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PHOTOCATALYTIC HYDROGEN PRODUCTION FROM A MIXTURE OF WATER AND 2-PROPANOL ON SOME SEMICONDUCTORS

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The photocatalytic production of H_2 and acetone from a mixture of water and 2-propanol in gas and liquid phases was studied on some semiconductor powders such as NiO supported $SrTiO_3$, CdS and TiO_2 etc. This reaction did not proceed without H_2O, indicating the coupling of the photodecomposition of H_2O and the photo-oxidation of 2-propanol.

The photo-oxidation of 2-propanol by O_2 to form acetone and H_2O has been studied on some semiconductors such as ZnO[1)] and TiO_2[2,3)]. In these systems, the reaction does not take place without O_2, which suggests some oxidizing agent is necessary for the dehydrogenation of 2-propanol. On the other hand, photocatalytic H_2 and CO_2 production from a mixture of H_2O and methanol on TiO_2 based catalysts was reported[4)].

We report here a photocatalytic dehydrogenation of 2-propanol to form H_2 and acetone in the presence of H_2O on some semiconductors. A characteristic feature of this reaction is that the dehydrogenation of 2-propanol does not proceed in the absence of H_2O.

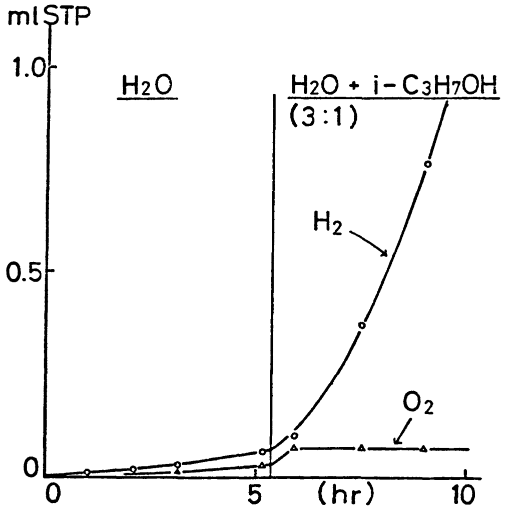

Fig. 1. Photocatalytic decomposition of H_2O + 2-propanol on NiO(2 wt%)-$SrTiO_3$.

The reaction was carried out in a closed circulation system (350 ml) equipped with a flat bottom vessel of a Pyrex glass. The catalyst powder (ca. 1 g) was spread over the bottom (15 cm^2) and irradiated through the bottom by a 450 W high pressure mercury lamp (USHIO, UV-452). The temperature of the catalyst was 308-313 K in the stationary state under irradiation. Catalysts were evacuated at 570-670 K for 3 to 10 h before the reaction. In the case of NiO (2 wt%) supported $SrTiO_3$, the catalyst was reduced by H_2 (at 670 K for 20 h) and reoxidized by O_2 (at 670 K for 3 h) after the evacuation. The reaction products, H_2 and acetone, were analyzed by gas chromatography.

When NiO-$SrTiO_3$ catalyst was suspended in the water, the photodecomposition of water proceeded steadily and stoichiometric amounts of H_2 and O_2 were evolved as has been reported in a previous paper[5]. By the addition of 2-propanol (25 vol%) during the photodecomposition of water in liquid phase, the rate of H_2 evolution was increased two hundred times and O_2 evolution stopped as shown in Fig. 1. Liquid phase analysis by gas chromatography demonstrated the formation of acetone (further oxidized products, such as acetic acids, were not detected) indicating that hydrogen was produced by the photodehydrogenation of 2-propanol. However, when only 2-propanol was introduced on the catalyst, very little amount of H_2 was evolved by irradiation, and it required the addition of water (30 vol%) for the steady formation of H_2.

CdS powder was also used for the catalyst of this reaction. When only 2-propanol (gas phase, ca. 50 Torr, H_2O impurity = 0.5 mol%) was introduced onto the

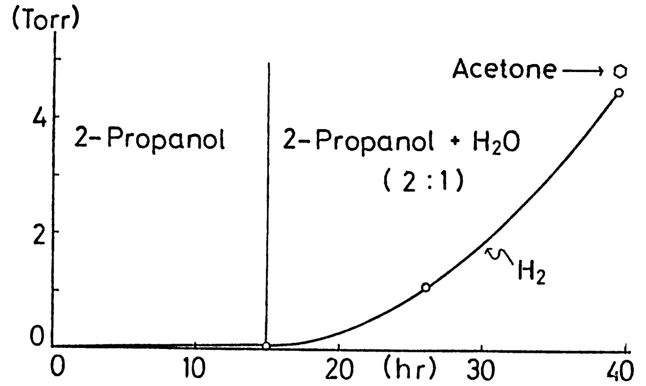

Fig. 2. Photocatalytic dehydrogenation of 2-propanol + H_2O on CdS (gas phase).

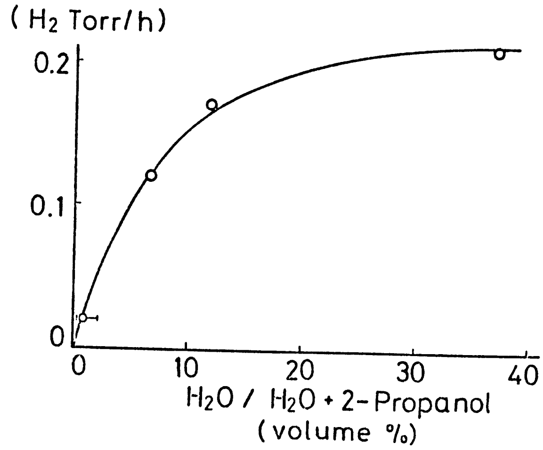

Fig. 3. Dependence of the activity of dehydrogenation of 2-propanol upon the concentration of H_2O on CdS.

catalyst, little amount of H_2 was produced, as shown in Fig. 2. After 15 h, H_2O (25 Torr) was added in the system and the H_2 began to be evolved in a way similar to NiO-$SrTiO_3$. The produced organic compound was only acetone, whose amount coincided with that of H_2 within a experimental error after 40 h reaction. The rate of H_2 evolution increased gradually after H_2O introduction, as shown in Fig. 2. This behavior may be associated with the reduction of the catalyst, because the color of CdS changed from bright yellow to dark yellow during the reaction.

The dependence of the activity upon the concentration of H_2O was studied. The result is shown in Fig. 3. The activity of H_2 evolution was extrapolated to zero at 0% of the concentration of water, and it was increased gradually with the increase of the volume % of H_2O. As CdS can not decompose water at all without proper modification$^{6)}$, at 100% of H_2O, the activity is zero. The effect of O_2 on this reaction was also studied. When O_2 (300 Torr) was introduced during the course of the photodecomposition of 2-propanol and H_2O (1:1, liquid phase) on NiO-$SrTiO_3$, the rate of H_2 evolution was decreased to 2/3 of that without O_2. In the case of CdS, the effect was more striking, that is, the evolution of H_2 stopped completely by the addition of O_2 (Fig. 4). When O_2 (300 Torr) was replaced by Ar (300 Torr), H_2 began to evolve again, but its rate was not as fast as that before the introduction of O_2.

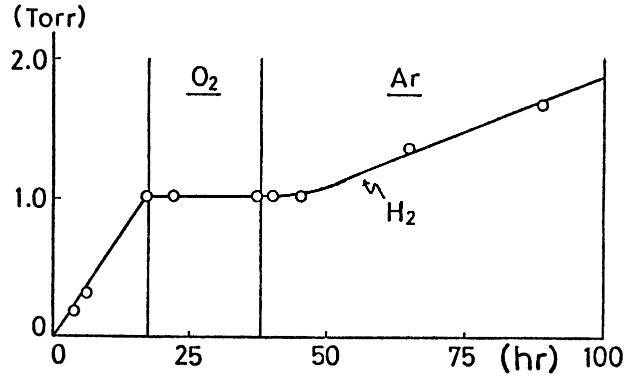

Fig. 4. Effect of O_2 on the photocatalytic dehydrogenation of 2-propanol + H_2O (2:1) (liq. phase) on CdS.

CAT.	PHASE	H_2 $^{b)}$	ACETONE$^{b)}$
TiO_2	G	9.6×10^{-3}	—$^{a)}$
$SrTiO_3$	G	~0	0
CdS	G	2.5×10^{-1}	2.7×10^{-1}
CdSe	G	0	0
WO_3	G	0	3.5×10^{-2}
ZnO	G	0	0
NiO-$SrTiO_3$	G	4.5×10^{-1}	—$^{a)}$
NiO-$SrTiO_3$	L	3.7	—$^{a)}$
Pt-CdS	L	3.9	—$^{a)}$

Table 1. Activities of photocatalytic dehydrogenation of 2-propanol + H_2O (1:1) on various semiconductor powders.

a): not measured

b): Torr/h

The results on some othre semiconductors are summarized in Table 1. $SrTiO_3$, CdSe and ZnO were inactive for this reaction. In the case of WO_3 powder, acetone was produced without the evolution of H_2. The color of the catalyst changed from yellowish green to blue as the reaction proceeded, indicating the photoreduction of WO_3 by 2-propanol.

Considering these results, we tentatively propose that the photocatalytic reaction on $NiO\text{-}SrTiO_3$, TiO_2 (anatase) and CdS should be regarded as a coupling reaction of photodecomposition of H_2O and (photo-)oxidation of 2-propanol as follows:

$$\begin{array}{lr}
2H_2O\ (l\ \text{or}\ g) \rightleftarrows 2H^+(a) + 2OH^-(a) & (1) \\
2H^+(a) + 2e^- \rightarrow H_2(g) & (2) \\
\text{2-propanol}(l) + 2OH^-(a) + 2h^+ \longrightarrow \text{acetone}(l) + 2H_2O(l) & (3) \\
\hline
\text{2-propanol}(l) \longrightarrow H_2(g) + \text{acetone}(l) & (4)
\end{array}$$

For the photodecomposition of water on these catalysts, the evolution of O_2, step (5), may be a rate determining step. Especially on CdS, the reaction does not proceed.

$$4OH^-(a) + 4h^+ \longrightarrow 2H_2O(l) + O_2(g) \qquad (5)$$

Since 2-propanol acts as a reducing agent for an oxidized species, H_2 can be evolved on CdS and also the rate of H_2 evolution is increased by the addition of 2-propanol on $NiO\text{-}SrTiO_3$.

The effect of O_2 may be explained by the composition of step (3) and step (6) on the surface.

$$\text{2-propanol}(l) + \frac{1}{2}O_2(g) \longrightarrow \text{acetone}(l) + H_2O(l) \qquad (6)$$

In the case of CdS catalyst, added oxygen may oxidize the surface, which causes the deactivation of the catalyst and also explains the reason why photodecomposition of H_2O does not proceed on the surface.

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