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Photocatalytic Decomposition of Water over NiO–$K_4Nb_6O_{17}$ Catalyst

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Photocatalytic decomposition of H_2O to form H_2 and O_2 over NiO–$K_4Nb_6O_{17}$ powder (1–10 μm, band gap = 3.3 eV), which is an ion-exchangeable layered compound, proceeds steadily more than 50 h under the bandgap irradiation. Maximum activity was obtained when the reaction was carried out in distilled water where the pH was ca. 11 by elution of K^+ and the quantum efficiency at 330 nm was 3.5 ± 0.5% at the initial stage of the reaction over pretreated NiO(0.1 wt%)–$K_4Nb_6O_{17}$. Several characteristic features of NiO–$K_4Nb_6O_{17}$ were discussed and compared with those of NiO–$SrTiO_3$. © 1988 Academic Press, Inc.

INTRODUCTION

Photodecomposition of H_2O has been studied extensively in recent years, and various homogeneous and heterogeneous systems have been reported (*1*). For the photocatalytic decomposition of water into H_2 and O_2, predominantly semiconductor powders such as $SrTiO_3$ (*2–6*) and TiO_2 (*7–9*) are used, because of the suitable band levels and their stability during reaction.

The activities of $SrTiO_3$ and TiO_2 themselves are negligible for the photodecomposition of water under bandgap irradiation. However, $SrTiO_3$ powder loaded with RhO_x (*2*) or NiO (*3–6*) evolves H_2 and O_2 in the stoichiometric ratio for a few tens of hours, although the activities decay gradually with irradiation time. The estimated quantum efficiencies were ca. 1% in both cases under bandgap irradiation (*2, 3*). Interestingly, $SrTiO_3$ loaded with Rh metal (*2*) or Ni metal (*3*) did not exhibit catalytic activity for the reaction. Several reports on Pt–TiO_2-based photocatalysts have also been published. Recent results, however, have shown that the sustained photodecomposition of H_2O into H_2 and O_2 is extremely difficult to accomplish (*10–12*), whereas the high efficiency of H_2 evolution from aqueous solution containing a sacrificial reagent has been well demonstrated (*1*). It is noteworthy that decomposition of water vapor into H_2 and O_2 proceeded over NaOH-coated Pt–TiO_2 (*7*), and the simultaneous evolution of H_2 and O_2 was also observed over a NiO–TiO_2 photocatalyst in aqueous NaOH solution (3 *N*) (*9*).

Several efforts to construct "integrated" systems for the photocatalytic reactions have been reported (*13*). Some of these consist of photocatalyst intercalated into clay, with layered structures, and exhibit the behavior characteristic of those specific structures. It is possible that these systems will provide further developments in this field.

Recently, the authors have reported preliminary results on a new type of photocatalyst, potassium niobate compounds, especially $K_4Nb_6O_{17}$ (*14, 15*). $K_4Nb_6O_{17}$ is composed of layers of niobium oxide sheets, in which potassium ions locate in two different kinds of interlayers (*16, 17*). One interlayer is easily hydrated but the other is not. Those potassium ions are replaced by various cations (*18*). It has been found that $K_4Nb_6O_{17}$ loaded with NiO

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decomposes H_2O into H_2 and O_2 steadily (*14*). Furthermore, the photocatalytic activity of ion-exchanged $K_4Nb_6O_{17}$ for H_2 evolution from aqueous methanol solution changes markedly depending on the cation; in particular, H^+-exchanged $K_4Nb_6O_{17}$ shows high activity (the quantum yield is ca. 50% at 330 nm) without the assistance of other materials such as Pt (*15*).

In this paper, the photodecomposition of water over some modified $K_4Nb_6O_{17}$ catalysts is reported in detail.

EXPERIMENTAL

$K_4Nb_6O_{17}$ powder was prepared from Nb_2O_5 and K_2CO_3 at 1573 K in air. The crystal structure was confirmed by X-ray diffraction (*19*). $K_4Nb_6O_{17}$ catalysts loaded with transition metal oxides (Cr, Mn, Fe, Co, Ni, and Cu) were prepared by the impregnation method; $K_4Nb_6O_{17}$ was added in aqueous solution which contained the required amount of metal nitrate. Then the sample was calcined at ca. 550 K in air for 1 h after the impregnated niobates were dried on a water bath. At this stage the catalyst is referred to as "untreated" catalyst. During this procedure, the potassium ions are replaced by transition metal cations. $K_4Nb_6O_{17}$ photocatalysts loaded with noble metal oxides (Pt, Ru and Rh) were prepared in aqueous metal chloride (H_2PtCl_6, $RuCl_3$, and $RhCl_3$) solutions in a manner similar to that mentioned above. They were calcined at ca. 800 K in air for 2 h.

Pretreatments of the calcined catalysts were carried out in a closed-gas circulation system connected to a vacuum line (*3*). The typical pretreatment was as follows: the catalyst was reduced by H_2 (ca. 40 kPa) at 773 K for 2 h (R773) and then oxidized by O_2 (ca. 16 kPa) at 473 K for 1 h (O473). (The catalyst is now referred to as the "R773–O473" catalyst.) During reduction of untreated catalysts with H_2, the transition metal cations are replaced by H^+ to maintain the electrical neutrality of the catalysts.

Catalysts were characterized by scanning electron microscopy (SEM), UV diffuse reflectance, and electron spin resonance (ESR). The quantum efficiency was determined by chemical actinometry using $(NH_3)_3Fe(COO)_3 \cdot 3H_2O$, an Xe lamp, and a monochromator.

Photocatalytic reactions, i.e., photodecomposition of H_2O (300 ml), H_2 evolution from aqueous methanol solution (CH_3OH 10 ml + H_2O 300 ml), and O_2 evolution from aqueous silver nitrate solution (0.01 mol/liter, 300 ml), were carried out in a closed-gas circulation reaction system. A mixture of a catalyst (1 g) and aqueous solution in an inner irradiation reaction cell (*3*) was degassed completely and then Ar (ca. 16 kPa) was introduced. The catalyst in solution was suspended by a magnetic stirrer and irradiated using a high-pressure mercury lamp (USHIO UM-452, 450 W).

The evolved gases were analyzed by gas chromatography (TCD, Ar carrier) with a molecular sieve 5A column as mentioned in a previous paper (*3*).

It is known that $K_4Nb_6O_{17}$ is normally hydrated and changes into $K_4Nb_6O_{17} \cdot xH_2O$ ($x = 3$ or 4.5) (*19*), which is probably the form during the photoreaction in aqueous solution. In this paper, however, the catalyst is described as "$K_4Nb_6O_{17}$."

RESULTS

Figure 1 shows an SEM photograph and a schematic view of the structure of $K_4Nb_6O_{17}$. The SEM photographs of the catalysts loaded with various materials and treated under various conditions were similar to those of $K_4Nb_6O_{17}$ itself. The basal and edge planes are discriminated in a rectangular parallelepiped shape. The particle size was estimated to be between 1 and 10 μm, and the BET surface area was small (≤ 1 m^2/g) (*14*).

The amounts of H_2 and O_2 evolved from distilled water for 10 h over $K_4Nb_6O_{17}$ and those loaded with various transition metal oxides are summarized in Table 1. The evolution of H_2 and O_2 was observed over

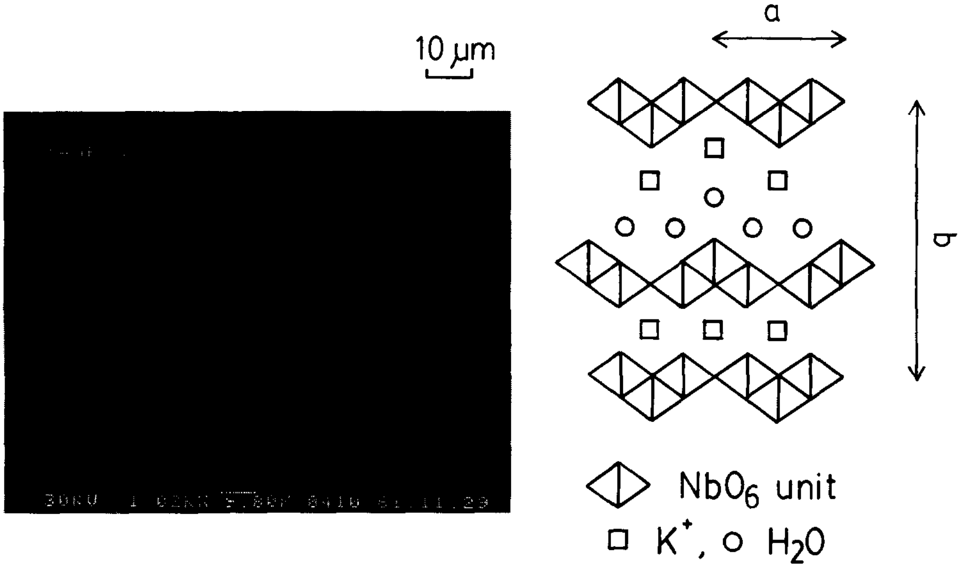

FIG. 1. SEM photograph (×600) and schematic view of $K_4Nb_6O_{17} \cdot 3H_2O$ photocatalyst with a layer structure.

TABLE 1

Photodecomposition of Water over $K_4Nb_6O_{17}$ Loaded with Metal Oxides

Metal oxide[a] (1 wt%)	Pretreatment[b]	Amount of gas evolved (μmol)	
		H_2	O_2
None	R773–O473	63	7
Cr_2O_3	R773–O473	27	0
Mn_3O_4	R773–O473	6	0
Fe_2O_3	R873–O473	8	0
Co_3O_4	R823–O473	32	0
NiO	R773–O473	630	310
CuO	R773–O473	12	1
PtO[c]	Untreated	19	0
	R773–O473	12	0
RuO_2[c]	Untreated	77	16
	R773–O473	9	0
Rh_2O_3[c]	Untreated	18	0
	R773–O473	3	0

Note. Catalyst, 1 g; H_2O, 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell; reaction time, 10 h.

[a] The metal oxides represented are the probable forms under the reaction conditions but were not confirmed.

[b] R773–O473 means reduction by H_2 at 773 K, then oxidation by O_2 at 473 K.

[c] 0.5 wt% loading.

$K_4Nb_6O_{17}$ alone as well as over catalysts loaded with NiO, CuO, and RuO_2. In other cases, only small amounts of H_2 were detected. Of all the catalysts, NiO–$K_4Nb_6O_{17}$ showed the highest activity and evolved H_2 and O_2 in the stoichiometric ratio. Therefore, the NiO–$K_4Nb_6O_{17}$ photocatalyst was examined in detail.

In Fig. 2, UV diffuse reflectance spectra of $K_4Nb_6O_{17}$ and NiO(1 wt%)–$K_4Nb_6O_{17}$ are shown. The bandgap of the catalyst was estimated to be 3.3 eV from the spectrum of $K_4Nb_6O_{17}$. The untreated NiO(1 wt%)–$K_4Nb_6O_{17}$ was light green. Judging from the spectrum the untreated NiO–$K_4Nb_6O_{17}$ catalyst contains mainly Ni^{2+} ions in the interlayer by replacing K^+ ions. The UV diffuse reflectance spectrum of the R773–O473 catalyst showed broad absorption of Ni metal and NiO in addition to that of $K_4Nb_6O_{17}$.

In Table 2, the photocatalytic activities of the decomposition of water, the H_2 evolution from aqueous methanol solution, and the O_2 evolution from aqueous silver nitrate solution over $K_4Nb_6O_{17}$ and catalysts loaded with NiO are summarized. It is clear that proper pretreatment of the catalysts is

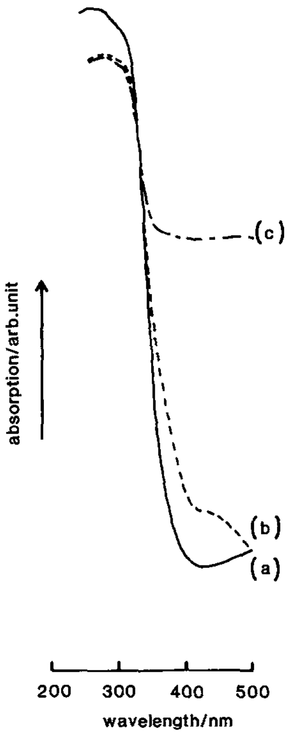

FIG. 2. UV diffuse reflectance spectra of $K_4Nb_6O_{17}$ and NiO–$K_4Nb_6O_{17}$ photocatalysts: (a) untreated $K_4Nb_6O_{17}$, (b) untreated NiO(1 wt%)–$K_4Nb_6O_{17}$, (c) R773–O473 NiO(1 wt%)–$K_4Nb_6O_{17}$.

indispensable to the photodecomposition of H_2O. The untreated NiO–$K_4Nb_6O_{17}$ catalyst showed very low activity. For the catalyst reduced by H_2 at 773 K, i.e., the R773 catalyst, the activity increased markedly and both H_2 and O_2 evolved in the stoichiometric ratio. Ni^{2+} was reduced into Ni metal by this pretreatment which is discussed later. When the R773 catalyst was oxidized at 473 K, i.e., the R773–O473 catalyst, the activity increased, whereas at a higher oxidation temperature, the R773–O773 catalyst, the activity decreased drastically.

In the case of H_2 evolution from aqueous methanol solution over NiO(0.1 wt%)–$K_4Nb_6O_{17}$, almost the same effects produced by the pretreatment in the photodecomposition of water were observed, although the change in activity was much smaller. On the contrary, the activities of the O_2 evolution from aqueous silver nitrate solution over those catalysts were low in all cases. Furthermore, the rates of O_2 evolution from distilled water were faster than those for O_2 evolution from aqueous silver nitrate solution for the R773 and R773–O473 catalysts.

TABLE 2

Photocatalytic Activities over $K_4Nb_6O_{17}$ and NiO–$K_4Nb_6O_{17}$ after Pretreatment

Catalyst	Pretreatment	H_2O		CH_3OH_{aq}[a]	$AgNO_{3_{aq}}$[b]
		H_2 (μmol/h)	O_2 (μmol/h)	H_2 (μmol/h)	O_2 (μmol/h)
$K_4Nb_6O_{17}$	Untreated	5	0	177	10
	R773	5	1		
	R773–O473	8	1		
NiO(0.1 wt%)–$K_4Nb_6O_{17}$	Untreated	4	1	667	2
	R773	55	28	1593	7
	R773–O473	77	37	1300	9
	R773–O773	4	1	814	5
NiO(1 wt%)–$K_4Nb_6O_{17}$	Untreated	3	1		
	R773	19	9		
	R773–O473	66	38		

Note. Catalyst, 1 g; solution, 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell.

[a] MeOH : H_2O = 1 : 30 (v/v).

[b] 0.01 mol/liter.

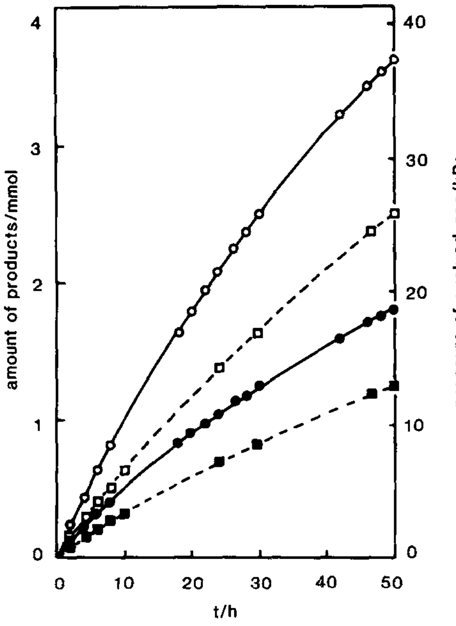

FIG. 3. Photocatalytic decomposition of distilled water over the R773–0473 NiO-$K_4Nb_6O_{17}$ catalysts. ○, H_2; ● O_2—over NiO(0.1 wt%)-$K_4Nb_6O_{17}$. □, H_2; ■, O_2—over NiO(1 wt%)-$K_4Nb_6O_{17}$. Catalyst, 1 g; distilled water, 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell.

The time courses of H_2 and O_2 evolution from distilled water over R773–0473 NiO(0.1 wt%)-and NiO(1 wt%)-$K_4Nb_6O_{17}$ catalysts are shown in Fig. 3. It was found that H_2 and O_2 evolved in a 2 : 1 ratio for a long period and the catalyst loaded with 0.1 wt% NiO showed higher activity than that loaded with 1 wt% NiO. In both cases, the activities decreased gradually with time. When the reaction continued after the evacuation of products at 50 h, the activity was the same as before the evacuation, which meant that there was no significant effect of the gaseous H_2 and O_2 evolved on the decomposition of water.

The quantum efficiency was measured by means of chemical actinometry, according to the relationship

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

The maximum quantum efficiency at the initial stage of the photodecomposition of water over R773–0473 NiO(0.1 wt%)-$K_4Nb_6O_{17}$ catalyst was 3.5 ± 0.5% at 330 nm.

Figure 4 shows the dependence of the activity of NiO(0.1 wt%)-$K_4Nb_6O_{17}$ upon the pretreatment temperature of the reduction by H_2 when the reoxidation temperature was kept at 473 K. The optimum reduction temperature was about 673–773 K.

The dependence of the activity on the amount of NiO loaded over $K_4Nb_6O_{17}$ was studied, as shown in Fig. 5. Optimum activity was obtained at NiO loading of 0.1 wt%. Activity was proportional to the amount of supported NiO in the low loading region (<0.1 wt%), while it decreased gradually in the high loading region (>0.1 wt%).

The effects of the addition of H_2SO_4 and KOH on the activity of the photodecomposition of water over NiO(0.1 wt%)-$K_4Nb_6O_{17}$ were studied (Fig. 6a). In Fig. 6b, the activity was plotted against the pH of the solution during the reaction. The pH of the solution of distilled water (300 ml) containing the NiO(0.1 wt%)-$K_4Nb_6O_{17}$ catalyst (1 g) was ca. 11, which meant about 5%

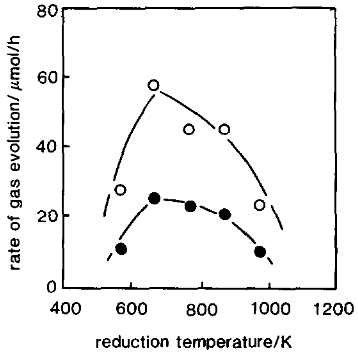

FIG. 4. Dependence of the activity of photodecomposition of distilled water over NiO(0.1 wt%)-$K_4Nb_6O_{17}$ upon the reduction temperature of pretreatment. ○, H_2; ● O_2. Catalyst, 1 g; distilled water, 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell; reoxidation temperature, 473 K.

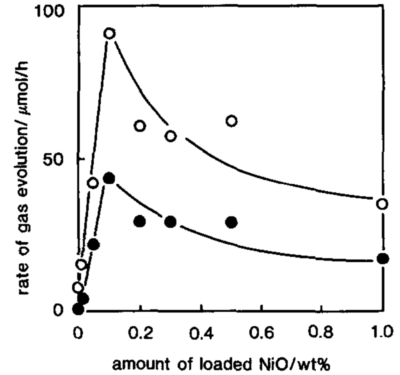

FIG. 5. Dependence of the activity of photocatalytic decomposition of distilled water over R773-O473 NiO-$K_4Nb_6O_{17}$ upon the amount of loaded NiO. ○, H_2; ●, O_2. Catalyst, 1 g; distilled water, 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell.

of the K^+ was released into the solution and replaced by H^+. Furthermore, the pH of the solution did not change that much, even after addition of H_2SO_4 or KOH, probably because of the buffer effect of $K_4Nb_6O_{17}$ caused by the reversible replacement between K^+ and H^+. In both cases, activity decreased as the amount of added H_2SO_4 or KOH increased.

The effect of the "neutralization" on photocatalytic activity is shown in Fig. 7. At first, the reaction over NiO(0.1 wt%)-$K_4Nb_6O_{17}$ was carried out in aqueous KOH solution (1 *N*), and only H_2 evolved slowly. After evacuation of the gas phase, an equivalent amount of H_2SO_4 was added. The rate of H_2 evolution increased and O_2 began to evolve. On the other hand, addition of KOH to the catalyst in aqueous H_2SO_4 solution did not lead to recovery of activity, as in the "neutralization" of aqueous KOH solution by H_2SO_4.

ESR spectra of $K_4Nb_6O_{17}$ and NiO(0.1 wt%)-$K_4Nb_6O_{17}$ after various treatments and the photodecomposition of water are shown in Fig. 8. When the NiO(0.1 wt%)-$K_4Nb_6O_{17}$ catalyst was reduced by H_2 at 773 K (R773), the intense ferromagnetic resonance line of metallic nickel particles was observed (d), while no signal was detected in the untreated sample (c). Even after reoxidation at 473 K (R773-O473), the metallic nickel particles remained almost unchanged (e). When the R773 catalyst was reoxidized at 773 K (R773-O773), the ferromagnetic resonance of metallic nickel particles disappeared (f). Figure 8g is the spec-

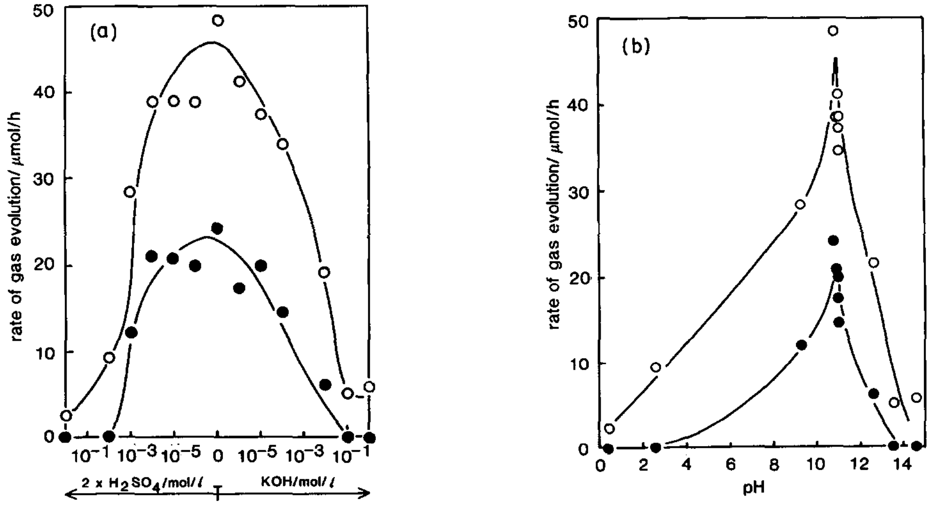

FIG. 6. (a) Effects of the addition of H_2SO_4 and KOH on the activity of photodecomposition of water over R773-O473 NiO(0.1 wt%)-$K_4Nb_6O_{17}$. (b) Dependence of the activity of photodecomposition of water over R773-O473 NiO(0.1 wt%)-$K_4Nb_6O_{17}$ upon pH. ○, H_2; ●, O_2. Catalyst, 1 g; solution, 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell.

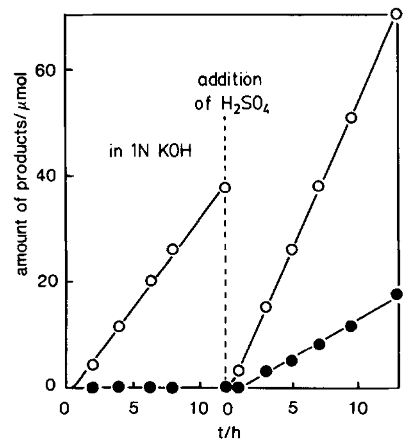

FIG. 7. Effect of the addition of H_2SO_4 on the activity of photodecomposition of water in aqueous KOH solution (1 *N*) over R773–0473 NiO(0.1 wt%)–$K_4Nb_6O_{17}$. ○, H_2; ● O_2. Catalyst, 1 g; KOH_{aq} (1 *N*), 300 ml; light source, high-pressure mercury lamp (450 W); reaction cell, inner irradiation reaction cell.

trum of the R773–0473 catalyst after a long period of irradiation (≳100 h); activity (H_2; 7 μmol/h, O_2; 4 μmol/h) decreased to the value almost comparable with that of the untreated catalyst. No ferromagnetic resonance due to the nickel metal particles was observed. Thus, the oxidation of Ni metal, which caused a decrease in activity, proceeded during the photodecomposition of water.

DISCUSSION

Catalytic Nature of the Photodecomposition of Water over Various $K_4Nb_6O_{17}$ Catalysts

In Table 1, the amounts of H_2 and O_2 evolved over $K_4Nb_6O_{17}$ loaded with various transition metal oxides are summarized. It is emphasized that pretreated $K_4Nb_6O_{17}$ evolved not only H_2 but also O_2 under irradiation. To our knowledge, $K_4Nb_6O_{17}$ is the first example of a catalyst that evolves H_2 and O_2 together without modifications by other materials. The amount of O_2 evolved was 75 μmol after 75 h, ca. 30% of the amount expected for the stoichiometric photodecomposition of water calculated from the amount of H_2 simultaneously evolved (550 μmol), as shown in Table 3. The rates of H_2 and O_2 evolution were almost constant during the reaction, as shown in a previous paper (*14*). There seems to be two possibilities to explain the shortage of evolved O_2. One is the effect of impurities that are oxidized instead of water; another is that the oxidized species of water is trapped in the catalyst, e.g., within the interlayer. At present, we favor the latter possibility because the effect of impurities was negligible in the case of NiO–$K_4Nb_6O_{17}$, i.e., the ratio of evolved H_2 to O_2 was 2 : 1, which was pretreated similarly to the $K_4Nb_6O_{17}$. In any event, the simultaneous evolution of O_2 and H_2 suggests potential applications of this material and this characteristic is probably due to the specific nature of niobium and the layered structure of the catalyst.

In most catalysts loaded with metal oxides, small amounts of H_2 but no O_2 are observed. Similar cases, i.e., lack of O_2 evolution, were also previously reported for the photodecomposition of water

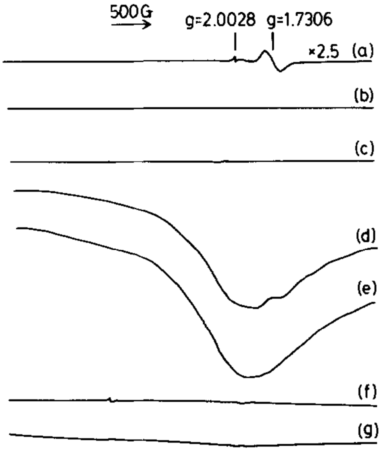

FIG. 8. ESR spectra of $K_4Nb_6O_{17}$ and NiO(0.1 wt%)–$K_4Nb_6O_{17}$ after pretreatment and the reaction of photodecomposition of water. (a)R773 $K_4Nb_6O_{17}$, (b) R773–0473 $K_4Nb_6O_{17}$, (c) untreated NiO(0.1 wt%)–$K_4Nb_6O_{17}$, (d) R773 NiO(0.1 wt%)–$K_4Nb_6O_{17}$, (e) R773–0473 NiO(0.1 wt%)–$K_4Nb_6O_{17}$, (f) R773–0773 NiO(0.1 wt%)–$K_4Nb_6O_{17}$, (g) R773–0473 NiO(0.1 wt%)–$K_4Nb_6O_{17}$ after the reaction of photodecomposition of water for 100 h.

TABLE 3

Comparison of the Amounts of Gases Evolved over $K_4Nb_6O_{17}$ Catalysts

Catalyst	Reaction time (h)	H_2 evolved (μmol)	O_2 evolved (μmol)	e^- (h^+) reacted (μmol)	Amount of Ni (μmol)	Amount of Nb (μmol)
$K_4Nb_6O_{17}$	75	550	75	1100 (300)	—	6000
NiO(0.1 wt%)-$K_4Nb_6O_{17}$	50	3600	1800	7200	13	6000
NiO(1 wt%)-$K_4Nb_6O_{17}$	100	4500	2200	9000	130	6000

Note. Catalyst, 1 g.

(*10–12*). Those cases were often explained as adsorption of oxygen species on the catalyst surfaces or attributed to the existence of impurities such as carbon species, which work as reducing agents. Although the reason is not clear at present, the amount of H_2 evolved was too small to discuss the catalytic nature, and we have never actually observed O_2 evolution over those catalysts, even after prolonged irradiation. On the other hand, $K_4Nb_6O_{17}$ catalysts loaded with RuO_2 and CuO evolved H_2 and O_2 simultaneously, although the amounts of O_2 evolved were less than expected from the stoichiometric decomposition. Even in these cases, it was still not clear whether the reaction proceeded catalytically, because the total amounts of gases evolved were not large enough to prove the catalytic cycle, even after prolonged irradiation. Furthermore, those activities were almost the same or less than that of $K_4Nb_6O_{17}$ itself. For all of these systems, sufficient evidence of the photocatalytic decomposition of water has not been obtained, at least with the present pretreatments and reaction conditions.

$K_4Nb_6O_{17}$ loaded with NiO showed the highest activity and H_2 and O_2 evolved in the stoichiometric ratio. The optimal amount of NiO loading was ca. 0.1 wt%. One of the roles of NiO or Ni metal is inferred to be promotion of the reduction of H^+ into H_2, as shown in Table 2. The catalytic property of the NiO surface for H_2 evolution was also demonstrated for NiO–$SrTiO_3$ catalyst (*3*). Another significant effect of NiO loading is the evolution of O_2 in the stoichiometric ratio. The amount of O_2 evolved without NiO loading was much less than expected, which might indicate the catalytic nature of NiO for O_2 evolution. When the loading of NiO exceeded 0.1 wt%, the activity decreased gradually although H_2 and O_2 evolved in the 2 : 1 ratio. This decline would be attributed to some extent to the absorption of photons ($h\nu \gtrsim 3.3$ eV) by Ni metal and/or NiO as shown in the UV diffuse reflectance spectra in Fig. 2c. It is clear that the amounts of products evolved far exceeded that of Ni atoms and that the calculated amounts of reacted e^- and h^+ for the reduction and oxidation of water were also greater than that of Nb atoms in the catalyst used, as shown in Table 3. Furthermore, even after long reactions (50–100 h), both catalysts, NiO(0.1 wt%)- and NiO(1 wt%)–$K_4Nb_6O_{17}$, maintained considerable activities. In view of these results, it is clear that the photocatalytic decomposition of H_2O occurs over the NiO–$K_4Nb_6O_{17}$ catalyst. Activity decayed gradually with reaction time, as mentioned above, probably because of the oxidation of loaded Ni metal by the positive hole in the valence band and/or by the oxidation products of H_2O. Thus, the oxidation of H_2O into O_2 and the oxidation of nickel metal into Ni^{2+} compete with each other during the reaction. Judging from the results in Table 3, the relative rate of Ni metal oxidation against that of O_2 evolution was less than 0.4% for NiO(0.1 wt%)–$K_4Nb_6O_{17}$. Thus, the deviation from the stoichiometric ratio of evolved H_2 and O_2 caused by the oxidation of Ni metal is negligible.

Comparison of NiO–$K_4Nb_6O_{17}$ and NiO–$SrTiO_3$

We have previously reported on the NiO–$SrTiO_3$ photocatalyst which also decomposes water into H_2 and O_2 in the stoichiometric ratio (*3–6*). This catalyst is activated in a manner very similar to the NiO–$K_4Nb_6O_{17}$ catalyst, i.e., reduction by H_2 at 773 K and reoxidation by O_2 at 473 K. The importance of the existence of Ni metal was also demonstrated both on $K_4Nb_6O_{17}$ and on $SrTiO_3$ (*20*). Nevertheless, several differences exist.

First, the effect of the pretreatment by H_2 at 773 K (R773 catalysts) was different. For NiO–$K_4Nb_6O_{17}$, the R773 catalyst evolved H_2 and O_2 in the 2 : 1 ratio, as shown in Table 2, whereas no O_2 evolved and the rate of H_2 evolution decayed rapdily for NiO–$SrTiO_3$ (*3*). In the latter case, instead of the water, the reduced Ni was oxidized into $Ni(OH)_2$ during the reaction (*20*). It was also found that Ni metal particles in R773 NiO–$K_4Nb_6O_{17}$ were rather stable in aqueous H_2SO_4 solution (1 *N*) for several days in the dark, although the Ni metal on $SrTiO_3$ dissolved completely in a day. Ni particles in pretreated NiO–$SrTiO_3$ were proved to be located over the $SrTiO_3$ surface (*20*). In view of these facts, the nickel in NiO–$K_4Nb_6O_{17}$ may be located at the interlayer of niobium oxide sheets and be protected from oxidation to some extent.

Second, a marked difference between these catalysts is the dependence of activity on the pH of aqueous solution. It has been known that over $SrTiO_3$ catalysts a concentrated alkaline solution is favorable for the decomposition of water (*2, 3, 6*) as well as TiO_2 catalysts (*7, 9*). However, over NiO–$K_4Nb_6O_{17}$ the optimum condition is obtained in distilled water (the pH of the solution was ca. 11 by elution of K^+) and in concentrated KOH solution, the rate of H_2 evolution decreased and no O_2 was detected.

Third, the activity of O_2 evolution from aqueous silver nitrate solution over NiO–$K_4Nb_6O_{17}$ is low; i.e., it was lower than that of the O_2 evolution from distilled water. Over NiO–$SrTiO_3$, O_2 evolution was much enhanced by the addition of Ag^+ as oxidizing agent (*3*). Ag^+ ions and Ag metal, which are intercalated, might be working as recombination centers for electrons and holes, reducing the efficiency of the photoreaction. A similar decrease in activity was observed previously for H_2 evolution as a result of the intercalation of Ni^{2+}, Co^{2+}, and Cu^{2+} (*15*).

Fourth is the effect of evolved O_2 on the photodecomposition of water. Along with the irradiation time, a considerable amount of O_2 accumulated, e.g., 19 kPa after 50 h in Fig. 3, in the system. In the case of NiO–$SrTiO_3$, moderate suppression of the H_2 evolution by O_2 was observed (*3*). However, no distinguishable effect was found over NiO–$K_4Nb_6O_{17}$ as stated above. Most of these differences seem to be related to the structure of the catalyst, i.e., Ni and/or NiO particles locate within the interlayer into which the migration of evolved O_2 may be hindered. A detailed study of the structure of this catalyst by SEM, XPS, EXAFS, and XRD and the mechanism of the photodecomposition of water will be reported in subsequent papers.

SUMMARY

Pretreated $K_4Nb_6O_{17}$ not modified by other materials evolved considerable amounts of H_2 and O_2 from water under irradiation, although the ratio of H_2 to O_2 was not exactly 2 : 1. Pretreated NiO–$K_4Nb_6O_{17}$ powder shows catalytic activity for the photodecomposition of water under bandgap (3.3 eV) irradiation. The catalyst loaded with 0.1 wt% NiO exhibited the highest activity and the optimum pretreatment conditions were H_2 reduction at 673–773 K for 2 h and O_2 oxidation at 473 K for 1

h. The quantum efficiency was 3.5 ± 0.5% at 330 nm in distilled water. Activity decreased gradually with reaction time, which was attributed to the oxidation of Ni metal produced by the pretreatment. The effect of the reverse reaction was negligible under the experimental conditions.

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