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THERMAL EVOLUTION OF NICKEL CHLORITE-LIKE PHASE DERIVED FROM MONTMORILLONITE

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ABSTRACT

A nickel chlorite-like compound was derived from montmorillonite by intercalation of nickel hydroxide layer between the silicate layers. The hydroxide layer was dehydrated in a temperature range of 300° to 400°C, and remained as the oxide between the silicate layers. The structural OH groups of montmorillonite are converted into the oxide ions by the reaction with the remained nickel oxide layer in a temperature range of 400° to 500°C. This conversion leads to a pronounced thermal stabilization of the silicate layers up to 800°C, though the untreated montmorillonite suffers a destructive dehydration starting at temperatures about 650°C.

Key words: Chlorite, Montmorillonite, Hydroxy nickel interlayer, Thermal behavior

INTRODUCTION

Montmorillonite is a reactive layered silicate mineral, which forms a variety of intercalation complexes with inorganic as well as organic guest species. If the interlayer cations are exchanged with voluminous metal-hydroxy cations such as $[Al_{13}O_4(OH)_{24}]^{7+}$ and $[Zr_4(OH)_{14}]^{2+}$, the resulting complexes are the precursors for microporous oxide-pillared structures (Yamanaka and Hattori, 1991; Yamanaka and Takahama, 1993; Yamanaka, 1994). Oxide sol particles can also be introduced between the silicate layers by ion-exchange, so long as the particles are positively charged (Yamanaka et al., 1992). Some insoluble metal hydroxides have been precipitated between the silicate layers by a titration method; the metal salt solutions are titrated with alkaline solutions in the presence of montmorillonite (Yamanaka and Brindley, 1978; Yamanaka et al., 1987; Ohtsuka et al., 1990). The respective metal hydroxide monolayers are precipitated between the layers, and chlorite-like complexes are formed. These are interstratified complexes consisting of two different types of layer structures. It will be interesting to study the thermal reaction of the two types of layers mixed homogeneously in a molecular level. In this paper, a nickel chlorite-like phase is derived from montmorillonite and the thermal evolution of the silicate layer is investigated.

EXPERIMENTAL

Preparation of nickel chlorite-like phase

Na-montmorillonite (Kunipia G) used was supplied by Kunimine Industrial Company. Its structural formula was determined to be $Na_{0.35}K_{0.01}Ca_{0.02}(Si_{3.89}Al_{0.11})(Al_{1.60}Mg_{0.32}Fe_{0.08})$-$O_{10}(OH)_2 \cdot nH_2O$, and the cation exchange capacity (CEC) was 100 meq/100 g. A nickel chlorite-like phase was prepared according to the method described in a previous paper (Yamanaka and Brindley, 1978); a 1% clay suspension in a 0.1 M $Ni(NO_3)_2$ solution was titrated with a 0.1 N NaOH solution slowly until nickel hydroxide layer was fully developed between the silicate layers of clay. After a continuous stirring for 3 days at room temperature under a nitrogen atmosphere, the product was separated by centrifugation and washed with water several times. A nickel ion-exchanged montmorillonite was prepared by simply dispersing the clay in a 1 M $Ni(NO_3)_2$ solution for one day followed by washing with water in a similar manner.

Analysis

The obtained chlorite-like phase was spread on silica glass slide in such a way that the silicate layers were preferred oriented with the basal plane parallel to the plane of the glass slide. The sample on the glass slide was heated stepwise up to 840°C. At each heating step, the glass slide was taken out, and the X-ray powder diffraction (XRD) pattern of the sample was measured by using graphite-monochromatized Cu $K\alpha$ radiation. Infra-red spectra were recorded on a KBr pellet using a Perkin-Elmer FT-IR spectrometer (model 1600). Thermogravimetric analysis (TGA) was carried out for a heating rate of 10°C/min under a stream of dry air.

RESULTS AND DISCUSSION

XRD study

If a $Ni(NO_3)_2$ solution was titrated with NaOH in the presence of montmorillonite, nickel hydroxide was selectively precipitated between the silicate layers until the interlayer space was fully covered with about three moles of nickel hydroxide on $O_{10}(OH)_2$ anion basis of the silicate composition. The resulting solid was a chlorite-like phase with a characteristic basal spacing of 14.7 Å. A series of XRD patterns measured at different heating steps are shown in Fig. 1. As can be seen, a peak due to the 001 basal reflection of the chlorite-like phase is missing. This can be interpreted in terms of the cancellation of the XRD scattering factors from the silicate and the nickel hydroxide layers (Ohtsuka et al., 1990; Fukuda et al., 1990).

The chlorite-like phase was thermally stable up to 300°C. On heating to a temperature range of 300° to 400°C, the structure may be disordered in the way of stacking the layers due to the decomposition of the hydroxide interlayer to nickel oxide. In a higher temperature range of 500° to 800°C, a new basal reflection appears at about 12.0 Å. Since the sample is well oriented with the basal plane parallel to the plane of the glass slide, the new reflection can also be attributed to the basal reflection. This spacing value is corresponding to that of the silicate layers having a single oxide interlayer. The structure is stable up to 800°C.

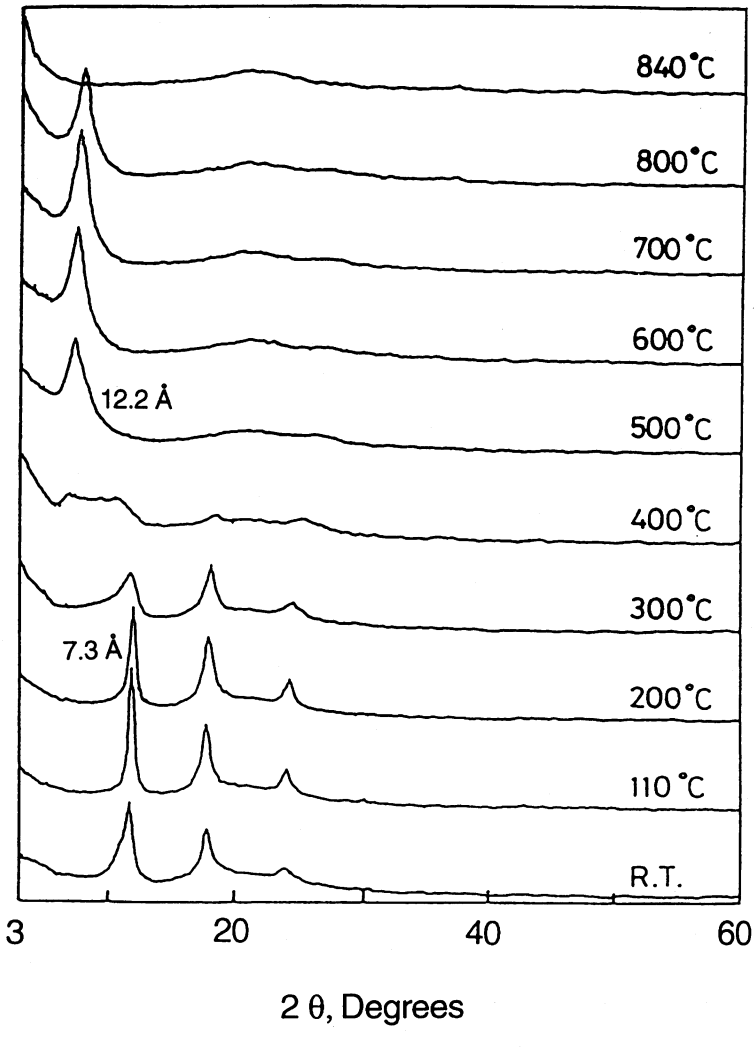


FIG. 1. A series of XRD patterns of Ni-chlorite-like phase calcined at different temperatures.

Thermogravimetric analysis

The TGA curve of the nickel chlorite phase is compared with those of Ni-montmorillonite and nickel hydroxide in Fig. 2. The nickel hydroxide bulk sample is converted into the oxide at about 300°C accompanied by an abrupt decrease in the weight; Ni-montmorillonite shows two-step dehydration; the first weight loss below 100°C is due to the dehydration of the absorbed water, and the second one at about 600°C is due to the dehydroxylation of the structural OH groups in the silicate layers. The chlorite-like phase having the nickel

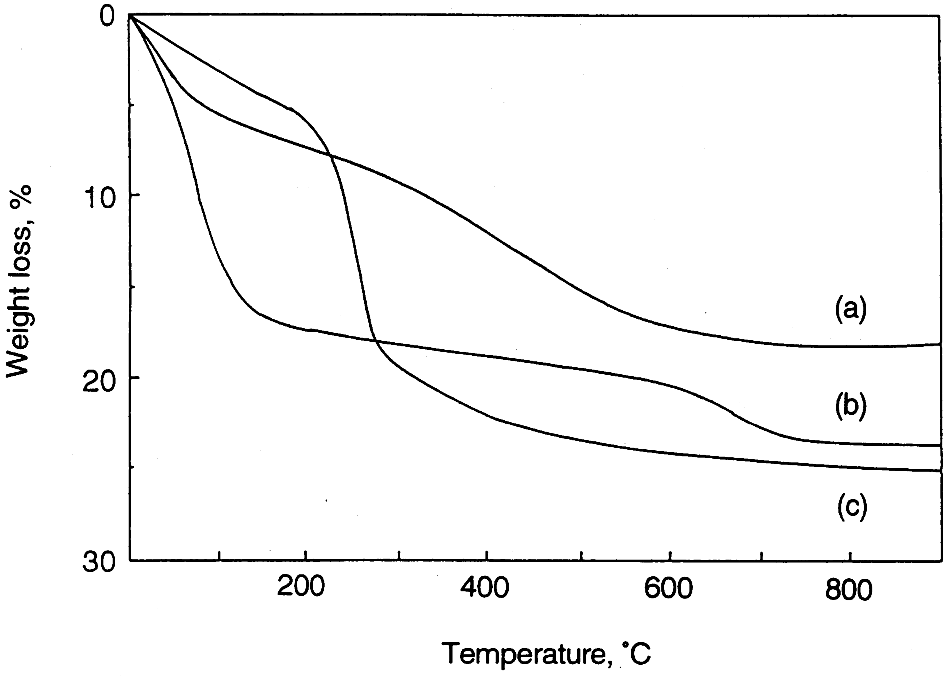


Fig. 2. Thermogravimetric analysis curves of (a) nickel hydroxide, (b) Ni-montmorillonite, and (c) Ni-chlorite-like phase.

hydroxide layers between the silicate layers decomposed gradually in a temperature range of 300° to 500°C. It is interesting to note that the dehydration of the silicate layers of the chlorite-like phase is completed at temperatures lower than that of the silicate layers without the hydroxide interlayers by about 100°C.

Infra-red spectra

The FT-IR spectra of Ni-montmorillonite and Ni-chlorite-like phase thermally treated at different temperatures are compared in Fig. 3. In the spectrum of the Ni ion-exchanged sample, the absorptions at 912 and 848 cm^{-1} are assigned to the librational modes of the di-octahedral OH groups, Al-OH-Al and Al-OH-Mg, respectively (Farmer, 1974). The absorption due to the stretching vibration of the OH groups appears at 3630 cm^{-1}. On heating to 400°C, the OH librational frequencies were shifted in wavenumber toward 938 and 879 cm^{-1}, respectively. Montmorillonite is a 2:1 di-octahedral clay mineral with one-third of the octahedral cation sites vacant. It is well known that small interlayer cations such as Li^+ can migrate into the vacant octahedral sites through the 6-membered oxygen ion rings of the silicate layers (Hofmann and Klemen, 1950; Sposito et al., 1983). Sakurai et al. (1990) reported that small and polyvalent interlayer cations such as Mg^{2+} and Al^{3+} could be fixed by migration to the octahedral vacant sites of tetrasilicic mica. Nickel ions

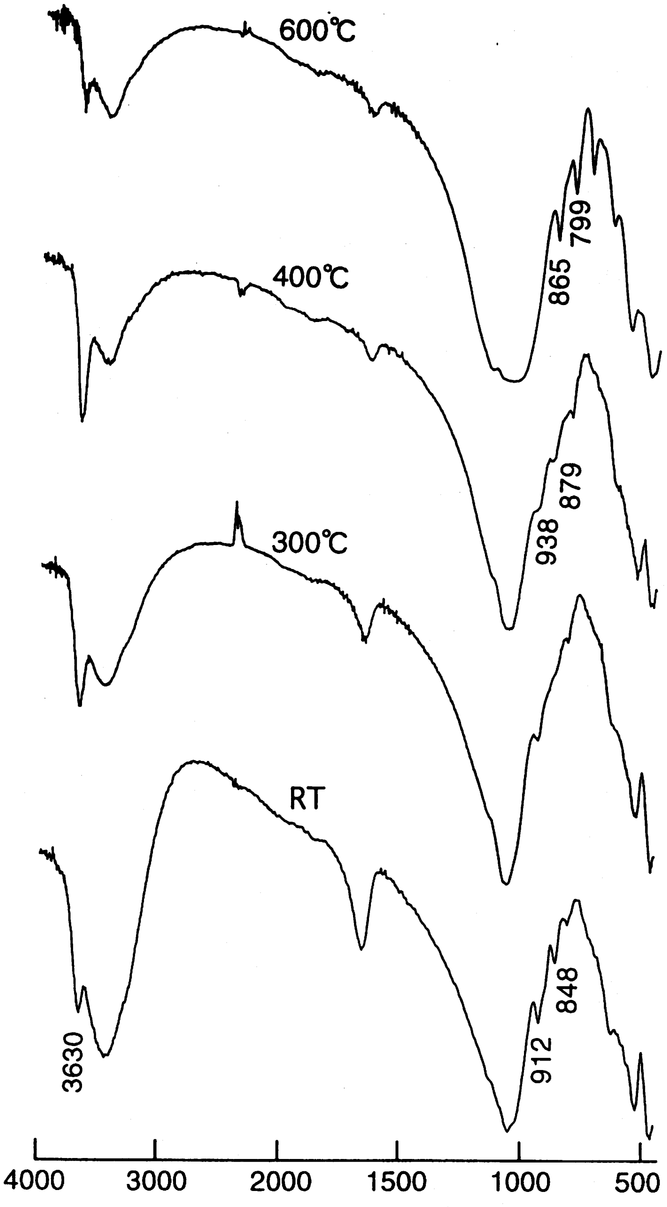
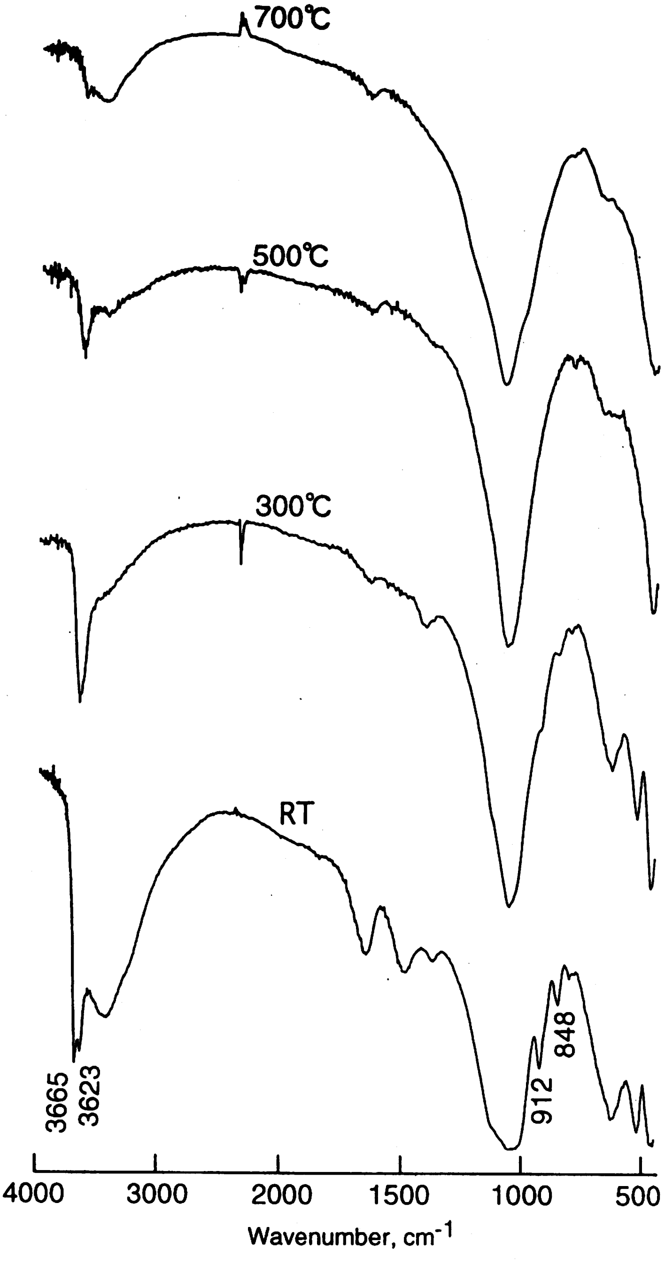


FIG. 3. FT-IR spectra of (a) Ni-montmorillonite and (b) Ni-chlorite-like phase thermally treated at different temperatures.


700℃
500℃
300℃
RT
3665
3623
912
848
4000
3000
2000
1500
1000
500
Wavenumber, cm^{-1}

(b)

have an ionic radius similar to that of Li^+ and it is reasonable to expect a similar migration to the octahedral vacant sites of montmorillonite. The shifts of the OH librational frequencies observed above on heating can be attributed to the migration of Ni^{2+} to the octahedral vacant sites.

On further heating to 600°C, the librational bands of the Ni-montmorillonite at 938 and 879 cm^{-1} were changed into new bands at 865 and 799 cm^{-1}. This change of the spectrum was interpreted in terms of the formation of five co-ordination structure with dehydroxylation in the octahedral sheet (Tennakoon et al., 1986). The OH stretching band was also much reduced in intensity on dehydroxylation.

The infra-red spectrum of the Ni-chlorite-like phase measured before thermal treatment (Fig. 3b) resembled that of Ni-montmorillonite in the sense that the OH stretching as well as the librational bands appeared at frequencies similar to those of Ni-montmorillonite, although some details of the two spectra were different. The splitting of the OH stretching band into 3660 and 3623 cm^{-1} appears to be due to the presence of nickel hydroxide interlayers. On heating to 500°C, however, the librational bands at 912 and 848 cm^{-1} due to Al-OH-Al and Al-OH-Mg, respectively, disappeared almost completely, and the OH stretching vibrational band was also much decreased in intensity. The stretching band disappeared completely at 700°C. As shown in the TGA analysis, the dehydration of the chlorite-like phase was almost completed at about 500°C. The disappearance of the IR bands related to the structural OH groups is in good agreement with the weight loss data.

The high thermal stabilization of the silicate layers of chlorite-like phase could be explained by the following mechanism schematically shown in Fig. 4. On heating the Ni-montmorillonite, the interlayer Ni^{2+} will migrate into the vacant octahedral sites through the hexagonal oxygen rings of the tetrahedral sheets. At temperatures above 600°C, a dehydration occurs within the silicate layers. In case of Ni-chlorite-like phase, a similar migration of Ni^{2+} will also occur on decomposition of nickel hydroxide interlayers. The interlayered Ni-hydroxide is converted into nickel oxide and remains between the silicate layers. The nickel oxide remained between the silicate layers reacts with the octahedral hydroxy groups of the silicate layers at temperature below 500°C:

$$2(OH^-)_{\text{octahedral}} + (NiO)_{\text{interlayer}} \rightarrow 2(O^{2-})_{\text{octahedral}} + (Ni^{2+})_{\text{interlayer}} + H_2O$$

The silicate layers are changed into oxide compositions and thermally stabilized up to 800°C.

Tennakoon et al. (1987) also found a marked decrease in the OH-stretching mode of alumina pillared clay on heating to 500°C. They explained the finding in terms of a condensation between the interlayer Al-hydroxy cations and the octahedral OH groups of the clay. Ohtsuka et al. (1990) prepared a series of chlorite-like compounds with intercalation of metal hydroxide (metal = Mg, Ca, Mn, Fe, Co, Ni, Zn, and Cd) by using fluor tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$). On heating to 500°C, the hydroxide layers were removed out of the interlayer space as oxides, and the compounds totally collapsed to a basal spacing of 9.6 Å. In the fluor mica, the hydroxy groups of montmorillonite are replaced with fluoride ions, which will not be subjected to the dehydration reaction with the interlayer oxide. The reactivity of the structural OH groups with the oxide interlayers appears to play an important role to hold the oxide layers between the silicate layers.

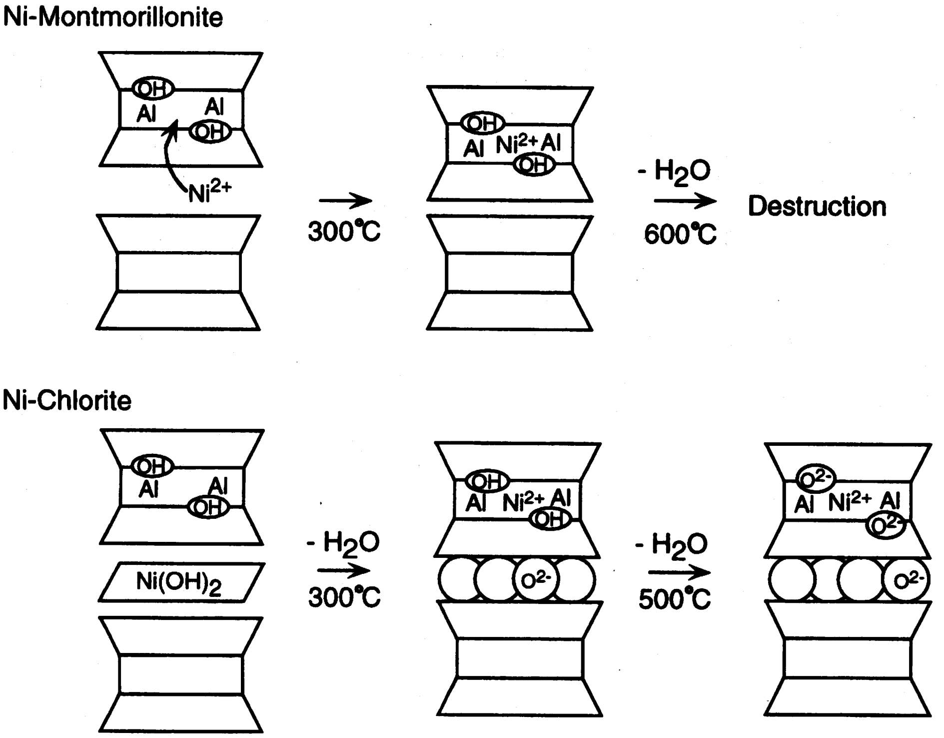


FIG. 4. Structural illustration of the conversion mechanisms of the silicate layers in Ni^{2+}-montmorillonite and Ni-chlorite-like phase on heating.

ACKNOWLEDGEMENTS

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