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# Water photolysis reaction on cerium oxide photocatalysts

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## Abstract

The photocatalytic reaction of water was studied on a cerium oxide photocatalysts system. Cerium oxide photocatalyst showed a high evolution rate of hydrogen with cesium loading. In comparison to the adsorption properties, the adsorption strength of oxygen was superior to that of hydrogen. The variation of product distribution during the water photolysis reaction was mainly influenced by the adsorption properties of hydrogen and oxygen. Metal carbonate additives to the water photolysis reaction accelerated hydrogen evolution by photodecomposition of themselves.

*Keywords:* Water photolysis; Cerium oxide; Cesium; Adsorption properties; Additives

## 1. Introduction

Hydrogen generation by water photolysis using photocatalysts is a clean technology. The development of highly photosensitive photocatalysts is the core of water photolysis. Fujishima and Honda [1,2] suggested a photoelectrochemical principle using a semiconductor metal compound such as $TiO_2$ for water photolysis. Domen et al. [3–5] reported that NiO-$SrTiO_3$ powder with proper pretreatment can steadily decompose water photocatalytically. Lehn et al. [6] also showed the activity of photodecomposition of water over $SrTiO_3$ powders modified with rhodium oxide. Recently, some alkali-layered metal oxide photocatalysts were suggested as highly photosensitive photocatalysts to improve the photocatalytic activity [7–9]. Various additives that accelerated the photodecomposition of water have been studied as a method of increasing hydrogen evolution [10–14].

In this study, the photocatalytic decomposition of water was studied to generate hydrogen on cerium oxide photocatalysts. The photocatalytic activity for hydrogen evolution was examined on modified cerium oxide photocatalysts by metal loading. In order to confirm the effect of additive addition in water, some carbonates were introduced to the photocatalytic reaction on cesium-loaded cerium oxide photocatalysts. The adsorption properties of the photocatalyst for hydrogen and oxygen gases were investigated to confirm the correlation of stoichiometric evolution between two gases during the photocatalytic decomposition of water.

## 2. Experimental

Cerium oxide (Aldrich, 99.9%) was introduced as a photocatalyst or photocatalyst sup-

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port. The photocatalysts were used in a water photolysis reaction after calcination for 2 h at 473 K. The metal-loaded cerium oxide photocatalysts were prepared by a typical incipient wetness method with a metal reagent such as $Cs_2CO_3$ (Janssen, 99.9%), $Li_2CO_3$ (Junsei, GR) and $Pt(NH_4)_3Cl_2$ (Aldrich, GR), controlled as 0.1 wt% of metal content for the amount of cerium oxide. The metal-loaded photocatalysts were also calcined for 2 h at 473 K.

The photocatalytic reaction was carried out in a completely air-free closed gas circulation system connected to a gas chromatograph and vacuum system. A schematic diagram of the photocatalytic reaction system is shown in Fig. 1. Evolved gases were analyzed quantitatively by the gas chromatograph (GC-8A, Shimadzu, 5A molecular sieves column). The reactants were irradiated by a high pressure Hg lamp (Ace glass Co., 450 W) inside the reactor. The remaining air inside the reaction system was excluded completely by the vacuum system, and then nitrogen gas was introduced to ca. 100 torr before reaction.

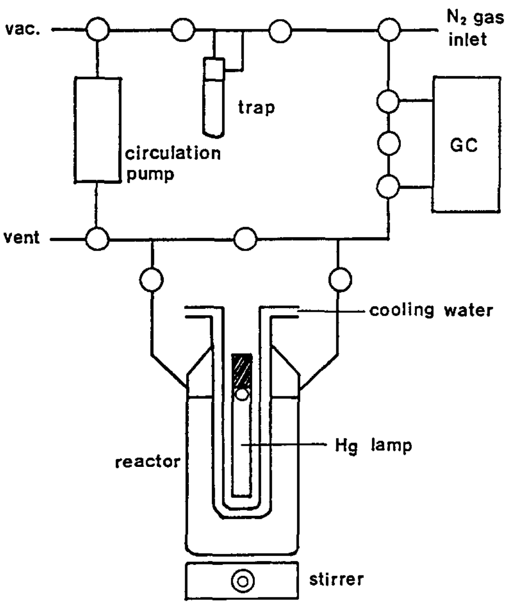

Fig. 1. Schematic diagram of the photocatalytic reaction system.

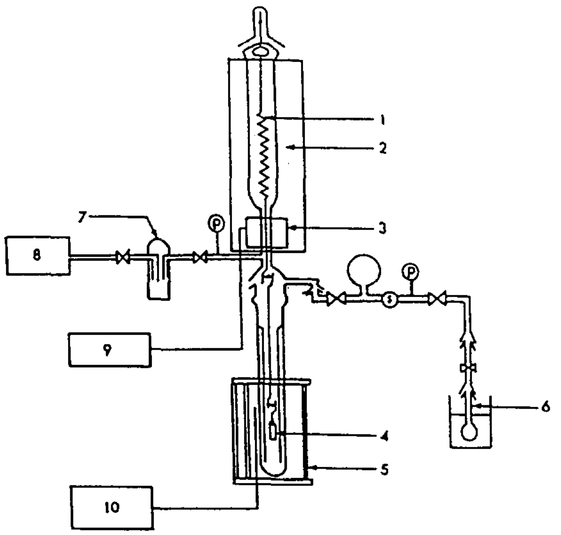

Fig. 2. Schematic diagram of the adsorption measurement apparatus: 1, quartz spring; 2, constant temperature chamber; 3, displacement meter; 4, sample; 5, heater or liquid $N_2$ dewar; 6, solvent; 7, liquid $N_2$ trap; 8, vacuum system; 9, recorder; 10, temperature control unit.

Pure water or 1 mol of additive containing water was used as reactant. The photocatalyst (1.0 g) was suspended with 500 ml of reactant by magnetic stirring. $Na_2CO_3$ (oriental Co., GR), $K_2CO_3$ (Ducksan Co., GR), $NaHCO_3$ (oriental Co., GR), and $(NH_4)_2CO_3$ (Ducksan Co., GR) were introduced as additives to the water photolysis reaction, respectively.

The properties of a single component adsorption for hydrogen and oxygen was investigated by gravimetric adsorption equipment installed on a quartz balance. A schematic of the adsorption equipment is shown in Fig. 2. Competitive adsorption between hydrogen and oxygen was performed by a volumetric adsorption apparatus. The adsorption amounts with process time of adsorption were analyzed by gas chromatograph (GC-8A, Shimadzu, 5A molecular sieves column) connected to the adsorption apparatus. Characterization of the photocatalysts was performed with an XRD (Rikagu, DIMAX-B), SEM (Jeol, JSM-840A), and a UV/VIS recording spectrometer (UV 2100, Shimadzu).

## 3. Results and discussion

### *3.1. Photocatalytic reaction of water on cerium oxide photocatalysts*

The photocatalytic activity of cerium oxide photocatalysts system for hydrogen evolution was examined. The photocatalytic decomposition of water produced hydrogen and oxygen gases. The results of the water photolysis reaction on cerium oxide photocatalysts and metal-loaded cerium oxide photcatalysts are presented in Table 1. The rate of hydrogen evolution on Cs(0.1)/$CeO_2$ was 81.60 μmol/h. It is as high as that of Pt/$K_4Nb_6O_{17}$ photocatalyst which is known as a highly active photocatalyst under the same conditions. The rate of hydrogen evolution improved with cesium loading on cerium oxide in comparison to that of the parent cerium oxide photocatalyst. However, other metals, such as Li and Pt, did not show an enhanced photocatalytic activity.

The results of the photocatalytic activity with various concentrations of cesium onto cerium oxide is shown in Fig. 3. The evolution rate of hydrogen decreased with increasing amounts of cesium. The highest evolution rate of hydrogen was given by 0.1 wt% of Cs-loaded on cerium oxide photocatalyst. Generally, it has been known that the electronic properties of metal/semiconductor type catalysts are improved by a decrease of the thickness of dispersed metal onto the semiconductor surface. Schwab [15] reported that as the thickness of NiO onto the semiconductor surface became thinner, the activity of NiO-loaded catalyst increased in the oxidation reaction. From our results, we also found that the photocatalytic activity was excellent on 0.1 wt% Cs-loaded cerium oxide photocatalyst.

Table 1
Rate of hydrogen evolution from water photolysis on various $CeO_2$ photocatalysts

| Photocatalyst | Rate of $H_2$ evolution (μmol/h) |
|---|---|
| $CeO_2$ | 7.08 |
| Cs(0.1)/$CeO_2$ | 81.60 |
| Li(0.1)/$CeO_2$ | 8.35 |
| Pt(0.1)/$CeO_2$ | 7.67 |

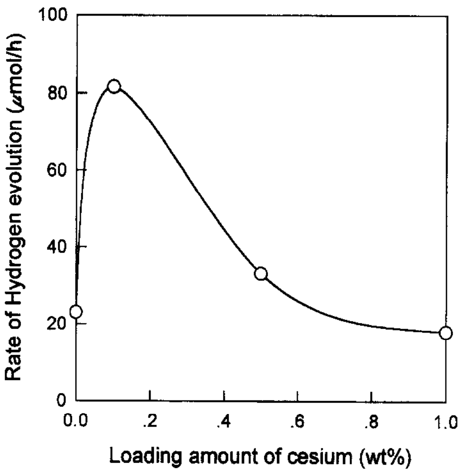

Fig. 3. Rate of hydrogen evolution with various loading amounts of cesium on $CeO_2$.

The evolution of hydrogen and oxygen with the time of the photoreaction is shown in Fig. 4. The amount of evolved hydrogen and oxygen increased continuously in spite of a long irradiation time (more than 70 h). It shows that no deactivation of photocatalyst occurred during the photocatalytic reaction. In the initial photocatalytic reaction, hydrogen was evolved domi-

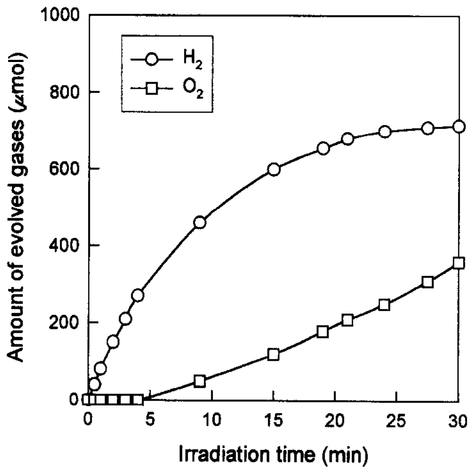

Fig. 4. Evolution of hydrogen and oxygen with time of water photolysis on Cs(0.1)/$CeO_2$ photocatalyst.

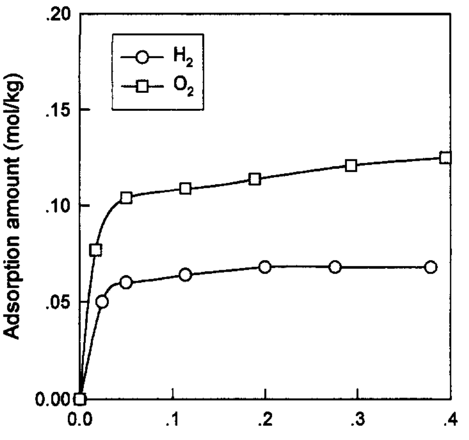

Fig. 5. Single component adsorption isotherm for hydrogen and oxygen on Cs(0.1)/CeO$_2$.

nantly compared to the oxygen evolution. In the process of the photoreaction, the amount of oxygen evolution increased gradually to the half that of the hydrogen evolution. It is considered that the oxygen evolution is interfered with in terms of its adsorption onto the photocatalyst. The reason is surmised that the adsorption strength for oxygen by the photocatalyst is superior to that of hydrogen. Therefore, the evolution of oxygen increased after saturated adsorption of oxygen on the photocatalyst.

### 3.2. Adsorption properties of hydrogen and oxygen

In order to confirm the variation of product distribution between hydrogen and oxygen during the photoreaction, we examined the adsorption properties for hydrogen and oxygen on Cs(0.1)/CeO$_2$ photocatalyst. Fig. 5 represents single component adsorption isotherms for hydrogen and oxygen, respectively. The amount of equilibrium adsorption of oxygen was much higher than that of hydrogen. From these results, we obtained the adsorption isotherm parameters by adopting the Freundlich isotherm equation. As shown in Table 2, the Freundlich isotherm coefficients ($k$ and $n$) of oxygen were larger than that of hydrogen. Therefore, we found that oxygen has a stronger adsorption ability on the photocatalyst compared to hydrogen in this system.

Table 2
Estimated Freundlich isotherm [a] coefficients for single component isotherm of hydrogen and oxygen on Cs(0.1)/CeO$_2$ photocatalyst

| Adsorbate | $k$ | $n$ |
|---|---|---|
| Hydrogen | 0.09 | 6.81 |
| Oxygen | 0.16 | 9.63 |

[a] Freundlich isotherm equation: $q = kC^{1/n}$.

The competitive adsorption property for the hydrogen–oxygen binary component is shown in Fig. 6. The adsorption curves were typical competitive adsorption curves. From these curves, oxygen was adsorbed dominantly during the initial adsorption time. In the process of adsorption, the adsorption of hydrogen took place gradually. However, the amount of adsorbed hydrogen was very small compared with that of adsorbed oxygen. It means that the adsorption strength of oxygen is stronger than that of hydrogen in hydrogen–oxygen competitive adsorption.

From the results of hydrogen and oxygen evolution in the photoreaction, the evolved oxygen amount was very small during the initial photoreaction time. However, the amount of evolved oxygen approached half the amount of

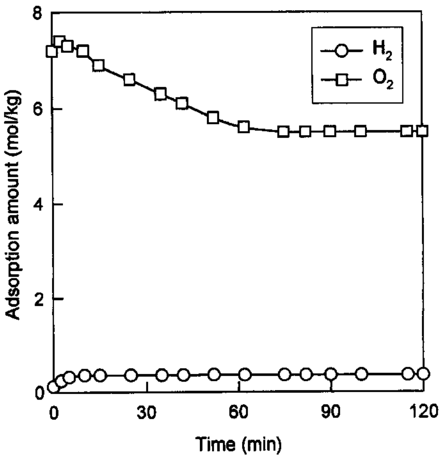

Fig. 6. Uptake curves of hydrogen and oxygen in binary component adsorption on Cs(0.1)/CeO$_2$.

evolved hydrogen photoreaction process. That is to say, the evolution of oxygen and hydrogen coincided with the stoichiometric mole ratio between the two gases. Therefore, it is surmised that the variation of product distribution between the two gases during the photoreaction is derived from the difference in the adsorption properties of the two gases.

As mentioned above, the adsorption strength of oxygen was superior to that of hydrogen. It means oxygen gas evolved can adsorb more easily onto the photocatalyst than the hydrogen gas evolved in the initial photoreaction. Therefore, the evolution of oxygen was negligibly small in the initial photoreaction. After saturation of oxygen adsorption on the photocatalyst, the evolution amount of oxygen increased gradually. From these results, it is shown that the variation of the evolution ratio between hydrogen and oxygen is mainly influenced by the adsorption properties of the two gases on the photocatalyst during the photoreaction.

### *3.3. The effect of metal carbonate addition in the water photolysis reaction*

The result of photocatalytic reaction of water with alkali metal carbonates addition is summarized in Table 3. Sodium carbonate and potassium carbonate did not increase the rate of hydrogen evolution. It resulted in the alkali metal ions in these additives interrupting the dissociation of the hydrogen bridge bonding of water. To the contrary, $(NH_4)_2CO_3$ and $NaHCO_3$ combined with the hydrogen bond showed an improved hydrogen evolution rate. This improvement derived from the addition of hydrogen evolved by decomposition of $(NH_4)_2CO_3$ or $NaHCO_3$ itself. Therefore, it is shown that the additives containing hydrogen bond would rather improve the hydrogen evolution by photodecomposition of themselves than accelerate the photodecomposition of water.

Table 3
Effect of carbonate addition to the photocatalytic reaction of water on $Cs(0.1)/CeO_2$ photocatalyst

| Additives | Rate of hydrogen evolution ($\mu$mol/h) |
|---|---|
| None | 81.60 |
| $(NH4)_2CO_3$ | 166.42 |
| $NaHCO_3$ | 132.31 |
| $Na_2CO_3$ | 20.23 |
| $K_2CO_3$ | 22.94 |

## 4. Conclusions

In the photocatalytic decomposition of water, modified cerium oxide photocatalysts showed a high photocatalytic activity for hydrogen evolution. Especially, cesium loaded on cerium oxide remarkably enhanced the hydrogen evolution activity in comparison with other metals.

The adsorption strength of oxygen was superior to that of hydrogen in single and binary component adsorption. The variation of the amount of hydrogen and oxygen evolved can be explained by their differences in adsorption properties during the photoreaction.

The increase of hydrogen evolution by the addition of carbonate additives was derived from addition of the hydrogen produced by decomposition of the additives which have hydrogen bonds.

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