Intercalation of Various Alcohols in $HLaNb_2O_7$

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Synopsis. The intercalation of various alcohols into the interlayer of $HLaNb_2O_7$ was investigated. Normal alcohols having carbon numbers from one to five were inserted into the interlayer in the presence of water. The intercalation of alcohols was ascribed to the hydrophilic property of *n*-alcohols.

The host material described in the theme consists of layered and double perovskite structures having an exchangeable cation in the interlayer.[1] In a previous paper[2] the intercalation of water was studied. Many investigations concerning the intercalation of alkylamines into natural clay minerals and synthesized materials have been reported. However, there have been relatively few reports concerning the intercalation of alcohols and aldehydes, probably due to the complex and hard intercalation resulting from their weak polarizability. Therefore, the intercalation of various alcohols was studied in order to clarify the factors controlling the reactions between the host and guest molecules.

Experimental

Host materials were prepared by the same method as described in previous papers.[2,3] Beforehand, the $HLaNb_2O\cdot nH_2O$ reaction (abbreviated as HLa) was carried out at 100 °C for several hours in order to remove a large part of the water. The intercalation of alcohols was generally carried out at room temperature for 3 d by stirring a suspended solution comprising of 1 g of the HLa, 30 ml of alcohol and 4 ml of water. The properties of the solid products were monitored using X-ray diffraction (Rigaku Rad-B) with Ni-filtered Cu $K\alpha$ radiation, TG-DTA (Rigaku), with an increasing temperature of 10 $°C\,min^{-1}$ and FT-IR (Perkin-Elmer 1600) spectroscopy. A sample used for an IR measurement was prepared by pressing a mixture of the intercalation compound and KBr.

Results and Discussion

Typical illustrations of the intercalation of 1-butanol into HLa are mainly described as below. An XRD measurement showed an expansion of d_{001} from 12.2 Å of the hydrated HLa, or from 10.45 Å of dehydrated HLa to 16.4 Å. The intercalation caused no change in the direction of the *a*- and *b*-axes of the resultant compound, indicating that the same tetragonal structure as that of the HLa[1] was retained. Alcohols other than 1-butanol exhibited similar XRD patterns to that for 1-butanol. The IR spectrum of the intercalation compound is illustrated in Fig. 1. Bands observed at around 2900 cm^{-1} are ascribable to C–H and at 1170 cm^{-1} to C–O stretching vibration, respectively. By comparing this data with the IR spectrum of 1-butanol (see Fig. 1(b)) the C–H bands were found to remain about the same as those in liquid 1-butanol, suggesting that the C–H bond in the alkyl chain of 1-butanol did not undergo any interaction with the surface of HLa. However, the wave number for the C–O band increased from 1050 cm^{-1} in 1-butanol, suggesting that the C–O–H bond in 1-butanol interacts with OH^- or O^- on the inner surface of the layer compound, $LaNb_2O_7$, having a negative charge. The band at 1650 cm^{-1}, which is ascribable to the bending vibration of water, was also observed, and did not disappear upon a treatment at 100 °C, indicating that water coexists in the interlayer with alcohol. Although the band shift for the C–O stretching vibration is considered to result from the formation of a metal alkoxide,[4,5] the observed shift does not seem to represent this case. This is because both lanthanum and niobium atoms are surrounded by oxygen atoms in a double-perovskite structure of HLa.[1] The result for TG-DTA is shown in Fig. 2, together with the basal spacing of a sample treated at various temperature. Below 100 °C, the removal of water and/or 1-butanol weakly adsorbed on the outer surface was observed, and at 300—400 °C the sample weight decreased due to the combustion of 1-butanol, accompanying a large decrease in the basal spacing. From the results mentioned above, the intercalation of 1-butanol was also confirmed. When water did not exist in the reaction system, the intercalation of alcohols did not take place for any of the reaction times and temperatures. Thus, water is neccesary for the intercalation of alcohols. When HLa was treated

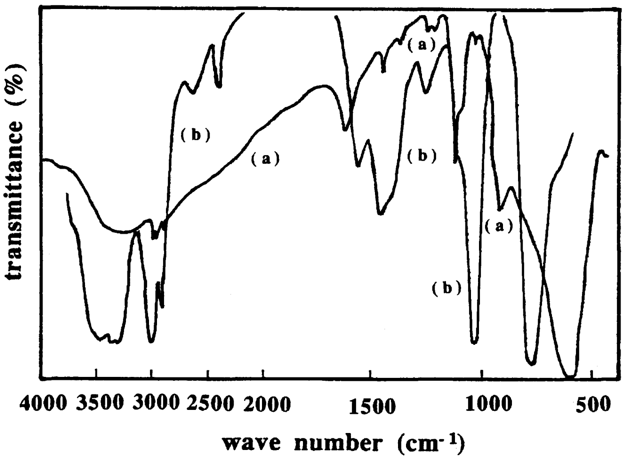

Fig. 1. (a) IR spectrum of the intercalation compound with 1-butanol. (b) IR spectrum of the 1-butanol.

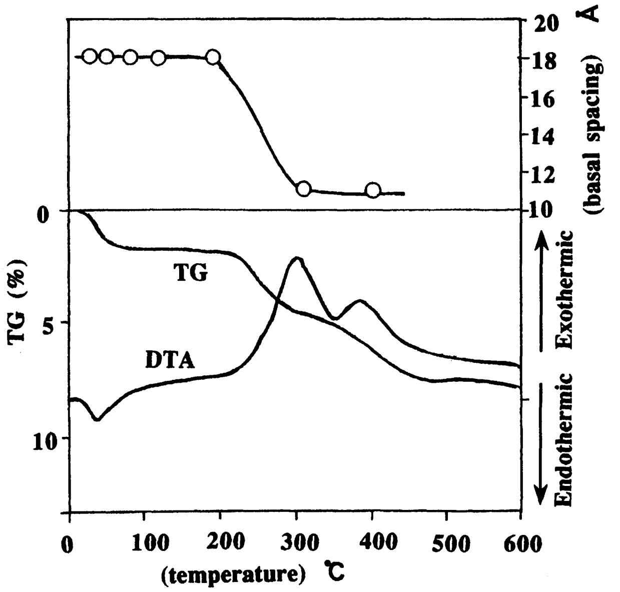

Fig. 2. Change in the basal spacing with temperature and DTA-TG results of the intercalated HLa with 1-butanol.

at temperatures higher than 400 °C, no intercalation of alcohols took place, even in the presence of water, resulting from a complete loss of the ability to insert water into the interlayer of HLa. The X-ray diffraction of the HLa treated at temperatures higher than 400 °C suggested a transformation into another crystal state,[2] thus providing additional evidence for the loss of the ability. Table 1 summarized the results of the intercalation of various alcohols, together with their solubility in water. Since alcohols having carbon numbers larger than 6 hardly (or do not) dissolve in water, they can not intercalate into HLa. It has been reported[2,4] that water in the interlayer dissociates 10^7 times higher than does liquid water. On the basis of the results mentioned above and the fact that water in the interlayer of HLa can easily enter, or go out, it is considered that water intercalates first, followed by alcohol. The polarizability of *n*-alcohols may be increased by the action of the water in the interlayer, which leads to intercalation. This explanation may be further supported by the result that ethylene glycol having good affinity for water cannot intercalate into the interlayer space, probably because of the lack of polarizability, due to its symmetrical structure. Further, although both 2-propanol and 2-butanol easily dissolve in water, no intercalation has been observed. Since the basal spacing of HLa is enlarged by ca. 2 Å by the intercalation of water,[1] it is considered that both alcohols penetrate between the layers. However, this was not found to be the fact. A steric hindrance may be the cause for the lack in intercalation of secondary alcohols.

The amounts of 1-butanol and water intercalated were determined from both elementary analysis and TG, as shown in Table 2. The weight loss (8.82%) obtained by TG measurements up to 700 °C was due to the removal of both 1-butanol and water. Consequently, the weight loss corresponds to 0.1633 mg. Since the amount of carbon in the sample was 5.14%, the amount

Table 1. Results of the Intercalation of *n*-Alcohols and Their Solubility in Water

Guest alcohol	Intercalation[a]	Solubility[b]
Methanol	○	∞
Ethanol	○	∞
1-Propanol	○	∞
2-Propanol	×	∞
1-Butanol	○	7.1 vol%
2-Butanol	×	18 vol%
1-Pentanol	△[c]	2.6 wt%
1-Hexanol	×	0.6 wt%
1,2-Ethanediol	×	∞
1,4-Butanediol	×	∞

a) ○ : Occurred × : not occurred. b) Solubility in water at room temperature. c) Partial intercalation at 130 °C.

Table 2. Results of the Elementary Analysis of the HLa Intercalated with 1-Butanol and Water and Their Molar Ratio

[Results]
The weight of the sample=1.852 mg
C ; 5.14%, H ; 1.39%
Weight loss=8.82%
[Calculation]
Molar ratio of 1-butanol and water=2.16 : 1
The molar ratio of each compounds
1-C_4H_9OH : H_2O : $HLaNb_2O_7$=0.51 : 0.24 : 1
Number of mol of $HLaNb_2O_7$ is assumed to be 1

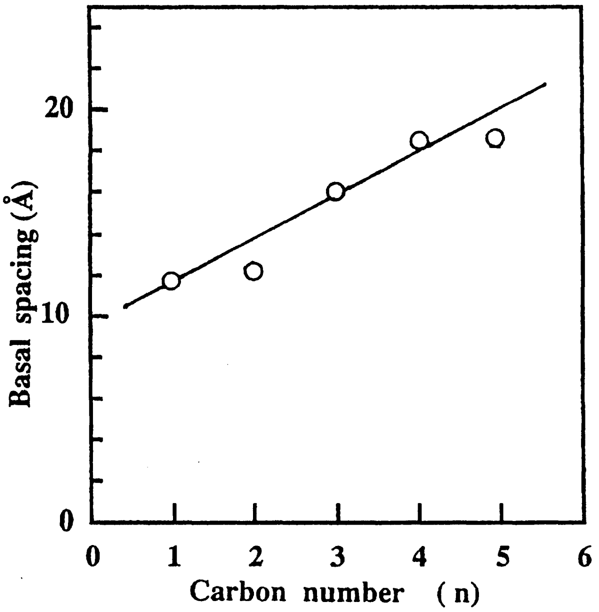

Fig. 3. Correlation between the basal spacing and carbon number of *n*-alcohols.

of carbon in 1-butanol was 0.0952 mg. The amount of 1-butanol corresponding to that of carbon was 0.1456 mg and the amount of water intercalated in the interlayer was about half the amount of 1-butanol.

The relationship between the carbon number of *n*-alcohols and the basal spacing is illustrated in Fig. 3. The slope of the straight line is 2.1 Å which corresponds to the increase in the basal spacing accompanying the increase of the single carbon number. Since the length increment of a linear chain of alcohols is 1.27 Å, the formation of bilayers of alcohol may be considered.

However, since the intercalation of methanol enlarged the basal spacing by only about 1 Å (see Fig. 3), further study concerning the formation of a bilayer, or on the state of alcohols inserted in the interlayer, is necessary.

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