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NOTES

LEAD HYDROXIDE-VERMICULITE COMPLEX: PREPARATION AND CHARACTERIZATION

Key Words—Lead hydroxide, Vermiculite.

Clay-inorganic complexes have been investigated as catalysts or absorbents by many researchers as reviewed by Kato (1991). In most cases smectite has been used as the host for complexes. Vermiculite-inorganic complex, however, has been reported (Sawhney 1960; de la Calle and Suquet 1988; Martin de Vidales *et al* 1990). Hayase *et al* (1978) have reported surite, a naturally occurring clay-inorganic complex intercalated with lead carbonate. The authors in this paper have attempted to synthesize the surite under different conditions. In the course of the synthesis study, we have obtained a basic lead carbonate-montmorillonite complex (Tsutsumi *et al* 1993) and a lead oxide-montmorillonite complex (Uehara *et al* 1993). The host material of these clay-inorganic complexes was smectite. In this present work, the synthesis of vermiculite-inorganic complex has been attempted. As a result, a lead hydroxide-vermiculite complex (LVC) was synthesized by hydrothermally treating a mixture of vermiculite and lead nitrate solution.

EXPERIMENTAL

Sample preparation

Vermiculite from Transvaal, ground to less than 45 μm in size, was used as the starting material and treated in a Morey-type bomb which contained a Teflon bottle of about 15 ml volume. Initially, 200 mg of starting material was placed in the Teflon bottle, and then 8.4 ml of a 0.25M $Pb(NO_3)_2$ solution was added. After the suspension had been well stirred, the bottle was sealed. The mixture was treated for 42 h at 200°C in an electric furnace. The product was then centrifugally separated from the solution and washed with distilled water.

Methods of analysis

X-ray powder diffraction and high-temperature X-ray powder diffraction were carried out using a Rigaku Geigerflex RAD-IB with graphite monochromatized Cu-Kα radiation (40 kV, 20 mA) and a Rigaku Geigerflex RAD-IC with high-temperature attachment and Ni-filtered Cu-Kα radiation (40 kV, 20 mA).

In order to determine the layer structure of the LVC, interlayer materials were removed by the following acid treatment method; the LVC was treated with 0.75% HCl at room temperature for two days and then washed with distilled water, the residue was then dispersed in a 1 M NaCl solution and stirred with a magnetic stirrer for 24 h. The product was centrifugally separated from the solution and washed five times with distilled water.

Chemical analysis was carried out using an energy-dispersive analysis system (Tracor Northern TN5400 EDS) installed in an electron probe microanalyzer (JEOL JXA733) which used an accelerating voltage of 15 kV and a beam current of 4.00×10^{-10} A. The measured values of the elements, except for the CO_2, NO_2, and H_2O, were corrected using the conventional ZAF correction method. The contents of CO_2 and NO_2 were determined using a YANACO Type MT-5 CHN corder. The water content was obtained by subtracting the CO_2 and NO_2 contents from the weight loss between room temperature and 1000°C using thermogravimetry.

RESULTS AND DISCUSSION

XRD data

Figure 1 (a and b) shows respectively XRD patterns of the LVC and the residue after treatment with HCl and Na-exchange. In the diffraction pattern of the LVC, the basal reflections corresponding to the *d*-spacing of 1.41 nm are observed up to the 12th order. The relative intensities of reflections differ from that of natural vermiculite in the point that the 002 and 005 reflections are remarkably intense. The basal spacing of the vermiculite has been reported to decrease to a spacing of about 1.0 nm on K-saturation because of K^+ fixation into the six-membered ring (MacEwan and Wilson 1980). However, no discernible changes were observed in the intensities and spacings of the peaks of the LVC on treatment with a 1 M KCl solution. This result indicates that the LVC contains compounds, and no exchangeable cations, in the interlayer that prevent contraction of the interlayer space on KCl treatment.

The XRD pattern of LVC treated with HCl and Na-saturated shows the basal reflection corresponding to the spacing of 1.47 nm and the sequential high-order reflections. The relative intensities of the reflections agree with that of the Na-form of vermiculite reported by MacEwan and Wilson (1980).

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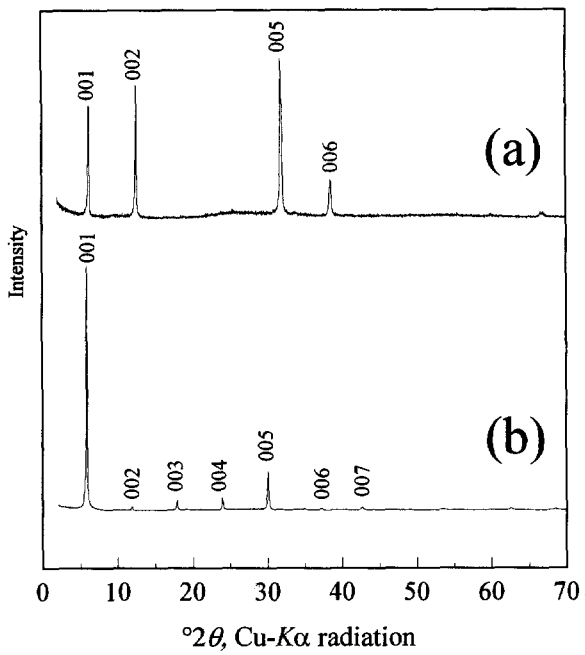


Figure 1. X-ray diffraction patterns of (a) the lead hydroxide-vermiculite complex (LVC); (b) residue obtained from the LVC powder treated with 0.75% HCl and Na-saturated.

Table 1. Chemical composition and structural formula of the lead hydroxide-vermiculite complex (LVC) (1), and the residue obtained from the LVC powder treated with 0.75% HCl and Na-exchanged (2).

	(1)	(2)
SiO_2	24.10	39.43
Al_2O_3	5.70	8.96
Fe_2O_3	3.45	6.08
MgO	14.93	24.06
CaO	trace	trace
Na_2O	trace	5.65
K_2O	trace	trace
TiO_2	0.57	0.90
PbO	42.32	trace
H_2O	8.94	14.91
Total	100.01	99.99
Composition per formula unit containing $O_{10}(OH)_2$		
Si	3.00	3.02
Al_{tet}	0.84	0.80
Fe_{tet}	0.16	0.18
Fe_{oct}	0.16	0.17
Mg	2.78	2.75
Ti	0.05	0.05
Interlayer composition		
Ca	—	—
Na	—	0.84
K	—	—
Pb	1.42	—
OH	2.00	—
H_2O	1.72	2.81

Chemical composition

Table 1 shows the chemical composition of the LVC and the residue after treatment with HCl and Na-exchange. The negative charge of the 2:1 layer was determined to be −0.84, as obtained from the structural formula of the Na-saturated residue, as shown in Table 1 (2). The Pb content of LVC was determined to be 1.42. This value is extremely large compared with the negative layer charge of 0.84. This leads to the inference that at least part of the H_2O coordinating with lead is in the form of a hydroxyl group. The small amounts of CO_2 and NO_2, which have been detected with CHN corder, originate from impurities of basic lead carbonate and lead nitrate. The basic lead carbonate was produced by taking CO_2 in air into the $Pb(NO_3)_2$ solution. These molecules were excluded from the chemical analysis of LVC. Hence, the LVC structural formula expressed as a half-unit cell can be represented as follows:

$$Pb_{1.42}(OH)_{2.00}1.72H_2O(Si_{3.00}Al_{0.84}Fe_{0.16})\cdot(Mg_{2.78}Fe_{0.16}Ti_{0.05})O_{10}(OH)_2$$

High-temperature X-ray powder diffractometry

Figure 2 shows the d_{001} values of the LVC and the residue after HCl treatment and Na-exchange, as a function of temperature. The basal spacing of the LVC gradually decreases from 1.41 nm to 1.23 nm with increasing temperature up to 300°C. At a higher temperature, the basal spacing of 1.23 nm is retained until dehydroxylation of the 2:1 layer occurs at 650°C. These results show that the lead compound contained in the interlayers prevents the layer collapse to 1.0 nm. For the acid-treated products, the basal spacing is 1.02 nm at 100°C, indicating complete interlayer collapse. This behavior is similar to that of the Na-form of vermiculite (MacEwan and Wilson 1980; de la Calle and Suquet 1988).

Structural model

The above properties of the LVC suggest that the material can be regarded as being composed of vermiculite intercalated with lead hydroxide. On the basis of this assumption, the atomic arrangement along the *z*-axis was determined using a one-dimensional Fourier synthesis method of electron density.

The LVC structure was considered to be a 14 Å intergrade. However, when one lead plane was assumed to be at the center (z = 0.705 nm) of the interlayer such as a chlorite, the one-dimensional electron density analysis did not give satisfactory results. Lead (II) in solution produces ions of composition $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$, etc. (Carell and Olin 1960; Taylor and Lopata 1984; Olin 1960a and b). Occurrence of $Pb_6(OH)_8^{4+}$ or higher hydroxides in the interlayers is precluded because the layer dimensions of these ions are larger than the observed 0.45 nm

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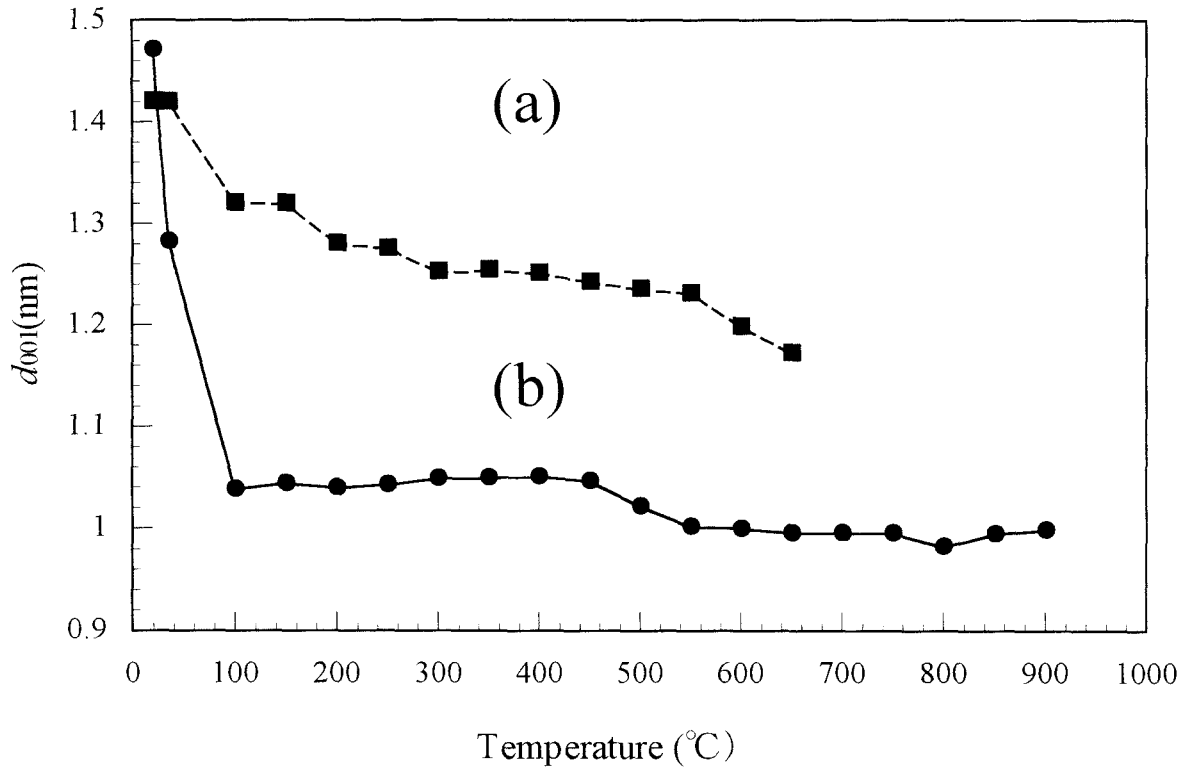


Figure 2. Values of the 001 reflections for (a) lead hydroxide-vermiculite complex (LVC); (b) residue obtained from the LVC powder treated with 0.75% HCl and Na-saturated as a function of temperature.

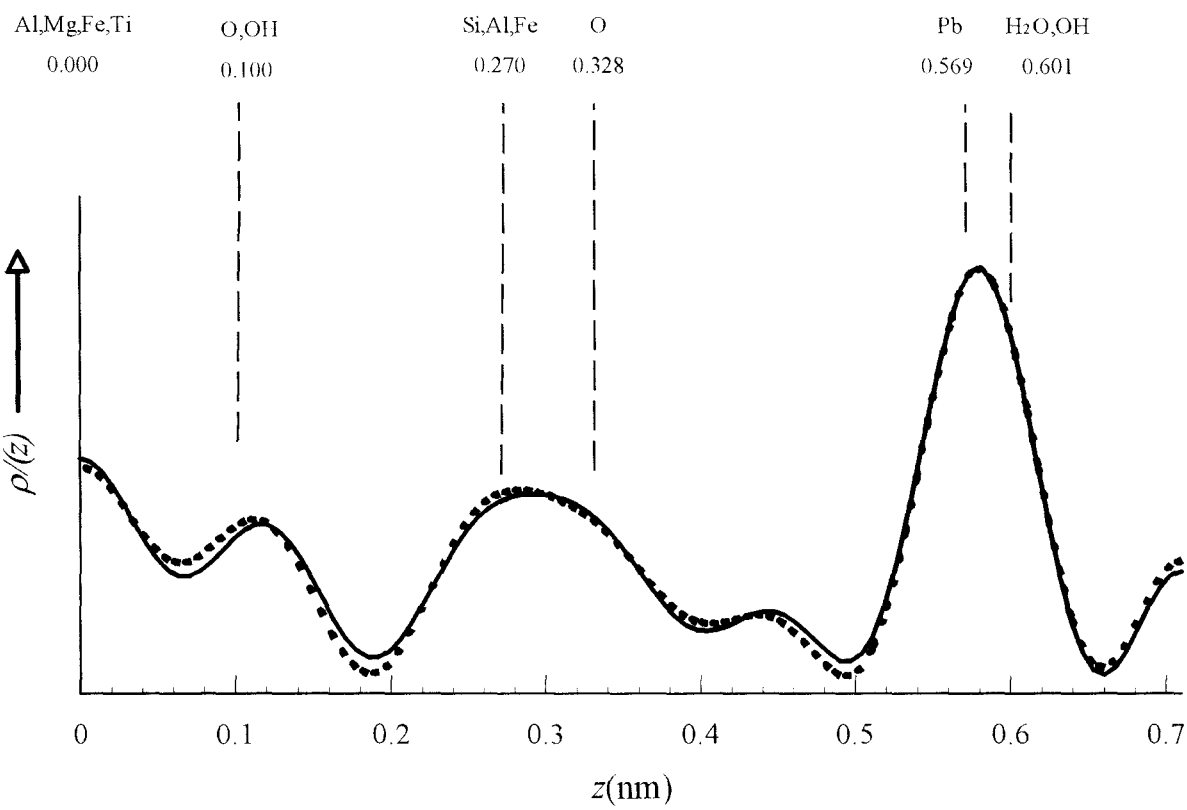


Figure 3. One-dimensional Fourier synthesis from 00*l* diffraction intensities of lead hydroxide-vermiculite complex (LVC).

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Table 2. Observed and calculated structure factors of 00*l* reflections for the lead hydroxide-vermiculite complex (LVC).

00*l*	d_{00l} (nm)	I/I_o	$\|F_{obs}\|$	F_{calc}*
1	1.415	51.00	173.81	−170.01
2	0.7053	52.60	356.21	319.08
3	0.4702	0.40	47.01	80.42
4	0.3527	0.62	79.01	−172.17
5	0.2810	100.00	1281.62	1271.77
6	0.2339	27.50	823.03	−800.95
7	0.2015	0.38	114.75	132.73
8	0.1763	1.04	221.67	−142.68
9	0.1567	1.53	308.23	−195.08
10	0.1416	7.99	792.25	794.15
11	0.1282	1.05	319.75	−333.14
12	0.1176	2.41	524.38	528.92

interlayer spacing. An arrangement involving three Pb planes in the interlayer was also dismissed because the electron density distribution curves based on this arrangement did not agree with those calculated from the observed peak intensities. Hence, provided that two lead planes exist, and $Pb_3(OH)_4^{2+}$ or $Pb_4(OH)_4^{4+}$ is involved in the exchange reaction with the interlayer cations of vermiculite, one-dimensional Fourier synthesis method of electron density shows a satisfactory result. The most satisfactory model is expressed with distribution of atom planes in Figure 3, when the *z* coordinates were refined on the basis of the structural model of $Pb_4(OH)_4^{4+}$ (Maroni and Spiro 1968). Figure 3 also shows the observed and calculated one-dimensional electron density distribution curves. Table 2 shows a comparison of $|F(00l)_{obs}|$ with $F(00l)_{calc}$. The reliability factor was 0.085 that the proposed structural model is reasonable. A more detailed discussion of structure is not possible from the restricted data along only the z-axis.

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