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Effect of Water on the Acidic Properties of Layered $HLaNb_2O_7$

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Synopsis. The irreversible water in the interlayer of $HLaNb_2O_7$ (HLa), which was removed in the temperature range of 350—400 °C, greatly affected the formation of acidic properties of the HLa. The reversible water removed at lower temperature than 350 °C did not greatly affect the acidic character of the HLa. The relations between the isoelectric points and heat-treatment temperature of the HLa were examined in connection with the acidity.

The solid compound used in this study, $HLaNb_2O_7$ (abbreviated as HLa), comprised a layered, double-perovskite structure having an exchangeable proton in the interlayer exhibiting an acidic character.[1] Gopalakrishnan et al.[1] only reported that as the HLa intercalated pyridine it showed Brönsted acidity. The relation between the water in the interlayer and acidity has not yet been investigated. Generally, HLa has several moles of water molecules in the interlayer per mol of HLa. The water in the interlayer in the laminar compounds, (for instance, as montmorilonite) easily dissociates 10^7 times faster than does liquid water.[2] It can therefore be considered that the water existing in the interlayer affects the acidic properties. In the case of montmorilonite there are two kinds of water between layers:[3] One is water molecules coordinated to cations in the interlayer by having a constant arrangment which is controlled by the interaction of the charge-dipole, and an another situating on the outer position from the former is the reversible and free water, which can easily desorb and recombine. Since HLa has water in the interlayer, it is interesting to study how the water operates regarding the formation of the acidic properties of HLa, in connection with the intercalation of water into HLa.

Experimental

The materials used in this study were prepared as follows: A stoichiometric mixture of La_2O_3 and Nb_2O_5 (adding 1.2-times excess of K_2CO_3) was calcined at 1100 °C for 48 h in air. The thus-prepared $KLaNb_2O_7$ (KLa) was refluxed at 60 °C in a 6 M HNO_3 aqueous solution (1 M=1 $\mathrm{mol\,dm^{-3}}$) for 36 h to transform it into $HLa\cdot nH_2O$. For estimating the acidity of HLa the isoelectric-point method, accompanied by the titration of aqueous ammonia and the adsorption method with ammonia in the gas phase, were employed. In the former case ca. 1.0 g of the HLa, which was treated at various temperatures in air for 1 h and then cooled to room temperature in a desiccator, was immersed in 100 ml of pure water, so as not to come into contact with air, as much as possible. A pH meter (Toha Denpa HM-85) was equipped in the suspended solution at 25 °C, being stirred in a nitrogen atmosphere. Reading the pH meter was carried out after the pH reached a constant value.

In the case of the latter, the adsorption of NH_3 was carried out at various temperatures by the spring-balance method with a measurement accuracy of 0.5 mg. The HLa was previously treated at the same temperature as the adsorption for 1 h under vacuum. The dissociation constant (K_a) of HLa was estimated from

$$\mathrm{pH} = -1/2 \log K_a - 1/2 \log A, \qquad (1)$$

where A is the concentration of the conjugated anion formed by the dissociation of acid. After attaining a constant pH, the suspended solution was titrated with 0.1 M aqueous ammonia under a nitrogen atmosphere until the pH of the solution reached the original value prior to introducing ammonia. The structure of the intercalated products with water was measured by X-ray diffraction (Rigaku Rad-B) with a Ni-filtered Cu $K\alpha$ radiation. The thermal behavior of water in HLa was measured by TG-DTA (Rigaku) with an increasing rate of 10 °C per minute.

Results and Discussion

The amount of water in HLa varies depending on the condition of preservation. Consequently, the large amount of water removed until around 100 °C (Fig. 1) varied from sample to sample. In any case, the removed water is weakly adsorbed one on the outer and/or the inner surface of the HLa. At above 100 °C the gradual weight decrease continued until around 350 °C; then, a slight large weight loss could also be detected in the

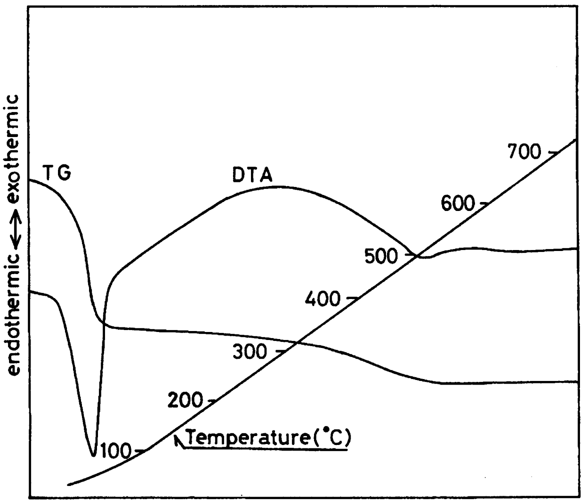

Fig. 1. Results of a DTA-TG analysis.

Table 1. Results of the Isoelectric Point Method, Acidity of the HLa and Surface Area

Treatment temperature °C	pH	K_a	Acidity[a)] mmol g^{-1}	Absorbed amount of NH_3 mmol g^{-1}	Ratio of H^+ [b)] %	Surface area m^2 g^{-1}
100	3.99	4.57×10^{-7}	1.70	2.26	44.7	18.4
200	4.23	1.51×10^{-7}	1.47	1.49	25.8	18.6
300	4.28	1.20×10^{-7}	1.11	1.13×10^{-1}	23.0	19.8
400	5.46	5.25×10^{-10}	1.10	7.43×10^{-2}	15.2	20.3
500	6.00	4.37×10^{-11}	0.0343	ca. 0	4.4	20.6

a) Acidity was estimated from the amount of NH_4OH titrated. b) Ratio=(the dissociated amount of H^+ in unit gram of the HLa)/(the amount of H in unit gram of the HLa).

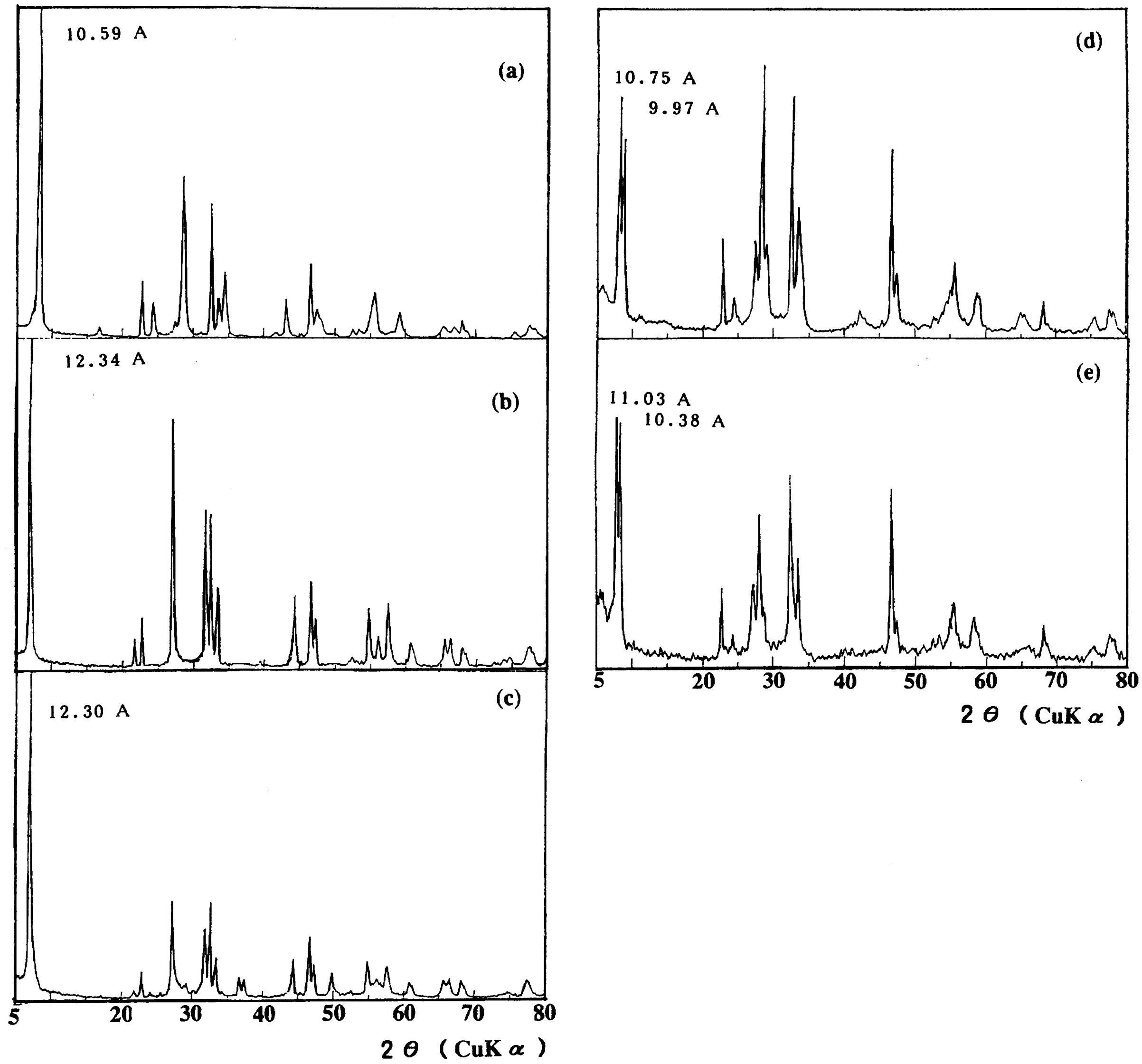

Fig. 2. XRD patten of the $HLaNb_2O_7$ (HLa), (a) after the heat-treatment at 100 °C; (b) hydrated HLa; (c) after dipping of the HLa treated at 300 °C in water for 3 d; (d) after a heat-treatment at 500 °C; (e) after dipping of (d) in water for ca. 3 d. The numericals in the figures denote the value of the basal spacing.

350—400 °C range. The desorbed materials were confirmed to be water using a mass filter. Thus, the water in the interlayer was removed in three stages. As a typical example, the amounts of water removed until 100 °C, in the temperature range of 100—400 °C, and over 400 °C by TG measurements, were 11.4, 0.15, and 0.6 mol per unit mol of the HLa, respectively. The ratio of the weight loss during the latter two stages was almost independent on the state of the sample preserved.

The results of the isoelectric point method and the acidity of the HLa treated at various temperatures are summarized in Table 1. The HLa treated at 100 °C exhibited the lowest pH value, i.e., the maximum acidity. The amount of H^+ obtained from the value of the pH was much less than that of H^+ in the HLa which could be calculated to be 2.28×10^{-3} $\mathrm{mol\,g^{-1}}$, and further the titrated amount of aqueous ammonia. This may be caused by the intercalation of ammonia in the interlayer.[1,4] With an increase of the temperature until around 350 °C, the pH value, gradually, and in the 350—400 °C region greatly decreased. This indicates that the water in the interlayer removed in the 350—400 °C range is strongly related with the acidic property. The layer compound, $LaNb_2O_7$ in the HLa, has a negative charge of one, i.e., A^-; its concentration can be assumed to be equal to that of $LaNb_2O_7$. Based on the assumption the amount of A^- ion in 1 g of the HLa is 2.28×10^{-2} $\mathrm{mol\,dm^{-3}}$. From Eq. 1, using the value of the dissociation constant, K_a could be calculated, as presented in Table 1. The values of K_a are 10^3—10^7 times higher than the dissociation constant of pure water. The values of K_a of the sample treated at the temperature until 300 °C happened to approximately agree with those obtained by the NMR method.[2] In any case, a large extent of the dissociation of H in the laminar compound (HLa) by the action of water inserted in the interlayer could be detected by a simple method, as in this study. The values of K_a are also in agreement with those given in the literature.[2]

The intercalation of water was carried out: HLa treated at a higher temperature of 100 °C interval from 100 °C in air was dipped into water for ca. 3 d and then submitted to XRD measurements. The typical XRD patterns are shown in Fig. 2. By a heat-treatment until 300 °C the basal spacing shrank from ca. 12.3 to 10.5 Å by removing the water in the interlayer. By treating with water the HLa was recovered to the original hydrated HLa (see Fig. 2(c)). However, at 400 °C the partial recovery of the basal spacing could be observed, i.e. both hydrated and dehydrated HLa was detected. At a higher temperature than 500 °C two peaks in the low-diffraction-angle region (see Fig. 2(d)) was observed, but could not be recovered to the original HLa by the reaction with water (see Fig. 2(e)), though a small extent of enlargement of the basal spacing was observed. From the results shown in Fig. 2, although the recovery to the original state at the heat-treatment until 300°C could be detected, the acidity was not recovered, as can be seen from Table 1. This indicates that the variation of the small amount of the water in the interlayer sensitively affects the acidity.

The adsorbed amount of NH_3 at 100 °C was greater than the titrated amount of aqueous ammonia. This could be caused by the dissociation of NH_3 into the water in the interlayer, since the HLa still has water, even after a treatment at 100 °C. With an increase in the treatment-temperature the adsorbed amount of NH_3 decreases to less than the titrated one of aqueous ammonia. This may be due to both the different measurement temperature and the different amount of water in the interlayer, though the cause of the latter may be pronounced.

The ratio of the amount of H^+ dissociated in the aqueous solution to that of H^+ in the HLa varies from 44.7% at a treatment of 100 °C to 4.4 at 500 °C, as presented in Table 1. It can therefore be concluded that nearly half of the H in HLa dissociates into H^+ in the presence of a relatively large amount of the reversible water; with a decrease in the amount of water in the interlayer the acidity of HLa also decreases.

The surface areas of HLa treated at various temperatures are illustrated in Table 1. With an increase in the temperature the surface area slightly decreased, perhaps due to removal of the water in the interlayer.

The two peaks appearing in the low diffraction angle shown in Fig. 2(d) and (e) may be due to a transformation to another crystal state of HLa. Although the cause is still obscure, the details will be examined elsewhere.

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