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Modification of the Interlayer in Lanthanum–Niobium Oxide and Its Catalytic Reactions

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The methods for preparation of pillared materials with ZrO_2, TiO_2, or SiO_2 in the interlayer of layered perovskite structural oxides, $HLaNb_2O_7$ (HLa), were examined in detail. HLa that had been intercalated with *n*-amines of different carbon chain lengths was used in pillaring ZrO_2. *N*-octyl- and decylamine were useful in the construction of the pillar. It is of critical importance to enlarge the interlayer spacing of the HLa by using filling with *n*-octylamine for the intercalation of the precursor of ZrO_2, TiO_2, or SiO_2. The precursor of ZrO_2 or TiO_2 could easily be intercalated by exchange with *n*-octylamine. When pillaring with SiO_2 was done, the preparation was not as easy as pillaring with ZrO_2 or TiO_2. The molar ratio of tetraethoxysilane (TEOS), the concentration of HCl, and the amount of ethanol was closely related in the preparation. The optimum preparation condition was a molar ratio of TEOS : ethanol : HCl (2 or 3 *M*) of 10 : 5 : 0.5 to 1 mol of $HLaNb_2O_7$ fully filled with *n*-octylamine at 40°C. Thus, the materials prepared (by pillaring with ZrO_2, TiO_2, or SiO_2) were used as a catalyst in the dehydration of 1-butanol. Enhancement of activity was detected on all the pillared catalysts. It was caused by interaction between the pillaring material and the host matrix. The TiO_2 pillared catalyst exhibited the highest activity in hydration, followed by the ZrO_2 and SiO_2 pillared catalysts. All of the catalysts that were examined consisted of a large amount of mesopore, in which the TiO_2 pillared catalyst exhibited the presence of a larger ratio of mesopore, as compared with other catalysts. © 1997 Academic Press

1. INTRODUCTION

Since the introduction of pillared clays by Barrer and Macload in 1955 (1), pillared clays with various organic cations and metal chelates have been successfully prepared; however, these pillared compounds were rather unstable when heated above 300°C. In 1975 Brindley and Semples (2) prepared robust pillared compounds with Al_2O_3 in montmorillonite from polyoxyaluminum. Yamanaka and Brindley (3) also reported the preparation of pillared compounds with ZrO_2 using multinuclear hydroxyzirconium. Thus, the synthesis of pillared compounds with stable inorganic materials has been carried out mainly in clay and clay minerals. Under the stimulus of research concerning modification such as the intercalation and ion exchange of the interlayer in clay minerals, the number of similar studies about synthesized layered materials (which are relatively stable at high temperatures) has also recently increased. Since a new series of layered oxides, $A\mathrm{LaNb_2O_7}$ (A = alkali metals, H, NH_4, and amines) with thermal stability have been reported (4, 5) the authors have studied copper compounds (6, 7), ion exchange (8, 9), the acidic properties (10), and the intercalation of types of alcohol (11) in $HLaNb_2O_7$ (HLa). In this study, new compounds that were pillared with ZrO_2, TiO_2, or SiO_2 in the interlayer between the $LaNb_2O_7$ layer were examined in detail [also see previous paper (9)], as were their catalytic properties.

2. EXPERIMENTAL

2.1. *Materials*

As the starting material for the preparation of all pillared compounds, HLa was first prepared according to the procedure described in previous papers (4, 5). It was then intercalated with *n*-octylamine to enlarge the interlayer, by which the intercalation of the precursors was facilitated. ZrO_2 or TiO_2 pillared samples were prepared according to the following procedures. A suspended solution of 100 ml of water and a sample that had been intercalated with *n*-octylamine (which had been prepared from 10 g of HLa) were added to 300 ml of 0.1 *M* zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) (ZOC) aqueous solution. The operation was performed by stirring for 3 days at room temperature. After the operation, the slurry was separated from the solution with a centrifugal separator and washed by suspension in water. This was followed by repetition of the separation and washing procedure until the washed water reached a pH of 7. It was then dried at 100°C.

The TiO_2 pillared sample was prepared by a method similar to that used for the ZrO_2 pillared sample. The suspended solution mentioned above was added to a hydrated titanium sol solution formed by mixing 23.8 g of titanium tetraisopropoxide (TIO), 5.28 g of ethanol, and 5.7 ml of HCl (2 *M*). The following procedure was the same as for the case of ZrO_2. Samples that was intercalated with ZOC or TIO that

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had been hydrated with HCl and ethanol were calcined at 500°C for 3 h in air to convert to ZrO_2 or TiO_2.

Preparation of the SiO_2 pillared compound was different from the above methods. Here, the different amounts of ethanol and tetraethoxysilane (TEOS) and the varying concentrations of HCl (which were arranged by means of dilution of 4.2 ml of 3 *M* HCl or 3.25 ml of 4 *M* HCl without dilution) were used. In the suspended solution, a colloidal solution consisting of 23.7 g of TEOS, 12.6×10^{-3} *M* HCl, and varying concentrations of ethanol (5.3—15.9 g) diluted with 100 ml of water was added and then stirred for 4 days at 40°C. After the operation, the same procedure used for ZrO_2 was carried out. All of the reagents used in this study are of a special grade purchased from Wako Junyaku Company Ltd.

2.2. *Characterization of Materials*

The amount of *n*-amines that was intercalated into the HLa interlayer was estimated from the weight decrease by thermogravimetric measurement. The contribution of the water content to the weight decrease could not be detected as expected because the intercalation of the *n*-amines was carried out in heptane (4). The acidity of the samples was estimated from the saturated adsorbed amount of NH_3 at room temperature using the Langmuir equation. This differed from the previous method (9). The previous method was accompanied by an evacuation procedure after the adsorption of NH_3 at room temperature occurred. After evacuation, NH_3 was adsorbed again and the difference between the amounts of NH_3 adsorbed in the first and second adsorption stages was defined as the acidity; however, it does not appear that this procedure is appropriate because it is doubtful if the NH_3 that had been inserted in the first stage was fully adsorbed on the surface of the interlayer. Therefore, for these reasons we decided not to use the previous method in this study.

The elementary analysis of the samples was performed as follows except for the SiO_2 pillared compound: A sample was dissolved in an equimolar solution of H_2SO_4 and HF by warming at ca. 190°C in a Teflon beaker. H_2O_2 solution was then slowly added, followed by dilution with water after cooling. The amounts of Zr and Ti in the dissolved solution were measured by inductively coupled plasma (ICP) emission spectroscopy (Emission Spectro Analyzer, Jobin Yvon-Rigaku 70C). The amount of Si was measured by means of fluorescent X-ray spectrometry (Phillips, PW-2400). TG-DTA measurements (Rigaku RTC-10A) were performed in the temperature range from room temperature to 800°C at the rate of 10°C/min.

Surface area, pore volume, and pore size distribution were obtained by the adsorption of nitrogen using micrometrics (Coulter Omnisorp Gas Sorption Analyzer 360). Before the measurement the sample was treated at 150°C for 3 h by evacuation.

2.3. *X-Ray Characterization*

The properties of the pillared compound and intercalated solid products were examined using X-ray diffraction (Rigaku Rad-B) with Ni- filtered Cu $K\alpha$ radiation (4, 7). The basal spacing was estimated from the length of the *c* axis based on a peak of $d(001)$, as calibrated by standard Si beforehand.

The atomic ratio of Si to Nb on the surface of the samples was estimated by XPS measurement as follows; each peak height on Si ($2p$) and Nb ($3d_{5/2}$) that was obtained by substitution of the background was divided by calibrated sensitivity factors of 0.16 and 1.01 for Si and Nb, respectively. The ratio of the values thus obtained by this simple calculation was defined as the atomic ratio.

2.4. *Dehydration of Alcohol*

The dehydration of 1-butanol was performed with a flow reactor at 320°C in a nitrogen flow of 20 ml/min as a diluent under atmospheric pressure. The distilled purified 1-butanol was fed through a microfeeder at the rate of 0.098 mol/min. The weight of the catalyst used in the reaction was 200 mg. It had been treated at 320°C for 1 h in a N_2 flow before the reaction. N_2 (research grade) was purified by flowing through a deoxygen column at 180°C which consisted of Cu–kieselguhr catalyst.

The reaction products were analyzed in a gas chromatograph (Hitachi Type 263-30 FID, capillary column OV-1, 50 m long at 110°C).

3. RESULTS AND DISCUSSION

3.1. *Pillared $HLaNb_2O_7$ with ZrO_2*

As *n*-octylamine can easily intercalate in the HLa interlayer, various types of other *n*-amines such as methyl-, propyl-, butyl-, hexyl-, and decylamine were examined. All the amines that were examined could be as easily intercalated as *n*-octylamine. The HLa that was intercalated with various kinds of amines was treated with an aqueous $ZrOCl_2$ (ZOC) solution insert zirconium precursor into the interlayer. It was then dried at 100°C and calcined at 500°C in air. The basal spacing of the samples that were intercalated with each amine and the amount of Zr inserted (expressed as the molar ratio of Zr/La) are given in Table 1. For reference, the values of the basal spacing of HLa are also given in Table 1. From the observations in Table 1, the expanded extent of the basal spacing by means of methyl- to hexylamine appears to not be large enough to intercalate a Zr precursor because the inserted amount of Zr was very small in comparison with the amount in the cases treated with *n*-octylamine or decylamine. Therefore, it is necessary

TABLE 1

Basal Spacing of Pillared $HLaNb_2O_7$ with ZrO_2 Prepared from Intercalated $HLaNb_2O_7$ with Various Amines

	Basal spacing (Å)			
		After calcination at		
Amine	Amine-$HLaNb_2O_7$	100°C	500°C	Zr/La atomic ratio
$HLaNb_2O_7$	—	12.1	10.7	—
Methyl-	12.1	11.8	10.7	0.0015
n-Propyl-	18.7	10.7	10.8	0.11
n-Butyl-	21.1	10.7	10.8	0.09
n-Hexyl-	24.9	10.9	10.8	0.08
n-Octyl-	28.8	14.3	11.7	0.71
n-Decyl-	30.6	16.2	12.4	0.64

to use amines that have a longer carbon chain length than 8 in the intercalation of zirconium compound. The basal spacing of the intercalated samples diminished due to its decomposition into ZrO_2 with a rather bulky zirconium precursor by treatment at 500°C. The decomposed product of the zirconium precursor was confirmed to be ZrO_2 by means of XRD.

The HLa that was intercalated with varying amounts of *n*-octylamine was prepared by treatment with a different amount of *n*-octylamine. The intercalation of ZOC in the samples thus treated was performed. The results are given in Table 2. From the results given in Table 2, one can see that 100% of *n*-octylamine cannot be intercalated into the interlayer even if it is treated with a molar ratio of 1 : 1 to the HLa. The amount of Zr that was inserted into the interlayer increased with an increase in the *n*-octylamine that was intercalated in the HLa. The basal spacing was almost constant except for HLa : *n*-octylamine = 1 : 0.2. From the results in Table 2 it can be considered that the Zr precursor intercalates by means of an exchange with *n*-octylamine, but does not insert in the interstice between *n*-octylamine pillars. ZOC easily dissolves in water and forms a complex of the form $[Zr(OH)_{14-n}(H_2O)_{8+n}]^{n+}$ in aqueous solution. Yamanaka *et al.* (3, 10) reported that this complex maintains the state of $n = 2$ in the interlayer of types of clay like montmorillonite. This complex had a length and breadth of 10 Å and thickness of 4.5 Å, respectively (3). The extent between the layers of the HLa intercalated with this complex is ca. 19 Å by means of XRD measurement, but due to subtraction of the net thickness (4) of the layer, the calibrated spacing becomes 11.2 Å. If the zirconium complex intercalates in the same form and size as does montmorillonite, the Zr complex may stay in the interlayer as a single molecule in a direction that is perpendicular to the surface or as double molecules piled toward the breadth. However, considering the value of the basal spacing of a sample intercalated with Zr complex, it is reasonable to believe that this complex molecule will remain in the interlayer in the former form. The basal spacing and surface area of the samples thus prepared that were calcined at 500°C are given in Table 4 together with data for other samples that will be described later.

TABLE 2

Effects of the Amount of *n*-Octylamine on Preparation of $ZrO_2 \cdot HLaNb_2O_7$

HLa : *n*-octylamine	Amount of *n*-octylamine inserted (%)[a]	Basal spacing (Å) after calcination at 100°C	500°C	Zr/La ratio
1 : 0.2	31.9	10.7	10.7	0.044
1 : 0.33	42.3	14.2	11.5	0.33
1 : 0.5	55.9	14.3	11.5	0.46
1 : 1	73.2	14.2	11.5	0.70
1 : 2	94.8	14.5	11.7	0.71

[a] Percentage $= a/(HLa + a) \times 100$, where $a =$ amount of *n*-octylamine inserted.

3.2. *Pillared $HLaNb_2O_7$ with TiO_2*

It was impossible to produce a pillar of TiO_2 without ethanol and HCl because TIO could not easily be hydrated without them. HLa with varying amounts of *n*-octylamine in the interlayer was treated with titanium sol (which may be a polycation that is formed by hydrolysis of the titanium sol) which had been produced by TIO hydration; the content of Ti (expressed as the Ti/La ratio) and the basal spacing of the samples in question are summarized in Table 3. Basal spacing before calcination was ca. 14.5 Å, which is larger than that of $HLa \cdot 2H_2O$ and smaller than that of HLa intercalated with *n*-octylamine, which has a basal spacing of 28.8 Å (see Table 1). Therefore it is assumed that titanium sol is intercalated in the interlayer. Even when HLa was intercalated with a relatively small amount of *n*-octylamine, the amount of titanium that was intercalated was not as small as was the amount of zirconium (see Table 3). Consequently, it seems that the intercalation of titanium sol is easier than the intercalation of Zr complex. We consider two possible intercalation mechanisms for the titanium sol: one is an exchange with *n*-octylamine and the other is insertion of the sol into the interstice between *n*-octylamine

TABLE 3

Ti/La Ratios and Basal Spacing in Samples Produced from $HLaNb_2O_7$ Intercalated with Varying Amounts of *n*-Octylamine

HLa : *n*-octylamine	Ti/La	Basal spacing (Å)
1 : 0.2	0.79	14.0
1 : 0.33	0.80	14.5
1 : 0.5	0.90	15.0
1 : 1	0.89	15.0
1 : 2	1.04	15.0

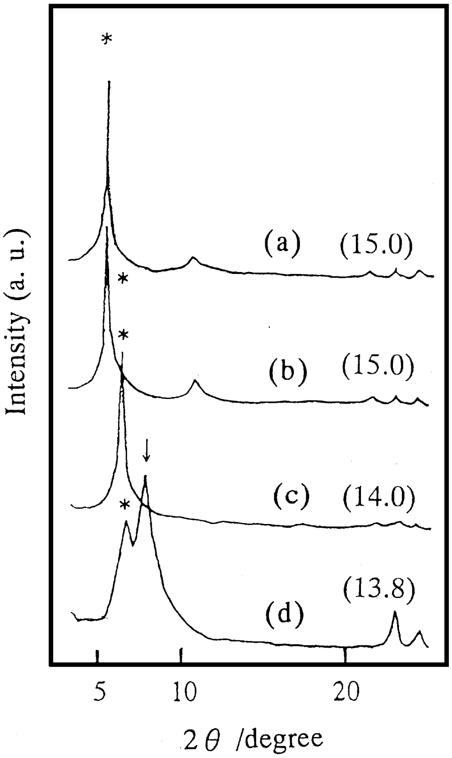

FIG. 1. XRD patterns of TiO_2 pillared samples prepared with varying concentrations of HCl: (a) 1 *M*, (b) 2 *M*, (c) 3 *M*, (d) 6 *M*. The figures in parentheses indicate the values of the basal spacing and are expressed in angstroms. The stars and the arrow indicate *d*(001) and $HLaNb_2O_7 \cdot 2H_2O$ peak, respectively.

pillars. From the results in Table 3, it is difficult to determine which mechanism is preferred; however, the former case may be preferred by using the analogy of a Zr compound. Figure 1 shows the effect of the concentration of HCl and XRD patterns on the samples along with varying concentrations of HCl. With an increase in HCl concentration, the *d*(001) peak shifted to a higher diffraction angle. When 6 *M* HCl was used, the HLa pattern appeared, indicating that the *n*-octylamine in the interlayer was exchanged with protons to partly return it to the original $HLa \cdot 2H_2O$ form. Therefore, it is clear that excessively high concentrations of HCl were not acceptable since the protons are preferentially inserted. It appears that a concentration of 1 or 2 *M* HCl was optimal. As a hydrated TIO product may be titanium tetrahydroxide which contains an undefined amount of water, its size cannot be estimated. Consequently the inserted state of the hydrated titanium compound in the interlayer is not clear as it is for a zirconium complex.

3.3. *Pillared $HLaNb_2O_7$ with SiO_2*

The synthesis of pillared HLa with SiO_2 was not as easy as the preparation of pillared HLa with TiO_2 or ZrO_2. The former has attractive characteristics like a large surface area and high catalytic activity (9); however, it is difficult to prepare the same material with good reproducibility. The reason why the preparation is so difficult may be because TEOS sol has a negative charge as compared with the zirconium and titanium complex sols, which have positive charges (10). In this study, we investigated in detail a method that was used to prepare pillared HLa with SiO_2 with good reproducibility. In the previous paper (9) we reported that pillared HLa with SiO_2 was successfully prepared when the HLa interlayer was filled with a small amount of *n*-octylamine (e.g., 33%), although it was not reproducible; however, even with the HLa with an interlayer that had been filled with enough *n*-octylamine, we discovered that SiO_2 pillaring could proceed sucecessfully with good reproducibility when the operation temperature was raised to 40°C with the appropriate amounts and concentrations of both ethanol and HCl. Consequently, at first the effect of the HCl concentration was examined by maintaining a constant concentration of ethanol, i.e., 0.23 *M*. As shown in Fig. 2, the sample prepared at a low concentration of HCl exhibited large basal spacing before calcination at 500°C; however, with an increase in the concentration, the basal spacing decreased. On the contrary, after calcination, the basal spacing of the sample prepared with a high HCl concentration tended to increase and to maintain a constant value. If the amount of basal spacing of a sample prepared with a low concentration before calcination is caused by intercalation in the interlayer with relatively large amounts of silica sol, large basal spacing will be maintained after calcination. Our observations showed the exact opposite. Therefore it can be considered that silica sol does not intercalate at low HCl concentration, but instead adheres onto

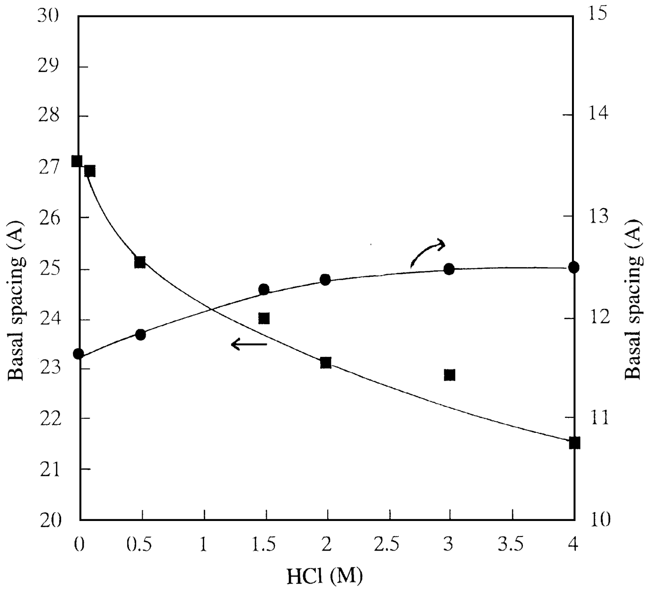

FIG. 2. Effect of HC1 concentration on the basal spacing of the SiO_2 pillared samples. Sample calcined at 100°C (■); sample calcined at 500°C (●).

the outer surface of the matrix, not on the inner surface in the interlayer. By calcination at 500°C, it is assumed that the silica sol that is adhering onto the outer surface will change into SiO_2 which will exhibit a large surface area. This consideration is reasonable due to the fact that SiO_2 prepared under the same conditions as was the SiO_2 pillar showed a large surface area of 358 m^2/g. On the other hand, at high concentrations silica sol intercalates in the interlayer and will stay in the SiO_2 state after calcination, thereby retaining some of the basal spacing. Generally, the decrease in basal spacing after calcination of the sample may be a result of turning bulky hydrated silica sol into SiO_2. The surface state of the samples prepared under both low (0.5 *M*) and high (3 *M*) HCl concentration and a constant concentration ethanol (0.23 *M*) were examined by XPS for comparison. The relative atomic ratios of Si to Nb of the samples prepared at low and high concentrations were 4.2 and 2.7, respectively. These values are not the exact atomic ratios, but are simply a measure of the atomic ratios, because the values were not calibrated by the use of the standard sample; however, the preceding results show that the surface of the samples prepared at low concentration is rich in Si, indicating SiO_2 coverage on the surface. The ratio of Si to Nb of the samples prepared at a HCl concentration of 1.5 *M* was 3.4 of the intermediate value. This result shows that SiO_2 partly intercalates in the interlayer and enlarges basal spacing and also covers the outer surface of the layer (though not completely), thereby resulting in a relatively large surface area.

When the HCl concentration were raised to 6 *M* (not shown in the figure), the basal spacing of the sample decreased and was nearly the same as that of $HLaNb_2O_7 \cdot 2H_2O$, which showed a trend similar to that for titanium. These observations indicate that HCl expels *n*-octylamine in the interlayer by the acid and base reaction and inserts preferentially protons accompanying water, resulting in inhibition of the SiO_2 sol intercalation. Therefore, in this case as well as in the case of titanium, high HCl concentrations (e.g., 6 *M*) are not applicable to SiO_2 pillaring. It can be assumed that of 2 or 3 *M* HCl is appropriate; however, even if the concentration is appropriate, the existence of a large amount of ethanol, i.e., 0.46 mol, does not lead to intercalation of silica sol. Therefore, because ethanol is hydrophilic, the dilution of HCl by ethanol will occur. The relationship between area and HCl concentration with varying amounts of ethanol is summarized in Fig. 3. Samples prepared with small amounts of ethanol with 2 or 3 *M* HCl exhibited basal spacings of 12.2 and 12.4 Å after calcination at 500°C, respectively. The precursor of SiO_2 might be intercalated from this, but the surface areas were 29 and 10 m^2/g, respectively, as shown in Fig. 3a. It appears that the preparation conditions for a small amount of ethanol, i.e., 0.115 mol, with 3 *M* HCl do not lead to a sample with a small surface area. As shown in Fig. 3c a sample prepared with a HCl concentration of 0.1 *M* exhibited a relatively small surface area. It can be considered that the SiO_2 intercalation in the interlayer does not occur because basal spacing of a sample after calcination at 500°C remains the same as that of the HLa after calcination; however, the fact that a surface area of 128 m^2/g was obtained seems to indicate that some TEOS hydrolysis will occur and will cover the outer surface of the layer matrix, leading to not so small a surface area. From the results in Figs. 2 and 3, it can be considered that the relationship between the molar ratios among TEOS, ethanol, and HCl at a concentration of 2 or 3 *M* with a constant amount of HLa intercalated with *n*-octylamine is important to prepare pillared HLa with SiO_2. Therefore, it can be concluded that the optimal preparation conditions are molar ratio of TEOS : ethanol : HCl (2–3 *M*) of 5 : 10 : 0.55 on a base of 1 mol of HLa filled with enough *n*-octylamine.

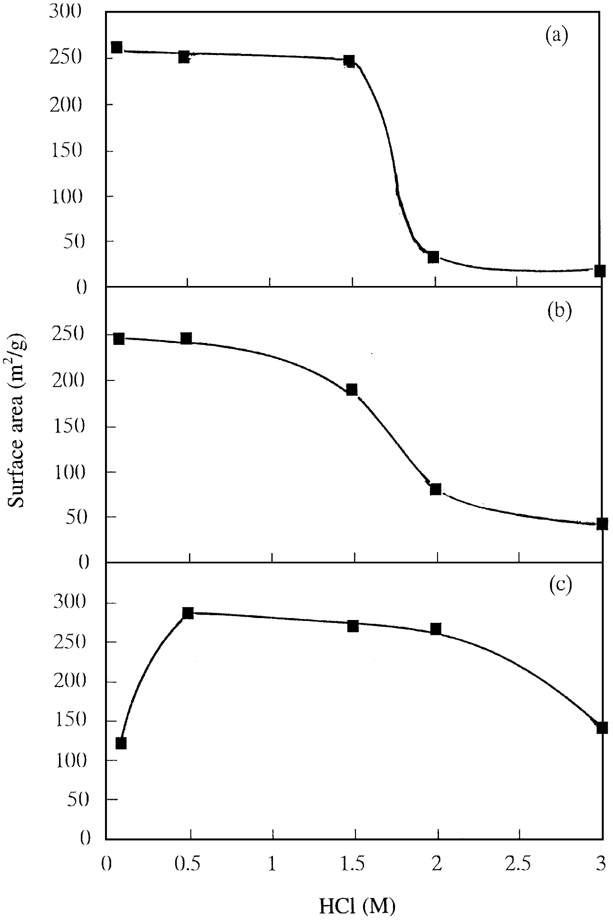

FIG. 3. Relationship between surface area and HC1 concentration with different concentrations ethanol (*M*): (a) 0.115, (b) 0.230, and (c) 0.346. Sample: $HLaNb_2O_7$ pillared with SiO_2.

From the observations mentioned above it appears that HCl promotes the hydrolysis of TEOS and gives protons that accompany water, i.e., H_3O^+, to a sol particle produced by hydrolysis which leads to easy intercalation of the sol and expels *n*-octylamine from the interlayer. On the other hand, however, ethanol functions as an active agent that occludes hydrophobic sol particles from connecting with water molecules, which introduces these particles into the hydrophilic interlayer.

3.4. Thermal Stability of Pillared Materials

Pillared samples with ZrO_2, TiO_2, and SiO_2 that were treated at different temperatures were examined by XRD. As shown in Fig. 4, the XRD patterns of the pillared ZrO_2 and SiO_2 samples treated at 700°C were somewhat distorted by the accompanying decrease in intensity as well as the broadening of the peaks, indicating that the layered structure was being destroyed. In contrast, the TiO_2 pillared sample was relatively stable with respect to temperature, since a variation in the pattern among all temperatures was hard to find.

The results for only the TG-DTA for a ZrO_2 pillared sample are shown in Fig. 5. This was a typical example. A large weight decrease near 100°C accompanied by a large endothermic peak causes the removal of the remaining water in the interlayer, thereby leading to shrinkage in the basal spacing, as shown by a shift in the *d*(001) peak to a high diffraction angle in the XRD pattern. With an increase in temperature from 100 to 800°C, the weight decreased slightly and no DTA peak could be detected. The other two samples also showed behavior similar to that of the ZrO_2 pillared sample.

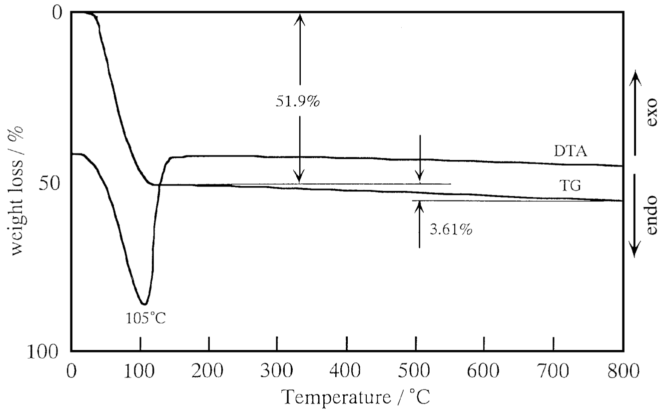

FIG. 5. TG-DTA of ZrO_2 pillared sample.

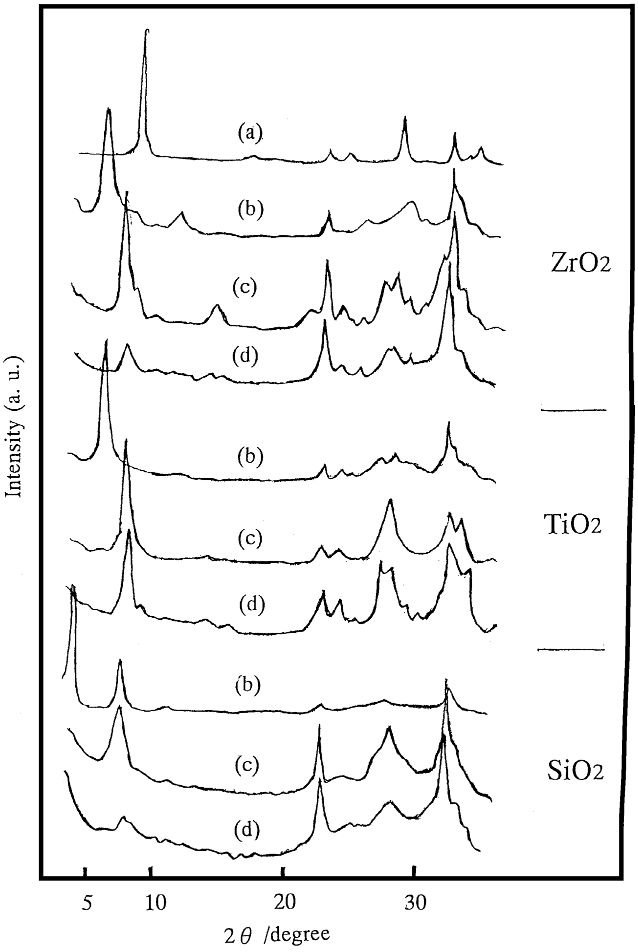

FIG. 4. XRD patterns of the samples calcined at various temperatures. Samples pillared with ZrO_2, TiO_2, and SiO_2. (a) $HLaNb_2O_7$ calcined at 100°C and the samples calcined at (b) 100°C, (c) 500°C, and (d) 700°C.

Consequently, all the samples that were examined appeared to be rather stable until near 800°C, although the samples pillared with ZrO_2 and SiO_2 appeared to be somewhat unstable at high temperatures.

3.5. Pore Size Distribution

The pore size distribution of the HLa and the other three types of pillared samples calcined at 500°C was examined. As expected, all of the samples examined exhibited the presence of a large amount of mesopores with radius >20 Å and a slight pore volume as given in Table 4. The ratio of the micropores of the samples is also given in Table 4 for reference. The pore radii in all of the samples were concentrated in the range 50–200 Å, although there are some differences

TABLE 4

Properties of Catalysts Used in the Dehydration of 1-Butanol and Turnover Frequency at 320°C

Catalyst[a]	Basal spacing (Å)	Surface area (m^2/g)	Acidity (mmol/g)	Pore volume (cm^3/g)	TOF[b]
$HLaNb_2O_7$	10.5	8	1.29	0.034(14.4)[c]	1.9
$TiO_2 \cdot HLaNb_2O_7$	11.3	15	0.50	0.060(6.1)	8.2
$SiO_2 \cdot HLaNb_2O_7$	12.2	78	0.82	0.082(29.4)	5.4
$ZrO_2 \cdot HLaNb_2O_7$	12.3	9	0.32	0.035(6.1)	5.6

[a] Catalysts were calcined at 500°C in air for 2 h.

[b] Turnover frequency (molecules/site · s).

[c] Figures in parentheses are the percentages of micropore volume below 20 Å of radius.

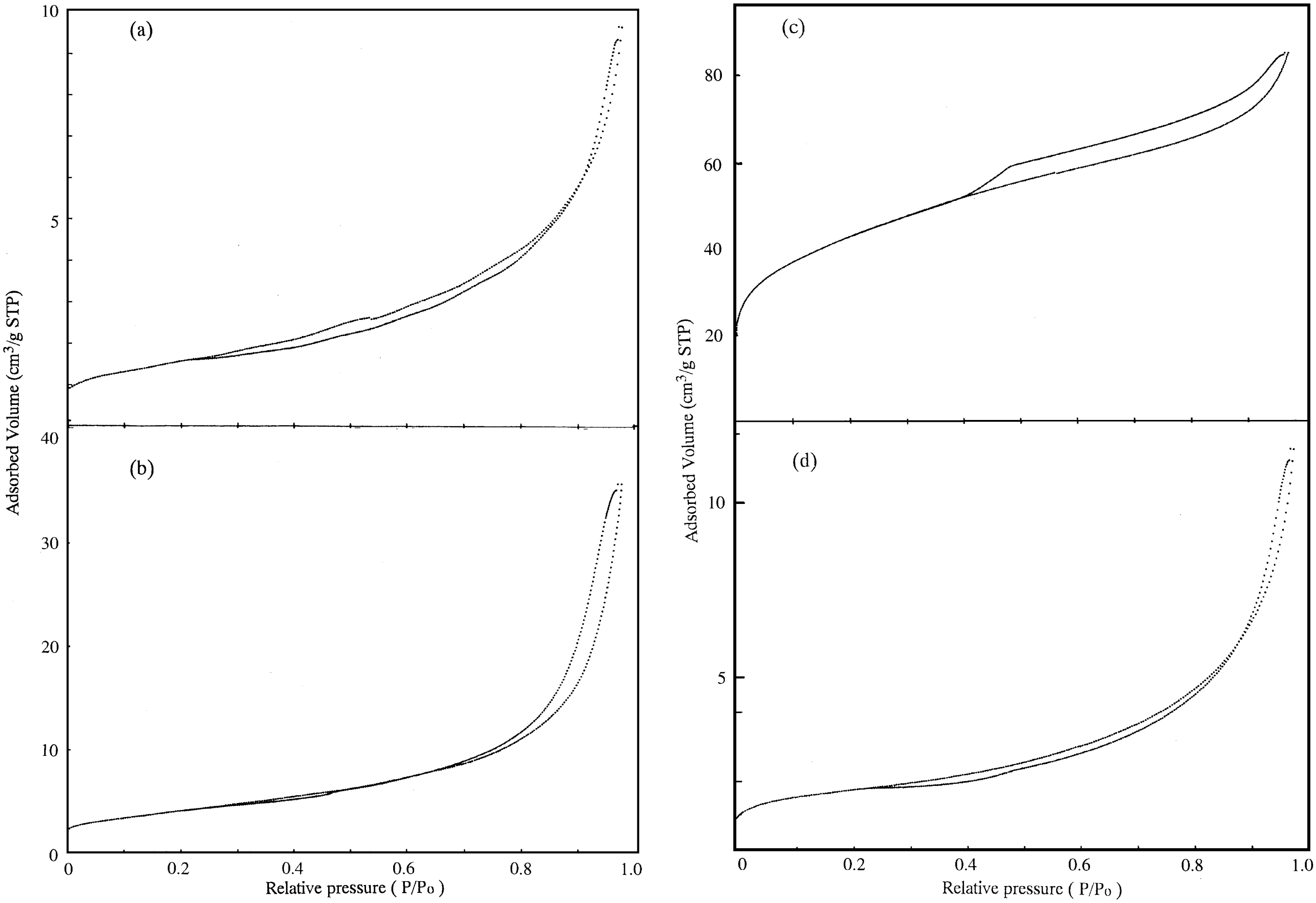

FIG. 6. Nitrogen adsorption–desorption isotherms of (a) $HLaNb_2O_7$ and samples pillared with (b) TiO_2, (c) SiO_2, and (d) ZrO_2.

in distribution. Nitrogen adsorption–desorption isotherms of the HLa and pillared samples are shown in Fig. 6. The sorption isotherm that was observed in all of the samples is similar to type IV in BDDT (13) classification. TiO_2 and SiO_2 pillared samples exhibited a hysteresis loop in a relatively high P/P_0 region; however, the HLa and ZrO_2 pillared samples exhibited it in rather a low region. The hysteresis loop curves are all similar to type B according to de Boer classification; however, the hysteresis of the latter samples is not as clear as that of the former two. The samples that show this type (especially the former two) are those that possess slit-shaped pores and spaces between the parallel plates. We suspected that molecules would be able to enter or leave the former samples relatively easily and would have a difficult time doing so in the latter samples.

3.6. Dehydration of n-Butanol on Pillared Catalysts

The catalytic performance of the pillared samples prepared according to the previously mentioned methods was compared with the catalytic activity from the dehydration of 1-butanol. The properties of the samples used as catalysts are summarized in Table 4. Both the basal spacing and the surface area of the pillared catalysts increased due to pillaring. The extent of increase in the SiO_2 pillared catalyst was especially remarkable. The acidity of the HLa catalysts was the highest, but its value is doubtful, because there was so much NH_3 adsorption that it may have led to an increase in basal spacing. On the other hand, the pillared catalysts cannot intercalate NH_3 enough to increase basal spacing, which produced a small amount of NH_3 adsorption compared with that on the HLa. Consequently, it may be assumed that it is valuable to compare the acidity among the three pillared catalysts. The acidity of the HLa catalyst is given in Table 4.

The dehydration rate of 1-butanol gradually decreased from the initial stage and then, after 1 or 2 h, reached a stationary state. This behavior was detected all over the catalysts examined. The activity of the catalysts was therefore defined by the values of the stationary state in this study. The reaction rates at the stationary state were rather lower than were those in the previous paper (9), because the reaction temperature was lowered by 30°C in this study to avoid 100% conversion. The reaction products were primarily butenes. A very small amount of *n*-butyl ether ($\lesssim$1%)

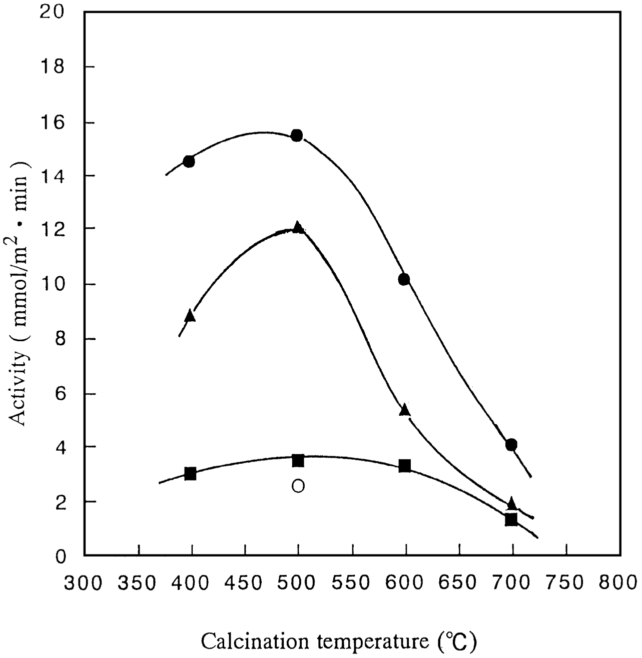

FIG. 7. Dehydration results on the pillared catalysts calcined at various temperatures. Catalyst pillared with (▲) ZrO_2, (●) TiO_2, (■) SiO_2, and (○) $HLaNb_2O_7$. Reaction temperature: 320°C.

was also detected. Of the butenes, mainly 1-butene was produced and this was almost in agreement with the previous paper (9). The results obtained for the SiO_2 pillared catalyst, however, were an exception. On the TiO_2 pillared catalyst, 1-butene selectivity was 68.7% and the ratio of *trans*- to *cis*-2-butene was 1.6. The other catalysts also showed both similar selectivity and similar *trans*- to *cis*-2-butene ratios. The SiO_2 pillared catalyst in the previous paper (9) exhibited a selectivity of ca. 70% to 2-butene; however, in this study a larger amount of 1-butene was produced, probably due to both the low reaction temperature and the use of a different kind of catalyst. With the dehydration of 1-butanol on acid-activated montmorillonite 2-butene was preferentially produced (14) by a pulse reactor. The difference in selectivity is probably due to the fact that the acid strength of the catalyst can promote isomerization from 1- to 2-butene.

The reaction activity on the pillared catalysts calcined at various temperatures for 2 h in air is shown in Fig. 7. When the catalysts were calcined at 500°C, maximum activity was obtained all over the pillared catalysts. By comparing the maximum activity of each catalyst, we can see that the TiO_2 pillared catalyst was the most active. Considering the fact that was occurring on the acidic site, the number of 1-butanol molecules reacted per unit number of acidic sites and per unit time (second), (i.e., turnover frequency, TOF) was calculated and is also given in Table 4. The TOF of the TiO_2 pillared catalyst was also the highest and those of the SiO_2 and ZrO_2 pillared catalysts were nearly the same. Therefore, the high activity of the TiO_2 pillared catalyst is caused by the interaction of TiO_2 intercalated in the interlayer with the host matrix. Both the SiO_2 and ZrO_2 pillared catalysts showed higher activity than the HLa catalyst. Here too the enhancement of this activity can also be ascribed to the interaction of SiO_2 or ZrO_2 with the host matrix, although it can be expected that this interaction will be weaker than that of TiO_2 with the host matrix. With an increase in calcination temperature to above 500°C, the activity decreased remarkably as shown in Fig. 7. This is probably due to a decrease of the concentration in the active sites (i.e., the acidic sites), accompanied by a decrease in surface area. The amount of decrease was small over 500°C.

The ratio of mesopores in the TiO_2 pillared catalyst is higher than that of the other catalysts (see Table 4). Consequently, 1-butanol or product molecules can easily enter or exit the pore. This may cause this high level of activity. To provide evidence that this enhancement of activity is related to the interaction of TiO_2 with the host matrix, two kinds of catalysts were prepared: one was a HLa catalyst impregnated in a titanium nitrate aqueous solution and the other was a mechanical mixture of HLa and TiO_2 (anatase) prepared by the hydration of TIO using the same method as was used for its intercalation. The amount of TiO_2 added is the same as the amount intercalated in the interlayer, i.e., a molar ratio of TiO_2 : HLa of 0.9 : 1. The results of the reaction on these catalysts including HLa are shown in Fig. 8. High activity was observed on the pillared

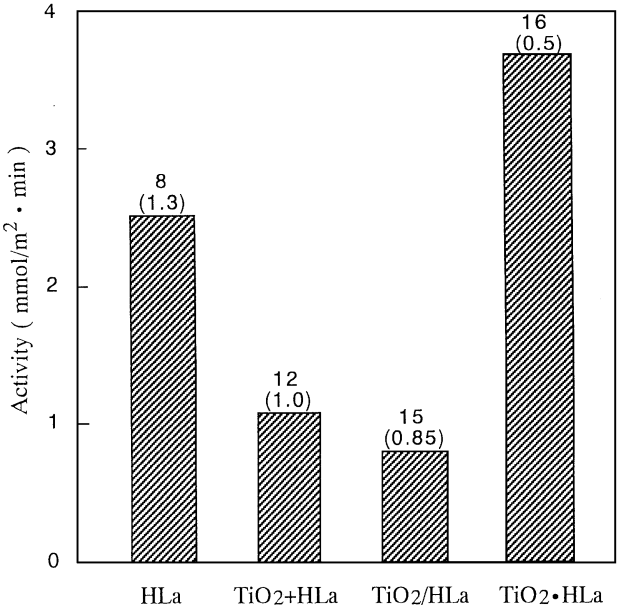

FIG. 8. Dehydration results on various TiO_2–$HLaNb_2O_7$ catalysts. TiO_2 + HLa, mechanical mixture (0.9 to 1 by weight) of TiO_2 and $HLaNb_2O_7$; TiO_2/HLa, $HLaNb_2O_7$ impregnated in a titanium nitrate aqueous solution; TiO_2 · HLa, $HLaNb_2O_7$ pillared with TiO_2. All catalysts were calcined at 500°C in air for 2 h. The amount of TiO_2 is 45%. Figures on the bar graph indicate surface area (m^2/g), and those in parentheses, acidity (mmol/g).

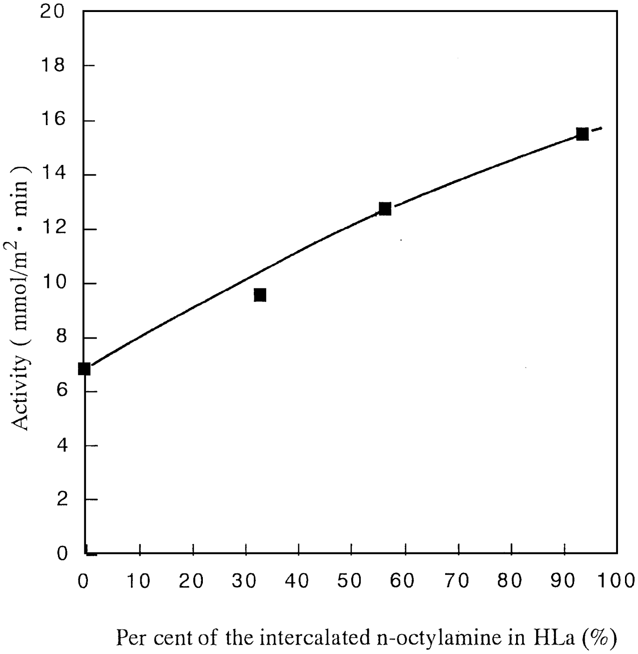

FIG. 9. Dehydration results on the catalysts pillared with TiO_2, which were prepared from $HLaNb_2O_7$ intercalated with varying amounts of *n*-octylamine.

catalysts, indicating that the above hypothesis is true. This hypothesis can be also substantiated from the following experimental results. TiO_2 pillared catalysts were prepared from HLa that had been filled with different amounts of *n*-octylamine (see Table 3). As shown in Fig. 9, the catalysts prepared with a small amount of *n*-octylamine (i.e., small amount of TiO_2 intercalated) showed low activity, indicating a low concentration of the active sites. Even with similar SiO_2 or ZrO_2 interactions with the host matrix, the active sites that were formed by the TiO_2 pillared catalyst were superior to the former. This difference is probably due to the existence of acidity as well as its strength. As illustrated in Fig. 10, the temperature-programmed desorption (TPD) profile for the TiO_2 pillared catalyst showed desorption peaks at 180°C; this may correspond to acidity with moderate strength. On the other hand, SiO_2 pillared catalyst is rather rich in stronger acid sites and ZrO_2 pillared catalyst has relatively weak acid sites. The HLa catalyst profile is unique and its acidity is the highest; however, the dehydration activity was low. This may be due to the less effective utilization of the active sites in the pore.

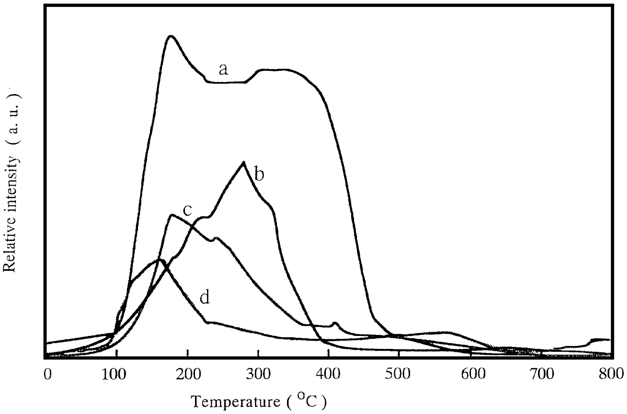

FIG. 10. TPD profiles of NH_3 adsorbed on (a) $HLaNb_2O_7$ and catalysts pillared with (b) SiO_2, (c) TiO_2, and (d) ZrO_2.

SiO_2 pillared catalyst has a relatively wide surface area and large acidity with respect to both strength and amount in comparison with other pillared catalysts. In fact, the dehydration activity per unit gram for the SiO_2 pillared catalyst was higher than that for other catalysts; however, the activity per unit surface area was the lowest due to the enlargement of the surface area by pillaring. If both TiO_2 and ZrO_2 pillared catalysts of large surface area are prepared, their activity will decrease and/or reach the same level as that of the SiO_2 pillared catalyst. The area of the desorption peaks decreased in the following order: SiO_2, TiO_2, and ZrO_2 pillared catalysts. The decrease in the concentration of acid sites is in the same order.

In conclusion, it is clear that, when TiO_2, SiO_2, or ZrO_2 is pillared into the layered host material $HLaNb_2O_7$, a highly active catalyst for the dehydration of 1-butanol is obtained.

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REFERENCES

1. Barrer, R. M., and Macload, D. M., *Trans. Faraday Soc.* **52**, 1290 (1955).
2. Brindley, G. W., and Semples, R. E., *Clay Miner.* **12**, 229 (1977).
3. Yamanaka, S., and Brindley, G. W., *Clay Clay Miner.* **27**, 119 (1979).
4. Goparakrishnan, J., Vasudeva, B., and Ravean, B., *Mater. Res. Bull.* **22**, 413 (1987).
5. Matsuda, T., Fujita, T., and Kojima, M., *J. Mater. Chem.* **1**, 559 (1991).
6. Matsuda, T., Fujita, T., Miyamae, N., Takeuchi, M., and Kunou, I., *J. Mater. Chem.* **4**, 955 (1994).
7. Matsuda, T., Fujita, T., Miyamae, N., and Takeuchi, M., *Bull. Chem. Soc. Japan* **66**, 1548 (1993).
8. Matsuda, T., Fujita, T., Miyamae, N., Takeuchi, M., and Kanda, K., *Bull. Chem. Soc. Japan* **66**, 1548 (1993).
9. Matsuda, T., Udagawa, M., and Kunou, I., "Catalysis by Microporous Materials," Studies in Surface Catalysis, Vol. 94, p. 71. Elsevier, Amsterdam, 1995.
10. Yamanaka, S., and Hattori, S., *Zeoraito [zeolite]* **6**, 10 (1989). [in Japanese]
11. Hattori, H., Tada, A., Kikuchi, E., Segawa, K., and Imizu, Y., "Atarasii Sjokubai Kagaku" ["New Catalytic Chemistry"], p. 144. Sankyo, Tokyo, 1988.
12. Ozaki, A., *et al.* (Eds.), "Shokubai Chousei Kagaku" ["Preparation Chemistry of Catalysts"], p. 28. Kodansha, Tokyo, 1980.
13. Brunauer, S., Deming, L. S., Deming, W. E., and Teller, E., *J. Am. Chem. Soc.* **62**, 1723 (1940).
14. Mokaya, R., and Jones, W., *J. Catal.* **153**, 76 (1995).