temperature. Incidentally, there are no data in Figs. 4 and 5, the FT-IR spectrum and TG-DTA curve of Ni-hectorite 1 are similar to those of Ni-hectorite 2.

The XPS measurement was applied to synthetic Ni-hectorite hitherto (Seyama et al., 2002; Korakianiti et al., 2004). The XPS spectra of the Ni-hectorites 2 and 3 and Mg-hectorite are indicated in Fig. 6. The Ni-hectorite 2 has the spectra assigned to Ni2p₁/₂ and Ni2p₃/₂, whose binding energy suggests that the Ni-hectorite 2 has...
Ni$_3$(OH)$_6$ trioctahedral sheets. It seems that XPS spectra of Ni-hectorites 1 and 3 are similar to that of Ni-hectorite 2 in consideration of likeness in their FT-IR spectra and TG-DTA curves.

The following cation exchange capacity (CEC) and adsorptive property of methylene blue (MB) are generally evaluated as a property of smectite. First, the structural formula and CEC of the Ni-hectorite have been investigated. Table 2 makes a summary of the results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structural formula</th>
<th>CEC (meq/100 g-clay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-hectorite 2</td>
<td>Na$<em>{0.36}$ (Ni$</em>{0.46}$Li$<em>{0.64}$)Si$</em>{17.48}$O$_{70}$(OH)$_4$</td>
<td>53</td>
</tr>
<tr>
<td>Ni-hectorite 3</td>
<td>Na$<em>{1.44}$ (Ni$</em>{1.3}$Li$<em>{0.14}$)Si$</em>{22.88}$O$_{70}$(OH)$_4$</td>
<td>90</td>
</tr>
<tr>
<td>Me-hectorite</td>
<td>Na$<em>{1.51}$ (Mg$</em>{0.44}$Li$<em>{0.56}$)Si$</em>{17.72}$O$_{70}$(OH)$_4$</td>
<td>115</td>
</tr>
<tr>
<td>Zn-hectorite</td>
<td>Na$<em>{1.06}$ (Zn$</em>{0.36}$Li$<em>{0.64}$)Si$</em>{18.34}$O$_{70}$(OH)$_4$</td>
<td>149</td>
</tr>
</tbody>
</table>

Ni$_3$(OH)$_6$ trioctahedral sheets. It seems that XPS spectra of Ni-hectorites 1 and 3 are similar to that of Ni-hectorite 2 in consideration of likeness in their FT-IR spectra and TG-DTA curves.

The following cation exchange capacity (CEC) and adsorptive property of methylene blue (MB) are generally evaluated as a property of smectite. First, the structural formula and CEC of the Ni-hectorite have been investigated. Table 2 makes a summary of the results. The Ni-hectorites 2 and 3 have the CEC values of 53 and 90 meq/100 g-clay, respectively. Because the Ni-hectorite 3 has a larger amount of Li in the trioctahedral sheets than the Ni-hectorite 2, the Ni-hectorite 3 has naturally more exchangeable cations than the Ni-hectorite 2 for neutralizing layer charge. Therefore, Ni-hectorite 3 has a larger CEC than Ni-hectorite 2. However, the CEC of the Ni-hectorites is less than that of the Mg-hectorite and Zn-hectorite, although Ni-hectorite 3 has more exchangeable cations compared to Mg-hectorite and Zn-hectorite. The explanation for this phenomenon is under consideration.

Then, the adsorptive ability of MB has been investigated. The adsorption isotherms of MB for the Ni-hectorites, Mg-hectorite and Zn-hectorite are represented in Fig. 7. The mathematical form of the Freundlich isotherm is

\[ q = kC^{1/n} \quad \text{or} \quad \log q = 1/n \log C + \log k, \]

where \( q \) is the amount (mmol) of MB adsorbed per 100 g of clay, \( C \) is the equilibrium concentration of MB aqueous solution (μmol/l) and \( n \) and \( k \) are constants. The plot of \( \log q \) against \( \log C \) gives straight lines, indicating that the Freundlich adsorption equation is applicable. Table 3 summarizes the slope (\( n \)) and intercept (\( k \)) on the Freundlich adsorption isotherms. The \( n \) values give information about surface heterogeneity and affinity of hectorite for MB species and the \( k \) values give values when \( C \) is 1 μmol/l. The Ni-hectorites 2 and 3
The modified electrode consisted of Ni-Al-Cl in phosphate to Ni²⁺. It was reported that layered double hydroxide the cathodic peak is attributed to the reduction of Ni³⁺, and then has an anodic peak at 0.75 V vs. SCE and a cathodic peak at 0.75 V vs. SCE using scanning speed of 100 mv/s (Qiu et al., 1995). The differences in the redox potentials between both cases are probably due to property of modified electrode, thickness of film, electrolyte and pH.

CONCLUSIONS

In this study, we have investigated the synthetic conditions of the Ni-hectorite as well as its physicochemical and electrochemical properties in detail. The Ni-hectorite has been synthesized by hydrothermal reaction of the starting slurry with the initial molar ratios Na: Ni: Li: Si = 0.7: 5.4: 0.8: 1.0, 1.4: 5.4: 1.2: 8.0, 1.4: 4.8: 1.2: 8.0 and 1.4: 4.8: 1.2: 7.5 at 300°C for 12 h. It has been found that the formation of Ni-hectorite needs the severe condition of higher temperature (300°C) and longer duration (12 h), and the resulting Ni-hectorite is relatively large massive plate-like particles with a characteristic tint of green and has a smaller CEC and lower MB adsorptive ability in comparison with the Mg-hectorite and Zn-hectorite. In addition, the Ni-hectorite modified electrode has been found to be active in electrochemistry, indicating an anodic peak attributed to the oxidation at 0.75 V vs. SCE and a cathodic peak attributed to the reduction at 0.65 V vs. SCE.

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We are grateful to Fuji Chemical Co., Ltd. for provision of water glass, CO-OP Chemical Co., Ltd. for provision of Mg-hectorite sample and Kuramoto Seisakusho Co., Ltd. for provision of In-doped SnO₂ coated glass.

REFERENCES


FIG. 8. Cyclic voltammogram of Ni-hectorite 3 modified electrode.
