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Photocatalytic Decomposition of Water over a Ni-Loaded $Rb_4Nb_6O_{17}$ Catalyst

K. SAYAMA, A. TANAKA,* K. DOMEN, K. MARUYA, AND T. ONISHI[1]

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 227; and *Nikon Company, 1-10-1 Asamizodai, Sagamihara 228, Japan*

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Nickel-loaded $Rb_4Nb_6O_{17}$, which has the same layered structure of niobium oxide sheets with interlayers as that of $K_4Nb_6O_{17}$, exhibits a high activity for photocatalytic water splitting to form H_2 and O_2 under band gap irradiation. In order to obtain an efficient catalyst, it was essential to treat the $Rb_4Nb_6O_{17}$ powder before nickel-loading by washing the $Rb_4Nb_6O_{17}$ with deionized water and then recalcining this powder in air in the temperature range 1153–1173 K for more than 10 h. The maximum activity was obtained when the reaction was carried out in distilled water where the pH was ca. 9.7 and the quantum efficiency at 330 nm was ca. 10% at the initial stage of the reaction over NiO(0.1 wt%)–$Rb_4Nb_6O_{17}$. © 1990 Academic Press, Inc.

INTRODUCTION

Photocatalytic water splitting is accompanied by a large energy conversion and has attracted considerable attention from the viewpoint of solar energy utilization. Several photocatalytic systems have been reported; however, the quantum efficiencies in most cases have remained at quite low levels (ca. 1%) (*8–10*). Some layered compounds with an ion-exchange capability show a characteristic photocatalytic behavior under band gap radiation (*1–5*). In particular, $K_4Nb_6O_{17}$ modified by Ni metal was found to decompose H_2O into H_2 and O_2 under band gap radiation (>3.3 eV). It is known that $A_4Nb_6O_{17}$ (A = K, Rb, Cs) has corrugated niobate sheets stacked along the *b*-axis of an orthorhombic unit cell. A unique structural feature of these compounds is the existence of four interlayer spaces in a unit cell, which are classified into two types (interlayers I and II) (*6, 7*). Hydration and ion exchange capabilities are different for interlayers I and II. Furthermore, it was suggested that the existence of two kinds of alternating interlayer spaces is essential for water splitting over a Ni-loaded $K_4Nb_6O_{17}$ (*5*).

Ni-loaded $K_4Nb_6O_{17}$ exhibited a relatively high quantum efficiency of 3.5–5% at 330 nm (*4, 5*). The high efficiency of this catalyst was thought to be due to the peculiar structure and a unique reaction mechanism in which the intercalated water molecules were decomposed into H_2 and O_2 at interlayers I and II, respectively. Although the response of this catalyst is limited in the UV region (<380 nm), it is worthwhile to investigate this new type of material in more detail.

$Rb_4Nb_6O_{17}$ has the same layered structure as that of $K_4Nb_6O_{17}$. As the ionic radii of K^+ and Rb^+ are 1.33 and 1.48 Å, respectively, the interlayer space length of $Rb_4Nb_6O_{17}$ is different from that of $K_4Nb_6O_{17}$. In this work, therefore, a $Rb_4Nb_6O_{17}$-based photocatalyst was examined in comparison with $K_4Nb_6O_{17}$. Consequently, it was found that Ni-loaded $Rb_4Nb_6O_{17}$ exhibits a higher efficiency (ca. 10% quantum efficiency at 330 nm) for overall water splitting. The result for $K_2Rb_2Nb_6O_{17}$ is also reported (*6*).

[1] To whom correspondence should be addressed.

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EXPERIMENTAL

$K_4Nb_6O_{17}$ and $K_2Rb_2Nb_6O_{17}$ powder catalysts were prepared as follows: stoichiometric mixtures of Nb_2O_5 (Mitsui Kinzoku), K_2CO_3 (Wako Junyaku), and Rb_2CO_3 (Wako Junyaku) were melted in a platinum crucible at 1573 K for ca. 15 min in air, then cooled rapidly (cooling rate ca. 100 K/min) (*6, 11*). The large crystalline product was crushed to small pieces (ca. 1–10 μm) in a mortar and these crystal structures were confirmed by XRD. The synthesis of $Rb_4Nb_6O_{17}$ was more complex; a mixture of Rb_2CO_3 (Wako Junyaku) and Nb_2O_5 powder in a molar ratio of 1 : 1.14 was heated at 1523 K for 20 h in air in a platinum crucible, then cooled down gradually to 1123 K (cooling rate 100 K/6 h) and to room temperature (*6*). In this manner, large transparent crystals of $Rb_4Nb_6O_{17}$ were obtained together with an unknown composition of rubidium niobate, which was white in color. Crystals of $Rb_4Nb_6O_{17}$ were crudely separated from the other phase by hand. The large crystals were then pulverized in a mortar to a particle size of 1–10 μm. $Rb_4Nb_6O_{17}$ was then washed in deionized water to remove excess rubidium. This sample is referred to as "H_2O-treated." Next, this powder was recalcined in air; this sample is designated "recalcined." These treatments of the catalyst were essential to obtain an efficient catalyst as shown below.

A $Rb_4Nb_6O_{17}$ catalyst loaded with nickel was prepared by an impregnation method. $Rb_4Nb_6O_{17}$ was added to an aqueous solution (4 ml) which contained the required amount of nickel nitrate. Then the sample was calcined at ca. 550 K in air for 1 h after drying in a water bath. The catalyst was activated as follows: the calcined sample was reduced by H_2 (ca. 40 kPa) for 2 h and then reoxidized by O_2 (ca. 16 kPa) for 1 h in a closed gas circulation system.

Photocatalytic reactions were carried out in a closed gas circulation system (*9*). A mixture of a catalyst (1 g) and distilled water (300 ml) in an inner irradiation reaction cell was degassed completely, and then Ar (ca. 16 kPa) was introduced. The catalyst was suspended by rapid stirring and irradiated using a high-pressure mercury lamp (USHIO UV-452, 450 W). The evolved gases were analyzed by gas chromatography (TCD, Ar carrier) with a molecular sieve 5A column, which was attached directly to the gas circulation system. The quantum efficiency (QE) was measured with the aid of a reaction cell equipped with a flat side-window which was irradiated with a Xe lamp (USHIO 500 W) with monochromatized light (H.20, ISA JOBIN YVON Instruments). The number of absorbed photons was measured by chemical actinometry with $(NH_4)_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and the QE was determined according to the equation

$$\mathrm{QE}(\%) = \frac{\text{amount of } H_2 \text{ evolved}}{\text{number of absorbed photons}} \times 2 \times 100.$$

RESULTS AND DISCUSSION

Table 1 shows the *b*-axis lengths of anhydrates and trihydrates of $K_4Nb_6O_{17}$, $K_2Rb_2Nb_6O_{17}$, and $Rb_4Nb_6O_{17}$. The *b*-axis length of $Rb_4Nb_6O_{17} \cdot 3H_2O$ is longer by 1.5 Å than that of $K_4Nb_6O_{17} \cdot 3H_2O$, while those of the anhydrates are the same (*6*). When wet, corresponding to the conditions in the photocatalytic reaction, the difference in the *b*-axis lengths between $K_4Nb_6O_{17} \cdot xH_2O$ and $Rb_4Nb_6O_{17} \cdot xH_2O$ increases.

TABLE 1

The *b*-Axis Lengths of $A_4Nb_6O_{17}$ (A = K or Rb)

	b-Axis length (Å)		
	Anhydrate	Trihydrate	Under wet conditions
$K_4Nb_6O_{17}$	33.2	37.6	41.7
$K_2Rb_2Nb_6O_{17}$	33.2	38.4	42.1
$Rb_4Nb_6O_{17}$	33.2	39.1	44.0

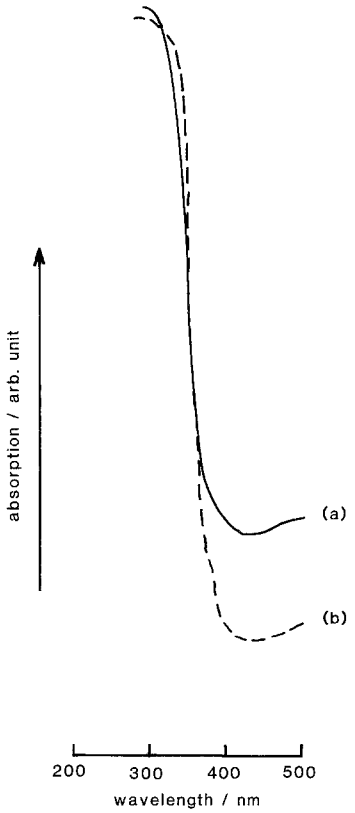

FIG. 1. UV diffuse reflectance spectra; (a) $Rb_4Nb_6O_{17}$, (b) $K_4Nb_6O_{17}$.

Figure 1 shows the UV diffuse reflectance spectra of $Rb_4Nb_6O_{17}$ and $K_4Nb_6O_{17}$. No significant difference was observed between them. In both cases the estimated band gaps were ca. 3.3 eV.

By the preparation mentioned above, needle-like crystallites were produced together with layered $Rb_4Nb_6O_{17}$. Figure 2 shows XRD patterns of those compounds. The XRD pattern (a) indicates the existence of a single-phase of $Rb_4Nb_6O_{17} \cdot 3H_2O$. The needle-like phase shows rather broad and weak diffraction peaks and the composition was not identified. The photocatalytic activity of the needle-like compound was negligible compared to that of $Rb_4Nb_6O_{17}$.

When $Rb_4Nb_6O_{17}$, separated from the needle-like crystallites, was impregnated with nickel nitrate solution and then pre-

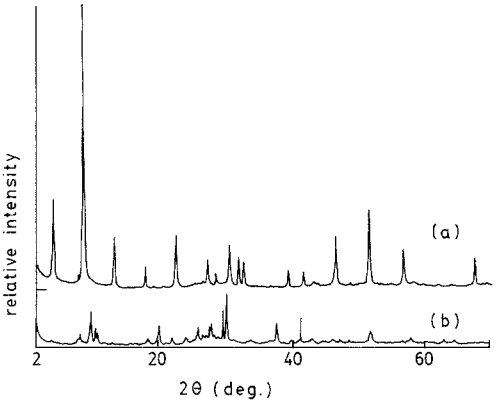

FIG. 2. X-ray diffraction pattern of (a) $Rb_4Nb_6O_{17} \cdot 3H_2O$ and (b) needle-like crystallites.

treated by H_2 reduction and O_2 oxidation, a rather low activity for photodecomposition of water was obtained as shown in Table 2. However, after the H_2O treatment and recalcination, the photodecomposition activity of water over Ni-loaded $Rb_4Nb_6O_{17}$ increased. Successive H_2O treatments and recalcinations produced the catalyst with the highest activity. It was confirmed that neither the H_2O treatment nor the recalcination caused any change in XRD pattern compared to the pattern of the untreated sample. This suggests that the increase in photocatalytic activity is not due to a transformation of the crystal structure of $Rb_4Nb_6O_{17}$ detectable by XRD. We

TABLE 2

The Effect of Treatment for Photodecomposition of Water

	Rate of gas evolution (μmol/h)	
	H_2	O_2
Nontreated	35	9
H_2O-treated	50	19
Recalcined	103	49
H_2O-treated + recalcined	228	110
Recalcined + H_2O-treated	136	66

believe that the increase in activity is due to the removal of excess rubidium compounds, such as RbOH and Rb_2CO_3, which remained after the $Rb_4Nb_6O_{17}$ preparation. The color of $Rb_4Nb_6O_{17}$ powder without H_2O treatment and recalcination did not change when the powder was impregnated in an aqueous nickel nitrate solution for about 1 h. However, the color of the catalyst receiving H_2O treatment and/or recalcination (the pH of the solution in the impregnation process was ca. 11) turned to green, indicative of Ni^{2+} ion-exchange with Rb^+ ions in the interlayer spaces. It seems that a basic medium is not favorable for the Ni^{2+} and Rb^+ exchange reaction.

Table 3 and Fig. 3 show detailed results for the recalcination of the powdered $Rb_4Nb_6O_{17}$, i.e., the dependencies of H_2 and O_2 evolution rates on the temperature and on the time of recalcination. The rates increased with an increase in treatment temperature and were optimized at 1153–1173 K, as shown in Table 3. It was necessary to maintain the samples at recalcination temperature for more than 10 h to increase the activity at 1123 K. In addition to removal of the excess rubidium compounds, recalcination may decrease the defect concentration in $Rb_4Nb_6O_{17}$ crystals, although there is no evidence.

TABLE 3

Dependence of the Activity of Photodecomposition of Water upon the Recalcination Temperature

Recalcination temperature (K)	Recalcination time (hr)	Rate of gas evolution (μmol/h)	
		H_2	O_2
1103	48	98	44
1123	12	102	50
1153	12	136	66
1173	12	136	67
1193	15	96	42
1223	20	51	11
1273	20	8	1

Note. NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$: 1 g; water: 300 ml. H_2 reduction at 773 K for 2 h; O_2 oxidation at 473 K for 1 h.

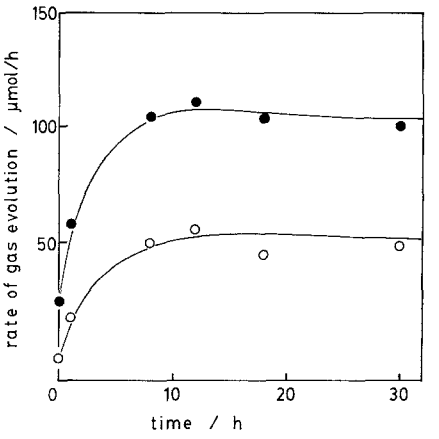

FIG. 3. Dependence of H_2 and O_2 evolution rates on the time of recalcination over NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$ in distilled water. (●) H_2, (○) O_2. Recalcination temperature, 1123 K; reduction temperature, 773 K; oxidation temperature, 473 K.

A typical time course of H_2 and O_2 evolution from distilled water over NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$ receiving H_2O treatment and recalcination is shown in Fig. 4. After an induction period of less than 1 h, H_2 and O_2 evolved steadily in a stoichiometric ratio. The activity, however, decayed gradually with irradiation time.

Figure 5 shows the dependence of the activity of photocatalytic decomposition of water over NiO–$Rb_4Nb_6O_{17}$ upon the amount of NiO loaded. It was found that the activity reached its maximum when the amount of loaded NiO was ca. 0.1 wt%. This value was equal to that found for $K_4Nb_6O_{17}$, but the molar ratios of Ni/Nb over $Rb_4Nb_6O_{17}$ and $K_4Nb_6O_{17}$ were 2.7×10^{-3} and 2.3×10^{-3}, respectively. Thus, $Rb_4Nb_6O_{17}$ seems to need larger amounts of nickel than does $K_4Nb_6O_{17}$ to achieve the same activity.

The dependencies of the activity upon the temperature of H_2 reduction and O_2 oxidation are shown in Fig. 6. The activity increased with reduction temperature up to

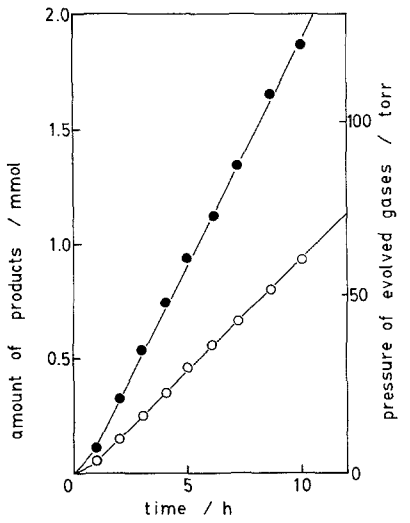

FIG. 4. Photocatalytic decomposition of distilled water over NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$. (●) H_2, (○) O_2. The catalyst was H_2O-treated and then recalcined. Recalcination temperature and time, 1153 K and 12 h; reduction temperature, 773 K; oxidation temperature, 473 K.

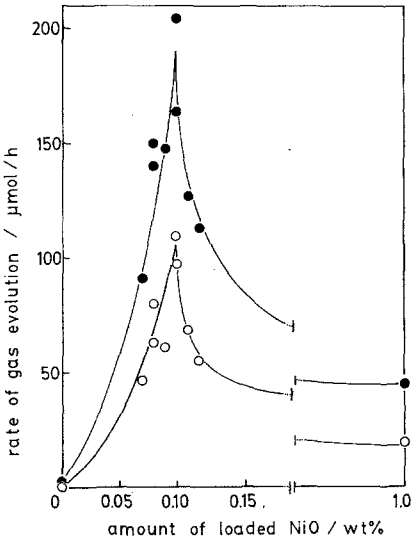

FIG. 5. Dependence of the activity of photocatalytic decomposition of distilled water over NiO–$Rb_4Nb_6O_{17}$ upon the amount of loaded NiO. (●) H_2, (○) O_2. The catalyst was H_2O-treated and then recalcined. Recalcination temperature and time, 1153 K and 12 h; reduction temperature, 773 K; oxidation temperature, 473 K.

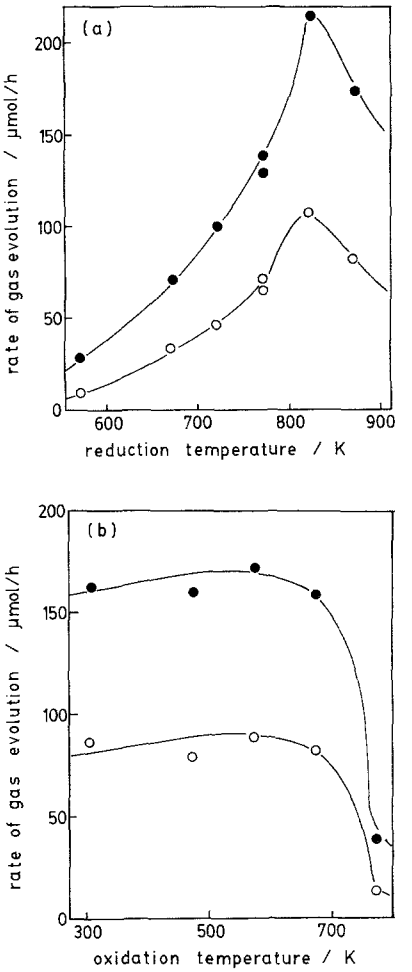

FIG. 6. Dependence of the photodecomposition activity of distilled water over NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$ upon the reduction temperature (a) and the oxidation temperature (b). (●) H_2, (○) O_2. The catalyst was H_2O-treated and then recalcined. Recalcination temperature and time, 1153 K and 12 h. (a) Reduction temperature, 773 K. (b) Oxidation temperature, 473 K.

823 K; above this temperature it decreased. In the case of $K_4Nb_6O_{17}$, the activity was maximal at 673–773 K. The activity increased by O_2 oxidation in the case of $K_4Nb_6O_{17}$ (*4*); however, there was no increase for $Rb_4Nb_6O_{17}$.

Figure 7 shows the dependence of the activity upon pH, which was examined by adding H_2SO_4 or RbOH to the reaction solution. The activity decreased with addition

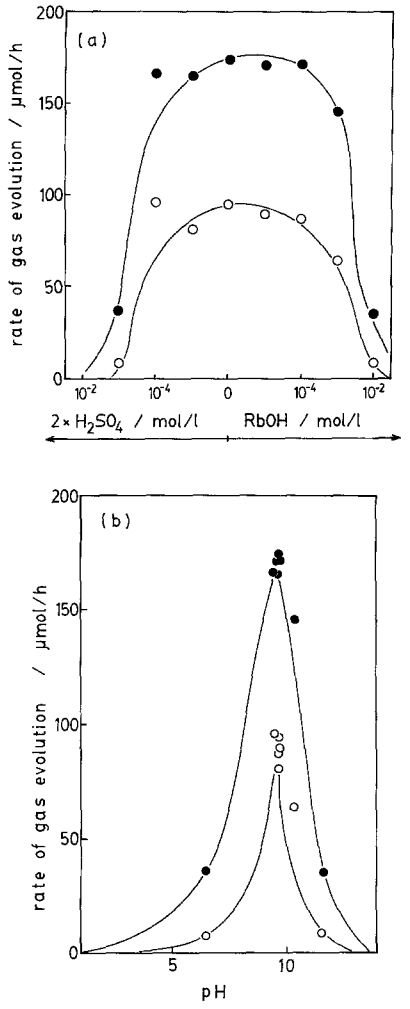

FIG. 7. (a) Effects of the addition of H_2SO_4 and RbOH on the activity of photodecomposition of water over NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$. (b) Dependence of the activity of photodecomposition of water over NiO (0.1 wt%)–$Rb_4Nb_6O_{17}$ upon pH. (●) H_2, (○) O_2. The catalyst was H_2O-treated and then recalcined. Recalcination temperature and time, 1153 K and 12 h; reduction temperature, 773 K; oxidation temperature, 473 K.

of either H_2SO_4 or RbOH. The optimum pH of the solution was obtained when just 1 g of Ni-loaded $Rb_4Nb_6O_{17}$ was suspended in 300 ml distilled water, pH ca. 9.7. A similar dependence of the activity was obtained in the case of NiO–$K_4Nb_6O_{17}$.

In Table 4, the highest steady-state activities are summarized for $Rb_4Nb_6O_{17}$- and $K_4Nb_6O_{17}$-based catalysts. Data for the $K_2Rb_2Nb_6O_{17}$-based catalyst are also shown, although in this case activity was not optimized. The rates of H_2 and O_2 evolutions were estimated from the values during the initial 5 h after an induction period under full irradiation from the high-pressure Hg lamp (450 W) in an inner irradiation cell. The most active catalyst was obtained from $Rb_4Nb_6O_{17}$; the quanum efficiency at 330 nm reached almost 10%.

TABLE 4

Photocatalytic Activity over $A_4Nb_6O_{17}$ (A = K or Rb) and Quantum Efficiency

	Rate of gas evolution (μmol/h)		Quantum efficiency (%)
	H_2	O_2	
$K_4Nb_6O_{17}$	124	62	5.2
$Rb_4Nb_6O_{17}$	228	110	10.0
$K_2Rb_2Nb_6O_{17}$	78	39	3.3

Finally, it should be noted that the activity of Ni-loaded $Rb_4Nb_6O_{17}$ is less stable than that of Ni-loaded $K_4Nb_6O_{17}$. This gradual decay of the activity appears to be due to the oxidation of the ultrafine Ni metal particles which exist in the interlayer spaces (*5*). Therefore a more rapid decay of the activity for $Rb_4Nb_6O_{17}$ suggests an increasesd tendency toward oxidation of ultrafine Ni particles in $Rb_4Nb_6O_{17}$ than that in $K_4Nb_6O_{17}$. A modification to protect the ultrafine Ni metal particles from the oxidation will provide a more stable photocatalyst for the overall water splitting.

CONCLUSION

$Rb_4Nb_6O_{17}$ has the same layered structure as that of $K_4Nb_6O_{17}$ but the interlayer space length of $Rb_4Nb_6O_{17}$ is longer than that of $K_4Nb_6O_{17}$ under reaction conditions. It is thought that the photodecomposition of water proceeds at the interlayer spaces. Therefore, this difference in the interlayer

space lengths is responsible for the photocatalytic activity. Since the synthesis of $Rb_4Nb_6O_{17}$ is different from that of $K_4Nb_6O_{17}$, it is necessary to use H_2O treatment and recalcination for $Rb_4Nb_6O_{17}$ powder before nickel-loading in order to obtain $Rb_4Nb_6O_{17}$ powder which has a high activity for photocatalytic water splitting under band gap irradiation. The catalyst loaded with 0.1 wt% NiO showed the highest activity and its quantum efficiency was almost 10% at 330 nm in distilled water.

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