

LETTERS

Effects of Acceptor Doping to KTaO_3 on Photocatalytic Decomposition of Pure H_2O

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It was found for the first time that controlling the charge density in oxide semiconductors with an acceptor was effective for improving the activity to photolysis of H_2O . Although the photodecomposition activity of NiO supported on nondoped KTaO_3 was negligibly small, doping small amount of acceptors such as tri- or tetravalent cations to KTaO_3 increased the formation rate of H_2 and O_2 . In particular, it was found that NiO supported on KTaO_3 doped with 8 mol % Zr^{4+} exhibits higher activity to the photocatalytic decomposition of H_2O than that of a well-known photocatalyst of Pt/TiO_2 .

1. Introduction

Hydrogen is an important molecule not only as a clean-energy source but also as a chemical reagent. However, production of hydrogen consumes a large amount of energy. Therefore, development of a production method of hydrogen with a small energy consumption is a critically important subject for creating a future energy-utilization system. Photolysis of H_2O with a semiconductor as the catalyst is an attractive method to produce H_2 , since a reactor system is simple and a small amount of energy is enough by using solar light. It is well-known that TiO_2 loaded with Pt is active in various photocatalytic reactions.¹ This catalyst is also active in the formation of H_2 from H_2O . However, the amount of oxygen formed is far smaller than the stoichiometric amount predicted for H_2O decomposition.^{1,2} Up to now, many catalysts have been studied in the photolysis of water. However, there is a limited number of catalysts which can form H_2 and O_2 in a stoichiometric ratio. Recently, it was reported that addition of boron is effective for photolysis of water with a stoichiometric amount.³ On the other hand, Kudo and Domen et al. reported that NiO supported on $\text{K}_4\text{Nb}_6\text{O}_{17}$ with a layered structure is active to the photolysis of water into H_2 and O_2 .⁴ In this catalyst, it is believed that the layered

structure of $\text{K}_4\text{Nb}_6\text{O}_{17}$ works effectively for separating a charge formed by photoexcitation. After their report, layered oxides consisting of Ti or Nb were extensively investigated as catalysts for photolysis of water.⁵ Recently, a mixed oxide of $\text{K}_3\text{Ta}_3\text{Si}_2\text{O}_{13}$, which has a similar large single-tunnel structure to BaTi_4O_9 ,⁶ was reported as a new catalyst for the decomposition of water.⁷ However, the catalyst reported for stoichiometric H_2O photolysis was the layer, or tunnel-structured oxide, and it is believed that the layered or tunnel structure is essential for stoichiometric photolysis of water. In addition, except for $\text{K}_3\text{-Ta}_3\text{Si}_2\text{O}_{13}$,⁶ the number of reports on a Ta-based catalyst for photolysis of water has been limited. For the photocatalytic reaction, it is expected that the improvement in life and/or mobility of photoexcited charge is important for the high activity. Therefore, control of the charge density seems to be important. It is well-known that the addition of small quantities of impurity atoms to a semiconductor has a dramatic effect on the charge density. However, the effects of dopant in an oxide semiconductor on the activity of photolysis of H_2O have not been reported. In this study, a Ta-based perovskite oxide was investigated for the decomposition of water, in particular, the effects of aliovalent cation substituted crystal lattice were studied.

TABLE 1: Photocatalytic Decomposition of Water on NiO Supported on Ta-Based Perovskite-Type Oxide^a

catalyst	formation rate/ $\mu\text{mol/h}$	
	H ₂	O ₂
LiTaO ₃	0.0	0.0
NaTaO ₃	0.8	0.0
Rb ₄ Ta ₆ O ₁₇	0.0	0.0
KTaO ₃	4.5	0.0
KTa _{0.9} M _{0.1} O ₃		
M = Zn ²⁺	29.1	0.0
Y ³⁺	4.4	0.0
Al ³⁺	9.7	2.7
Ga ³⁺	67.7	22.3
In ³⁺	21.3	8.1
Ce ⁴⁺	trace	0.0
Ti ⁴⁺	50.6	12.6
Zr ⁴⁺	93.5	42.1
Hf ⁴⁺	98.5	39.8
Si ⁴⁺	17.2	4.1
Ge ⁴⁺	8.3	0.0
Nb ⁵⁺	3.7	0.0
Sb ⁵⁺	trace	0.0
W ⁶⁺	1.0	0.0
Pt/TiO ₂ (0.3 wt %)	106.1	0.0

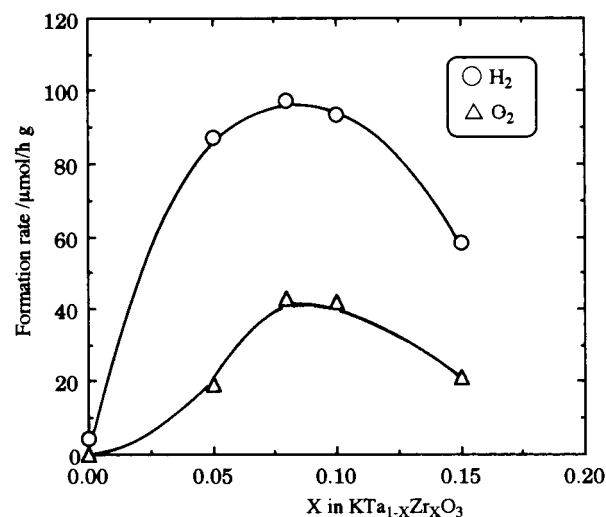
^a NiO loading; 1 wt %.

2. Experimental Section

Doped Ta-based perovskite oxide was prepared by calcination of a mixture of Ta₂O₃ (Kishida, 99.9%), alkaline carbonate (Wako, reagent grade), and a commercial metal oxide (Wako, 99.9%) as a dopant at 1173 K in air. The single phase of perovskite-structured KTaO₃ was always obtained (as assessed by X-ray diffraction measurement using Cu K α line (Rigaku Rint 2000)). Loading nickel oxide onto the obtained KTaO₃ was performed by an impregnation method with a Ni(NO₃)₂ (Wako, reagent grade) aqueous solution. The prepared sample was reduced in flowing H₂ (100 mL/min at 673 K for 6 h) and then reoxidized in flowing O₂ (100 mL/min at 773 K for 6 h). The photodecomposition of water was performed with a closed circulating system with a dead volume of ca. 400 mL. The catalyst (100 mg) was suspended in 30 mL of commercial deionized water (Takasugi), which was presaturated with Ar. The Pyrex reaction cell was irradiated (50 mm in diameter) by an external light source of a 500 W xenon lamp (Ushio). During the H₂O photodecomposition, water and catalyst was mixed with a magnetic stirring bar. Ar gas at a pressure of 13.36 kPa was used as the circulating carrier gas. The H₂ and O₂ formed were measured with a TCD gas chromatograph which was connected with a circulating line. The formation rate was estimated within the first few hours by assuming a first-order reaction. UV-visible spectra of KTaO₃-based oxide was measured with a diffuse reflection method (Hitachi, U 3410) by using an Al₂O₃ disk as a reference.

3. Results and Discussion

Table 1 shows the formation rate of H₂ and O₂ on the Ta-based perovskite oxide. Although no photodecomposition reaction occurred on LiTaO₃ and Rb₄Ta₆O₁₇, formation of H₂ was observed on NaTaO₃ and KTaO₃ catalysts. In contrast, no oxygen was formed on any of the catalysts. Among the measured Ta-based perovskite oxides, the formation rate of H₂ is the highest on KTaO₃, albeit a much smaller H₂ formation rate compared with that of Pt/TiO₂ shown in Table 1. Consequently, effects of dopant on the photodecomposition activity were studied on KTaO₃.

**Figure 1.** Formation rate of H₂ and O₂ as a function of Zr content in KTaO₃ (1 wt % NiO loaded).

It is expected that addition of a small amount of an aliovalent cation would form a donor or acceptor state in the band structure of KTaO₃ and will affect the excitation of the electron and hole by light irradiation. Table 1 also summarizes the effects of metal cations substituted on the Ta site in KTaO₃ on the formation rate of H₂ and O₂. It is obvious that the formation rate of H₂ was drastically changed by doping a small amount of aliovalent cation. Among the investigated dopant, tri- or tetravalent cation seems to be the most effective for improving the photodecomposition activity of KTaO₃. In particular, tetravalent cations of Hf⁴⁺ and Zr⁴⁺ and the trivalent cation of Ga³⁺ exhibit the best dopant effect for improving the formation rate of H₂. On the other hand, formation of oxygen is also observed on some catalysts which generally exhibited a large formation rate of H₂. On the photodecomposition of water, formation of O₂ is generally difficult and sometimes catalyst was deactivated by accumulation of a peroxidized phase. For example, titanium oxide supporting Pt (Pt/TiO₂) was active for the formation of H₂, however, oxygen hardly formed (see Table 1). Therefore, catalysts which form a stoichiometric amount of O₂ in the decomposition of water are required from a long-term stability point of view. On this point, NiO supported on KTaO₃ doped with Hf⁴⁺, Zr⁴⁺, or Ga³⁺ are attractive, since almost a stoichiometric amount of oxygen was formed. Among the investigated acceptor-doped KTaO₃, Hf⁴⁺-doped catalyst exhibited the highest rate of H₂ formation. However, the formation rate of O₂ on this Hf⁴⁺-doped catalyst was slightly smaller than one-half of H₂ formation rate. In contrast, the O₂ formation rate almost corresponded with one-half of that of H₂ on Zr⁴⁺-doped KTaO₃. Consequently, Zr⁴⁺-doped catalyst may be more promising than the Hf⁴⁺-doped one. In the following part, the photodecomposition of H₂O on the Zr⁴⁺-doped KTaO₃ catalyst was studied in detail.

Figure 1 shows the formation rate of H₂ and O₂ as a function of the amount of Zr⁴⁺ doped for the Ta site of KTaO₃. It is obvious that the formation rate of H₂ and O₂ increased with increasing the amount of doped Zr⁴⁺ attaining a maximum at 8 mol %. At this composition, the formation rate of H₂ and O₂ were 94 and 42 $\mu\text{mol}/(\text{g h})$, respectively. It is also noted that the formation rate of H₂ on 8 mol % doped catalyst was larger than that of nondoped KTaO₃ by an order of magnitude. Therefore, doping of a small amount of Zr⁴⁺ was highly effective for increasing the activity of NiO/KTaO₃ catalyst to photodecomposition of water. The effect of the amount of NiO

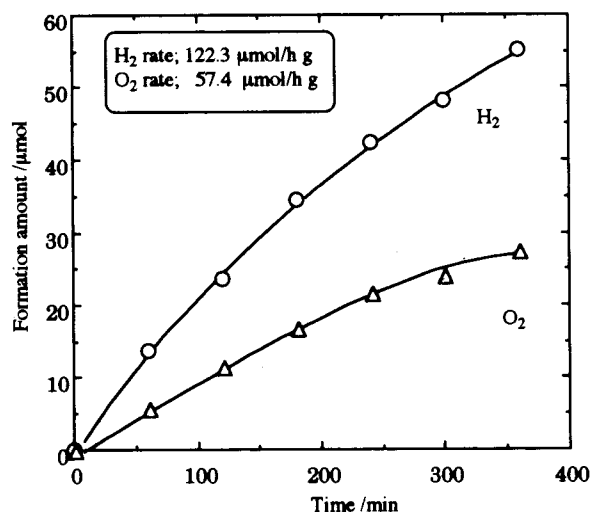


Figure 2. Formation rate of H₂ and O₂ on NiO (1.5 wt %)/K_{1.15}Ta_{0.92}Zr_{0.08}O₃ as a function of reaction time.

loading on the activity to photodecomposition of water was further studied. The formation rate of H₂ and O₂ increased with increasing amount of NiO and attained a maximum at 1.5 wt % NiO loading. Reoxidation of H₂ into H₂O seemed to occur when the amount of NiO was in excess. Consequently, the optimized NiO loading seems to exist around 1.5 wt %. On the other hand, the activity to photodecomposition of water was also strongly dependent on the molar ratio of K to Ta, and the largest rate of H₂ and O₂ production was obtained on KTaO₃ at K/Ta = 1.15, when 1 wt % NiO was loaded. Consequently, the optimized composition for KTaO₃ was K_{1.15}TaO₃ in a starting composition.

Figure 2 shows the amount of H₂ and O₂ on the optimized catalyst of 1.5 wt % NiO loaded K_{1.15}Ta_{0.92}Zr_{0.08}O₃ (which denoted simply as NiO/KTa(Zr)O₃) as a function of reaction time. The largest H₂ and O₂ formation rate was attained on this catalyst. It is clear that the amounts of H₂ as well as O₂ monotonically increase with increasing reaction time on this catalyst. The amounts of H₂ and O₂ formed after 3 h were 34.5 and 16.8 μmol, respectively, i.e., almost in correspondence with the stoichiometry of H₂O decomposition. The initial rate of H₂ and O₂ formation on this catalyst were 122.3 and 57.4 μmol/(h g), respectively. The formation rate of H₂ on Pt/TiO₂, a well-known active catalyst under the same condition, was 106.1 μmol/(h g), as shown in Table 1. Therefore, it is clear that the formation rate of H₂ was larger on NiO/KTa(Zr)O₃ than that on Pt/TiO₂ under same reaction conditions, although the activity of photocatalyst should be compared with quantum yield. Consequently, it can be said that NiO/KTa(Zr)O₃ catalyst was highly active to the photodecomposition of H₂O among the reported catalysts. At present, the mechanism for the great improvement by the substitutional solid solution of Zr⁴⁺ is under investigation. Figure 3 shows UV-vis spectra of Zr-doped KTaO₃. The UV-vis spectra suggest that no significant change in the band gap (ca. 3.8 eV) of KTaO₃ is caused by doping Zr⁴⁺. Therefore, improvement in photodecomposition activity to H₂O is not assigned to the change in the band structure of KTaO₃ semiconductor. This may result of the wider band gap of ZrO₂ compared with that of KTaO₃. Since the electrical conductivity was monotonically increased with decreasing oxygen partial pressure, KTaO₃ is an n-type semiconductor under these conditions. Doping a lower valenced cation of Zr⁴⁺

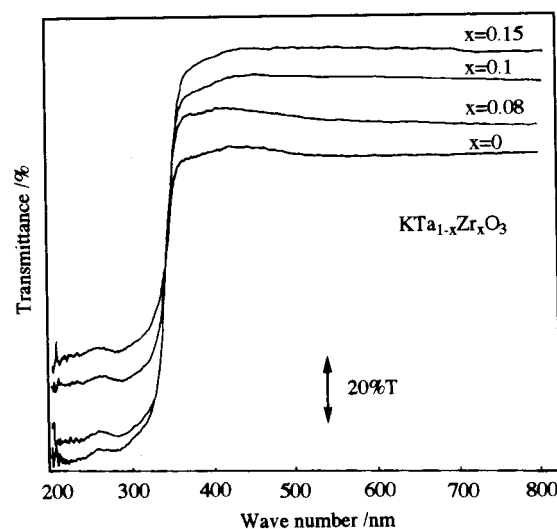
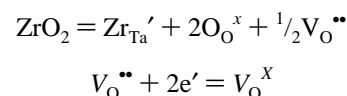


Figure 3. UV-vis spectra of Zr⁴⁺-doped KTaO₃.

to the Ta site will decrease the free electron density in KTaO₃ according to the following Kröger-Vink notation



where V_O and e' mean the oxygen vacancy and electron, respectively. In fact, the electrical conductivity was monotonically decreased with increasing amount of doping Zr⁴⁺. The mobility of the hole or electron would not be increased by doping Zr⁴⁺, because the electrical conductivity was decreased. Therefore, it is most likely that increased photolysis activity of H₂O was brought about by an increase in the lifetime of the photoexcited charge, which was caused by a decrease in the charge density. It is believed that H₂ and O₂ are formed on NiO and KTaO₃, respectively. Therefore, free electron generated in KTaO₃ by photoirradiation has to migrate to NiO to decompose H₂O into H₂. An increase in the lifetime of the photoexcited charge will increase the quantum yield. Consequently, photodecomposition activity to H₂O seems to be improved by doping an acceptor of Zr⁴⁺ to KTaO₃. So far, in the literature the effect of controlled charge density by acceptor to improve the photodecomposition activity has not been reported. In addition, the number of bulk catalysts which can produce H₂ and O₂ stoichiometrically in H₂O photolysis is limited, while it is clear that NiO/KTa(Zr)O₃ is a promising bulk photocatalyst for the decomposition of H₂O.

This study reveals that doping a small amount of acceptor is effective for increasing the catalytic activity for the photodecomposition of water. Also, NiO/KTa_{0.92}Zr_{0.08}O₃ is a novel active catalyst for the complete photodecomposition of pure water.

References and Notes

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