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Formation of a Methoxy-Modified Interlayer Surface via the Reaction between Methanol and Layered Perovskite $HLaNb_2O_7 \cdot xH_2O$

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The reactions between methanol (CH_3OH, CH_3OD, CD_3OD, $^{13}CH_3OH$) and layered $HLaNb_2O_7 \cdot xH_2O$ were investigated. X-ray powder diffraction (XRD) analysis showed that a peak corresponding to the basal spacing of $HLaNb_2O_7 \cdot xH_2O$ (1.05 nm) disappeared and a new peak appeared at 1.18 nm. Carbon-13 NMR spectra revealed the presence of two environments of the methyl group; the broad 67 ppm signal is ascribed to the rigid species located in the interlayer space, and the 50 ppm signal is ascribed to mobile methanol on the external surface. The amount of the latter species was negligibly small. Deuterium NMR spectra revealed the presence of a Pake doublet with an effective quadrupole coupling constant (QCC) of 47 kHz and an asymmetry factor (η) of zero, indicating that the CD_3O group was rigidly bound to the interlayer surface. In addition, when both CD_3OD and CH_3OD were used, no signal corresponding to the OD group was observed. Hence, although XRD results can be interpreted as intercalation of methanol, the ^2H NMR results indicate that methanol was dissociatively adsorbed to the interlayer surface. The observed very high thermal stability of the methyl group is consistent with methoxy formation. The structure of the product is discussed on the basis of the results with larger *n*-alcohols.

Introduction

A series of layered perovskite-related niobates, titanates, and titanoniobates has recently been prepared.[1] Their structures are very closely related to the Ruddlesden−Popper phase,[2] and their general formulas are presented as $M[A_{n-1}B_nO_{3n+1}]$, where M is the interlayer cation, A is the cation surrounded by 12 oxygen atoms, B is Ti and/or Nb hexacoordinated by oxygen atoms, and *n* describes the thickness of the perovskite slab. These compounds can be regarded as two-dimensional perovskite structures, and their properties can be controlled by changing the thickness of the perovskite slab; hence, they are interesting hosts for intercalation chemistry. Actually, they undergo intercalative ion-exchange reactions, and their protonated derivatives further form intercalation compounds via Brønsted acid−base reactions.[1] Moreover, pillaring of interlayer space has been reported.[3]

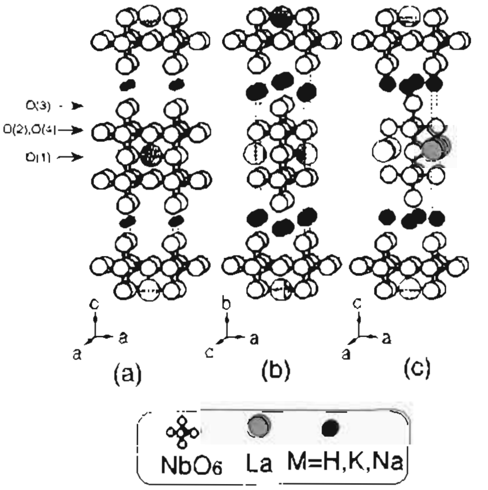

Figure 1. Structures of (a) $HLaNb_2O_7$, (b) $KLaNb_2O_7$, and (c) $NaLaNb_2O_7$.

$HLaNb_2O_7$, obtained by the acid treatment of $KLaNb_2O_7$, possesses a double perovskite slab (Figure 1) and contains water in the interlayer space at ambient temperature. The advantage of this compound is that its structure has been characterized precisely,[4] but studies on the intercalation chemistry of $HLaNb_2O_7$ have been limited. The interlayer proton was exchangeable with Na^+, Ag^+, and Cu^{2+},[5] and also, as described above, organic bases (*n*-octylamine, pyridine, and ammonia) were intercalated via acid−base reactions.[6] Recently, the intercalation of alcohols has been reported, and the X-ray powder diffraction (XRD) results were interpreted as the bilayer formation of alcohols in the interlayer space.[7] The possible intercalation of alcohols was also suggested by Domen et al.[8] for interpreting the effect of

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alcohols as sacrificial agents on photochemical activities of layered perovskite-related niobates. To our knowledge, however, no studies have so far been reported on the nature of the guest species.

The present study provides a detailed characterization of the reaction products between methanol and $HLaNb_2O_7{\cdot}xH_2O$. In addition to standard analytical techniques in intercalation chemistry, we have used ^2H NMR spectroscopy, which has been applied to layered material-alcohol systems for the first time, and have identified the guest species as the methoxy group. The present results expand the intercalation chemistry of layered perovskite-related oxides, as well as the approach to the surface modification of layered materials.

Experimental Section

Preparation of $HLaNb_2O_7$. $KLaNb_2O_7$ was prepared from K_2CO_3, La_2O_3, and Nb_2O_5 by heating at 1100 °C for 72 h according to the literature.[6] La_2O_3 was dehydrated by heating at 1100 °C for 1 h before use. A 10% excess of K_2CO_3 was added for possible loss due to volatilization. XRD analysis of the product showed the formation of essentially single-phase $KLaNb_2O_7$ with very weak peaks due to $LaNbO_4$.

$HLaNb_2O_7$, an anhydrous protonated derivative of $KLaNb_2O_7$, was prepared by treatment with 6.5 M HNO_3 for 24 h at ambient temperature and subsequent overnight drying at 40 °C. XRD analysis revealed that the product was indexed for tetragonal symmetry with $a = 0.389$ nm and $c = 1.047$ nm, these results being similar to those of previous work.[6] ICP analysis showed that 94% of potassium ions were removed by the acid treatment. A hydrated phase ($HLaNb_2O_7{\cdot}xH_2O$) was prepared by stirring $HLaNb_2O_7$ in an absolute amount of water. Water content determined by thermogravimetry (TG) was 2–2.5 mol/$HLaNb_2O_7$, which was similar to the value (3.4) reported previously.[6]

Intercalation of Alcohols. For the reaction with methanol (CH_3OH), 0.3 g of $HLaNb_2O_7{\cdot}xH_2O$ was stirred in 40 mL of methanol containing ~10 mass % of water[7] at ambient temperature for 1 d. $HLaNb_2O_7{\cdot}xH_2O$ was allowed to react with ethanol similarly at the longer reaction time of 7 d. When the other *n*-alcohols possessing longer alkyl chains ($C_nH_{2n+1}OH$; $n = 3-6, 8, 10, 12$) were used, a mixture of $HLaNb_2O_7{\cdot}xH_2O$ and a given alcohol (containing ~10 mass % of water) was allowed to react at 80 °C for 7 d in a sealed glass ampule. The products were centrifuged and air-dried.

Moreover, the reactions between methanol (CD_3OD, Aldrich, 99.8 atom % D; CH_3OD, Aldrich, 99.8 atom % D) and $HLaNb_2O_7{\cdot}xH_2O$ were carried out similarly under a dry protective nitrogen atmosphere using the standard Schlenk technique.[9] About 10 mass % of water was added as H_2O. Furthermore, ^{13}C-enriched CH_3OH (Aldrich, 99 atom % ^{13}C) was allowed to react with $HLaNb_2O_7{\cdot}xH_2O$ similarly in an ambient atmosphere.

Analyses. XRD patterns were obtained by a Mac Science MXP^3 diffractometer with monochromated Cu Kα radiation. Differential thermal analysis (DTA) curves were recorded using a Shimadzu DT-20 instrument with a heating rate of 10 °C/min. TG analysis was performed using a Shimadzu TG-40 thermobalance. IR absorption spectra were obtained with a Perkin-Elmer FTIR-1640 instrument using the KBr disk technique.

Deuterium NMR spectra were recorded with a Bruker MSL400 spectrometer at 61.42 MHz by the quadrupole echo technique using a $(\pi/2)_x-\tau_1-(\pi/2)_y-\tau_2$ pulse sequence ($\pi/2$ pulse width, 3.5 μs; τ_1, 15 μs; τ_2, 17.6 μs) at ambient temperature. Chemical shifts were reported with respect to external D_2O. Deuterium contents were determined on the basis of signal intensities by using the external standard of perdeuterated poly(methylmethacrylate). Line shape analysis was performed by simulating spectra.[10] Hydrogen contents were estimated from ^1H NMR measurements with the same equipment at 400.14 MHz using adamantane as an external standard.[10]

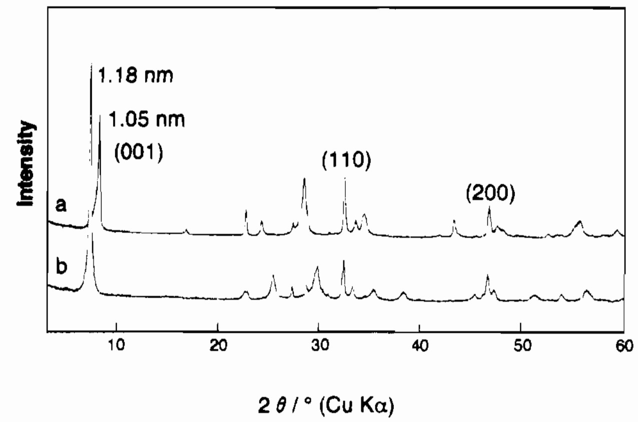

Figure 2. XRD patterns of (a) $HLaNb_2O_7{\cdot}xH_2O$ and (b) the reaction product with CH_3OH.

Carbon-13 magic angle spinning (MAS) NMR spectra were obtained at 100.54 MHz using a JEOL NM-GSX400 spectrometer with and without the cross polarization technique (CP) (spinning rate, ~5 kHz; 64 scans). For a single-pulse dipolar decoupling (DD)/MAS spectrum, a $\pi/2$ pulse (pulse width, 4.5 μs) and a repetition time of 10 s were used. A CP/MAS spectrum was obtained using the contact time of 2 ms and the repetition time of 5 s. Chemical shifts were reported with respect to external tetramethylsilane (TMS).

Results

Reaction Product with Methanol. Figure 2 shows the XRD patterns of $HLaNb_2O_7{\cdot}xH_2O$ and its reaction product with CH_3OH. In the reaction, the basal plane peak ((001) diffraction peak) at 1.05 nm disappears and a new low-angle peak appears at 1.18 nm, which is a result consistent with that of previous work.[7] It should be noted that peaks due to the perovskite-type slab ((100), (110), and (200) peaks) do not shift after the reactions. The reactions with deuterated and ^{13}C-enriched methanol led to essentially similar XRD results, but we observed shoulders at higher angles for the reaction products with deuterated methanol.

IR spectroscopy was also applied to characterize the guest species. In the spectrum of the reaction product between $HLaNb_2O_7{\cdot}xH_2O$ and CH_3OH, absorption bands due to the methyl group[11] were observed (2927 cm^{-1}, $\nu_{as(CH_3)}$; 2823 cm^{-1}, $\nu_{s(CH_3)}$; 1440 cm^{-1}, $\delta_{(CH_3)}$). In addition, a very intense absorption band was observed at 1130 cm^{-1}. This band could not be assigned to the $\nu_{(CO)}$ mode of methanol, since gaseous methanol shows a $\nu_{(CO)}$ band at 1033.5 cm^{-1}.[11] We attempted to assign this band by using deuterated and ^{13}C-enriched methanol, but we cannot interpret the behavior of the band on the basis of a reasonable assignment, possibly due to vibrational coupling with other modes.

The DTA curves of $HLaNb_2O_7{\cdot}xH_2O$ and its reaction product with CH_3OH are demonstrated in Figure 3. In the DTA curve of the reaction product, two endothermic peaks, which are also present in the DTA curve of $HLaNb_2O_7{\cdot}xH_2O$, are observed. Thus these two endothermic peaks should be mainly due to dehydration and dehydroxylation, respectively.[12] In addition, an exothermic peak starting at 330 °C is present. Since this is not observed in the DTA curve of $HLaNb_2O_7{\cdot}xH_2O$, it should be ascribed to oxidative decomposition of the methyl group. This is supported by the IR results, which show that the bands due to the methyl group are clearly present in the spectrum of

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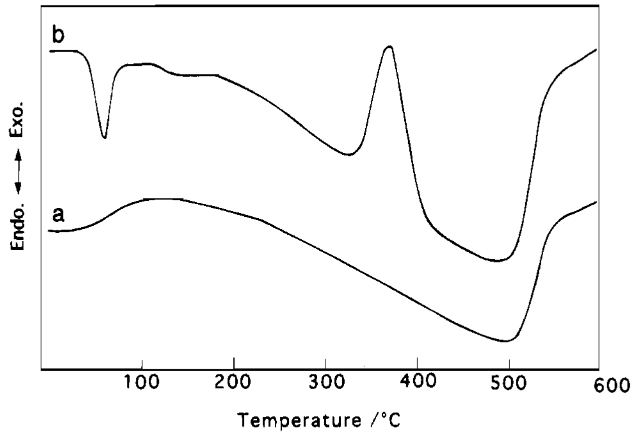

Figure 3. DTA curves of (a) $HLaNb_2O_7 \cdot xH_2O$ and (b) the reaction product with CH_3OH.

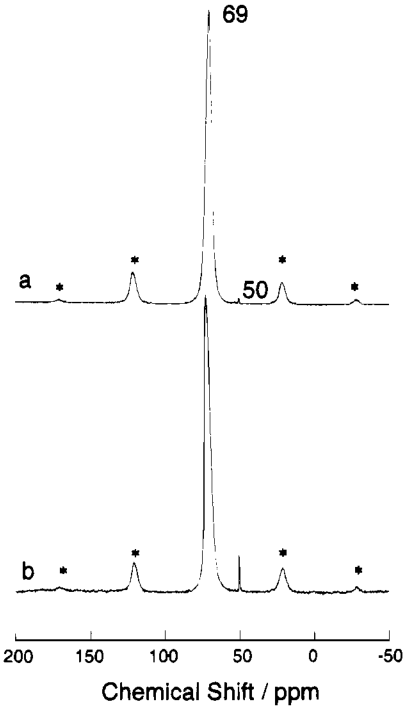

Figure 4. ^{13}C NMR spectra of the reaction product between $HLaNb_2O_7 \cdot xH_2O$ and CH_3OH: (a) CP/MAS spectrum and (b) DD/MAS spectrum.

the sample heated even at 320 °C. The DTA curve in the present study is similar to that reported for the reaction product between $HLaNb_2O_7 \cdot xH_2O$ and *n*-butanol.[7]

Carbon-13 CP/MAS and DD/MAS NMR spectra of the reaction product between $HLaNb_2O_7 \cdot xH_2O$ and ^{13}C-enriched CH_3OH are shown in Figure 4. In both spectra, a broad intense signal is observed at 69 ppm and also a narrow weak one at 50 ppm. It should be noted that the intensity of the narrow 50-ppm signal is relatively larger in the DD/MAS spectrum.

Figure 5 demonstrates ^2H NMR spectra of the reaction products between $HLaNb_2O_7 \cdot xH_2O$ and CD_3OD and between $HLaNb_2O_7 \cdot xH_2O$ and CH_3OD. In the spectrum of the reaction product between $HLaNb_2O_7 \cdot xH_2O$ and CD_3OD (Figure 5 a), a Pake doublet pattern is observed, where the interval between the two intense peaks is about 33 kHz. From simulation, an effective quadrupole coupling constant (QCC) of 47 kHz and an asymmetry factor (η) of zero are determined. The QCC value is typical of rigidly-bound CD_3 groups reorienting rapidly only about their 3-fold symmetry (C_3) axis,[13] indicating that the C−O axis of OCD_3 is fixed. In addition to the Pake doublet, a zero-frequency singlet is observed. A similar singlet is also present in the spectrum of $HLaNb_2O_7 \cdot xH_2O$ and CH_3OD (Figure 5 b), and the intensity of the singlet for the product between $HLaNb_2O_7 \cdot xH_2O$ and CD_3OD is estimated to be comparable with that for the product between $HLaNb_2O_7 \cdot xH_2O$ and CH_3OD.

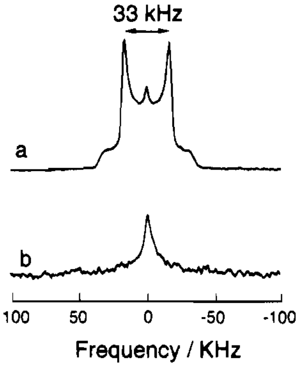

Figure 5. ^2H NMR spectra of the reaction products (a) between $HLaNb_2O_7 \cdot xH_2O$ and CD_3OD and (b) between $HLaNb_2O_7 \cdot xH_2O$ and CH_3OD.

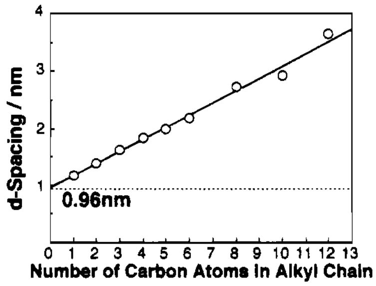

Figure 6. Variation in the *d*-values of the low-angle peak of the reaction products between $HLaNb_2O_7 \cdot xH_2O$ and *n*-alcohols with the number of carbon atoms in alkyl chain.

The amount of the methyl group in the product between $HLaNb_2O_7 \cdot xH_2O$ and CH_3OH was estimated from the carbon content determined by conventional CHN analysis (C, 1.06 mass %); 0.45 mol of the methyl group was present per $HLaNb_2O_7$ unit. A TG curve of the product showed the mass loss of 5.2% up to 900 °C.

Reaction Products with Other *n*-Alcohols. Reactions with alcohols possessing *n*-alkyl chains were also performed. All the *n*-alcohols reacted with $HLaNb_2O_7 \cdot xH_2O$. Figure 6 summarizes the variation in the d-values of the low-angle peaks with *n* in $C_nH_{2n+1}OH$. Although a previous report[7] described that only $C_nH_{2n+1}OH$ with $n \le 5$ reacted with $HLaNb_2O_7 \cdot xH_2O$, we observe successful reactions even for $6 \le n \le 12$ in the present study, possibly because of the different preparation procedure. In analogy with the reaction with methanol, XRD showed that (100), (110), and (200) peaks did not shift after the reactions.

The DTA results on these products were similar to those of the product with methanol. All of the products showed exothermic peaks at >300 °C. Also, two endothermic peaks were present, but the first one (at ~100 °C, due to dehydration) was much smaller, when $n \ge 3$.

Discussion

Guest Species in the Interlayer Space of the Reaction Products between $HLaNb_2O_7 \cdot xH_2O$ and Methanol. The possible states of methanol are (1) a mobile molecule with weak

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interaction, (2) an intercalated molecule with restricted motion, and (3) methoxy species formed by dissociative adsorption of methanol. XRD shows both the appearance of the low-angle peak at 1.18 nm and the retention of the layer structure, and spectroscopic results reveal the presence of the methyl group. Although these observations are consistent with the intercalation of methanol molecules, the NMR results, discussed in detail below, have led us to conclude that the methoxy species form in the interlayer space.

Carbon-13 NMR reveals the presence of two signals. The smaller one has a much narrower line shape, and its chemical shift (50 ppm) is close to that of liquid methanol (49.3 ppm)[14 a] and mobile adsorbed methanol,[14] suggesting that this signal is due to mobile methanol on the external surface of the product. The broad 69 ppm signal, which represents a large shift from the region described above, shows spinning side bands, indicative of chemical shift anisotropy of the nuclear site due to restricted motion. A relatively higher CP efficiency of the 69 ppm signal further indicates that the motion of the species for the 69 ppm signal is more restricted than that of the 50 ppm species.[15]

Deuterium NMR reveals further information on the guest species. The line shape analysis of the Pake doublet indicates that the motion of the CD_3 group is restricted only about the C−O axis. The observed QCC (47 kHz) and η (0) indicate that narrowing due to other motions such as wobbling and fluctuation of the C−O axis is negligible, indicating that the oxygen of the CD_3O group is immobilized very rigidly. Such stability has been reported for the dynamics of other guest species (molecules and a complex) in intercalation compounds, where the guest species bound in the interlayer space of hosts rigidly.[16] On the contrary, the Pake doublets of loosely-bound deuterated methanol (for example in zeolite cages) collapsed to give structureless singlets at ambient temperature.[13]

The intensities of the singlets at ~0 kHz are comparable between parts a and b of Figures 5, indicating that the contribution of the CD_3 group with isotropic motion is small; most of the CD_3 groups are at the rigid sites. The signal of the CD_3 group in mobile methanol, which shows the ^{13}C signal at 50 ppm, should be included in the singlet, but its amount should be small. The singlet is, therefore, mainly ascribed to mobile D_2O and HDO formed by H−D exchange.

If the guest species is present as molecular methanol, the dynamics of the OD group in CD_3OD (and also the OD group in CH_3OD) should also be restricted because of the rigidity of the CD_3O group; another doublet with a much larger splitting (~200 kHz) should be expected. In Figure 5, however, no signals corresponding to this splitting are observed. Although we should consider the H−D exchange of the OD group, the amount of the exchangeable proton (added as H_2O and present in the host) is less than half of the exchangeable deuterium in the OD group in the system, suggesting that, if methanol is intercalated without its dissociation, a considerable amount of the OD group should be present in the system under the present experimental conditions. Furthermore, quantitative analysis of hydrogen and deuterium in the reaction product between $HLaNb_2O_7{\cdot}xH_2O$ and CH_3OD reveals that the H:D ratio is estimated to be 1:0.04, indicating that most of the OD groups are lost during the drying. Hence, we have interpreted these observations as methanol being dissociatively adsorbed on the interlayer surface to form the methoxy species according to the following reaction:

$$O_5NbOH + MeOH \rightarrow O_5NbOMe + H_2O$$

The thermal stabilities reported for various methanol-intercalated layered compounds strongly support methoxy formation in the present system. When methanol was intercalated in the interlayer space of halloysite,[17] hydrated kaolinite,[18] zirconium phosphate,[19] molybdenyl hydrogen phosphate,[20] vanadyl phosphate,[21] vanadyl sulfate,[21] and vanadyl organophosphonates,[22] methanol was deintercalated below 70 °C or even at ambient temperature. Even when methanol interacted with the interlayer cations of montmorillonite, the temperature for maximum desorption of methanol was ~110 °C.[23] On the contrary, when the methoxy species, bound to the layer directly, formed in the interlayer space, thermal stability drastically increased; methoxy groups were lost at ~225 and ~300 °C for the methanol-reacted products of molybdenum trioxide dihydrate[24] and vanadium pentoxide hydrate,[25] respectively. These reports are consistent with the temperature-programmed desorption spectroscopy studies, which showed that adsorbed methanol on the oxides desorbed at a lower temperature than the methoxy species.[26] Thus, the very high thermal stability observed in the present study (>300 °C) is consistent with methoxy formation.

Structure of the Reaction Products between $HLaNb_2O_7{\cdot}xH_2O$ and Methanol. XRD shows the retention of the perovskite slab structure (corresponding to the ordering of oxygen and metal cations) and the expansion of the interlayer distance due to the presence of the methoxy group in the interlayer space. Although methoxy groups should be stabilized by coordinating to metals, both lanthanum and niobium are fully surrounded by oxygen. Thus, we propose a structural model where apical oxygen facing the interlayer space (oxygen (3) in Figure 1) is replaced with the methoxy group. Since charge balance requires the loss of additional positive charge, one interlayer proton appears to be released if one methoxy group is introduced. Taking into account the fact that approximately one methoxy group is present per two $HLaNb_2O_7$ units, a schematic model of the interlayer space is proposed in Figure 7. Half of oxygen (3) is replaced with the methoxy group to form an organically-modified interlayer surface. It should be noted that the proposed structure is consistent with the retention of the ordering of oxygen and metal cations (La and Nb).

Since the relationship between the number of carbon atoms and the *d*-values of the low-angle peaks is linear (Figure 6) and DTA shows exothermic peaks for all the products at >300 °C,

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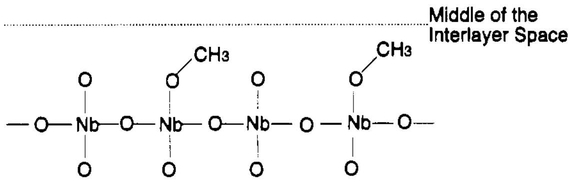

Figure 7. Proposed schematic model of the methoxy-modified interlayer surface of the reaction product between $HLaNb_2O_7 \cdot xH_2O$ and methanol.

all the reaction products with *n*-alcohols should possess alkoxy groups with similar structures. Since the slope in Figure 6 (0.214 nm/carbon atom) is much larger than a maximum increase of all-*trans* monolayers of alkyl chains (0.127 nm/carbon atom), the behavior corresponds to bilayer-formation of all-*trans* alkyl chains with a tilt angle of about 57°. The extrapolation of the straight line to $n = 0$ gives the intercept of 0.96 nm, which, if no structural change occurred, should correspond to the host compound. Thus, the fact that 0.96 nm is smaller than the basal spacing of anhydrous $HLaNb_2O_7$ (1.05 nm) strongly suggests that the stacking of the host layer changes upon reaction with *n*-alcohols. It was reported that the stacking of the $[LaNb_2O_7]^-$ layer depends on the interlayer cations (Figure 1).[4] In anhydrous protonated form, $HLaNb_2O_7$, the apical oxygen faces the corresponding apical oxygen in the adjacent $[LaNb_2O_7]^-$ layer via an interlayer proton. When the proton is replaced with a potassium ion to form $KLaNb_2O_7$, the adjacent $[LaNb_2O_7]^-$ layer stacks with a relative displacement by translating $^1/_2$ unit along one *a*-axis only. On the contrary, in the sodium-form of $NaLaNb_2O_7$, the adjacent layer displaces by translating $^1/_2$ unit along two diagonal *a*-axes in a tetragonal cell. Hence, we assume that the contraction is ascribed to a similar displacement, which makes the void space of the perovskite slab available for accommodation of alkoxide groups.

The observed mass loss of the reaction products between $HLaNb_2O_7 \cdot xH_2O$ and methanol (5.2 mass %) is much higher than the amount of the methyl group calculated from carbon content (1.3 mass % as CH_3). In addition, the endothermic peak due to dehydration is clearly observed on the DTA curve at ~100 °C (Figure 3b). Thus, water should be present in the product. Since the amount of water estimated from TG and carbon content is comparable with that of the methoxy group, we assume that water should also be present in the interlayer space. The amount of the methoxy group suggests that about half of the protons are still present for charge compensation. Thus, we speculate that water molecules are mainly present as hydronium ions (H_3O^+) in the interlayer space. When larger alcohols are used, the amount of water adsorbed in the products decreased because of the hydrophobic nature of the interlayer surface.

Conclusions

We have demonstrated that a methoxy group formed in the interlayer space of $HLaNb_2O_7 \cdot xH_2O$ by reaction with methanol. As well as the external surface of oxide particles, the interlayer surface of layered materials can be modified, and it should be noted that the structure of the perovskite slab is retained. Thus, the properties of the products (for example catalytic and electrical ones) are of interest. Furthermore, the present results indicate that the molecular design of interlayer space is possible under mild conditions.

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