Photocatalytic decomposition of hydrogen iodide on Ta-based oxides for solar hydrogen production

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Abstract: Photocatalytic hydrogen production from hydrogen iodide (HI) aqueous solution was demonstrated on Ta-based metal oxides. Photocatalytic activity of HI decomposition was strongly influenced on noble metal co-catalysts, and hydrogen and iodine formation were observed by using Pt- or Pd-loaded $KTaO_3$ photocatalysts. These results indicate that there is a possibility to establish new solar water splitting process, which can separately convert light and thermal energy in sunlight.

Keywords: Photocatalysis, Hydrogen production, Iodine–sulfur process.

1. Introduction

Development of efficient energy conversion process from the renewable energy to hydrogen has been an important issue to maintain the sustainable growing of human society. Photocatalytic water splitting is one of an ideal hydrogen production process because it can produce hydrogen from sunlight without exhaust CO_2 gas. On the other hand, the iodine–sulfur process (IS process), which is one of a thermochemical water splitting cycles, can potentially use for waste heat conversion to chemical energy.[1] The IS process consists of three chemical reactions as shown in below:

$$2HI \rightarrow H_2 + I_2 \qquad \text{(endothermic, 673 K)} \qquad (1)$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2O_2 \qquad \text{(endothermic, 1173 K)} \qquad (2)$$

$$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \qquad \text{(exothermic, 393 K)} \qquad (3)$$

The IS process totally results in the thermal decomposition of water to H_2 and O_2 using high temperature heat. In this IS process, HI decomposition should be improved because HI decomposition ratio is relatively low (ca. 20% at 673 K) at thermal equilibrium. To overcome this disadvantage, we applied a photocatalytic reaction to the HI decomposition. If the HI decomposition reaction occurs on photocatalysts under UV or visible light and the sulfuric acid decomposition proceeds by heat from infrared light in sunlight, the IS process proceed by solar energy. Based on these backgrounds, the photocatalytic HI decomposition was investigated. In this study, the photocatalytic HI decomposition on tantalum-based metal oxides, which have been reported as highly active photocatalyst for water splitting,[2,3] was investigated to achieve hydrogen production by the solar IS process.

2. Experimental

Photocatalyst preparation: All reagents were used without further purification. $LiTaO_3$, $NaTaO_3$ and $KTaO_3$ were synthesized by solid-state reaction method. Ta_2O_5 and alkali carbonates (Li_2CO_3, Na_2CO_3, or K_2CO_3) were mixed in an alumina mortar for 30 min, and then calcined in alumina crucible at 1273 K for 10 h. Pt-loading was performed by evaporation to dryness method with $Pt(NH_3)_4(NO_3)_2$ aqueous solution.

Photocatalytic reaction: Photocatalyst was dispersed in quartz tube cell containing 10 mM HI aqueous solution. The cell was irradiated by using a 500 W Xe lamp (2.0 W cm^{-2}) with magnetic stirring. After the photocatalytic reaction, the catalyst was gathered by using centrifugation, and separated from reaction solution by decantation. The evolved gasses were detected by gas chromatograph with thermal conductivity detector. The amounts of triiodide ion (I_3^-) and iodide ion (I^-) were determined by titration method with aqueous solution of $Na_2S_2O_3$ and $AgNO_3$, respectively.

3. Results and discussion

Figure 1 shows the results of photocatalytic decomposition of HI on Ta-based metal oxides. Formation of H_2 and I_2 was confirmed with all the catalysts under the light irradiation. Among the Ta-based oxides, it was found that $KTaO_3$ showed a specifically high photocatalytic activity for HI decomposition. Furthermore, compared to the result of $KTaO_3$, Pt-loaded $KTaO_3$ showed high photocatalytic activity. These results suggested that the loading co-catalyst is effective on the photocatalytic activity of $KTaO_3$ for HI decomposition. Therefore, effect of loading co-catalyst on the photocatalytic activity of KTaO3 was investigated. Table 1 summarized the results of photocatalytic HI decomposition on $KTaO_3$ with various co-catalysts. Production of H_2 was confirmed with all the catalysts studied, and Pt- or Pd- loaded $KTaO_3$ showed high catalytic activity. On the other hand, in the case of Rh- or Ir- loaded $KTaO_3$, O_2 formation was observed simultaneously with the formation of I_3^-, and the yield of the oxidation products of I^- decreased. Thus, it can be seen that the products of HI decomposition on $KTaO_3$ is greatly affected by the co-catalysts. From XPS analysis of the $KTaO_3$ photocatalyst after the reaction, I 3d peak was clearly observed from the sample modified with Pt, Pd, and Rh, while not observed from $KTaO_3$ without loading co-catalyst. Furthermore, the peak area of the I 3d peak tended to be larger for catalysts with higher I_2 production amounts in the HI photodecomposition. Therefore, it was suggested that the oxidation reaction of I^- on the catalyst surface was promoted by providing I^- adsorbed on the co-catalyst surface. The HI photodecomposition activity of $KTaO_3$ is greatly affected by co-catalysts, and it was found that photocatalytic HI decomposition proceeds efficiently by using Pt as a co-catalyst.

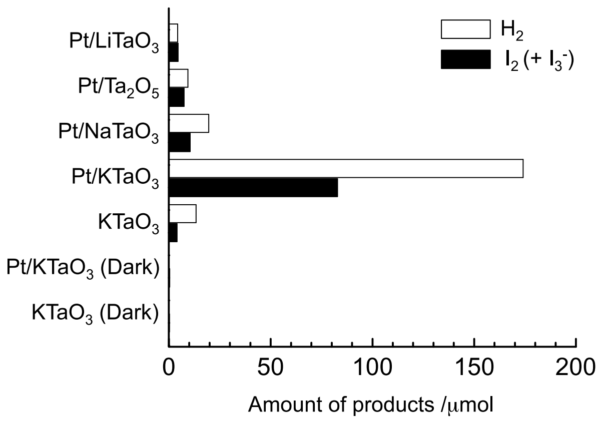

Figure 1. Amount of products formed by photocatalytic HI decomposition on the Ta-based oxide catalysts under white light irradiation from Xe lamp (2.0 W cm^{-2}) for 12 h.

Table 1. Photocatalytic HI decomposition on $M/KTaO_3$.

M	Formed H_2 /μmol	Formed I_2 /μmol	I^- conv. /%	I_2 yield /%
Pt	174.0	82.8	96.7	59.7
Pd	94.4	51.5	54.5	65.8
Ag	22.5	9.0	10.1	62.1
Rh	18.4	12.0	26.4	31.6
Au	15.7	5.3	5.2	71.1
None	13.3	4.2	12.1	24.2
Ir	12.2	13.1	48.8	18.7
Ru	10.0	0.8	2.0	28.6

Amount of cocatalyst: 0.2 wt%, Light source: 500W Xe lamp (Full arc, 2.0 W cm^{-2}), Reaction time: 12h.

4. Conclusions

The photocatalytic activity of Ta-based oxides for HI decomposition was investigated in this study. Modification with Pt co-catalyst was found to be effective for elevating the photocatalytic HI decomposition activity of $KTaO_3$. Although $KTaO_3$ only work under UV light irradiation, if it responds to visible light by narrowing the band gap (e.g. nitrogen doping), it has a potential to become a suitable material for solar IS process.

References

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