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Modification of the interlayer in $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and their photocatalytic performance for water cleavage

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Layered compounds $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($3 \leqq n \leqq 6$) were prepared by solid reaction at high temperatures, and the processes for the modification of the interlayers by protonation, intercalation and pillaring were investigated. *n*-hexylamine could easily be intercalated into the interlayers of $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and enhanced significantly the interlayer distance, which facilitated the incorporation and reaction of tetraethyl orthosilicate with *n*-hexylamine intercalated compounds. The analysis of XRD, TG-DTA and TEM indicated that silica-pillared layered compounds were formed and had high thermal stability. By comparing the rates of hydrogen evolution from water cleavage on various compounds, the enhancement in the activity of proton-exchanged and silica-pillared compounds was examined in the case of loading Pt. The promotion effect might be due to the adsorption and combination of Pt on the surface of compounds proton-exchanged and pillared.

1. Introduction

There has been intense research activity in the synthesis and characterization of layered metal oxides due to the properties of ion exchange and intercalation [1–6]. A novel class of porous materials can be prepared from proton-exchanged layered compounds by pillaring method, which cannot be prepared by heating mixtures of the starting materials, such as alumina-pillared layered $H_2Ti_3O_7$ [4], silica-pillared $H_2Ti_4O_9$ [5] and $HLaNb_2O_7$ [6]. This kind of layered porous materials is excepted to be applied as photocatalysts [7–10]. The series of layered compounds $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ being structurally related to perovskite $KCa_2Nb_3O_{10}$ but differing in the thickness of the perovskite layers was synthesized and shown to have intercalation reactivity [11]. Domen *et al.* [12] reported the preparation of SiO_2-pillared $KCa_2Nb_3O_{10}$ through the processes of proton-exchange and intercalation with *n*-octylamine/heptane, and showed a photocatalytic activity. The present authors have also reported that the photocatalytic property of mixed metal oxides having tunnel or layered structures as well as the influence of ion-exchange on their catalytic property [13, 14], and the preparation of silica-pillared layered titanium niobium oxide [15]. This paper reports that the preparation of layered metal oxides $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($3 \leqq n \leqq 6$), and the modification of their interlayers by ion-exchange, intercalation reaction with *n*-hexylamine, silica-pillaring, as well as their influence on photocatalytic performance for water cleavage.

2. Experimental

As the starting material for the preparation of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($3 \leqq n \leqq 6$), $KCa_2Nb_3O_{10}$ was first prepared by high temperature reactions at about 1200°C for 10 h in air from $CaCO_3$ (Wako), K_2CO_3 (Katayama) and Nb_2O_5 (Wako). Excess K_2CO_3 (~10 mol%) was added to compensate for the loss due to volatilization. After the reaction, the product was washed with distilled water and dried. The next member of the series $KCa_2NaNb_4O_{13}$ was prepared by using $KCa_2Nb_3O_{10}$ and $NaNbO_3$, which was obtained by calcining the mixture of Nb_2O_5 and Na_2CO_3 in stoichiometric amounts at 1050°C in air. The compounds with $n > 4$ were prepared by reaction of $KCa_2NaNb_3O_{13}$ with stoichiometric amounts of $NaNbO_3$ at higher temperatures, *ca.* 1230–1300°C. The potassium phases in $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ were converted to the hydrogen compounds $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ by ion exchange in HNO_3 (6 M) for 3 days at room temperature.

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In order to prepare silica-pillared compounds, n-hexylamine ($CH_3(CH_2)_5NH_2$) and tetraethyl orthosilicate ($(C_2H_5O)_4Si$) were employed as an interlayer exchange guest and a pillar precursor, respectively. n-hexylamine-intercalated compounds were prepared firstly by adding $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ to a 50% n-hexylamine (Wako)-ethanol (Wako) solution and stirring at room temperature for one week, followed by filtered and washing successively with ethanol-water (1:1) and distilled water. Obtained n-hexylamine-intercalated compounds (3.0 g) were then added to 120 ml of tetraethyl orthosilicate (Wako), and stirred for 3 days at *ca.* 80°C. After reaction, the product was separated and washed, dried and finally calcined at serial temperatures. All of obtained products were confirmed by X-ray diffraction (Rigaku Geigerflex, Cu-K_α radiation). The differential thermal analysis (DTA) and the thermogravimetric analysis (TG) were performed using a thermal analysis system (Rigaku TAS-200). Nitrogen adsorption (Autosorb-1, Yuasa Aionikusu), transmission electron microscopy (TEM, JEOL JEM-200CX microscope) and UV-Vis diffuse reflectance (Shimadzu UV-3100) were also employed in the study.

Photocatalysis for water cleavage was carried out in a photoreactor as reported previously [14]. Simply, a reaction mixture was prepared by introduction of catalyst powder (0.1 g) and distilled water of 20 cm^3, and then was externally irradiated for 6 h with a high-pressure mercury lamp of 150 W. The amount of evolved H_2 was analyzed by a gas chromatograph with molecular sieve 5 A column (KOR-70, Gas Chromatograph).

3. Results and discussion

3.1. $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and proton-exchange

Fig. 1 shows powder X-ray diffraction patterns of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($3 \leqq n \leqq 6$). The pure phases of the compounds with $n = 3$, 4 were obtained, but different members of series were observed in the compounds with $n > 4$. For example, a small of phases with $n = 4$ and 6 was detected in the $n = 5$ compound, and a little phase with $n = 5$ was observed in the $n = 6$ compound. The peak shifted into lower 2θ with increasing the value of n, indicating that the increase in the thickness of the perovskite layers is consistent with the addition of $NaNbO_3$. As summarized in Table I, in terms of the calculation on the unit cell parameters, the basic interlayer distance (c-axis dimension) increased linearly with increasing n, being 14.72, 18.61, 22.37 and 26.22 Å, respectively, when n increased from 3 to 6. It was also found that the interlayer distance of the proton-exchanged products was dependent on the drying methods. The compound dried at room temperature in vacuum has a larger interlayer distance as compared with that dried at 110°C in air. This demonstrated that hydrated phases $H[Ca_2Na_{n-3}Nb_nO_{3n+1}] \cdot xH_2O$ with $x = 1$–1.5 [11] were obtained from the proton-exchanged products without heating, and transferred to anhydrous phases at 110°C. The Fig. 2 shows the UV-Vis diffuse reflectance spectra of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($3 \leqq n \leqq 6$). No apparent shifts were observed in the series of compounds with different n values. The absorption edge is around 350 nm, being corresponded to the band gap energy of 3.5 eV.

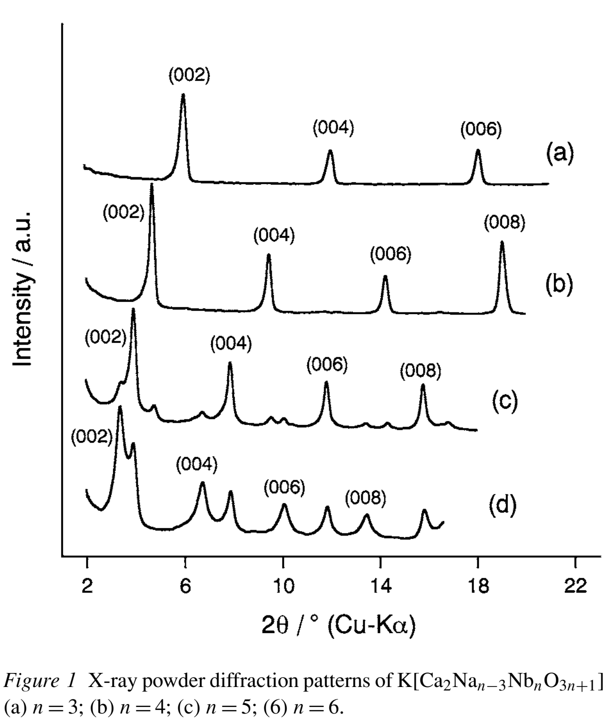

Figure 1 X-ray powder diffraction patterns of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$. (a) $n = 3$; (b) $n = 4$; (c) $n = 5$; (6) $n = 6$.

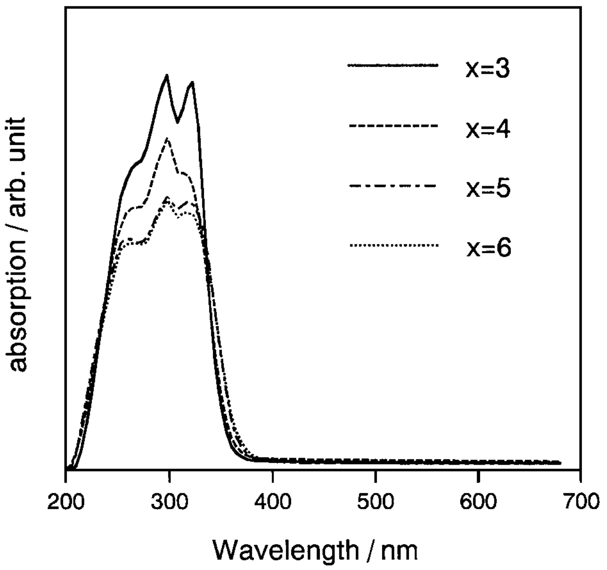

Figure 2 UV-Vis diffuse reflectance spectra of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$.

3.2. Intercalations and silica-pillared $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$

Since $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ cannot react directly with tetraethyl orthosilicate to form an intercalate, n-hexylamine-$H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ intercalated compound was prepared first to increase the interlayer distance and lower the charge density.

X-ray diffraction (XRD) patterns of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($n = 3$, 4) during protonation, intercalation and pillaring processes were analyzed. The change of XRD patterns for the compound with $n = 3$ is shown in Fig. 3, as an example. n-hexylamine readily intercalated layered $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and led to an extremely strong peak and lower 2θ. The

TABLE I Basic interlayer distance of M[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$] compounds on c-axis dimension

Processes	Formulas of compounds	Interlayer distance/Å			
		$n=3$	$n=4$	$n=5$	$n=6$
Original	K[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$]	14.72	18.61	22.37	26.22
Proton-exchange	H[Ca$_2$Na$_{n-3}$ Nb$_n$O$_{3n+1}$] · xH$_2$O[a]	16.49	20.00	23.90	27.55
	H[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$][b]	14.42	18.48	22.32	26.18
n-hexylamine intercalation	C$_6$H$_{13}$NH$_3$[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$]	28.68	32.97	/	/
Tetraethyl orthosilicate intercalation	[Si(OEt)$_4$H][Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$][c]	30.26	33.98	/	/
	SiO$_2$-pillared H[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$][d]	17.19	20.36	/	/

[a] obtained by drying at room temperature in vacuum from the proton-exchanged compounds.

[b] obtained by drying at 110°C from the proton-exchanged compounds.

[c] obtained by drying at 110°C from the tetraethyl orthosilicate intercalated compounds.

[d] obtainedby heating at 500°C from the tetraethyl orthosilicate intercalated compounds.

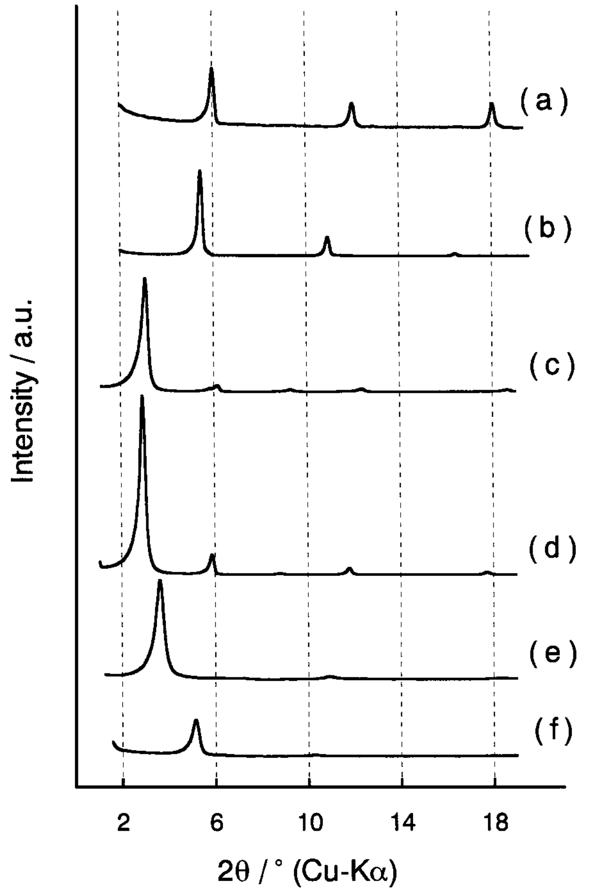

Figure 3 X-ray powder diffraction patters of (a) K[Ca$_2$Nb$_3$O$_{10}$]; (b) proton-exchanged by 6 M HNO$_3$; (c) reaction product of H[Ca$_2$Nb$_3$O$_{10}$] with n-hexylamine solution; (d) reaction product of tetraethyl orthosilicate intercalated compound; (e) calcined in air at 330°C for 2 h; (f) calcined in air at 500°C for 2 h.

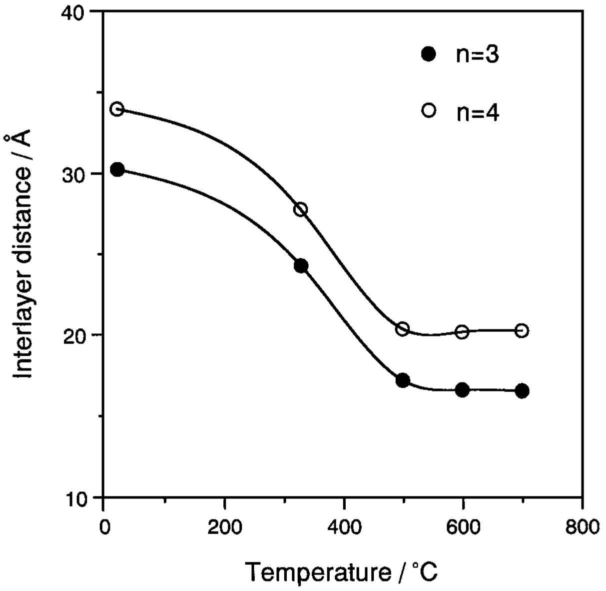

Figure 4 Effect of calcination temperature on the interlayer distance of tetraethyl orthosilicate intercalated compounds.

interlayer distance on c-axis dimension increased to 28.68 Å and 32.97 Å for the compound with $n=3$ and that $n=4$ respectively, being close to twice that of the proton-exchanged compounds (14.4 Å and 18.48 Å, respectively). It was also found that the obtained n-hexylamine-H[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$] has a slightly smaller interlayer distance, as compared to n-octylamine-H[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$] [11]. The n-hexylamine intercalated compounds have rather low thermal stability, and collapsed after calcination at about 400°C. However, the opened layers could facilitate the reaction of layered-hexylamine intercalated compounds with tetraethyl orthosilicate, which gave rise to a slightly lower 2θ and a larger interlayer distance (Table I).

Fig. 4 shows a change in the interlayer distance for the tetraethyl orthosilicate intercalated compounds with heating temperature in air. As a result of decomposition of organic matter with heating up to 500°C, the interlayer distance decreased remarkably to 17.19 and 20.36 Å for the compounds with $n=3$ and 4, respectively, and kept in a stationary state over that temperature. This indicates the layered compounds have rather high thermal stability.

The results of TG-DTA for silica-pillared compounds ($n=3$, 4) are showed in Fig. 5. The TG curve shows a continuous weight loss, and reaches the completion of 15.5% and 12.5% at *ca.* 500°C for those with $n=3$ and 4, respectively. As seen in Figs 4 and 5, the curves of weight losses are coincident with the curves of interlayer distance in the temperature dependence. This suggests that the weight losses originated from the decomposition of organic matter incorporated into the interlayers, hence the interlayer distance decreased with increasing the heating temperature. It can be speculated that the both exothermic peaks at *ca.* 300 and 400°C in Fig. 5 were attributed to the decomposition and combustion of the organic matter, but its interlayer

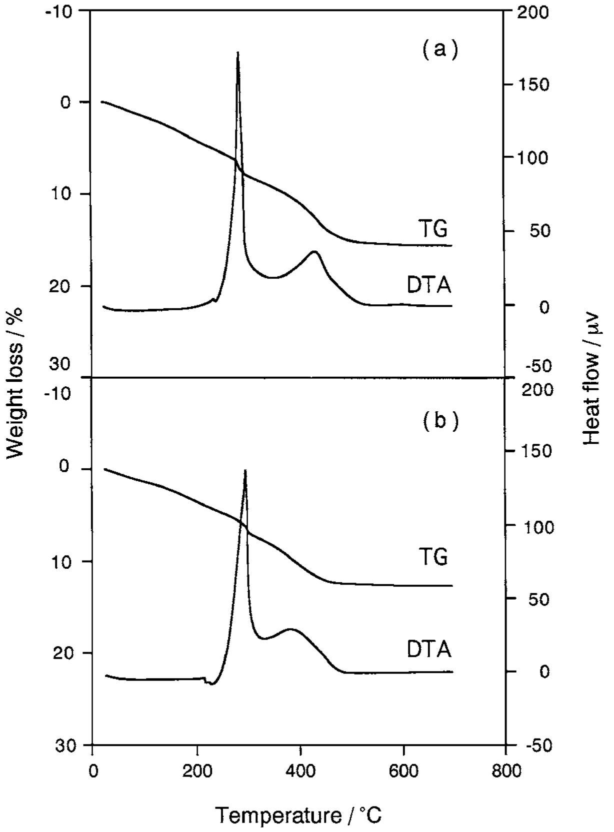

Figure 5 TG-DTA curves for the tetraethyl orthosilicate intercalated compounds with (a) $n = 3$ and (b) $n = 4$ in an air flow of 100 ml/min at a heating rate of 5°C/min.

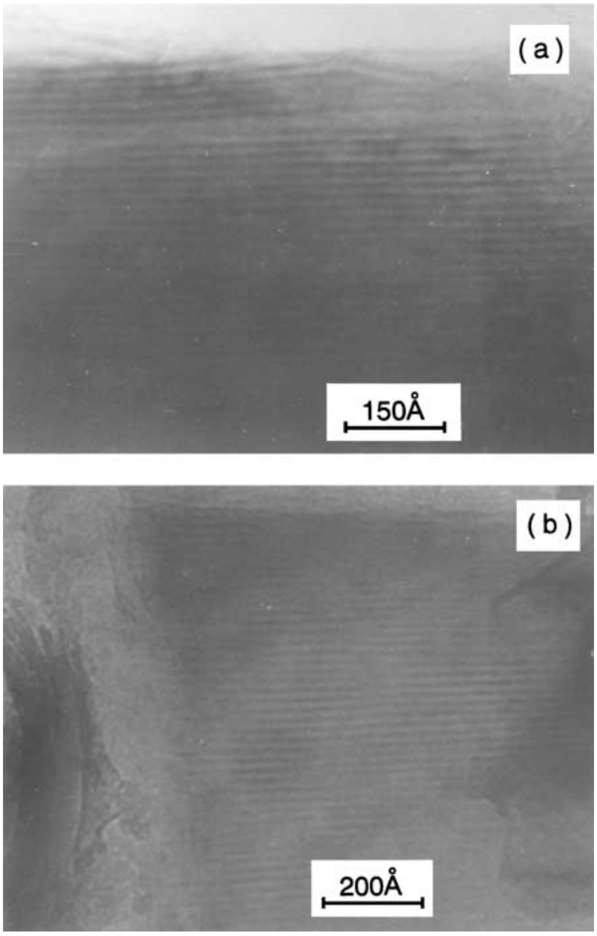

Figure 6 TEM images of silica-pillared compounds calcined at 500°C. (a) silica-pillared $H[Ca_2Nb_3O_{10}]$; (b) silica-pillared $H[Ca_2NaNb_4O_{13}]$.

combination and exhaustion processes are still unclear. As shown in Fig. 4 and Table I, the fact that the interlayer distance of the pillared compound calcined at 500°C hasn't been changed even heating to 700°C and is larger than that of original $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ demonstrated that silica-like clusters were formed in the interlayers, which acted as pillars to prop up the $[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ layers after interlayer organic matter was removed. By comparing the pillared compounds calcined at 500°C with the proton-exchanged compounds dried at 110°C, it can be found that the increment in the interlayer distance is 2.77 Å for that with $n = 3$ and 1.88 Å for that with $n = 4$, respectively. It seems that the pillaring process becomes difficult with increasing the interlayer distance of original compounds. Fig. 6 shows the images of the pillared compounds ($n = 3, 4$) calcined at 500°C. BET analysis indicated that the surface area increased from 1.0 and 1.4 m^2g^{-1} for the original $K[Ca_2Nb_3O_{10}]$ and $K[Ca_2NaNb_4O_{13}]$ to 14.3 and 6.1 m^2g^{-1} for those pillared compounds calcined at 500°C, respectively. The BET surface area is lower than that expected. The reaction of intercalations and synthesis of pillared products concern a series of complexed processes, and are depended on preparation conditions and starting material structures [6, 9, 15]. Recently, in our laboratory a new silica-pillared compound with high surface area has been synthesized from $K[Ca_2Nb_3O_{10}]$ in which partial Nb is substituted with Cr [16].

3.3. Photocatalysis for water cleavage

The rates of hydrogen evolution from water cleavage under the irradiation of high-pressure mercury lamp (150 W) were measured on $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ compounds and their modifications obtained from proton-exchange and silica-pillaring processes. As summarized in Table II, these compounds without

TABLE II Rates of H_2 evolution on $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ compounds under irradiation of a high-pressure mercury lamp (150 W)

Catalysts		H_2 evolution/$\mu mol \cdot h^{-1} \cdot m^{-2}$			
Compounds	Pt-loading	$n = 3$	$n = 4$	$n = 5$	$n = 6$
$K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$	None	87	105	18	42
	0.3 wt%	486	167	296	173
$H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$	None	55	30	24	36
	0.3 wt%	776	279	241	170
SiO_2-pillared $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$[a]	None	31	33	/	/
	0.3 wt%	246	930	/	/

[a] Calcined at 500°C.

Pt-loading have nearly the same level on the hydrogen evolution, and the loaded Pt enhanced remarkably the photocatalytic activity of original K[$Ca_2Na_{n-3}Nb_nO_{3n+1}$], proton-exchanged H[$Ca_2Na_{n-3}Nb_nO_{3n+1}$], and silica-pillared H[$Ca_2Na_{n-3}Nb_nO_{3n+1}$]. Overall, while the activity of the unloaded compounds is not so obviously depended on the interlayer distance (n value), the activity of the Pt-loaded compounds decreased with increasing the value of n. On the other hand, comparing the rate of hydrogen evolution on the compounds with $n = 3$ and 4, the deteriorate in the activity occurred somewhat in the case of Pt-unloading by the processes of proton-exchange and pillaring, as compared to that of original K[$Ca_2Na_{n-3}Nb_nO_{3n+1}$], but the promotion effect of the processes was found on the compounds loading Pt, except the pillared compound with $n = 3$. It seems that the proton-exchanged and silica-pillared compounds might facilitate the adsorption and combination of Pt on the surface, hence the activity increased. Band gap excitation produces an electron-hole pair in the semiconductor particle when adsorption of light. The electron is subsequently channeled to Pt sites where hydrogen evolution occurs. The combination between Pt and the semiconductor particle promotes the electron transfer and the hydrogen evolution [17–19].

In conclusion, n-hexylamine is effective for the intercalation of K[$Ca_2Na_{n-3}Nb_nO_{3n+1}$] compounds, hence facilitates the incorporation of tetraethyl orthosilicate and the formation of silica-pillared compounds. The photocatalytic activity for water cleavage can be enhanced by the modification with proton-exchange, intercalation and silica-pillaring for the compounds loading Pt.

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