

Preparation of Porous Niobium Oxides by Soft-Chemical Process and Their Photocatalytic Activity

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A new porous material was prepared from a layered compound $K_4Nb_6O_{17}$, by using a soft-chemical method. Two-dimensional niobate sheets which were obtained from exfoliation of $H^+/K_4Nb_6O_{17}$ were precipitated by MgO fine particles and new composites were synthesized. Porous niobium oxides were obtained by modification of the composites and they showed high photocatalytic activities for H_2 evolution from various alcohol aqueous solutions.

Introduction

One of the layered metal oxides, $K_4Nb_6O_{17}$, is known as a typical photocatalyst for an overall decomposition of water into H_2 and O_2 .^{1–6} As shown in Figure 1, $K_4Nb_6O_{17}$ consists of octahedral units of NbO_6 which form a two-dimensional layered structure via bridging oxygen atoms.^{7,8} The layers are negatively charged, and K^+ ions exist between the layers to compensate for the negative charges of the layers. There exist two types of interlayers (interlayers I and II) alternately, and they are different from each other in their properties of hydration and ion exchange.^{8,9} The unique structure has been considered to enable the $K_4Nb_6O_{17}$ to decompose water by Ni loading. The ion-exchanged $K_4Nb_6O_{17}$ had also photocatalytic activity for H_2 evolution from aqueous MeOH solution, and among them $H^+/K_4Nb_6O_{17}$ shown the highest activity.¹ However, modification of the interlayer space of $K_4Nb_6O_{17}$ is not facile, except for the ion exchange. For example, expansion of the interlayer space by silica pillaring was not accomplished while it was successfully performed for clays and $KCa_2Nb_3O_{10}$.¹⁰ Therefore, the photocatalysis of $K_4Nb_6O_{17}$ is only effective for small molecules such as H_2O and MeOH, and sudden decrease in photoreactivity was found for bulky reactants.

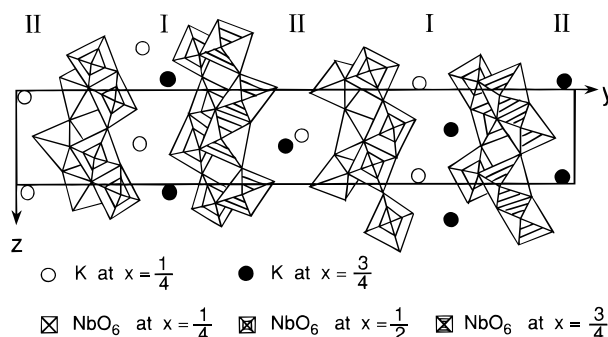


Figure 1. Crystal structure of $K_4Nb_6O_{17}$.

It has been reported by Mallouk et al. that layered metal oxide semiconductors such as $K_4Nb_6O_{17}$ and $CsTi_2NbO_7$ were acid exchangeable and exfoliated with tetra-*n*-butylammonium hydroxide (TBA^+OH^-) solution in much the same way as α -ZrP.^{11,12} The exfoliated niobate sheets could be precipitated by addition of cations such as H^+ .¹³ Application of this exfoliation–precipitation method may enable us to create new types of materials; porous materials with large surface area or new types of composite consisting of different kinds of sheet. Functionalities involving catalysis of such materials have not been reported although interesting properties and unique catalysis may be found.

In this paper, construction of new type of layered compound is attempted by exfoliation of the $K_4Nb_6O_{17}$ sheets and by precipitation with MgO fine particles. The obtained material was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), BET surface area and pore size distribution, and the photocatalytic abilities of the modified composites are studied.

Experimental Section

Materials. $K_4Nb_6O_{17}$ was prepared by calcination of a stoichiometric mixture of K_2CO_3 and Nb_2O_5 in a platinum crucible at 1473 K in the air for 15 min. The melt mixture

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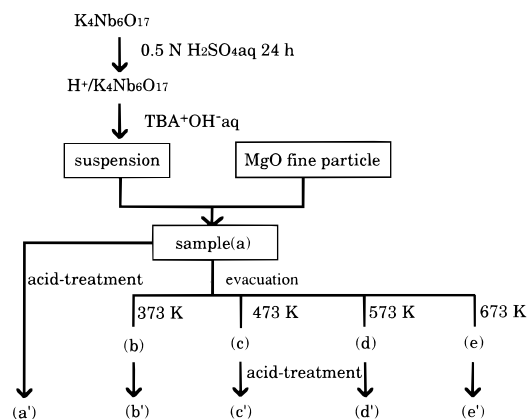


Figure 2. Synthetic process of samples (a)–(e').

was cooled rapidly to room temperature and was pulverized in a mortar to form powder with particle size of 1–10 μm . The proton exchange of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was carried out in 0.5 N sulfuric acid aqueous solution at room temperature for 24 h. Degree of exchange of cations was determined by atomic absorption spectrometry, and about 55–65% of K^+ ions was found to be exchanged to H^+ . Exfoliation of $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ was carried out by stirring in 100 mL of TBA^+OH^- aqueous solution at room temperature for 24 h. TBA^+OH^- was added in 8 times more molar quantity than $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$. The suspension was centrifugated at 2000 rpm, and the precipitation was removed from the suspension, about 80% of $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ being found to remain in the suspension. The same weight of MgO fine particles (ca. 100 Å, Ube Industry Ltd.) as $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ was added to the suspension, and the mixture was stirred for 1–2 h at room temperature until precipitation was formed. The composite of $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ and MgO was obtained by filtration. Other fine particles such as SiO_2 (Nihon Aerosil 300), TiO_2 (Nihon Aerosil P25), and Al_2O_3 (Nihon Aerosil Oxide C) were also used for precipitation.

Amorphous Nb_2O_5 was prepared from $\text{K}_8\text{Nb}_6\text{O}_{19}$ and was used as a reference of photocatalytic reaction.¹⁴

Thermal Treatment of Composite. The composite was evacuated at various temperatures for 1 h. The original composite is referred to as sample (a), and composites evacuated at 373, 473, 573, and 673 K are referred to as samples (b)–(e), respectively.

Acid Treatment of the Composite. To obtain porous materials that consist of only niobate sheets by removal of MgO particles, samples (a)–(e) were stirred in 0.5 N H_2SO_4 aqueous solution for 12 h. Disappearance of MgO and TBA^+ was confirmed by energy-dispersive X-ray spectrometry (EDX, Philips EDAX 9100) and Fourier transform FT-IR (JASCO FT-IR 7300) spectrometer, respectively. The acid-treated samples (a)–(e) are referred to as (a')–(e'), respectively. The above process of preparation of the samples is summarized in Figure 2.

Characterizations. The structural studies were carried out by means of XRD (Geigerflex RAD-B system Cu $\text{K}\alpha$ 15 mA, Rigaku) and TEM (JEM-2010F, JEOL). BET surface area of each composite was measured by N_2 adsorption at 77 K. All the samples except the sample (a) and (b) were evacuated at 473 K for 2 h as a pretreatment. The samples (a) and (b) were evacuated at room temperature and 373 K for 2 h, respectively. Pore size distributions were measured by N_2 adsorption at 77 K (Omnisorp 100cx, Coulter), where all the sample were evacuated at 473 K for 4 h as a pretreatment.

Photocatalytic Reaction. Photocatalytic reaction was performed using a closed gas-circulating system with an inner irradiation Pyrex reactor equipped with 450 W high-pressure Hg lamp. Pt (0.1 wt %) was loaded from H_2PtCl_6 (aq) to the catalyst (0.3 g) by in situ photochemical deposition method, and reaction was carried out in an alcohol aqueous solution (H_2O 300 mL, alcohol 30 mL). The evolution of H_2 was

measured by gas chromatography (Ar carrier, MS-5A column). The used photoreactor was described in our previous paper.¹⁵

Results and Discussions

Exfoliation and Precipitation. The suspension containing the exfoliated layers and TBA^+OH^- was suspended in aqueous solution even after centrifugation at 2000 rpm, although some precipitates were observed. These precipitates presumably correspond to the unreacted or very large niobates. Electrokinetic potential (ζ potential) of the suspension was measured after dilution of the suspension with water. At $\text{pH} = 9.6$, the ζ potential of the suspension was measured as -9.9 mV. This result suggests that the exfoliated layers have a negative charge as a whole even with the TBA^+ cations bounded to the niobate sheets. On the other hand, the ζ potential of MgO fine particles in aqueous solution was $+47.3$ mV at $\text{pH} = 9.8$. It is, therefore, presumed that the composite was formed by electrostatic force of attraction. No precipitates were formed when other fine particles such as SiO_2 , TiO_2 , and Al_2O_3 were used instead of MgO, because all of which had negative ζ potentials at the pH values around 10. The composite obtained from $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ and MgO was examined in detail below.

XRD. XRD patterns of the composites are shown in Figure 3a, and those of the original $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$, MgO, and JPPDS data of MgO and $\text{Mg}(\text{OH})_2$ are also shown for comparison. A strong (040) diffraction peak ($2\theta = 9.4$) which indicates well ordered stacking of niobate sheets is observed in the XRD pattern of the original $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$. On the other hand, a broad peak ($2\theta = 7.3$) and some peaks attributed to the mixture of $\text{Mg}(\text{OH})_2$ and a small amount of MgO were observed for the composite (sample (a)). The broad peak ($2\theta = 7.3$) is considered to be attributed to the layered structure because the 2θ value of the composite is similar to the one of the original $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$. The increase of the 2θ value from 9.4 to 7.3 is attributable to larger hydration rate of the interlayer of the composite than that of the $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$.

In Figure 3b, the XRD patterns of samples (a)–(e) which were evacuated at various temperatures are shown. With a rise of temperature the XRD pattern of the composite changed, especially between 473 and 573 K. The peaks attributed to $\text{Mg}(\text{OH})_2$ changed to those attributed to MgO, and the broad peak at ca. $2\theta = 7.3$ decreased and shifted to larger value of 2θ . The similar phenomenon was observed for the original $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ above 573 K. The interlayer space of $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ also shrunk, and this shrinkage was caused by the desorption of H_2O from the two hydroxyls which are perpendicularly neighboring, likewise other layered materials.^{16,17} The $\text{H}^+/\text{K}_4\text{Nb}_6\text{O}_{17}$ evacuated at 573 K has a somewhat broad peak at ca. $2\theta = 11.0$, which decreased and shifted likewise the case of the sample (d) which was evacuated at 573 K. Therefore, the shift of the broad peak at around 7–11 degree is suspected to be due to the dehydration of the interlayer of the niobate sheets in the composite. In other words, some layered

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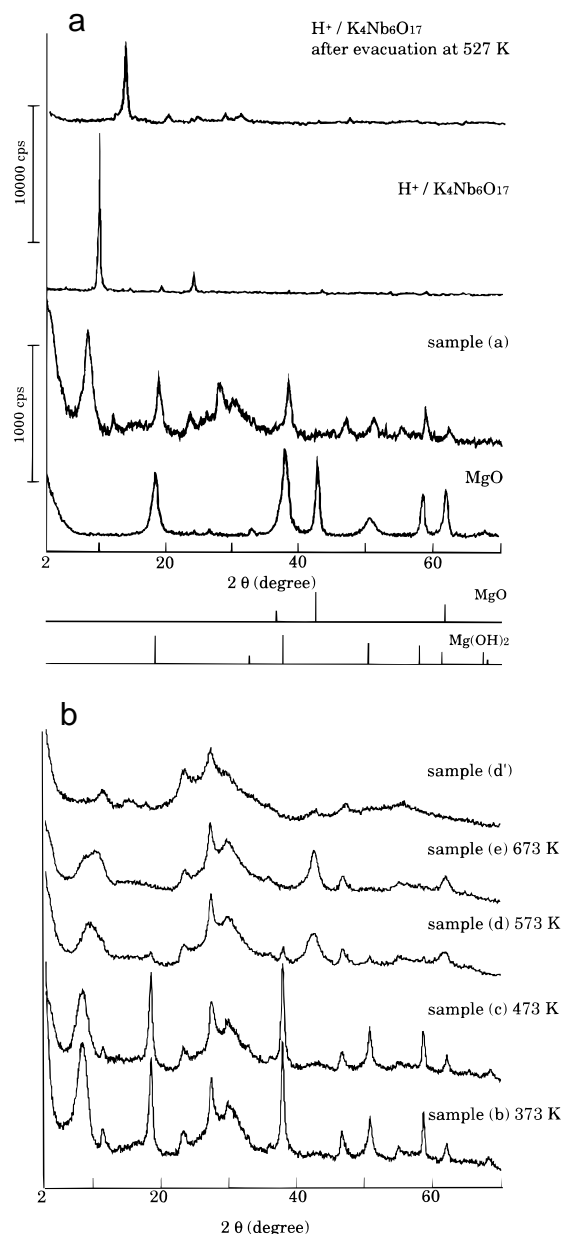


Figure 3. (a) XRD patterns of $H^+/K_4Nb_6O_{17}$ after evacuation at 527 K for 1 h, $H^+/K_4Nb_6O_{17}$, sample (a), MgO (Ube Industry Ltd.), and JPPDS data of MgO and $Mg(OH)_2$. (b) XRD patterns of the composites after evacuation at respective temperature.

structure is considered to remain after the exfoliation of the layers.

TEM. TEM photographs of the sample (a) are shown in Figure 4. Some rodlike dark stripes and pale particles are observed in Figure 4a, and they are mixed randomly without any particular structure. The rodlike materials must be exfoliated layers consisting of several niobate sheets. This materials are made of dark and bright parts; the dark part corresponds to the niobate sheets, and the bright parts corresponds to the interlayers. The pale particles surrounded by exfoliated layers are regarded as MgO particles, and they are seen as to ensure spaces among the exfoliated layers. In Figure 4b, two-dimensional exfoliated thin layers are observed as being piled up with MgO particles. It is worth noting that the exfoliated layers do not consist of a single niobate sheet but of some niobate sheets as clearly confirmed in Figure 4c, expanded image from Figure 4b. In Figure 4c, the presence of six niobate

sheets are clearly observed. It is also evidenced by the XRD pattern of the composite shown in Figure 3a that a broad peak ($2\theta = 7.3^\circ$) indicating a layered structure was still observed as described above. The thickness of four niobate sheets which was estimated from Figure 4a is about 40–50 Å. It agreed approximately with the *b*-axis length (ca. 45.6 Å) of the composite which was calculated from (040) peak of the XRD pattern.

From the results, it is found that the exfoliated thin layers are observed from the lateral direction in Figure 4a, that is, *a*-axis or *c*-axis directions. In the case of Figure 4b the estimated thickness of four niobate sheets is about 30–40 Å, indicating that the exfoliated thin layers are observed obliquely. It is further interesting that the most of the layers consist of 2, 4, or 6 (i.e., multiple of two) sheets as can be seen from the detailed observation of Figure 4a,b. That is to say, exfoliation of the layers occurred by the unit consisting of even-numbered niobate sheets in the present experimental condition. Although the detailed mechanism of proton exchange and exfoliation of $K_4Nb_6O_{17}$ have not been clarified yet, it is likely taking account the differences between interlayer I and II and the degree of proton exchange (55–65%) that K^+ ions remain in one interlayer and exfoliation occurs at the other. Since it is known that the interlayer space I is easily hydrated even in the air while the interlayer space II is not hydrated in the air but is hydrated under a highly humid condition or in water, it is reasonable to consider that proton exchange occur more readily in the interlayer space I than the interlayer space II and that K^+ ions remain in the interlayer space II. Therefore, the exfoliation which is caused by acid–base reaction between H^+ and TBA^+OH^- is considered to occur in the interlayer space I.

BET Measurements. BET surface areas of samples (a)–(e) and (a')–(e') are listed in Table 1. The surface area of the original $H^+/K_4Nb_6O_{17}$ was 1–2 $m^2 g^{-1}$, and that of a MgO particle was 110 $m^2 g^{-1}$. In the samples (a) ~ (e), the BET surface area increased with a rise of temperature from 373 to 573 K and decreased at 673 K. The decrease of surface area at 673 K may be due to destruction of the niobate sheets, or adhesion of carbon deposit derived from decomposition of TBA^+ . The adhesion of carbon deposit is more likely by considering the gray color of the sample after evacuation at 673K, and by the fact that there are no changes between the XRD patterns of samples (d) and (e).

The surface areas of the acid-treated samples that consists of only niobate sheets are also large, as shown in Table 1. It indicates that the large surface area of the composites is attributable not only to the surface area of MgO particles but also to that of exfoliated layers. Although all of the acid-treated samples (a')–(e') have a relatively large surface area, the surface area of each samples is dependent on the evacuation temperature of the composites. In the case of sample (a), which was evacuated at room temperature, the surface area decreased remarkably after acid treatment (from 100 to 37 $m^2 g^{-1}$). On the other hand in the case of sample (d), which was evacuated at 573 K, the surface area increased after acid treatment (from 110 to 145 $m^2 g^{-1}$). The point is that the surface areas of the samples (d) and (e) which were evacuated above 573 K

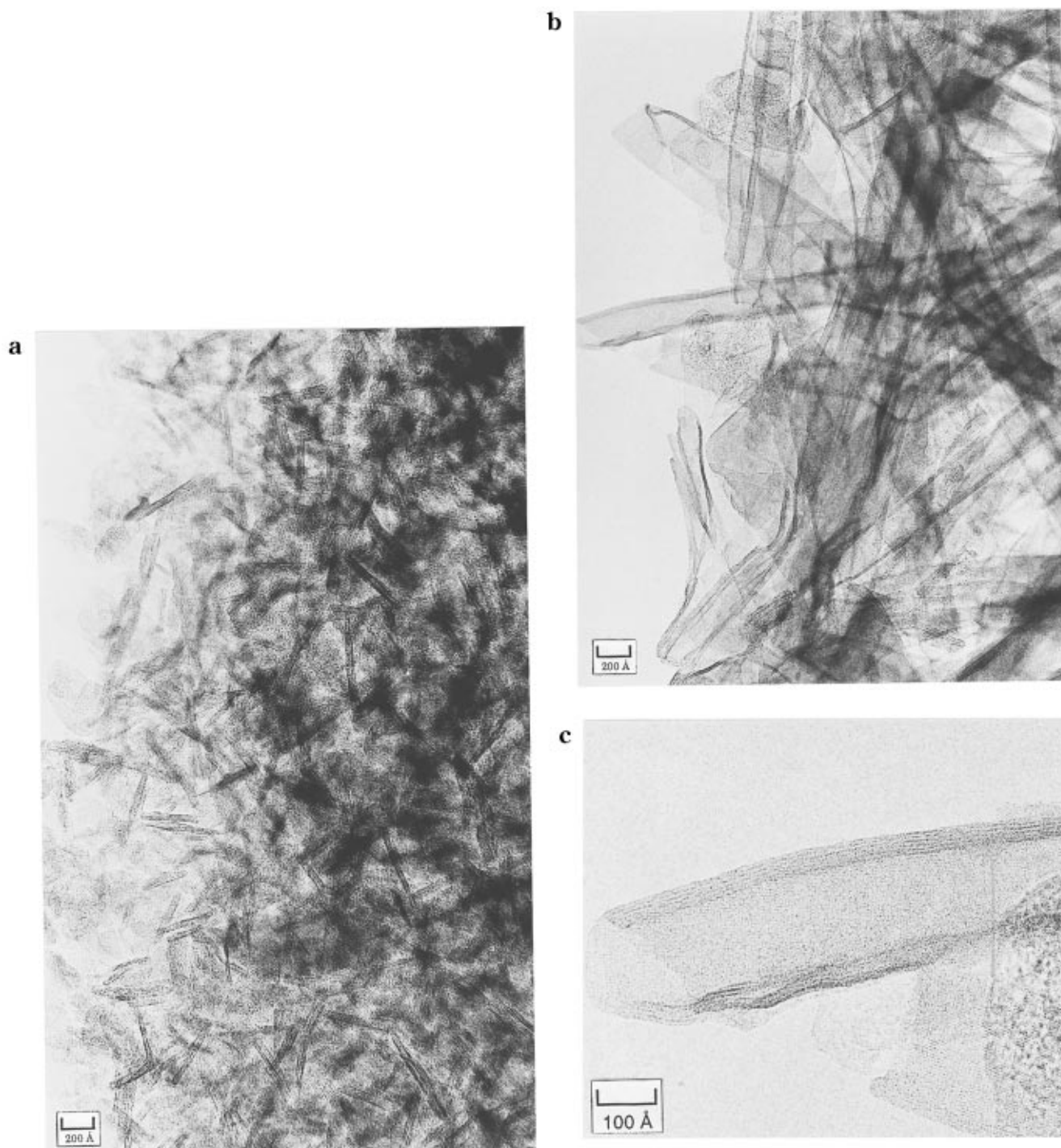


Figure 4. (a) TEM photograph of sample (a). (b) TEM photograph of sample (a). (c) TEM photograph expanded from Figure 4b.

Table 1. BET Surface Area of Samples^a

evacuation temp, (K)	BET surface area ($\text{m}^2 \text{g}^{-1}$)			
	sample	sample	sample	sample
373	(a)	100	(a')	37
	(b)	80	(b')	50
473	(c)	85	(c')	70
573	(d)	110	(d')	145
673	(e)	77	(e')	87

^a All the samples except samples (a) and (b) were evacuated at 473 K for 2 h as a pretreatment. Samples (a) and (b) were evacuated at room temperature and 373 K for 2 h, respectively.

increased after acid-treatment, in contrast to the samples (a)–(c) whose surface areas decreased after acid-treatment. This results may be caused by the formation of the more rigid structure of niobate after evacuation

above 573 K. Taking into account the structure of the composite, removal of MgO and TBA⁺ from the composite may cause destruction of the spaces between each set of the niobate sheets that were supported by MgO particles and TBA⁺ and cause the decrease of surface area and spaces. For sample (a') the niobate sheets were considered to pile up parallel to each other, and as a result the narrow spaces between the niobate sheets were undetected as surface area. But if each set of the niobate sheets attach partly to each other by the thermal treatment, it is likely that the spaces ensured by MgO and TBA⁺ remain even after removal of them, and as a result samples (d) and (e) have large surface areas after acid treatment. This speculation is taken up in the next chapter.

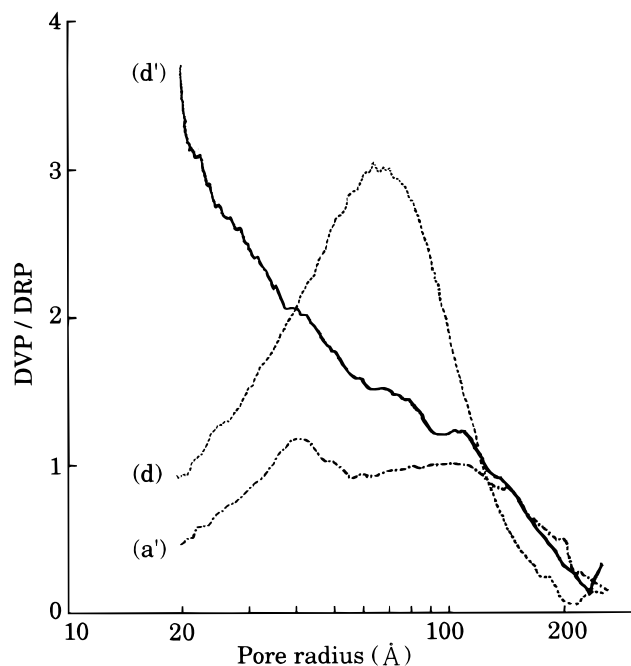


Figure 5. Pore size distributions of sample (d) (---), sample (a') (· - ·) and sample (d') (—).

Pore Size Distribution. Pore size distributions of samples (d), (a'), and (d') were measured and shown in Figure 5. Sample (d) was found to have a mesoporous structure, and some regularity was observed in pore size distribution at about 60–70 Å. This distribution corresponds to the space preserved by MgO particles (ca. 100 Å) existing between niobate sheets. Similarly, the acid-treated samples (a') and (d') were found to have mesoporous structure, although the pore size distribution was changed by disappearance of the MgO particles and TBA⁺. The pore size distribution of sample (a') between 40 and 100 Å is much smaller than that of sample (d). In the case of sample (d'), the pore size distribution between 40 and 100 Å similarly decreased, but the decrease is less than sample (a'), and the pore size distribution between 20 and 40 Å increased remarkably. The pore size between 20 and 40 Å corresponds to the space ensured by TBA⁺, and that between 40 and 100 Å corresponds to the spaces ensured by the MgO particles. Therefore, it is considered that in the case of sample (a) the mesopores were lost by acid treatment, while in the case of sample (d) which was evacuated at high temperature the mesopores remained even after acid treatment. This result agreed with the experimental results of BET and indicates that the formation of the rigid structure of niobate after evacuation above 573 K as expected in BET section. The temperature 573 K is above 523 K where the desorption of H₂O from two hydroxyls occurs, as described in the XRD section. Then it is not unlikely that the exfoliated niobate sheets partly attach to each other by the desorption of H₂O. An expected scheme of the formation of samples (a') and (d') is shown in Figure 6. In the case of (a') the spaces decrease with the disappearance of TBA⁺ and MgO particles due to destruction of the structure. Each set of the niobate sheets attach partly to each other by evacuation at 573 K, and the sample (d) was formed. Then the spaces which were ensured by TBA⁺ and MgO particle between each set of exfoliated niobate sheets are retained even after acid treat-

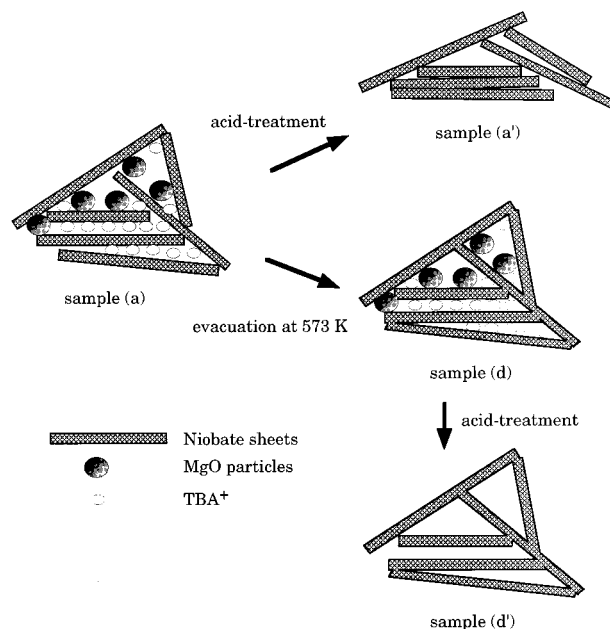


Figure 6. Expected Scheme of the formation of samples (a') and (d').

Table 2. Table of Photocatalytic Activities of H₂ Evolution from MeOH(aq)^a

sample	H ₂ evolution (μmol h ⁻¹)
H ⁺ /K ₄ Nb ₆ O ₁₇	1700
(a)	220
(d)	263
(a')	682
(d')	2200

^a Reaction conditions: catalyst: 0.3 g, Pt (0.1 wt%) was loaded from H₂PtCl₆(aq), solution: H₂O 300 mL + MeOH 30 mL, high-pressure mercury lamp (450 W), an inner irradiation type Pyrex reaction cell.

ment because they are attached each other at above 573 K. The reason for the increase of the pore size distribution between 20 and 40 Å of sample (d') is considered as follows: Since the spaces between each set of exfoliated niobate sheets whose pore size distributed from 20 to 40 Å are densely packed with TBA⁺ before acid treatment, the pore size distribution between 20 and 40 Å was not observed much in sample (d). In sample (d') the spaces occupied by TBA⁺ appear with the disappearance of TBA⁺, and as a result the pore size distribution between 20 and 40 Å is observed largely.

Photocatalytic Activity. Photoproduction of H₂ from MeOH aqueous solution was examined over samples (a), (d), (a'), (d'), and original H⁺/K₄Nb₆O₁₇. The blank and dark reactions were carried out, and no H₂ evolution was detected. The photoreactions proceeded steady. As shown in Table 2, sample (d') has the highest activity among them as expected from the results of BET. A little difference in activity between sample (d') and the original one indicate that the interlayer spaces of the H⁺/K₄Nb₆O₁₇ effectively act as reaction sites for small reactants such as MeOH. The decrease of photocatalytic activity of samples (a) and (d) was probably caused by the MgO and TBA⁺ which binded to the niobate sheets and obstructed surface-active sites. The lower activity of sample (a') compared with sample (d') is attributable to the smaller surface area and number of active sites of sample (a').

Next photoproduction of H₂ from various alcohols was examined over sample (d'). The activities of the original

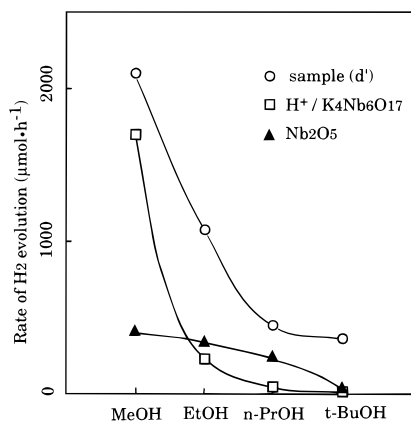


Figure 7. Photocatalytic activities from various alcohol aqueous solutions on sample (d') (○), H⁺/K₄Nb₆O₁₇ (□), and amorphous Nb₂O₅ (▲).

H⁺/K₄Nb₆O₁₇ and amorphous Nb₂O₅ were also examined for comparison. All the reactions proceeded steadily. As shown in Figure 7 the activity decreased drastically with increasing of carbon number of alcohol over the original H⁺/K₄Nb₆O₁₇, because bulky alcohols are difficult to intercalate to the active sites in the interlayer. On the other hand, sample (d') has high activity for bulky alcohol compared with the original one. This tendency is evident for *t*-BuOH, where about 25 times higher activity was obtained. However, compared with amorphous Nb₂O₅, the decrease of activity for bulky reactant was still observed for the sample (d'), likewise the original H⁺/K₄Nb₆O₁₇. The XRD pattern indicates that sample (d') still has a layered structure (Figure 4b), although the peak is very weak and the *b*-axis length shortened. Then the activity and mechanism of reaction over the sample (d') are explained as follows. The reaction proceeds at both external and interlayer space

of niobate sheets, while the contribution of interlayer space is less than external for bulky alcohol. As a result, the activity of external of the sheets increase in proportion to the increase of surface area, although the activity of interlayer space is similar to original H⁺/K₄Nb₆O₁₇. Therefore, the activity of sample (d') is higher than the original H⁺/K₄Nb₆O₁₇ for all alcohols, whereas it decreased for bulky ones and also the original H⁺/K₄Nb₆O₁₇. If exfoliation of a single layer is possible, a much higher but similar tendency of the activity for various alcohols to the amorphous Nb₂O₅ may be observed.

Conclusion

Porous niobium oxides were obtained from the layered compound K₄Nb₆O₁₇ by using the so-called soft-chemical method. The exfoliated niobate sheets were precipitated by addition of the MgO fine particles, and the exfoliated thin sheets were visually observed by TEM photograph. The most active photocatalyst with the largest surface area was prepared when the composite was treated with acid after evacuation at 573 K. This soft-chemical method by exfoliation and precipitation is useful for synthesis of new materials, because it does not require any particular condition such as high pressure or high temperature, and there are many kinds of layered compound whose layer can be exfoliated. The materials obtained from this method have a large surface area and porous structure and are expected as active catalysts.

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