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. The IS process consists of three chemical reactions as shown in below:

\[ 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \] (endothermic, 673 K) (1)
\[ \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \] (endothermic, 1173 K) (2)
\[ \text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4 \] (exothermic, 393 K) (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, 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$_2$O$_5$ and alkali carbonates (Li$_2$CO$_3$, Na$_2$CO$_3$, or K$_2$CO$_3$) 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...
The amounts of triiodide ion (I$^-_3$) and iodide ion (I$^-$) were determined by titration method with aqueous solution of Na$_2$S$_2$O$_3$ 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 KTaO$_3$ 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.

<table>
<thead>
<tr>
<th>M</th>
<th>Formed H$_2$</th>
<th>Formed I$_2$</th>
<th>I$_2$ conv.</th>
<th>I$_2$ yield</th>
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<tr>
<td></td>
<td>/µmol</td>
<td>/µmol</td>
<td>/%</td>
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<tr>
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<tr>
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</tr>
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</table>

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