Preparation of Silica Pillared $Ca_2Nb_3O_{10}$ and Its Photocatalytic Activity

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Silica pillared $Ca_2Nb_3O_{10}$ was prepared from the layered perovskite $KCa_2Nb_3O_{10}$ via alkylammonium ion intercalated $Ca_2Nb_3O_{10}$. The obtained materials were characterized by XRD, TEM, NMR, and BET measurements. The interlayer spacing increased in parallel with the length of the alkyl chain of intercalated alkylamines although the BET surface area was not reflected in this increase. The photocatalytic activity of the silica pillared $Ca_2Nb_3O_{10}$ was studied for H_2 evolution from aqueous alcohol solutions. Marked increase by ca. 30 times in activity was obtained for silica pillared $Ca_2Nb_3O_{10}$ compared with the original $HCa_2Nb_3O_{10}$ in an aqueous propanol or butanol solution, while no difference was observed in an aqueous methanol solution. The result was interpreted in terms of the intercalation of the reactant alcohol molecules into the interlayer space.

Introduction

Recently, several layered metal oxides have been demonstrated to be highly active photocatalysts under bandgap irradiation.[1−8] One of the characteristics of such layered photocatalysts is to utilize intercalated molecules as reactants. For example, $A_4Nb_6O_{17}$ (A = K, Rb) with loading of ultrafine Ni metal particles at the interlayer space shows high activity of an overall photodecomposition of water, e.g., 10% of quantum efficiency on Ni (0.1 wt %)−$Rb_4Nb_6O_{17}$ under irradiation at 330 nm.[1,4,5,7]

Layered perovskite type niobates, $AB_{n-1}Nb_nO_{10}$ (A = K, Rb, etc.; B = La, Ca, Pb, etc.; $n = 2$ or 3), also possess high activity for photocatalytic H_2 evolution from an aqueous methanol solution.[3,8] It should be noted that the family of layered perovskite type niobates has a wide variety of derivatives produced by replacing A and B sites with various metal cations. For example, when Pb was incorporated in the B site, $RbPb_2Nb_3O_{10}$, photocatalytic H_2 evolution under visible light irradiation ($\lambda > 420$ nm) proceeded.[8] H_2 evolution rates of the niobates in an aqueous methanol solution was noticeably increased by substituting H^+ ions for the alkali-metal cations at the interlayer space because the intercalation of the reactant molecules, water and methanol, became possible.[9] In general, however, reactant molecules including water are hardly intercalated into the interlayer space of the layered perovskite type niobates except for the H^+ forms, which is probably due to the high charge density of the niobate layer. This makes the proper modification and utilization of the interlayer space difficult to prepare further functionalized photocatalysts.

One of the approaches to overcoming the difficulty is to mechanically expand the interlayer space by introducing “pillar” material. Recently, several procedures for introducing pillars into various layered compounds have been reported.[10] A frequently used method to introduce oxide pillars is to intercalate bulky multinuclear ions as precursors by the ion-exchange method.[10] When this method was applied to layered perovskite type niobates, however, only the stuffed structure of the oxide where multinuclear ions densely occupied the interlayer space was obtained probably because of the high charge density,[11,12] and the interlayer was not available for chemical reactions. It was recently reported by Landis et al.[13] that construction of pillars of silica was possible even for the oxides with high charge density by hydrolysis of intercalated tetraethyl orthosilicate (TEOS) after expansion of the interlayer space by alkylammoiun ions with long alkyl chains. It was also found that the same type of silica pillars were possible to be formed by employing (4-aminobutyl)-triethoxysilane[14−17] or (4-aminopropyl)trimethoxysilane.[18]

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In this study, a similar procedure to that of Landis et al. was applied to prepare a silica pillared $Ca_2Nb_3O_{10}$, and characterization of the obtained materials was carried out together with the estimation of the photocatalytic abilities.

Experimental Section

Layered Materials. $KCa_2Nb_3O_{10}$ was prepared by heating a stoichiometric mixture of K_2CO_3, $CaCO_3$, and Nb_2O_5 in a platinum crucible in the air at 1473 K for 10 h. The XRD pattern coincided with that in the literature.[19-21] The H^+-exchanged form, $HCa_2Nb_3O_{10}$, was prepared by ion exchange of $KCa_2Nb_3O_{10}$ (20 g) in 5 mol dm^{-3} HNO_3 (400 cm^3) solution for 72 h at room temperature (degree of H^+ exchange > 95%). Alkylamines (alkyl = octyl, dodecyl, and octadecyl, in 2 equiv) were intercalated into $HCa_2Nb_3O_{10}$ (20 g) by refluxing in heptane (100 cm^3) for 1−3 days (bath temperature 403 K).

Pillaring. A method similar to that previously reported by Landis et al. was employed.[13] An alkylammonium-exchanged niobate (20 g) was stirred in TEOS (100 cm^3) at 353 K for 72 h, followed by filtering. The filtrate was washed with ethanol and then dried. Calcination at 773 K was conducted at 773 K for 4 h for the once-treated sample. The TEOS treatment was repeated twice without calcination for the twice-treated sample. The twice-treated sample was finally calcined at 773−973 K for 4 h in air. The difference of once- and twice-treated samples is mentioned in Results and Discussion.

Characterization. For characterization of the products, X-ray powder diffraction (XRD, Rigaku Geigerflex RAD-B, Cu Kα), X-ray photoelectron spectroscopy (XPS, Shimazu ESCA 750), transmission electron microscopy (TEM, Hitachi HF-2000, 200 kV), and ^{29}Si CP/MAS NMR (JEOL GX-270) were used.

Photocatalytic Reaction. Photocatalytic reactions were carried out in an airfree closed gas circulation system with a reaction cell of inner irradiation type made of Pyrex (250 cm^3). The catalyst (1 g) was dispersed in an aqueous solution (330 cm^3) by magnetic stirring and was irradiated under an Ar atmosphere (about 13.3 kPa) by a high-pressure Hg lamp (450 W). H_2 evolution was carried out in a 10 vol % aqueous alcohol solution. Pt was loaded by a photodeposition method with addition of H_2PtCl_6 into the aqueous alcohol solution.[22,23] The amount of evolved gas was analyzed by gas chromatography (MS-5A column, Ar carrier) through a gas sampler (10 cm^3) which was directly connected to the reaction system to avoid any contamination from the air.

Results and Discussion

(1) Characterization of Silica Pillared $Ca_2Nb_3O_{10}$.

XRD. Materials obtained at each step of the silica pillaring process were examined by XRD. The XRD pattern of $HCa_2Nb_3O_{10}$ is shown in Figure 1a. The (001) reflection indicated the c-axis length of 1.57 nm. The interlayer spacing was increased to 3.26 nm by octylamine intercalation as shown in Figure 1b, a result that coincided with a previously reported one.[9] The sample after the first TEOS treatment and calcination at 773 K (once-treated sample) showed a considerable shrinkage of the interlayer spacing; the weak and broad (001) reflection was observed at almost the same position as that of $HCa_2Nb_3O_{10}$ (Figure 1c). Therefore, it was found that the pillars formed by first TEOS treatment were not stable after calcination at 773 K. However, as observed in Figure 1d, the sample after the second TEOS treatment followed by calcination at 773 K (twice-treated sample) retained the *c*-axis length of 2.93 nm which was longer by 1.36 nm than that of the original $HCa_2Nb_3O_{10}$. The length of the interlayer space appeared to be 1.77 nm after subtracting the length of a niobate sheet (1.16 nm). The difference between the once- and twice-treated samples by TEOS is discussed below on chemical components of the pillars with the results of NMR. It is noted that (*hk*0) reflections appeared at the same position for all samples, indicating that the intralayer structure of the niobate sheet was maintained through the above treatments.

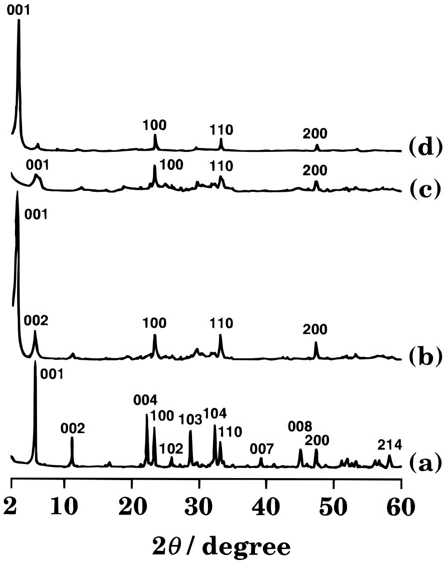

Figure 1. XRD patterns of modified $KCa_2Nb_3O_{10}$. (a) $HCa_2Nb_3O_{10}$, (b) $(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$, (c) silica pillared $Ca_2Nb_3O_{10}$ (TEOS treatment × 1), and (d) silica pillared $Ca_2Nb_3O_{10}$ (TEOS treatment × 2).

The effect of the calcination temperature after the second TEOS treatment was then studied by XRD as shown in Figure 2. After calcinations at 873 and 973 K for 4 h the c-axis lengths decreased to 2.50 and 2.00 nm, respectively. When the sample was calcined at 573 K for 48 h, although the c-axis length was the same as that calcined at 773 K, the color was gray. Therefore, the calcination condition was fixed at 773 K for 4 h to maintain the interlayer spacing and to remove completely the alkylamine residual.

TEM, XPS, and NMR. The obtained silica pillared $Ca_2Nb_3O_{10}$ was characterized by TEM, XPS, and NMR. A high-resolution TEM photograph is shown in Figure 3. A calcium niobate layer ($Ca_2Nb_3O_{10}^-$) with a perovskite structure was observed as dark triple stripes. A white colored interlayer space of 1.6 nm thickness was observed between calcium niobate layers of 1.2 nm thickness. These values coincided well with those obtained by XRD. Any particles or aggregates of silica were not identified by our TEM study.

XP spectra of $HCa_2Nb_3O_{10}$ and silica pillared $Ca_2Nb_3O_{10}$ via octylamine intercalation were compared. New peaks attributed to Si 2s and 2p, and an additional peak of O 1s at higher binding energy were observed

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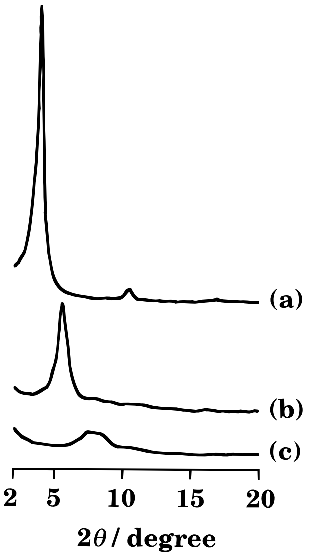

Figure 2. Dependence of *c*-axis length upon the calcination temperature of silica pillared $Ca_2Nb_3O_{10}$ calcinated for 4 h in air at (a) 773, (b) 873, and (c) 973 K.

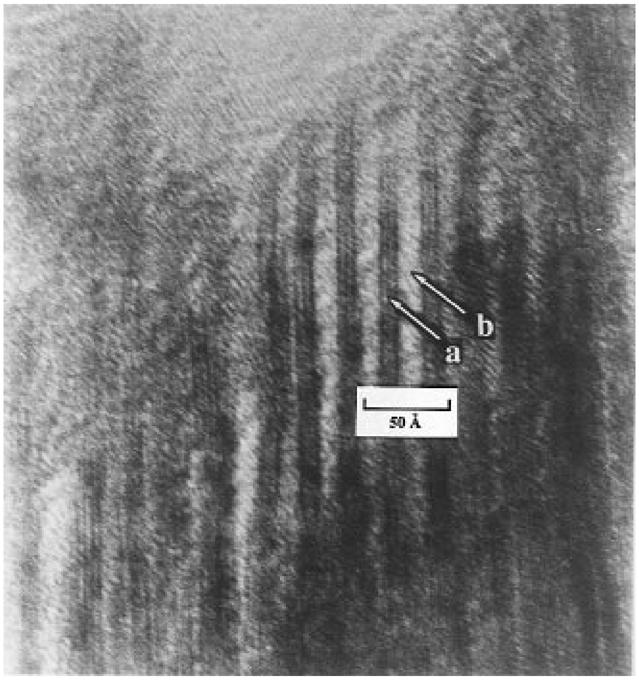

Figure 3. TEM photograph of silica pillared $Ca_2Nb_3O_{10}$ (352 × 385 Å^2). (a) $Ca_2Nb_3O_{10}^-$ layer and (b) interlayer.

for the pillared sample. From the chemical shifts, these peaks were assigned to silica, but there was no appreciable difference in peak intensities of the other peaks between two spectra, indicating no significant amount of segregation of silica at the external surface for the silica pillared $Ca_2Nb_3O_{10}$. Actually the estimated ratio of Si and Nb at the external surface, with taking into account the relative sensitivity, was Nb:Si = 1:0.71.

In Table 1 results of $^1H-^{29}Si$ CP/MAS NMR of $(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$ during TEOS treatment are summarized with the assignment of each peak. The numbers 0−4 indicate the number of silicon bonding to the relevant SiO_4 unit. The sample after the first TEOS treatment possessed two peaks at −88.4 and −100.5 ppm, while a single peak at ca. −100 ppm appeared for the sample after the second TEOS treatment and also for that after calcination at 773 K. The peak at −88.4 ppm and those around −100 ppm are assigned to Q^2 and Q^3 (for the meaning of the abbreviation Q^n, see Table 1[24]). It is noted that no appreciable peak assigned to Q^4 was observed for all samples. It was also found that neither Q^0 nor Q^1 was observed for any of the samples. From these results, hydrolysis of TEOS in the interlayer space proceeded during the TEOS treatment. Q^2 appeared for the sample after the first TEOS treatment and disappeared after the second TEOS treatment. It was suggested, therefore, the hydrolysis after the first TEOS treatment was not sufficient to make a stable silica pillar after the calcination. It was also found that the stable SiO_2 pillar mainly consisted of Q^3 Si.

Effect of Alkyl Chain Length of Intercalated Alkylamines. In the same manner as in case of octylammonium ion ($C_8H_{17}NH_3^+$), dodecylammonium ion ($C_{12}H_{25}NH_3^+$) and octadecylammonium ion ($C_{18}H_{37}NH_3^+$) were intercalated before TEOS treatment. All samples were treated twice by TEOS and were calcined at 773 K. The *c*-axis lengths and BET surface areas are summarized in Table 2. The *c*-axis length after the calcination increased with the alkyl chain length of the alkylamines as reported by Landis et al.[13] BET surface areas of pillared materials greatly increased from the unpillared starting material, $HCa_2Nb_3O_{10}$. The largest BET surface area was measured for pillared $Ca_2Nb_3O_{10}$ with $C_8H_{17}NH_3^+$ as a precursor. Even though *c*-axis length was increased with increasing the length of alkyl groups of alkylammonium precursor, BET surface area was not increased or even decreased. This is probably due to an increase in pillar diameter.

(2) Photocatalytic Activity of Silica Pillared $Ca_2Nb_3O_{10}$. *H_2 Evolution from an Aqueous Methanol Solution.* The rates of photocatalytic H_2 evolution as obtained for an aqueous methanol solution are compared in Figure 4 between $HCa_2Nb_3O_{10}$ and silica pillared $Ca_2Nb_3O_{10}$ prepared from $(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$. The pillared catalyst was less active (400 μmol h^{-1}) than $HCa_2Nb_3O_{10}$ (2200 μmol h^{-1}) without Pt loading. Pt loading, however, markedly enhanced the activity of the silica pillared $Ca_2Nb_3O_{10}$ and a comparable (or even higher) rate of H_2 evolution (10800 μmol h^{-1}) with that of Pt-loaded $HCa_2Nb_3O_{10}$ (8400 μmol h^{-1}) was obtained. From our previous work,[3] it is known that $HCa_2Nb_3O_{10}$ intercalates methanol and oxidizes it into CO_2 at the interlayer space.

The lower rate of H_2 evolution of silica pillared $Ca_2Nb_3O_{10}$ than $HCa_2Nb_3O_{10}$ without Pt loading may be interpreted as follows: silica is an inert material for photocatalytic H_2 evolution and it blocks the active sites, especially H_2 evolution sites of $Ca_2Nb_3O_{10}^-$ layers. An efficient catalyst for H_2 evolution was obtained by introduction of Pt, because the disadvantage was overcome probably due to the high mobility of photoexcited electrons that migrate to Pt sites.

Rates of H_2 evolution from an aqueous methanol solution were compared between three silica pillared $Ca_2Nb_3O_{10}$ catalysts prepared from different alkylammonium-exchanged precursors. Among them with Pt loading, the catalyst prepared from $(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$ with the largest surface area, 200 m^2 g^{-1}, showed the highest H_2 evolution rate, 10 800 μmol h^{-1},

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Table 1. Results of $^1H-^{29}Si$ CP/MAS NMR during TEOS Treatment of $(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$ and Type and Chemical Shift of Solid Silicates[a]

sample	chemical shift	
after the first TEOS treatment	−88.4 ppm (Q^2)	−100.5 ppm (Q^3)
after the second TEOS treatment		−101.6 ppm (Q^3)
calcination of twice treated by TEOS (773 K)		−98.6 ppm (Q^3)

type of silicon−oxygen tetrahedra	Q^0 single	Q^1 end group	Q^2 middle group	Q^3 branching group	Q^4 cross-linking group
structure	O^- $^-OSiO^-$ O^-	O^- $SiOSiO^-$ O^-	O^- $SiOSiOSi$ O^-	Si O SiOSiOSi O^-	Si O SiOSiOSi O Si
^{29}Si chemical shift range from Me_4Si	−60 to −83	−67 to −85	−70 to −93	−90 to −102	−105 to −120

[a] Reference 24.

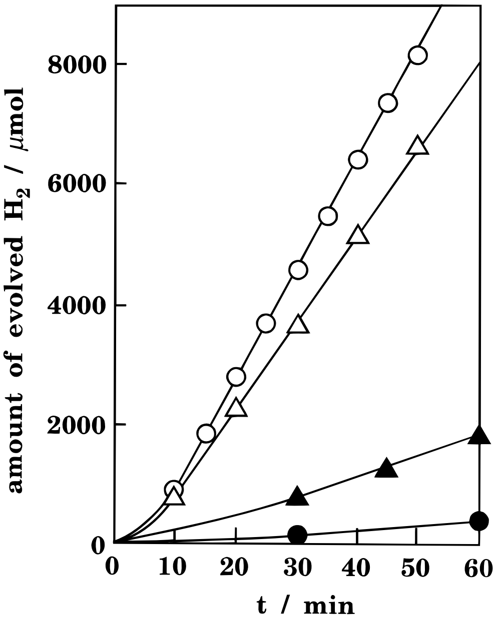

Figure 4. H_2 evolution from an aqueous methanol solution (10 vol %) over modified $KCa_2Nb_3O_{10}$. (▲) $HCa_2Nb_3O_{10}$; (●) silica pillared $Ca_2Nb_3O_{10}$; (△) Pt(0.1 wt %)−$HCa_2Nb_3O_{10}$; (○) Pt(0.1 wt %)−silica pillared $Ca_2Nb_3O_{10}$.

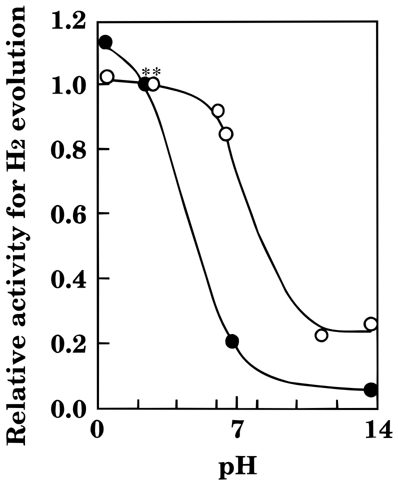

Figure 5. Dependence of H_2 evolution rate over Pt(0.1 wt %)−silica pillared $Ca_2Nb_3O_{10}$ and Pt(0.1 wt %)−$HCa_2Nb_3O_{10}$ upon pH from an aqueous methanol solution. (○) Pt(0.1 wt %)−silica pillared $Ca_2Nb_3O_{10}$; (●) Pt(0.1 wt %)−$HCa_2Nb_3O_{10}$. (*) No added electrolyte (pH = 3).

Table 2. *c*-Axis Length and Surface Area of Silica Pillared $Ca_2Nb_3O_{10}$

precursor	*c*-axis length (nm) before calcination	after calcination	BET surface area ($m^2\ g^{-1}$)
$(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$	3.26	2.93	200
$(C_{12}H_{25}NH_3)Ca_2Nb_3O_{10}$	3.92	3.36	180
$(C_{18}H_{37}NH_3)Ca_2Nb_3O_{10}$	5.00	4.31	50
$HCa_2Nb_3O_{10}$	1.57		2

Table 3. Rate of H_2 Evolution from Aqueous Alcohol Solutions (μmol h^{-1})

alcohol	catalyst[a] $HCa_2Nb_3O_{10}$	silica pillared $Ca_2Nb_3O_{10}$	TiO_2
MeOH	4700	8100	4000
EtOH	380	5500	5200
PrOH	40	1100	3500
BuOH	30	1060	2800

[a] Pt(0.1 wt %) was loaded from H_2PtCl_6.

and the one prepared from $(C_{18}H_{37}NH_3)Ca_2Nb_3O_{10}$, with a smallest surface area, 50 $m^2\ g^{-1}$, exhibited the lowest rate, 6700 μmol h^1.

Dependence on the Kinds of Alcohols as Reducing Reagents. In Table 3, H_2 evolution rates are compared between $HCa_2Nb_3O_{10}$ and a silica pillared $Ca_2Nb_3O_{10}$ prepared from $(C_8H_{17}NH_3)Ca_2Nb_3O_{10}$ in several aqueous alcohol solutions. The rates for TiO_2 (P25) are also shown as a reference. In all cases 0.1 wt % of Pt was loaded by a photodeposition method. In the case of TiO_2 no remarkable difference of H_2 evolution rates was observed, although an aqueous ethanol solution gave the highest rate. For $HCa_2Nb_3O_{10}$, however, the rate of H_2 evolution dramatically decreased from methanol to ethanol and further for propanol and butanol. A similar result was previously reported,[1] and it was interpreted as the difference of the facility for the intercalation of each alcohol, i.e., methanol easily intercalates into the highly ionic interlayer space but alcohols with longer alkyl chains occurs less easily. Compared with $HCa_2Nb_3O_{10}$, the rates were remarkably increased for silica pillared $Ca_2Nb_3O_{10}$ in aqueous ethanol, propanol, and butanol solutions. This clearly indicates that in a silica pillared $Ca_2Nb_3O_{10}$ alcohols with longer alkyl chains are also intercalated and oxidized at the expanded interlayer space.

Effect of pH. Shown in Figure 5 is the relative rates of H_2 evolution from methanol aqueous solutions with various pH values on $HCa_2Nb_3O_{10}$ and a silica pillared $Ca_2Nb_3O_{10}$. For both catalysts 0.1 wt % of Pt was loaded. The pH of the solution was adjusted by HCl or KOH addition. The pH values as immersed in an aqueous methanol solution are indicated by arrows for both catalysts, and the rates of H_2 evolution at those pH's were used for the normalization of the H_2 evolution rates. For both catalysts, the rates of H_2 evolution were slightly increased at the lower pH (pH $\approx$ 0.3), while they decreased markedly at the higher pH region. The decrease of the H_2 evolution rates at the higher pH region for $HCa_2Nb_3O_{10}$ was understood as follows: at pH above 7, KOH was added and the ion-exchange reaction of H^+ and K^+ at the interlayer space proceeded in the solution, which inhibited the intercalation of water and methanol into the catalyst. The XRD pattern after the reaction confirmed the decrease of the interlayer spacing, the *c*-axis length decreased from 1.57 to 1.46 nm. On the other hand, in the case of a silica pillared $Ca_2Nb_3O_{10}$ the H_2 evolution rate were still high even at pH = 7. At this pH most H^+ ions were substituted by K^+ ions. This result, therefore, clearly indicates that methanol is still possible to intercalate into a silica pillared $Ca_2Nb_3O_{10}$ at pH = 7 due to the expanded interlayer spacing. Another point to be noted is that the H_2 evolution reaction proceeds efficiently without a large amount of H^+ ions in the interlayer space. In other words, the controlling factor of the H_2 evolution reaction is the intercalation of methanol molecules. When the pH became higher than 7, however, the rate of H_2 evolution decreased even for a silica pillared $Ca_2Nb_3O_{10}$. XRD revealed that in the high-pH region the silica pillar dissolved and the pillar structure collapsed. After the reaction the *c*-axis length decreased from 2.93 to 1.81 nm. This again confirms the importance of the intercalation of the reactant molecules.

Summary

In this study, some silica pillared $Ca_2Nb_3O_{10}$ were characterized by several methods and their photocatalytic H_2 evolution was examined. Main results are summarized as follows:

The interlayer spacing of the prepared silica pillared $Ca_2Nb_3O_{10}$ was expanded and showed a porous structure.

Silica existed dominantly in the interlayer space and was found to mainly consist of Q^3 Si by XPS and $^1H-^{29}Si$ CP/MAS NMR.

The photocatalytic activity of H_2 evolution rate of a silica pillared $Ca_2Nb_3O_{10}$ from aqueous solutions of alcohols with longer alkyl chains was much higher than that of $HCa_2Nb_3O_{10}$. This effect was attributed to the expanded interlayer space which facilitated the intercalation of those alcohols.

The silica pillar was collapsed by calcination above 873 K or in a solution of pH above 11.

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