

Reactions of Alkoxy Derivatives of a Layered Perovskite with Alcohols: Substitution Reactions on the Interlayer Surface of a Layered Perovskite

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Organic derivatives of a layered perovskite compound, $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLN), with interlayer surfaces possessing n -alkoxy groups (n -decoyl and n -propoxyl) have been allowed to react with various alcohols and a diol (ethylene glycol) to form new organic derivatives via substitution reactions. The reaction of an n -propoxyl derivative of HLN with n -decanol leads to the formation of n -decoyl groups bound to the interlayer surface of the perovskite-like $[\text{LaNb}_2\text{O}_7]$ slab. In a similar fashion, the reaction of an n -decoyl derivative of HLN with 2-propanol results in the formation of an isopropoxyl derivative. The reaction of the n -decoyl derivative of HLN with *tert*-butyl alcohol also proceeds, though the reaction is not completed even after 14 days. After the reaction of the n -decoyl derivative of HLN with ethylene glycol, only one of the two hydroxyl groups in ethylene glycol is reacted, and $-\text{OCH}_2\text{CH}_2\text{OH}$ groups are present on the interlayer surface. Water is required for proceeding the substitution reaction between the n -propoxyl derivative of HLN and n -decanol, and the reaction mechanism involving hydrolysis of the alkoxy groups on the interlayer surface and subsequent esterification is proposed.

Introduction

Inorganic–organic hybrids have attracted increasing attention as a new class of materials. Various inorganic layered compounds can accommodate organic ions and molecules in the interlayer space to form intercalation compounds, where inorganic sheets and layers of the organic molecules or ions are interstratified at a molecular level.^{1–4} Intercalation compounds are generally prepared via ion-exchange reactions and/or adsorption based on interactions with interlayer cations or surfaces. In addition, grafting reactions (alternatively called substitution reactions) of some layered compounds can be utilized to form two-dimensional inorganic–organic hybrids, where organic groups are covalently bound to the surfaces of inorganic sheets. For example, layered polysilicates (such as magadiite and kenyaite) can be modified via the reaction of their interlayer surfaces, where silanol (SiOH) groups are located, with silylation agents (such as chlorosilanes and alkoxy silanes)^{5,6} and alcohols.⁷ Similar reactions involving AlOH groups were

reported for kaolinite recently.^{8,9} FeOCl can also react with various compounds including amines and alcohols.^{2,10} Another typical example is zirconium phosphate, which reacts with phosphoric ester groups.^{11,12}

Ion-exchangeable layered perovskites ($M_m[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$; $M = \text{Rb}, \text{K}, \text{etc.}$, $\text{A} = \text{Sr}, \text{Ca}, \text{La}, \text{etc.}$, $\text{B} = \text{Ti}, \text{Nb}, \text{Ta}$, $m = 1$ or 2) consist of perovskite-like slabs (n : thickness of the perovskite-like slab) and interlayer cations, and various cations including proton, alkali-earth metal ions, and divalent cations are successfully intercalated.^{13,14} Some of their protonated forms accommodate alkylamines, and intercalated alkylamines form alkylammonium ions in the interlayer space via acid–base reactions.^{15–23} It is also possible to replace protons

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with organic cations via ion-exchange reactions.^{24,25} We have demonstrated that the reaction of a protonated form of a Dion–Jacobson phase (ion-exchangeable layered perovskite with $m = 1$, $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$) with n -alcohols did not result in simple intercalation,²⁶ but led to the formation of n -alkoxy derivatives, whose interlayer surfaces were covered with alkoxy groups.²⁷

Metal alkoxide chemistry has been investigated for decades since metal alkoxides are attractive precursors for metal oxides via a sol–gel process.²⁸ Among their reactions, those with alcohols have been studied extensively since such reactions are utilizable for preparing metal alkoxides possessing various alkoxy groups.²⁹



These reactions are called alcohol-exchange (or alcohol-interchange) reactions or alcoholysis reactions, and niobium alkoxides were reported to undergo these reactions.^{30–33}

Here, we report substitution reactions of alkoxy derivatives of the protonated form of the Dion–Jacobson-type layered niobate ($\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$; HLN) with alcohols (n -decanol, 2-propanol, and *tert*-butyl alcohol) and ethylene glycol. The overall reaction resembles the alcohol-exchange reactions of the metal alkoxides. Reaction products were analyzed by X-ray diffraction (XRD), solid-state nuclear magnetic resonance (NMR) spectroscopy, differential thermal analysis (DTA), and compositional analyses. The reaction mechanism is discussed by focusing on the role of water in the reaction process.

Experimental Section

Preparation of $\text{RbLaNb}_2\text{O}_7$. $\text{RbLaNb}_2\text{O}_7$ was prepared from a mixture of Rb_2CO_3 , La_2O_3 , and Nb_2O_5 by calcining at 1100 °C for 48 h with intermediate grinding after 24 h.¹⁷ La_2O_3 was calcined at 1100 °C for 1 h for dehydration before use. Excess Rb_2CO_3 (30% as Rb) was added to compensate for the loss of Rb during calcination. The crude product was washed with distilled water and dried at 120 °C. All the XRD reflections of the washed product can be assigned to $\text{RbLaNb}_2\text{O}_7$. Inductively coupled plasma emission spectrometry (ICP) showed that the cation ratio of the washed product corresponded to $\text{RbLaNb}_2\text{O}_7$. All of these analytical results indicated the successful formation of $\text{RbLaNb}_2\text{O}_7$.

Preparation of $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLN). A protonated form ($\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$; HLN) was prepared by the treatment of $\text{RbLaNb}_2\text{O}_7$ with 6 M HNO_3 at 60 °C for 72 h. The product was centrifuged and washed with distilled water. The product was then dried at ambient temperature, and further drying at 120 °C led to the formation of a single-phase anhydrous phase (HLaNb_2O_7). The XRD pattern of the product dried at 120 °C showed a tetragonal structure with $a = 0.3891(4)$ nm and $c = 1.0578(6)$ nm, consistent with the previous work ($a = 0.38886(4)$ nm and $c = 1.05483(12)$ nm).³⁴ ICP analysis revealed that 100% of Rb was leached during the acid treatment.

Modification of HLN with n -Propanol. HLN was modified with n -propanol based on the previous report.²⁷ Typically, 2 g of HLN, 35 mL of n -propanol, and 5 mL of distilled water were allowed to react in a sealed glass ampule at 80 °C for 3 days. The resultant product was centrifuged and air-dried to obtain a white powder. XRD analysis revealed the increase in the interlayer distance to 1.53 nm. The solid-state ¹³C CP/MAS NMR revealed the presence of three carbon environments (12, 26, and 80 ppm) assignable to n -propyl groups. A DTA curve of the product exhibited exothermic peaks at >300 °C. All of these analytical results indicated the formation of an n -propoxy derivative of HLN (n -propoxy-HLN).

Reaction of n -Propoxy-HLN with n -Decanol. Typically, 2 g of n -propoxy-HLN was reacted with 40 mL of n -decanol in a sealed glass ampule at 80 °C for 7 days. After centrifugation, the crude product was washed with acetone and dried at ambient temperature to obtain a white powder. To investigate the effect of water, the reaction was also conducted with a small amount of water; about 0.2 g of n -propoxy-HLN was reacted with 39 mL of n -decanol and 1 mL of distilled water [corresponding to 3 mass % of the total liquid (n -decanol and water)] in a sealed glass ampule at 80 °C for 1 or 7 days. The same reaction was also conducted under dry conditions; n -propoxy-HLN (0.2 g) previously dried under reduced pressure and n -decanol (40 mL) distilled over CaH_2 under a nitrogen atmosphere were utilized, and they were sealed in a glass ampule under a nitrogen atmosphere.

Reactions with Other Alcohols. Typically, 1.5 g of the reaction product between n -decanol and n -propoxy-HLN was reacted with 30 mL of 2-propanol, *tert*-butyl alcohol, or ethylene glycol (EG) in a sealed glass ampule at 80 °C for 7 days (2-propanol and EG) or 14 days (*tert*-butyl alcohol). After the centrifugation, the crude product was washed with acetone and dried at ambient temperature to obtain a white powder. The reaction product with EG was further dried at 200 °C. The reactions with 2-propanol were also conducted using HLN and the n -propoxy-HLN in a similar fashion.

Deintercalation Reactions of the Reaction Product between n -Decanol and n -Propoxy-HLN. About 0.1 g of the reaction product between n -decanol and n -propoxy-HLN was hydrolyzed with 2 mL of distilled water, 3 M HNO_3 , or 3 M KOH at ambient temperature for 24 h with stirring. The resultant hydrolyzed product was centrifuged and air-dried. To identify organic species formed via hydrolysis, the reaction product between n -decanol and n -propoxy-HLN was hydrolyzed with an excess of 3 M KOH (prepared using D_2O) for 24 h. Organic species were extracted from 3 M KOH using deuterated benzene (C_6D_6). Similarly, the reaction product between n -decanol and n -propoxy-HLN was dispersed in an excess of C_6D_6 overnight. The hydrolysis of the reaction product between EG and n -propoxy-HLN was performed with 3 M KOH (prepared using D_2O) in a similar fashion.

Deintercalation Reactions at High Temperature. The hydrolysis behavior at 80 °C was investigated as follows. About 0.2 g of n -propoxy-HLN or the reaction product between n -decanol and n -propoxy-HLN was reacted with 40 mL of distilled water in a sealed glass ampule at 80 °C for 4 days. After centrifugation, the crude product was washed with

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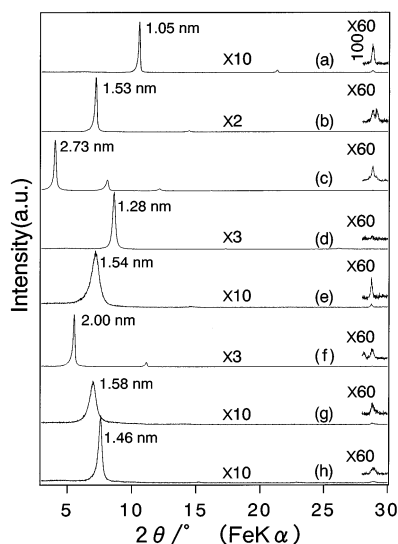


Figure 1. XRD patterns of (a) HLaNb_2O_7 (anhydrous HLN), (b) *n*-propoxyl derivative of HLN (*n*-propoxyl-HLN), (c) *n*-propoxyl-HLN after the treatment with *n*-decanol (*n*-decoxy-HLN), (d) *n*-decoxy-HLN hydrolyzed with 3 M KOH, (e) *n*-decoxy-HLN treated with 2-propanol, (f) *n*-decoxy-HLN treated with *tert*-butyl alcohol, (g) *n*-decoxy-HLN treated with ethylene glycol (EG), and (h) (g) heated at 200 °C.

acetone and dried at ambient temperature. The same reaction was also conducted by using a mixture of 39 mL of 2-pentanone and 1 mL of distilled water. The amounts of distilled water corresponded to 3 mass % of the total liquid (2-pentanone and water).

Analyses. XRD patterns of the products were obtained with a Mac Science $\text{M0}^3\text{XHF}^{22}$ diffractometer (Mn-filtered Fe $K\alpha$ radiation). Solid-state ^{13}C NMR spectra were recorded on a JEOL NM-GSX400 spectrometer with cross polarization and magic angle spinning techniques (CP/MAS) at 100.40 MHz. Contact time was 2 ms and pulse delay was 5 s. Chemical shifts were all reported with respect to external TMS. Liquid-state ^1H (270.17 MHz) and ^{13}C (61.94 MHz) NMR was performed with a JEOL NM-EX270 spectrometer. Chemical shifts were reported using internal 2,2'-dimethyl-2-silapentane-5-sulfonate (DSS) for aqueous solutions. DTA curves were obtained with MacScience TG-DTA2000S under a flow of air. The heating rate was 10 °C/min and $\alpha\text{-Al}_2\text{O}_3$ was utilized as a standard. The amounts of metals were determined by ICP using Nippon Jarrell Ash ICAP575 Mark II. The amounts of carbon were determined by an internal service at Waseda University Materials Characterization Center. The compounds released during the reactions were identified by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard H.P. 5971A instrument.

Results and Discussion

Reaction of *n*-Propoxyl-HLN with *n*-Decanol.

Figure 1 shows XRD patterns of *n*-propoxyl-HLN and its reaction product with *n*-decanol. The interlayer distance calculated from the low-angle XRD reflection increases from 1.53 to 2.73 nm after the reaction with *n*-decanol. In contrast, the XRD reflection at $2\theta = 28.8^\circ$, the (100) reflection of HLN, is present after the reaction with *n*-decanol, indicating the preservation of the structure of the perovskite-like slabs. Takahashi et al. prepared an *n*-decoxy derivative of HLN by the direct reaction between HLN and *n*-decanol and observed a similar interlayer distance.²⁷

The DTA curves of *n*-propoxyl-HLN and its reaction product with *n*-decanol are demonstrated in Figure 2. The DTA curve of *n*-propoxyl-HLN exhibits two exo-

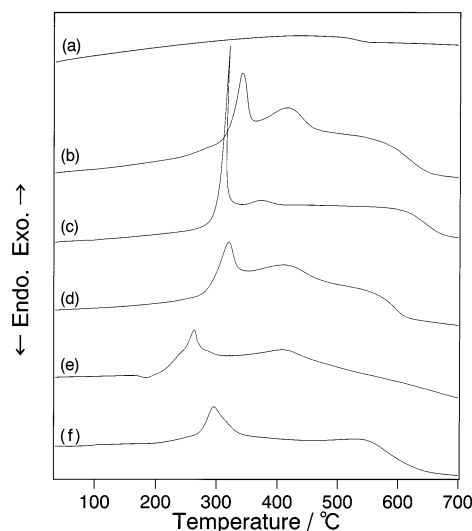


Figure 2. DTA curves of (a) HLaNb_2O_7 (anhydrous HLN), (b) *n*-propoxyl derivative of HLN (*n*-propoxyl-HLN), (c) *n*-propoxyl-HLN after the treatment with *n*-decanol (*n*-decoxy-HLN), (d) *n*-decoxy-HLN treated with 2-propanol, (e) *n*-decoxy-HLN treated with *tert*-butyl alcohol, and (f) *n*-decoxy-HLN treated with ethylene glycol (EG).

thermic peaks at 342 and 415 °C. After the reaction with *n*-decanol, the first peak becomes sharper and shifts to lower temperature (321 °C), and the second peak becomes weaker.

Solid-state ^{13}C NMR spectra of *n*-propoxyl-HLN and its reaction product with *n*-decanol are shown in Figure 3. After the reaction with *n*-decanol, the three signals assignable to *n*-propyl groups disappear and new signals appear at 15, 24, 28, 33 (with a shoulder at lower frequency), and 80 ppm. All of these new signals can be ascribed to *n*-decyl groups. Thus, *n*-propyl groups are removed and *n*-decyl groups are introduced in the reaction product with *n*-decanol.

The amount of *n*-decyl groups is estimated from the carbon content by assuming that all the carbon atoms are present as the decyl groups (Table 1). The estimated value is 0.87 groups per $[\text{LaNb}_2\text{O}_7]$ unit. This value is close to the number of propoxyl groups in starting *n*-propoxyl-HLN (0.85).

The supernatant liquid was separated after the reaction and analyzed with GC-MS. In addition to *n*-decanol, *n*-propanol was clearly detected, indicating that *n*-propoxyl groups were released as *n*-propanol molecules.

Deintercalation of the Reaction Product between *n*-Decanol and *n*-Propoxyl-HLN.

After the C_6D_6 treatment of the reaction product between *n*-decanol and *n*-propoxyl-HLN, no organic species was extracted. Hence, the reaction product between *n*-decanol and *n*-propoxyl-HLN was treated with an excess of water (distilled water, 3 M HNO_3 , or 3 M KOH) to remove the guest species from the interlayer space via hydrolysis. When distilled water was utilized, the XRD pattern was unchanged, indicating no reaction. A similar result was obtained for the treatment with 3 M HNO_3 . In contrast, the interlayer distance decreases to 1.28 nm [close to that of HLN (1.22 nm; hydrated phase)¹⁷] after the treatment with 3 M KOH (Figure 1d). A DTA curve of the KOH-treated product showed an endothermic peak, and no exothermic peak was detected. These observations indicate the successful re-

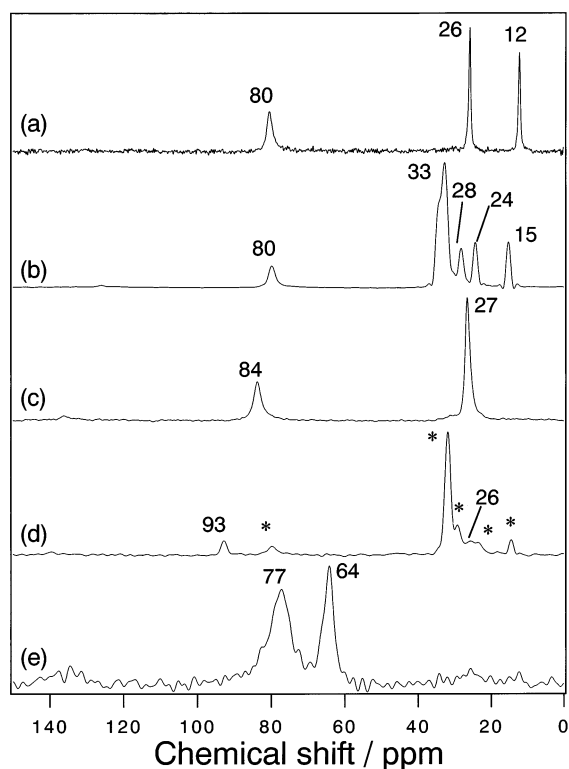


Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of (a) *n*-propoxyl derivative of HLN (*n*-propoxyl-HLN), (b) *n*-propoxyl-HLN after the treatment with *n*-decanol (*n*-decoxy-HLN), (c) *n*-decoxy-HLN treated with 2-propanol, (d) *n*-decoxy-HLN treated with *tert*-butyl alcohol, and (e) *n*-decoxy-HLN treated with ethylene glycol (EG). Signals for *n*-decoxy groups are indicated by asterisks in Figure 3d (see text).

Table 1. Amounts of Alkoxy Groups Bound to HLN after the Treatments with Alcohols

alcohol	carbon contents (mass %)	amount of groups per $[\text{LaNb}_2\text{O}_7]$
<i>n</i> -propanol ^a	6.45	0.85
<i>n</i> -decanol ^b	18.6	0.87
2-propanol ^c	7.85	1.0
ethylene glycol ^c	4.68	0.93

^a Prepared by the direct reaction with HLN (*n*-propoxyl-HLN).

^b Prepared by the reaction with *n*-propoxyl-HLN (*n*-decoxy-HLN).

^c Prepared by the reaction with *n*-decoxy-HLN.

removal of the organic component from the interlayer space after the KOH treatment.

After the hydrolysis with 3 M KOH, organic compounds in 3 M KOH were extracted using C_6D_6 , and *n*-decanol was clearly identified by ^1H and ^{13}C NMR. As water-soluble species, only a trace of *n*-propanol was detected by ^1H and ^{13}C NMR.

Guest Species in the Reaction Product between *n*-Decanol and *n*-Propoxyl-HLN. The *n*-decyl groups can be present as *n*-decanol intercalated in the interlayer space or *n*-decoxy groups bound to the surface of the perovskite-like slabs. The removal of *n*-decoxy groups from the interlayer space should involve hydrolytic bond cleavage, while *n*-decanol intercalated as a molecule is expected to be easily removed by dispersing intercalation compounds in organic solvents. Since no organic compound was extracted from the reaction product using C_6D_6 , the presence of *n*-decanol as intercalated molecules is very unlikely; the presence of *n*-decoxy groups is strongly suggested. The presence of

n-decoxy groups appears to be further supported by a large downfield shift of its α -carbon signal from the signal position observed for the liquid-state ^{13}C NMR (62.7 ppm) since the methoxy group signal of a methoxy derivative of HLN was observed at 69 ppm,²⁷ which is shifted from the liquid-state ^{13}C NMR signal of methanol (49.3 ppm).³⁵ A similar large downfield shift of the α -carbon signal was observed for *n*-propoxyl-HLN (63.4 \rightarrow 80 ppm). Furthermore, ^{13}C NMR study on $\text{Nb}(\text{OEt})_5$ demonstrated that the α -carbon signals of ethoxyl groups exhibited large downfield shifts (>10 ppm at 34 $^\circ\text{C}$) from that of ethanol.³⁶ Thus, we conclude that the product is an *n*-decoxy derivative of HLN. The *n*-decoxy derivative of HLN, hereinafter labeled as *n*-decoxy-HLN, was further utilized as an intermediate of the syntheses described below.

Reactions of *n*-Decoxy-HLN with 2-Propanol and *tert*-Butyl Alcohol. The reactions of *n*-decoxy-HLN with bulky alcohols have been examined. After the reactions with 2-propanol and *tert*-butyl alcohol, the interlayer distance decreases to 1.54 and 2.00 nm, respectively (Figure 1). The preservation of the (100) reflection position ($2\theta = 28.8^\circ$) indicates that the structure of the perovskite-like slabs is retained after the reactions.

DTA curves of the reaction products with 2-propanol and *tert*-butyl alcohol exhibit exothermic peaks (Figure 2): a peak starting from $\sim 270^\circ\text{C}$ for the product with 2-propanol and a peak starting from $\sim 190^\circ\text{C}$ for the product with *tert*-butyl alcohol. It should be noted that the DTA curve profiles are changed from that of *n*-decoxy-HLN after the reactions.

Solid-state ^{13}C CP/MAS NMR spectra of the products treated with 2-propanol and *tert*-butyl alcohol are shown in Figure 3. In the spectrum of the product with 2-propanol, the signals due to decyl groups disappear, and two signals which can be assigned to isopropyl groups are detected at 27 and 84 ppm. The α -carbon signal (at 84 ppm) shifts considerably from that of 2-propanol (63.4 ppm), suggesting the formation of isopropoxyl groups. Thus, it is concluded that *n*-decoxy groups are exchanged with isopropoxyl groups. Similarly, signals due to *tert*-butyl groups are detected at 26 and 93 ppm in the spectrum of the product treated with *tert*-butyl alcohol. The relative weakness of the 26-ppm signal is ascribed to a weaker ^{13}C - ^1H dipole-dipole interaction caused by rapid motion of the methyl groups in the *tert*-butyl groups.³⁷ The α -carbon signal (at 93 ppm) also exhibits a considerable downfield shift from that of *tert*-butyl alcohol (68.7 ppm), suggesting that organic species are present as *tert*-butoxyl groups. In the spectrum, however, the signals assignable to *n*-decyl groups (marked with asterisks) are also present. Thus, the reaction with 2-propanol is essentially completed, while that with bulkier *tert*-butyl alcohol is not completed even after 14 days under the present experimental conditions. On the basis of these observations, we conclude that the bulkiness of the reacting alcohol affects this type of reaction.

The amount of alkoxy groups is estimated for the product treated with 2-propanol and is determined to

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be 1.0 per $[\text{LaNb}_2\text{O}_7]$ unit (Table 1). This is slightly larger than that of starting *n*-decoyl-HLN, but does not exceed the amount of proton in HLN (1.0 per $[\text{LaNb}_2\text{O}_7]$ unit).

Reactions of *n*-Decoyl-HLN with Ethylene Glycol (EG). The XRD patterns of a reaction product between EG and *n*-decoyl-HLN are demonstrated in Figure 1. After the reaction, the interlayer distance decreases from that of *n*-decoyl-HLN (2.73 nm) to 1.58 nm. The interlayer distance further decreases to 1.46 nm upon drying at 200 °C.

A DTA curve of the air-dried product with EG exhibits an exothermic peak at ~300 °C (Figure 2). It should be noted that the profile of the DTA curve is changed from that of *n*-decoyl-HLN.

The solid-state ^{13}C CP/MAS NMR spectrum of the product heated at 200 °C exhibits two signals at 64 and 77 ppm (Figure 3). It is clearly shown that the *n*-decyl groups are removed during the reaction. The guest species were extracted via hydrolysis using 3 M KOH, and EG was clearly identified by both ^1H and ^{13}C NMR.

Since the ^{13}C NMR signals of α -carbon atoms in NbOR groups show downfield shifts from those of corresponding alcohols in this study, the 77-ppm signal, which shifts from the chemical shift of EG (63.8 ppm), can be ascribed to the α -carbon ($\text{Nb}-\text{OCH}_2\text{CH}_2\text{O}-$). This is not consistent with the solid-state ^{13}C NMR analysis of several organic derivatives of layered compounds (magadiite,³⁸ kaolinite,^{39–40} and boehmite⁴²) prepared by the reactions with EG since detected signals were near that of EG (62–65 ppm). This discrepancy appears to be ascribed to the effect of metal atoms to which alkoxy groups are bound, as indicated by the different ^{13}C NMR signal positions of methoxy groups in the methoxy derivative of HLN (69 ppm)²⁷ and that of kaolinite (51.1 ppm).⁴¹ Consequently, the 64-ppm signal is ascribed to the carbon atoms attached to hydroxyl groups ($\text{Nb}-\text{OCH}_2\text{CH}_2\text{OH}$).

The amount of C_2H_4 groups is estimated from the carbon content (Table 1). The amount is 0.93 groups per $[\text{LaNb}_2\text{O}_7]$ unit and is close to that of *n*-decoyl-HLN. Since 0.5 EG per $[\text{LaNb}_2\text{O}_7]$ unit is required by assuming both of the hydroxyl groups in the EG molecule are reacted, this value indicates that only one of the two hydroxyl groups in EG molecule is reacted. Similar grafting styles of EG were reported for other derivatives of layered materials.^{38,42}

Reaction Processes. To investigate the effect of the intermediates, a direct reaction between HLN and 2-propanol was attempted, and no reaction was observed; intermediates should be utilized for the reaction with 2-propanol. Furthermore, when *n*-propoxyl-HLN was utilized as an intermediate instead of *n*-decoyl-HLN, no reaction was observed with 2-propanol, indicating that an intermediate with appropriate alkoxy groups should be selected.

In terms of an NbO_6 octahedron, the present results can be summarized in the following "alcohol-exchange"

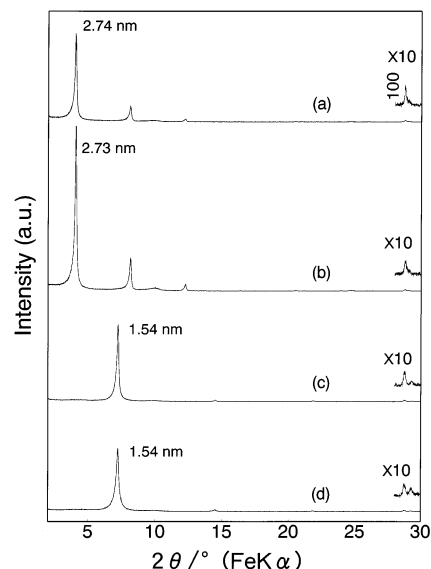
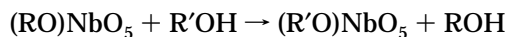


Figure 4. XRD patterns of (a) *n*-propoxyl-HLN after the treatment with *n*-decanol containing 3 mass % of distilled water for 1 day, (b) *n*-propoxyl-HLN after the treatment with *n*-decanol containing 3 mass % of distilled water for 7 days, (c) *n*-propoxyl-HLN after the treatment with distilled *n*-decanol for 1 day, and (d) *n*-propoxyl-HLN after the treatment with distilled *n*-decanol for 7 days.

type equation as an overall reaction:



Two reaction mechanisms appear to be possible for the observations. One possible mechanism is the nucleophilic attack of an alcohol molecule to the $(\text{RO})\text{NbO}_5$ site and subsequent release of ROH, which is similar to those for alcohol-exchange reactions of metal alkoxides.²⁹ The other one is a two-step process, which consists of hydrolysis of the $(\text{RO})\text{NbO}_5$ site by water (present in the system as an impurity and produced by water-generating esterification of an unmodified site $[(\text{HO})\text{NbO}_5]$) and subsequent esterification of the $(\text{HO})\text{NbO}_5$ site with alcohol.

To explore the reaction mechanism, the role of water is investigated (Figure 4). During the reaction of *n*-propoxyl-HLN with *n*-decanol containing 3 mass % of distilled water, the reflection due to *n*-propoxyl-HLN (1.53 nm) disappears within 1 day, and the reflection due to *n*-decoyl-HLN (2.73–2.74 nm) develops after 7 days. It should also be noted that the protonated form (HLN) is not detected in the XRD patterns. In contrast, the reaction of *n*-propoxyl-HLN with distilled *n*-decanol under dry conditions does not lead to the appearance of new reflections, and only the reflection due to *n*-propoxyl-HLN is observed at $d = 1.54$ nm, even after 7 days. Thus, it is likely that the reaction proceeded via a hydrolysis–esterification mechanism.

The hydrolysis behavior was further monitored by heating *n*-decoyl-HLN or *n*-propoxyl-HLN in distilled water or 2-pentanone containing 3 mass % of distilled water. As a solvent, 2-pentanone was selected because it dissolves water and bears no hydroxyl groups. When *n*-propoxyl-HLN was heated in distilled water, partial hydrolysis was observed, as shown by the presence of two XRD reflections corresponding to *n*-propoxyl-HLN (1.53 nm) and anhydrous HLN (1.07 nm). In contrast,

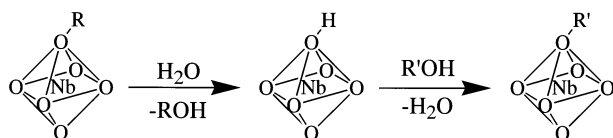
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Scheme 1. Proposed Reaction Mechanism

n-decoyl-HLN was not hydrolyzed after 4 days. Thus, without base catalysis, the hydrolysis of the *n*-decoyl groups was very slow even at 80 °C, consistent with the hydrolysis behavior at ambient temperature (described in the “Deintercalation of the Reaction Product between *n*-Decanol and *n*-Propoxyl-HLN” section). Since the interlayer space of *n*-decoyl-HLN is more hydrophobic than that of *n*-propoxyl-HLN, partial hydrolysis occurred only for *n*-propoxyl-HLN. When the water-containing 2-pentanone was utilized, both *n*-propoxyl-HLN and *n*-decoyl-HLN were hydrolyzed. Interestingly, an opposite tendency was observed; the hydrolysis proceeded to a large extent for *n*-decoyl-HLN, while the degree of hydrolysis for *n*-propoxyl-HLN was very low. Thus, it is likely that the *n*-alkoxy groups in the intermediates (*n*-decoyl-HLN and *n*-propoxyl-HLN) were hydrolyzed by a small amount of water in organic solvents that can dissolve water, such as alcohols and diols.

On the basis of these observations, the reaction mechanism is proposed as shown in Scheme 1. Initially, the (RO)NbO₅ site is hydrolyzed to form the (HO)NbO₅ site. The (HO)NbO₅ site then undergoes the esterification reaction with a reactant alcohol (R'OH) (or ethylene glycol) to form a new modified site, (R'O)NbO₅. For the unmodified (HO)NbO₅ site, which is present initially in the intermediate, the esterification can occur directly, and generated water further reacts with an (RO)NbO₅ site. Since the direct reaction between HLN and 2-propanol did not proceed, it is reasonable to assume that the esterification reaction proceeds before collapse of the layers by complete hydrolysis of the *n*-alkoxy groups in the same interlayer space; the unhydrolyzed site,

(RO)NbO₅, expands the interlayer space to make the intercalation of the reactant alcohol or diol molecules possible. The advantage of *n*-decoyl-HLN over *n*-propoxyl-HLN as an intermediate appears to be ascribed to faster hydrolysis of *n*-decoyl groups in organic solvents and/or a larger interlayer distance.

Conclusions

We have demonstrated that the alkoxy groups bound to the surface of the [LaNb₂O₇] slab can be substituted with other alkoxy groups and -OC₂H₄OH groups by heating in the corresponding alcohols (*n*-decanol, 2-propanol, and *tert*-butyl alcohol) and the diol (EG). The reactions are affected by both the kind of *n*-alkoxy groups in the intermediates and the bulkiness of reactant alcohols. The advantage of this type of reaction is clearly demonstrated by the unsuccessful direct reaction between HLN and 2-propanol. Water, which is present as an impurity and produced in situ by esterification of an unmodified site, plays an important role, and the reaction mechanism via the hydrolysis of the alkoxy groups on the surface of the perovskite-like slabs and subsequent esterification is proposed. The present results provide a new methodology for modifying the interlayer surface of layered perovskites and appear to be useful for designing their interlayer spaces via chemical modifications.

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