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# Hydrosilylation in the 2D interlayer space between inorganic layers: reaction between immobilized C=C groups on the interlayer surface of layered perovskite $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ and chlorohydrosilanes

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## Abstract

The C=C bonds immobilized in the interlayer space of layered perovskite,  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ , have undergone hydrosilylation reactions with chlorohydrosilanes. The C=C bonds are immobilized by the reaction between an *n*-propoxyl derivative of  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  and 4-penten-1-ol to form a  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-$  derivative of  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ , and a corresponding increase in the interlayer distance from 1.54 to 1.85 nm is observed. The  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-$  derivative is further treated with dichloromethylsilane or trichlorosilane, and the interlayer distance increases to 2.41 (dichloromethylsilane) or 2.07 (trichlorosilane) nm. Solid-state  $^{13}\text{C}$ -CP/MAS-NMR spectroscopy and infra-red (IR) spectroscopy reveal that the C=C groups disappear after the treatment with dichloromethylsilane or trichlorosilane, and  $^{13}\text{C}$ -NMR signals assignable to the hydrosilylated products are clearly observed. Besides hydrosilylation reactions, siloxane formation involving hydrolysis of the Si–Cl groups also proceeds. The structure of the perovskite-like slabs in  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  is preserved throughout the process, indicating the successful modification of immobilized C=C groups via hydrosilylation with no structural change in the inorganic host layers.

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**Keywords:** Layered perovskite; Dion–Jacobson phase; Hydrosilylation; Chlorosilane; Grafting reaction; Interlayer surface modification

## 1. Introduction

It is well known that some layered compounds can accommodate ions and molecules in the interlayer space to form intercalation compounds [1–3]. These intercalation reactions are generally considered to be reversible; guest species can be deintercalated under appropriate conditions. It is also possible to immobilize organic or organometallic groups on the interlayer surface. These reactions, called ‘grafting reactions,’ have been applied for layered compounds possessing reactive groups on the interlayer surface. Typical host compounds are layered polysilicates, whose interlayer surface bears silanol (SiOH) groups [4]. The silanol groups can react with organochlorosilanes (such as  $\text{R}_3\text{SiCl}$ ) [5] and alcohols [6] to form covalent Si–O–Si and Si–O–C

bonds, respectively. Other typical examples are kaolinite, [7,8] FeOCl, [9] and zirconium phosphate [10]. Interlayer space environments can therefore be modified through these reactions. Zirconium phosphate [11] and layered polysilicate [12] with grafted long alkyl chains can selectively adsorb molecules, for example. Another example is zirconium phosphate with grafted polyether chains which can solvate  $\text{LiClO}_4$ , and resulting  $\text{LiClO}_4$ -intercalated zirconium phosphate exhibited ionic conductivity [13].

Ion-exchangeable layered perovskites consist of perovskite-like slabs  $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$  and interlayer cations (M) [14]. Based on the layer charge, ion-exchangeable layered perovskites can be classified into the Dion–Jacobson phases ( $\text{M}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ ) [15,16] and the Ruddlesden–Popper phases ( $\text{M}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ ) [17,18]. These phases can be converted into their protonated forms by acid treatment [14,19].  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  (HLN), one of the protonated

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Dion–Jacobson-type layered perovskites, can react with *n*-alcohols to form *n*-alkoxyl groups, which are directly bound to niobium [20]. Direct reactions have been reported only for *n*-alcohols, and additional types of alcohols can be dissociatively immobilized via a hydrolysis-esterification mechanism using *n*-alkoxyl derivatives as intermediates [21]. Even with the use of appropriate intermediates, however, the reaction is affected by a steric factor: when an *n*-propoxyl derivative was treated with bulky *tert*-butanol, the substitution reaction was not completed. A more versatile method of designing interlayer space environments is therefore required.

Hydrosilylation has been known for decades in silicon chemistry [22–25]. The use of this type of reaction is not limited to molecular chemistry, and it has also been applied extensively to the surface modification of solids possessing SiH and C=C groups on their surfaces [26–30]. It is therefore expected that a hydrosilylation reaction can be employed to immobilize desirable functional groups in the interlayer space if appropriate groups (such as C=C, C≡C, and SiH groups) can be bound covalently on the interlayer surface. To date, the use of such approaches has been very limited, however. To the best of our knowledge, only one research group has reported the hydrosilylation on the surface of layered compounds: 2D silicate frameworks possessing alkenyl and alkynyl groups were prepared via reactions of a silicate mineral, apophyllite, with alkenylchlorosilanes and alkynylchlorosilanes and resulting organically-modified 2D silicates subsequently underwent hydrosilylation reactions with pentamethyldisiloxane [31,32].

We report here hydrosilylation of C=C groups immobilized on the interlayer surface of HLN with chlorohydrosilanes [ $\text{Cl}_x(\text{H})\text{SiMe}_{3-x}$ ] (Scheme 1). We first report the immobilization of  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -groups on the interlayer surface of HLN, after which we present the results for hydrosilylation reactions between the C=C groups in the  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -groups and chlorohydrosilanes,  $\text{Cl}_x(\text{H})\text{SiMe}_{3-x}$  (mainly  $x = 2, 3$ ). Since the purpose of this study is modification of the interlayer space of HLN via hydrosilylation, attention has been paid to providing evidence for the preservation of the perovskite-like slab structures of HLN during the grafting and hydrosilylation reactions.

## 2. Experimental

### 2.1. Immobilization of 4-penten-1-ol on the interlayer space of $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLN)

The preparation of  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  (HLN) and its conversion into the *n*-propoxyl derivative (*n*-propoxyl-

HLN) were described elsewhere [21]. About 1.3 g of *n*-propoxyl-HLN and 40 ml of 4-penten-1-ol were sealed in a glass ampoule and heated at 80 °C for 7 d. After centrifugation, the resultant product was washed with acetone and air-dried to give a  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -derivative ( $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN).

### 2.2. Reaction between chlorohydrosilanes ( $\text{Cl}_x(\text{H})\text{SiMe}_{3-x}$ ) and $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN

All the procedures were performed based on the standard Schlenk technique under protective nitrogen atmosphere [33] or in a glove box filled with nitrogen. About 0.3 g of  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN and 20 ml of  $\text{Cl}_x(\text{H})\text{SiMe}_{3-x}$  ( $x = 1, 2, 3$ ) were heated at reflux for 3 d. As a catalyst,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (as an acetonitrile solution) was employed with a Pt/Si ratio of  $5 \times 10^{-4}$ . The resultant product was washed with hexane and dried under reduced pressure.

### 2.3. Analyses

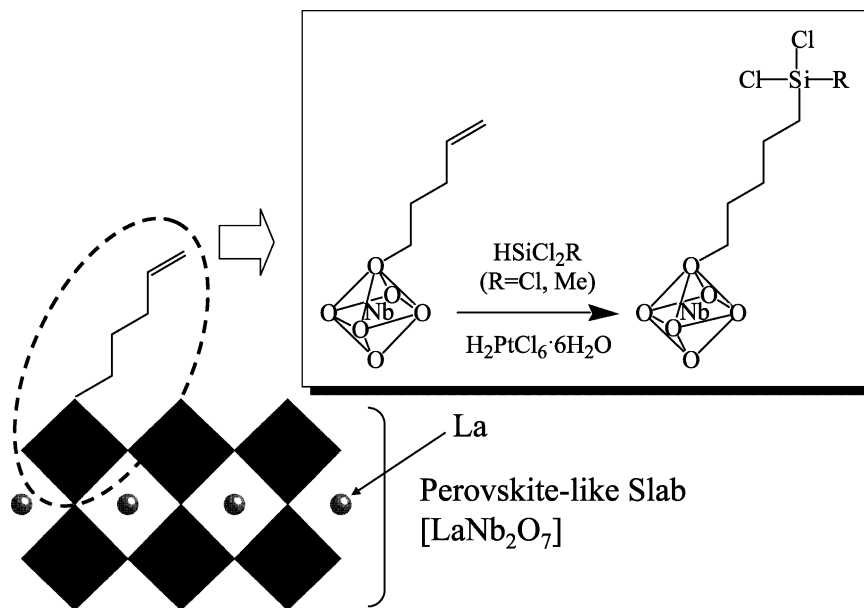
X-ray diffraction (XRD) patterns were obtained using a MacScience M03XHF<sup>22</sup> with Fe- $K_\alpha$  radiation. Infrared (IR) spectra were recorded on a Perkin–Elmer Spectrometer One. Solid-state <sup>13</sup>C- and <sup>29</sup>Si-NMR with magic angle spinning and a cross polarization technique (<sup>13</sup>C- and <sup>29</sup>Si-CP/MAS-NMR) were obtained using a JEOL CMX-400 spectrometer operated at 100.52 (<sup>13</sup>C) and 79.42 (<sup>29</sup>Si) MHz with a spinning rate of ~5 kHz. The carbon content was determined by internal service at the Waseda Material Characterization Center.

## 3. Results and discussion

### 3.1. Immobilization of 4-penten-1-ol on the interlayer space of $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLN)

Fig. 1 shows the XRD patterns of *n*-propoxyl-HLN and *n*-propoxyl-HLN treated with 4-penten-1-ol. The low-angle reflection expressing its interlayer distance shifts to a lower angle upon treatment with 4-penten-1-ol, indicating that the interlayer distance increases from 1.54 to 1.85 nm. The reflection at  $2\theta = 28.8^\circ$ , a (1 0 0) reflection of HLN, can be observed in the same position only when the structure of the perovskite-like slabs does not change. The observation of the reflection at  $2\theta = 28.8^\circ$  therefore indicates that treatment with 4-penten-1-ol affects the interlayer distance only.

The <sup>13</sup>C-CP/MAS-NMR spectra of *n*-propoxyl-HLN and its reaction product with 4-penten-1-ol are demonstrated in Fig. 2. Signals A, B and C observed in the spectrum of *n*-propoxyl-HLN are assigned to *n*-propoxyl groups [21]. In the spectrum of the reaction



Scheme 1. Schematic representation of hydrosilylation in the interlayer space of the organic derivative of layered perovskite  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ .

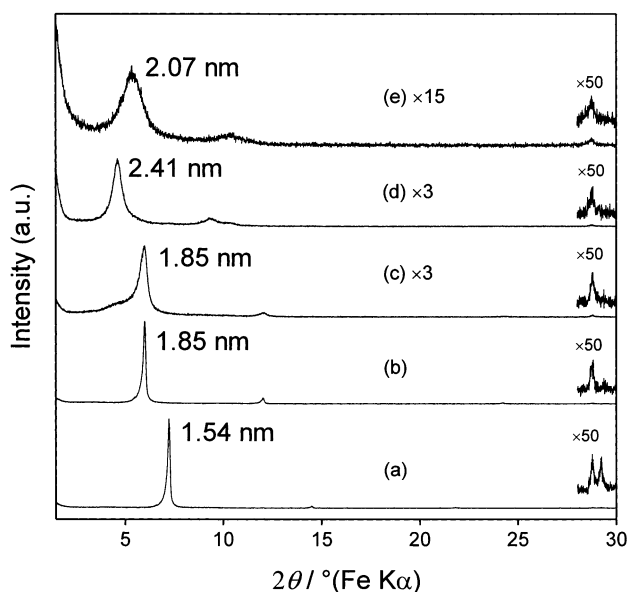


Fig. 1. XRD patterns of (a) *n*-propoxyl-HLN; (b)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN; (c)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with chlorodimethylsilane; (d)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with dichloromethylsilane and (e)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with trichlorosilane.

product with 4-penten-1-ol, these three signals disappear and new signals D–H appear (signal D at 31 ppm, signal E at 33 ppm, signal F at 80 ppm, signal G at 115 ppm and signal H at 139 ppm). These signals are assignable to the  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ - groups, as shown in Fig. 2b. The large downfield shift of the carbon atom attached to oxygen (signal F) from 62 ppm (a typical value in liquid-state  $^{13}\text{C}$ -NMR of molecular  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{OH}$ ) to 80 ppm indicates that the  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ - groups are

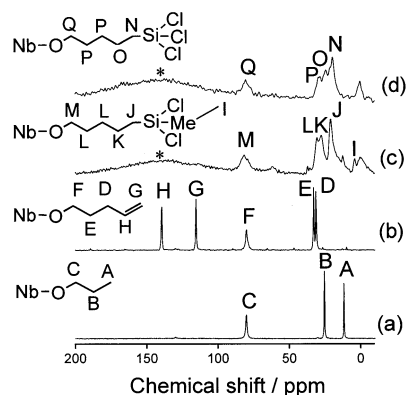


Fig. 2. Solid-state  $^{13}\text{C}$ -CP/MAS-NMR spectra of (a) *n*-propoxyl-HLN; (b)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN; (c)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with dichloromethylsilane and (d)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with trichlorosilane. Broad signals masked by asterisks are backgrounds.

present in the form of  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{Nb}$ , since similar downfield shifts have been observed for other alkoxy-derivatives of HLN, [20,21] for example, signal C of *n*-propoxyl-HLN at 81 ppm in Fig. 2a.

The IR spectra of *n*-propoxyl-HLN and *n*-propoxyl-HLN treated with 4-penten-1-ol are shown in Fig. 3. In the spectra of *n*-propoxyl-HLN and its reaction product with 4-penten-1-ol,  $\nu_{\text{CH}}$  bands of  $\text{CH}_3$  and  $-\text{CH}_2-$  groups are observed in the range of  $2800\text{--}3000\text{ cm}^{-1}$  [34]. In the spectrum of the reaction product with 4-penten-1-ol, additional bands assignable to  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ - groups ( $\nu_{\text{CH}}$ ,  $3074\text{ cm}^{-1}$ ;  $\nu_{\text{C}=\text{C}}$ ,  $1640\text{ cm}^{-1}$ ) are clearly observed besides the  $\nu_{\text{CH}}$  bands of the  $-\text{CH}_2-$  groups. These results show good consistency with the solid-state  $^{13}\text{C}$ -NMR results.

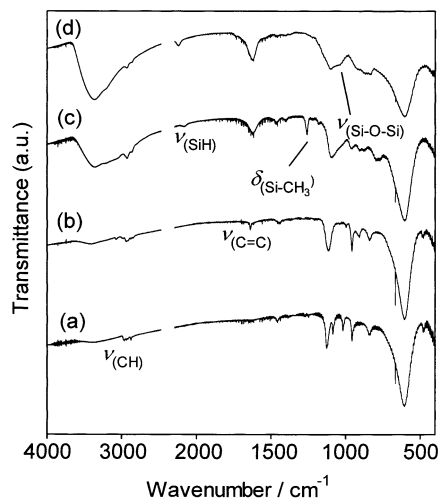


Fig. 3. IR spectra of (a) *n*-propoxyl-HLN; (b)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{HLN}$ ; (c)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{HLN}$  treated with dichloromethylsilane and (d)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{HLN}$  treated with trichlorosilane.

These results indicate that 4-penten-1-ol is dissociatively immobilized on the interlayer surface of HLN in a way similar to the reaction between *n*-alkoxyl derivatives of HLN and alcohols [21]. The amount of  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-$  groups is estimated from the carbon content (9.96%) to be 0.81 group per  $[\text{LaNb}_2\text{O}_7]$  unit, indicating that 81% of the protonated site  $[(\text{HO})\text{NbO}_5]$  in  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  is converted into a  $[\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}]\text{NbO}_5$  site.

### 3.2. Hydrosilylation in the interlayer space of HLN

The XRD patterns of the products after treatment of the  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-$  derivative of HLN ( $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{HLN}$ ) with chlorohydrosilanes are shown in Fig. 1. After the treatment with chlorodimethylsilane  $[\text{Cl}(\text{H})\text{SiMe}_2]$ , no clear variation in the XRD pattern is observed; only a weak shoulder reflection appears at  $2\theta = \sim 4.56^\circ$  ( $d = 2.43$  nm). After the treatments with dichloromethylsilane  $[\text{Cl}_2(\text{H})\text{SiMe}]$  and trichlorosilane ( $\text{HSiCl}_3$ ), on the contrary, the XRD patterns change drastically; the reflection corresponding to the interlayer distance of  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{HLN}$  ( $d = 1.85$  nm) disappears, and new low-angle reflections appear (dichloromethylsilane-treated product,  $d = 2.41$  nm; trichlorosilane-treated product,  $d = 2.07$  nm). It should be also noted that the reflection at  $2\theta = 28.8^\circ$ , the (1 0 0) reflection of HLN, is observed in these two XRD patterns. Thus, the treatments with dichloromethylsilane and trichlorosilane lead to expansion of the interlayer distance without changing the perovskite-like slab structure. The lower reactivity of chlorodimethylsilane in comparison with those of dichloromethylsilane and trichlorosilane is ascribed to the electronic effect of chlorine substituent on the reactivity of hydrosilanes toward Pt-catalyzed hydrosilylation

reactions [22,35,36]. Hereafter, further characterization results are presented for these two products only.

The solid-state  $^{13}\text{C}$ -CP/MAS-NMR spectra of the products treated with chlorohydrosilanes are demonstrated in Fig. 2. After the treatments with dichloromethylsilane and trichlorosilane, the signals due to  $\text{C}=\text{C}$  groups (signals G and H) disappear, and new signals appear. It is known that hydrosilylation of 1-alkenes with hydrosilanes readily proceeds in the presence of various transition metal catalysts including Pt(0) complexes to give 1-silylalkanes ( $\beta$ -adduct) [37]. It seems that a similar addition reaction also proceeds in our system, and thus, major signals in the  $^{13}\text{C}$ -CP/MAS-NMR spectra can be assigned to the structures assumed based on hydrosilylation reactions. For the product treated with dichloromethylsilane, signal I (4 ppm), signal J (21 ppm), signal K (27 ppm), signal L (30 ppm) and signal M (82 ppm) are assigned to carbon atoms in a  $[\text{CH}_3(\text{Cl})_2\text{Si}(\text{CH}_2)_5\text{O}]\text{NbO}_5$  site, as shown in Fig. 2c [38]. In the spectrum of trichlorosilane-treated product, signals assignable to a  $[\text{Cl}_3\text{Si}(\text{CH}_2)_5\text{O}]\text{NbO}_5$  site appear at 22 (signal N), 27 (signal O), 31 (signal P with a shoulder at 32 ppm) and 83 (signal Q) ppm (Fig. 2d) [39]. Thus, taking the observed expansion of the interlayer distances into account, we conclude that hydrosilylation proceeds successfully in the interlayer space of HLN.

The IR spectra of the products treated with chlorohydrosilanes are shown in Fig. 3. Compared with the spectrum of  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}-\text{HLN}$ , the  $\nu(\text{CH})$  band of the  $\text{CH}_2=\text{CH}-$  groups at  $3074$   $\text{cm}^{-1}$  disappears in the spectrum of the product treated with dichloromethylsilane. A new band appears at  $1259$   $\text{cm}^{-1}$  and can be ascribed to the  $\delta(\text{Si}-\text{CH}_3)$  mode [34]. These observations show good consistency with the  $^{13}\text{C}$ -CP/MAS-NMR results, which indicate the occurrence of hydrosilylation. The occurrence of hydrosilylation is also shown clearly by the disappearance of the  $\nu(\text{CH})$  band of the  $\text{CH}_2=\text{CH}-$  groups in the spectrum of the product treated with trichlorosilane. In both the spectra,  $\nu(\text{SiH})$  bands are detected at  $2160$   $\text{cm}^{-1}$  for the product treated with dichloromethylsilane and at  $2238$  and  $2248$   $\text{cm}^{-1}$  for the product treated with trichlorosilane [34]. In addition, a weak shoulder at  $1039$   $\text{cm}^{-1}$ , which could be assigned to the  $\nu(\text{Si}-\text{O}-\text{Si})$  mode, appears in the spectrum of the product treated with trichlorosilane. The appearance of the  $\nu(\text{SiH})$  band and the  $\nu(\text{Si}-\text{O}-\text{Si})$  band will be discussed below.

Fig. 4 shows solid-state  $^{29}\text{Si}$ -CP/MAS-NMR spectra of the products treated with chlorohydrosilanes [40]. In the spectrum of the product treated with dichloromethylsilane, an intense signal that can be assigned to a  $\text{Cl}_2(\text{CH}_3)\text{SiCH}_2-$  environment is observed at 33 ppm. Similarly, an intense signal assignable to the  $\text{Cl}_3\text{SiCH}_2-$  environment is present at 14 ppm for the product treated with trichlorosilane. The presence of these two signals

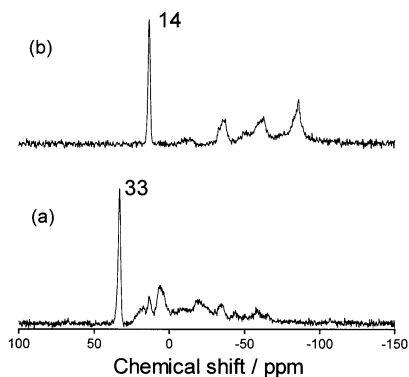


Fig. 4. Solid-state  $^{29}\text{Si}$ -CP/MAS-NMR spectra of (a)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with dichloromethylsilane and (b)  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -HLN treated with trichlorosilane.

shows good consistency with the occurrence of hydrosilylation in the interlayer space. Besides these signals, weak signals are present in an upfield region. In the spectrum of the product treated with dichloromethylsilane, the signals at  $-20$  and  $-35$  ppm are ascribable to the  $\text{Cl}(\text{CH}_3)\text{Si}(\text{O}-)\text{CH}_2-$  and  $\text{H}(\text{CH}_3)\text{Si}(\text{O}-)_2$  environments, respectively. In addition, the signal at  $6$  ppm appears to be due to the  $(\text{CH}_3)\text{Si}(\text{O}-)_2\text{CH}_2-$  environment. In the spectrum of the product treated with trichlorosilane, the signals at  $-35$ ,  $-62$  and  $-86$  ppm can be ascribed to the  $\text{HSiCl}_2(\text{O}-)$ ,  $\text{HSiCl}(\text{O}-)_2$  and  $\text{HSi}(\text{O}-)_3$  environments, respectively. These environments can be formed by the formation of siloxane bonds via the hydrolysis of Si-Cl groups and subsequent condensation. When siloxane formation occurs without hydrosilylation, SiH groups remain (as an  $\text{H}(\text{CH}_3)\text{Si}(\text{O}-)_2$  environment for the product treated with dichloromethylsilane and as  $\text{HSiCl}_2(\text{O}-)$ ,  $\text{HSiCl}(\text{O}-)_2$  and  $\text{HSi}(\text{O}-)_3$  environments for the product treated with trichlorosilane), which is consistent with the IR results. Hydrolysis could proceed during the synthesis process because of the presence of a trace of impurity water and/or during the washing procedures, since Si-Cl groups are highly reactive to water.

#### 4. Conclusions

We have demonstrated that hydrosilylation involving the C=C bonds immobilized on the interlayer surface of a layered perovskite  $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  (HLN) occurs if dichloromethylsilane and trichlorosilane are employed as hydrosilylation reagents. The  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -groups are successfully bound to the interlayer surface of HLN via the reaction between *n*-propoxyl-HLN and 4-penten-1-ol, as clearly shown by spectroscopic analyses, and the interlayer distance increases correspondingly from  $1.54$  to  $1.85$  nm. The C=C bonds in the  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ - groups can be further reacted with the chlorohydrosilanes (dichloromethylsilane and trichlor-

osilane) by hydrosilylation. The interlayer distance of the  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ - derivative ( $1.85$  nm) increases further to  $2.41$  nm (dichloromethylsilane) and  $2.07$  nm (trichlorosilane). Besides hydrosilylation reactions, siloxane formation involving hydrolysis of the Si-Cl groups also proceeds. It should be noted that the reflection at  $2\theta = 28.8^\circ$ , which is the (1 0 0) reflection of HLN and which indicates the ordering of the perovskite-like slabs along the *ab* plane, remains in the same position during the modifications with 4-penten-1-ol and hydrosilylation, indicating that the perovskite-like slab structure is preserved throughout the whole process. The present results offer a versatile approach for grafting functional groups on the interlayer surface of layered perovskites, and this approach may be applicable to other layered compounds undergoing grafting reactions.

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- [38] If an  $\alpha$ -addition occurs to form a  $[\text{CH}_3(\text{Cl})_2\text{Si}(\text{CH}_3)\text{CH}(\text{CH}_2)_3\text{O}]\text{NbO}_5$  site, signals with similar chemical shifts are expected. The presence of unidentified weak signals at 0, 12 and 62 ppm indicates the presence of an unidentified side reaction (or unidentified side reactions).
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