

Photocatalytic decomposition of water over cesium-loaded potassium niobate photocatalysts

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Abstract

Hydrogen evolution from photocatalytic decomposition of water has been studied over cesium-loaded potassium niobate photocatalysts. Various photocatalyst supports and loading metals were used to obtain an active photocatalyst on the hydrogen evolution. The effect of additives in photoreaction as well as of the photocatalyst were also investigated. Cesium loaded on potassium niobate improved the hydrogen evolution due to its low ionization energy. The maximum rate of hydrogen evolution was about 37.4 mmol h^{-1} over cesium-loaded potassium niobate photocatalyst from photocatalytic decomposition of formaldehyde solution. Hydrogen evolution increased in formaldehyde solution, but oxygen evolution did not occur. Oxygen evolution increased by addition of formic acid in water. Additives enhanced the photodecomposition behavior of water and made an influence on the evolution rate of hydrogen or oxygen. © 1998 Elsevier Science B.V.

Keywords: Photocatalytic decomposition; Cs-potassium niobate; Additives

1. Introduction

Hydrogen is one of the important materials needed in making an industrial commodity. It is used in the reduction of metal oxides and in other metalworking operations. Some of the industrial syntheses using hydrogen include the production of ammonia, hydrochloric acid, aluminum alkyls, methanol, higher alcohols, and aldehydes.

The method of the hydrogen production by water photolysis using photocatalysts has been known as an economic and clean technology.

The development of highly photoresponsible photocatalysts is the core of water photolysis. Fujishima and Honda [1,2] have suggested a photoelectrochemical principle which uses the semiconductor metal oxide such as TiO_2 on water photolysis. Domen et al. [3–5] reported that NiO-SrTiO_3 powder pretreated properly can steadily decompose water photocatalytically. Lehn et al. [6] also have showed the catalytic activity from the photodecomposition of water over SrTiO_3 powders which were modified by rhodium oxide. Recently, some alkali-layered metal oxide photocatalysts have been presented as highly photoresponsible photocatalysts improving the photocatalytic activity [7–9].

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Loading metals on photocatalyst supports can also enhance the photocatalytic activity for hydrogen evolution. Addition of additives in water is also one of the methods to increase the hydrogen evolution [10–12]. Therefore, the investigations of highly photoresponsible metal-loaded photocatalysts as well as of effective additives are very important to improving hydrogen evolution ability.

In the present work, to obtain high activity for hydrogen evolution from photocatalytic decomposition of water, the photocatalyst supports and loading metals have been investigated in various metals and metal compounds. Photocatalytic reaction in additive solution has been studied to improve the photocatalytic activity for hydrogen evolution. The role of additives was also proved to the photocatalytic reaction.

2. Experimental

Photocatalyst supports were prepared by the calcination of metal oxide (Nb_2O_5 , TiO_2 , ZrO_2 , V_2O_5 , Ta_2O_5) with alkaline carbonate (K_2CO_3 , Cs_2CO_3 , NaCO_3) at 1573 K for 15 min in air. Products were washed by distilled water and dried after calcination. Metal-loaded photocatalysts were prepared by typical incipient wetness method with various metal reagent which makes control as 0.1 wt% of metal content according to the photocatalyst support. The metal-loaded photocatalysts were calcined at 473 K for 2 h before photocatalytic reaction.

The photocatalytic reaction was carried out in a completely air-free closed gas circulation system connected to a gas chromatograph and vacuum system. We can indicate the schematic diagram of the photocatalytic reaction system in Fig. 1. The reactants were irradiated by a high pressure Hg lamp (Ace glass, 450 W) installed within the reactor. The remained air in the reaction system was excluded completely by the vacuum system, and then N_2 gas was introduced by ca. 200 Torr before the reaction. Evolved gases from the reaction were quantita-

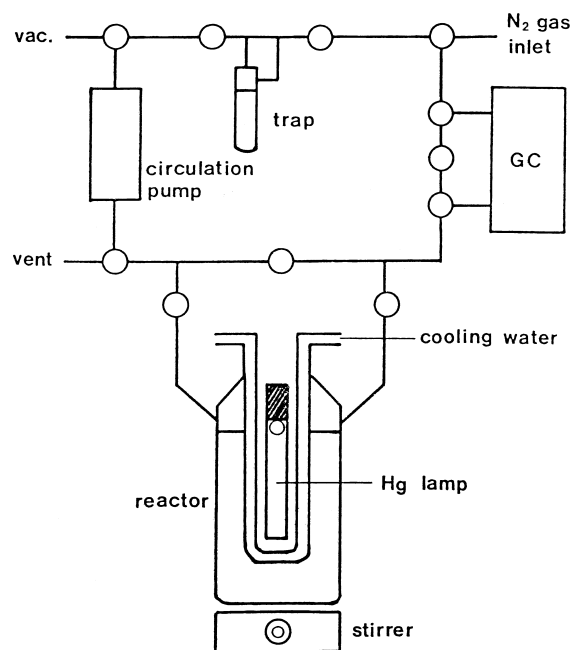


Fig. 1. Schematic diagram of the photocatalytic reaction system.

tively analyzed by gas chromatograph (GC-8A, Shimadzu, molecular sieve 5A column).

Pure water or additive solution could be used as a reactant. Photocatalyst (1 g) was suspended with 500 ml of reactant by magnetic stirring. Formaldehyde (Ducksan, GR) and formic acid (Ducksan, GR) were used as additives.

The characterization of photocatalysts was performed by XRD (Rikagu, D/MAX-B), SEM (Jeol, JSM-840A), and UV/VIS Recording Spectrometer (UV 2100, Shimadzu). The liquid reactant remained after reaction was analyzed by gas chromatograph (Hewlett Packard, 5890 Series II, Porapak Q column) to identify new liquid products.

3. Results and discussion

3.1. Hydrogen evolution over Pt-loaded photocatalysts

The photocatalytic activity of Pt-loaded photocatalysts was examined to the hydrogen evolution from water photodecomposition. Hydrogen

Table 1

The rate of hydrogen evolution from pure water over Pt-loaded photocatalysts

Photocatalysts	Rate of H ₂ evolution (mmol h ⁻¹)
Pt(0.1)/K ₄ Nb ₆ O ₁₇	0.03
Pt(0.1)/K ₂ Ti ₄ O ₉	0.01
Pt(0.1)/Na ₄ Nb ₆ O ₁₇	0.02
Pt(0.1)/Ca ₂ Nb ₆ O ₁₇	—
Pt(0.1)/K ₂ Zr ₄ O ₉	—

and oxygen gas were produced from the photocatalytic decomposition of water. Table 1 summarized the rates of hydrogen evolution over various Pt-loaded photocatalysts. Pt(0.1)/K₄Nb₆O₁₇ photocatalyst was presented as the highest photocatalytic activity to increase the hydrogen evolution among the various Pt-loaded photocatalysts. Potassium niobate (K₄Nb₆O₁₇) is an ascertaining excellent photocatalyst support one among the various metal compound supports.

Potassium niobate has the layered metal compound structure. As we have shown in Fig. 2, the conjugated layers were found within the single crystal of potassium niobate. When metals were loaded on potassium niobate support, it has been known that the metals have their place in the interlayer of the support [7]. The elec-

trons, produced from layers of potassium niobate support by ultraviolet irradiation, were transferred to the loaded metal in the process of the photoreaction [7]. The reduction of hydrogen ion by these electrons evolves hydrogen gas. It is because the Pt-loaded potassium niobate showed high photocatalytic activity for hydrogen evolution is presumably due to vigorous electronic behavior between layer and metal.

The rate of hydrogen evolution over metal-loaded potassium niobate photocatalysts was summarized in Table 2. In this result, some of metals, such as Fe, Co, Cu, Zn and Al, did not exhibit the photocatalytic activity on the hydrogen evolution. Cs-loaded potassium niobate photocatalyst, however, evolved great amount of hydrogen compared with the other metal-loaded potassium niobate photocatalysts. It can explain that the high photocatalytic activity is due to the low ionization energy of cesium, since the electrons of cesium could be excited easily.

3.2. Hydrogen evolution over Cs-loaded photocatalysts

The photocatalytic activity on the hydrogen evolution was examined over various Cs-loaded

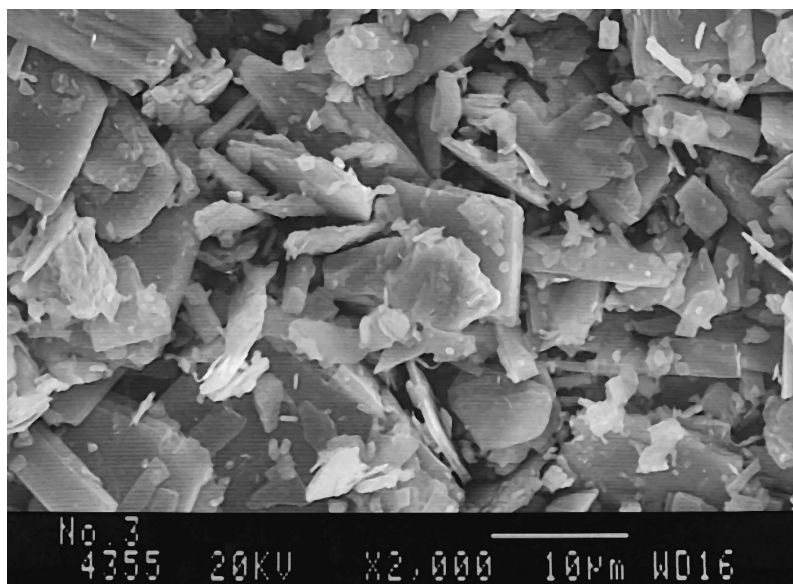


Fig. 2. SEM photograph of potassium niobate photocatalyst support.

Table 2

The rate of hydrogen evolution from pure water over various metal-loaded potassium niobate photocatalysts

Loaded metal ^a	Rate of H ₂ evolution (mmol h ⁻¹)
Cs	1.47
Pt	0.03
Ru	trace
Ir	trace
Ni	trace
Fe, Co, Cu	—
Zn, Al	—

^aLoading amount 0.1 wt%.

photocatalyst supports to investigate loading effect of cesium. The photocatalyst supports were prepared from metal compounds in IVb and Vb groups which have semiconductor properties.

Most of the Cs-loaded photocatalysts showed the photocatalytic activity for hydrogen evolution. Cs(0.1)/K₄Nb₆O₁₇ photocatalyst exhibited the highest evolution rate of hydrogen among the various photocatalysts. Cs-loaded K₂Ti₂O₅ and K₄Ta₆O₁₇ photocatalysts also represented the same photocatalytic activity.

UV adsorption spectrum of Cs(0.1)/K₄Nb₆O₁₇ photocatalyst was shown in Fig. 3. The band gap energy estimated from this spectrum, that is, extrapolating the adsorption edge as shown in the former figure, was ca. 3.5 eV.

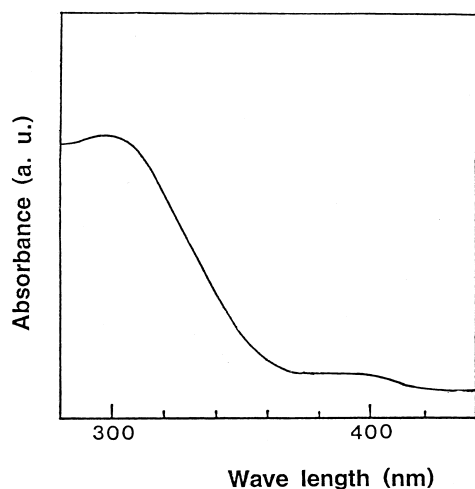


Fig. 3. UV adsorption spectrum of Cs(0.1)/K₄Nb₆O₁₇ photocatalyst.

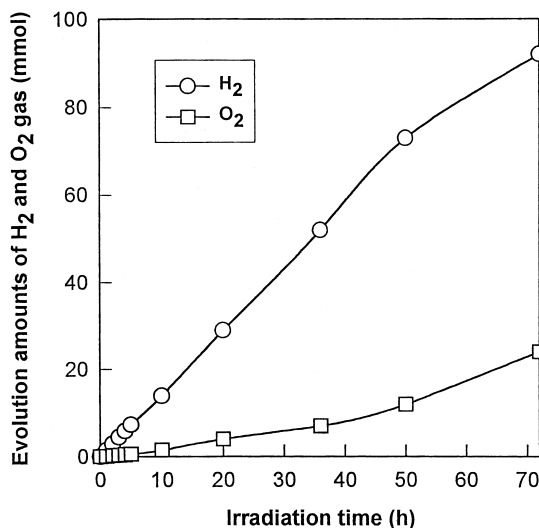


Fig. 4. Evolution amounts of hydrogen and oxygen evolution on Cs(0.1)/K₄Nb₆O₁₇ photocatalyst from water photolysis.

The evolutions of hydrogen and oxygen with irradiation time over Cs(0.1)/K₄Nb₆O₁₇ photocatalyst were shown in Fig. 4. The amount of hydrogen evolution increased continuously in spite of a long irradiation time of more than 72 h. From the above results, we can explain that deactivation of catalyst did not occur in the process of the photocatalytic reaction. By photocatalytic decomposition of water over Cs(0.1)/K₄Nb₆O₁₇ photocatalyst, the rate of hydrogen evolution was 1.47 mmol h⁻¹, but that of the oxygen evolution was only 0.04 mmol h⁻¹. The evolved oxygen gas was very little compared with the hydrogen gas. It has been guessed why the oxygen evolution is interfered owing to the formation of peroxy species on the catalyst during irradiation [13–16], and it could be certified, for the adsorption properties of oxygen on the photocatalyst were superior to that of hydrogen [17]. Furthermore, it is known that cesium has an explosive oxidation ability [18].

Fig. 5 represents the rate of hydrogen evolution with various Cs-loading amount on potassium niobate support. The rate of hydrogen evolution decreased as the Cs-loading amount get increased. The highest evolution rate of

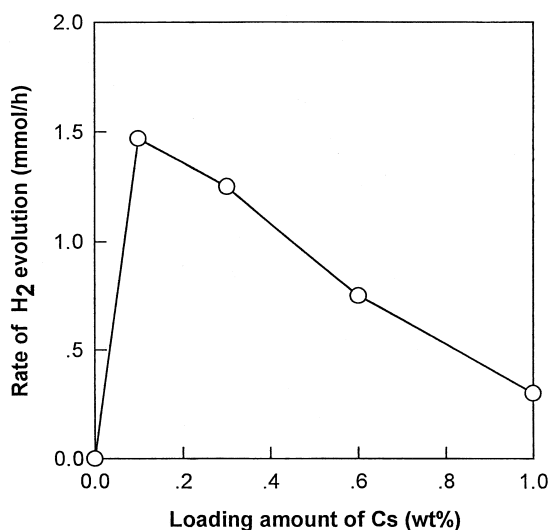


Fig. 5. Rate of hydrogen evolution by various loading amount of cesium on potassium niobate support from water photolysis.

hydrogen exhibited on 0.1 wt% of Cs-loading photocatalyst. Generally, it has been known that the electronic properties of metal/semiconductor type catalysts much improved as the thickness of dispersed metal onto semiconductor surface get decreased. Schwab et al. [19] reported that if the thickness of NiO onto semiconductor surface decreases, the activation energy of

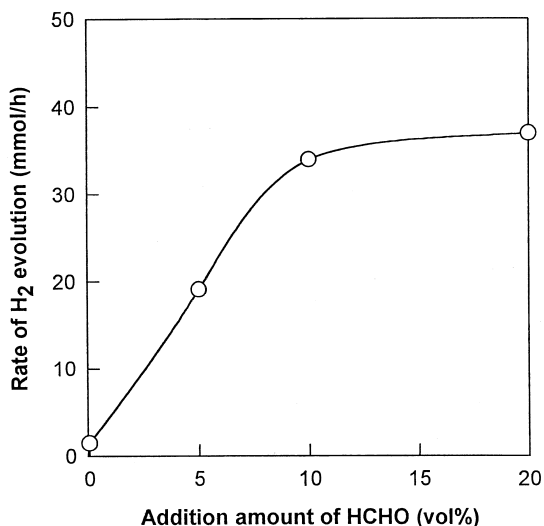


Fig. 6. Rate of hydrogen evolution by addition of formaldehyde on Cs(0.1)/K₄Nb₆O₁₇ photocatalyst from water photolysis.

NiO-loaded catalyst increased according to the oxidation reaction of carbon monoxide.

3.3. Effect of additives in hydrogen evolution

Photocatalytic activity on the hydrogen evolution was observed with the help of the additive solution over Cs(0.1)/K₄Nb₆O₁₇ photocatalyst. Fig. 6 showed how the rate of hydrogen evolution changed according to the addition amount of formaldehyde in water. The rate of hydrogen evolution was 1.47 mmol h⁻¹ in the photodecomposition of pure water, whereas it increased abruptly to 19.1 mmol h⁻¹ in the photodecomposition of 5 vol% formaldehyde solution (Table 3). In the photoreaction of 10 vol% formaldehyde solution, the rate of hydrogen evolution increased about 30 times in comparison with that of hydrogen evolution in the pure water photodecomposition. Particularly, no oxygen gas was evolved in the photoreaction of formaldehyde solution, and a little amount of CO gas was observed after 4 h of irradiation time.

The rate of hydrogen evolution improved as the addition amount of formaldehyde increased. When the amount of formaldehyde increased from 5 to 10 vol%, the rate of hydrogen evolution also increased about doubly. But the increment of the rate, if the formaldehyde addition increased from 10 to 20 vol%, was not so much as the double one. From this result, it can be suggested that formaldehyde acts as an accelerator promoting the photodecomposition of water, because the increase of the hydrogen evolution was not according with the increment of formal-

Table 3

The rate of hydrogen evolution from pure water over Cs-loaded photocatalysts

Photocatalyst	Rate of H ₂ evolution (mmol h ⁻¹)
Cs(0.1)/K ₄ Nb ₆ O ₁₇	1.47
Cs(0.1)/K ₂ Ti ₂ O ₅	0.25
Cs(0.1)/K ₂ Zr ₂ O ₅	0.08
Cs(0.1)/K ₄ V ₆ O ₁₇	0.01
Cs(0.1)/K ₄ Ta ₆ O ₁₇	0.14

dehyde addition. Accordingly, in this study, we determined that the most effective addition amount of additives was 10 vol%.

To identify the reaction pathway from photocatalytic reaction in formaldehyde solution, the liquid products after the reaction could be analyzed by gas chromatograph. A little amount of methanol and acetic acid were observed as new liquid products in the result. The main gas product was only hydrogen, but oxygen was not produced. As we mentioned above, a little amount of CO was detected in gas products.

The typical photoreaction pathway could be surmised from this product distribution. Water was decomposed into hydrogen and oxygen through the photocatalytic reaction like Eq. (1). Formaldehyde could be decomposed into CO and hydrogen as shown in Eqs. (2) and (3). Simultaneously, the oxidation of formaldehyde might occur by the oxygen generated from water decomposition. It seems that the reaction Eqs. (1)–(3) occurred mainly in this photoreaction behavior. As we mentioned in the result of pure water photodecomposition, in reaction Eq. (1), the amount of oxygen by water decomposition would be small. Therefore, we could surmise that the amount of formic acid generated by the oxidation reaction of formaldehyde would be very small. However, formic acid was not observed according to the result of gas chromatogram. Therefore, it can be suggested that the formic acid was decomposed into CO and H₂O, immediately.



The weak secondary reactions could be surmised as Eqs. (4) and (5). It has been known that the hydrogenation of formaldehyde into methanol occurs easily [20]. Therefore, methanol might be produced from reaction Eq. (4). Acetic

acid might be produced from the reaction of the methanol with CO as shown in Eq. (5).



From this photoreaction pathway, it can be explained why the oxygen evolution did not occur in this reaction. It is because the evolved oxygen was exhausted by the oxidation reaction of formaldehyde in the process of the reaction. We can suggest that formaldehyde acted as accelerator which could promote the decomposition of water like the function of an electrolyte in electrolysis. Furthermore, the additive can help to increase the amount of hydrogen generation with its decomposition.

Fig. 7 showed the evolutions of hydrogen and oxygen, when they are estimated by the irradiation time, according to the photocatalytic reaction of formic acid aqueous solution over Cs(0.1)/K₄Nb₆O₁₇ photocatalyst. The evolution rates of hydrogen and oxygen with addition to the formaldehyde and formic acid in water were summarized in Table 4. The evolution rates of hydrogen and oxygen by addition to the formic acid were 2.90 and 3.01 mmol h⁻¹, respectively. The rate of hydrogen evolution

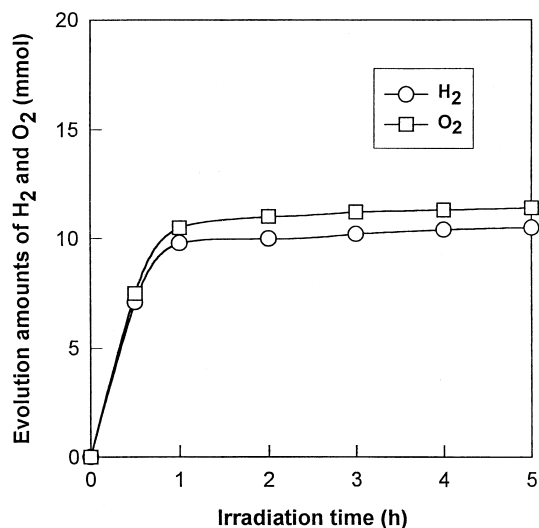


Fig. 7. Hydrogen and oxygen evolutions by addition of formic acid on Cs(0.1)/K₄Nb₆O₁₇ photocatalyst from water photolysis.

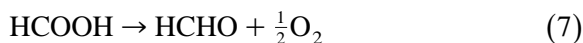
Table 4

The result of photocatalytic decomposition from additive containing water over Cs(0.1)/K₄Nb₆O₁₇ photocatalyst

Additives	Evolved gas (mmol h ⁻¹)	
	hydrogen	oxygen
Formaldehyde	33.31	0
Formic acid	2.90	3.01

was smaller than that of hydrogen evolution by addition of formaldehyde. On the contrary, the rate of oxygen evolution increased remarkably to the rate of hydrogen evolution.

To identify the photoreaction pathway, the products of gas and liquid were analyzed. No new products were found in gas products but hydrogen and oxygen. Formaldehyde was only observed by the analysis of gas chromatogram of liquid products after the reaction. The typical photoreaction pathway could be surmised as shown in reaction Eqs. (6) and (7) from this product distribution.



Reaction Eq. (6) represents the typical water photodecomposition of water. Formic acid might be decomposed into formaldehyde and oxygen by photoreaction. The amount of evolved oxygen was as much as that of evolved hydrogen owing to the above reactions. Although hydrogen was only generated from the water photodecomposition, the rate of hydrogen evolution by additive solution was higher than that of hydrogen evolution from pure water. It is suggested that the two kinds of additives act as an accelerator which improves the photodecomposition of water in the process of the photocatalytic reaction.

4. Conclusions

In photocatalytic decomposition of water, the Cs-loaded potassium niobate photocatalyst ex-

hibited high photocatalytic activity on the hydrogen evolution. Cesium enhanced notably the rate of hydrogen evolution in comparison with other metals.

Formaldehyde accelerated remarkably the rate of hydrogen evolution by addition in water over Cs(0.1)/K₄Nb₆O₁₇ photocatalyst. Furthermore, it could restrain the evolution of oxygen. On the contrary, the evolution rate of oxygen increased by addition of formic acid in water.

The additives not only acted as an accelerator for photodecomposition of water but also affected the evolution rates of hydrogen and oxygen.

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