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THE ROLE OF SULFITE ANION AS A HOLE SCAVENGER IN THE PHOTOCATALYTIC HYDROGEN FORMATION FROM WATER ON CdS SEMICONDUCTOR UNDER ILLUMINATION OF VISIBLE LIGHT

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Photocatalytic hydrogen evolution from water by visible light was investigated employing CdS as a semiconductor. It was demonstrated that sulfite anion (SO_3^{2-}) is a sufficient hole scavenger to prevent the photocorrosion of CdS. The effect of doped Pt on CdS was also investigated, which enhanced the rate 45 times compared to the case of CdS alone.

Photocatalytic decomposition of water has been attracted attention of many investigaters in connection with solar energy conversion. Proposed heterogeneous systems so far studied were mainly based on TiO_2[1,2,3] or $SrTiO_3$[4,5], which have too wide band gaps for this purpose. Cadmium sulfide (CdS) possesses relatively narrow band gap (ca. 2.4 eV) and shows a strong absorption of light whose wave length is shorter than 520 nm. But when illuminated, CdS itself dissolves into the solution according to the following reactions, and sulfur formed on the surface inhibits the reaction.

$$[\,CdS\,] + h\nu \longrightarrow h^+_{val.} + e^-_{cond.} \quad (1)$$

$$[\,CdS\,] + 2\,h^+_{val.} \longrightarrow S(ads) + Cd^{2+} \quad (2)$$

Some efforts have been made to prevent this photocorrosion process by adding some reducing agents like $Fe(CN)_6^{4-}$, I^-[6], or polysulfide ions[7] to scavenge a hole in competition to reaction (2). Recently, Grätzel et al.[8] succeeded in producing hydrogen and oxygen in stoichiometric proportion by illuminating the aqueous CdS dispersion loaded with Pt and RuO_4 with visible light.

We have also investigated an effective hole scavenger and found that the reaction (2) is supressed by adding sulfite anion (SO_3^{2-}) into the water and hydrogen evolves steadily from this solution under illumination of visible light. The reaction was performed in a conventional closed gas circulation system (ca. 320 ml), equipped with a reaction vessel of a flat bottom (ca. 15 cm^2). About 0.6 g of CdS powder (from Nakarai Chemicals Ltd.) was suspended in an aqueous solution of Na_2SO_3 (from Wako Chemicals Ltd.) and irradiated through the bottom by a 500 W xenon lamp (Ushio USH-500).

Figure 1 shows the typical time courses of hydrogen evolution, which was followed by gas chromatography (molecular seive 5A column, Ar carrier). When the suspension of CdS in water only or in 0.01 M aqueous solution of Na_2SO_3 was irradiated, no hydrogen evolution was detected within 30 hours. When the Na_2SO_3 solution higher than 0.1 M was employed, steady evolution of hydrogen was observed after an induction period of 5 ∿ 10 hours as seen in Fig. 1. The concentration dependence of Na_2SO_3 solution upon the rate of hydrogen formation was positive order, but too high concentration tended to supress the reaction. The dependence of the rate of hydrogen formation upon the light wave length was studied as shown in the table. Although the dependency does not correspond exactly to the absorption spectra of CdS, it is suggested that light absorption by CdS (reaction(1)) causes the hydrogen evolution. To determine the dependence of the rate on the light intensity,

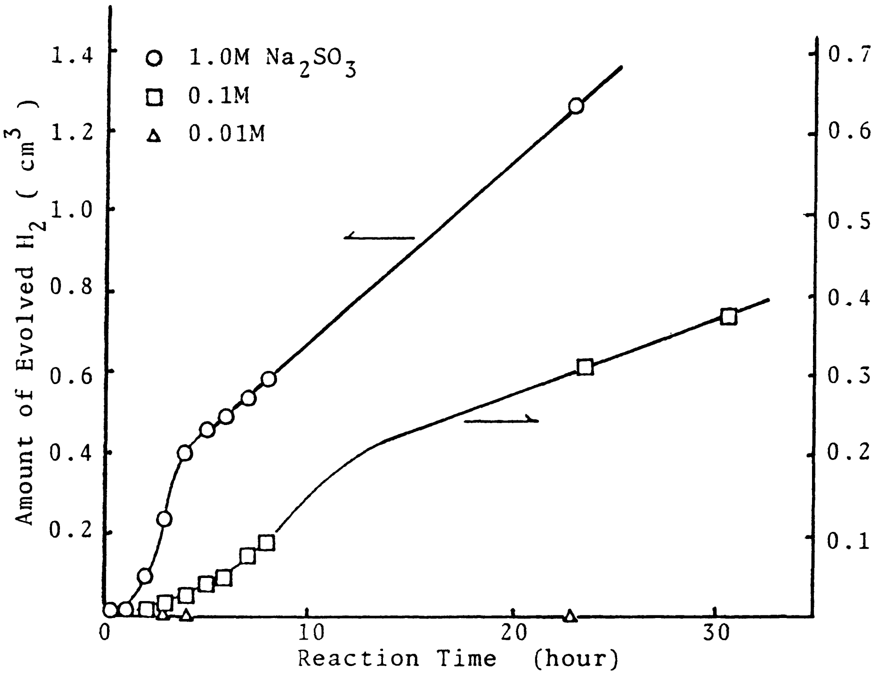

Fig. 1. Time courses of H_2 evolution from the suspension of CdS in various concentrations of aq-Na_2SO_3 soln. under illumination of 500W xenon lamp.

Table. Dependence of the rates of H_2 evolution upon the wave length by the suspension of CdS or CdS-Pt in 1 M aq-Na_2SO_3 solution.

wave length (nm)	rate of H_2 evolution (cm^3 h^{-1})	
	CdS	CdS-Pt
without filter	0.043	0.790
390	0.009	0.118
500	0.004	0.027
620	0.000	0.000

the light shorter than 390 nm was cut by a filter, and then the intensity was reduced by another proper neutral density filter (HOYA Glass Works). The rate of hydrogen evolution was proportional to the intensity of light under the investigated conditions as shown in Fig. 2. This also suggests that reaction (1) is responsible for hydrogen evolution.

After 70 hours irradiation of the suspension of CdS in 1 M Na_2SO_3 aqueous solution, the amount of Cd^{2+} in the solution was determined by EDTA titration method. Only 1.6 mol % of Cd^{2+} correponding to the total amount of produced hydrogen was detected, indicating that the reaction of holes in the valence band with SO_3^{2-} on the surface of CdS takes place in place of reaction (2). The amount of SO_4^{2-} formed in the solution was analyzed by using Ba^{2+} cation, which reasonably corresponded to the amount of H_2 evolved.

Similar experiments were performed with a Pt(6 wt%)-CdS catalyst which was prepared by mixing platinum black (from Nippon Engelhard) and CdS with an agate mortor. The rate of hydrogen evolution on Pt-CdS was 45 times as fast as that on CdS alone, which is summarized in the table. The dependences of the rate upon the light wave length and also upon the light intensity were quite similar to the case of CdS alone as shown in Fig. 2 and in the table. Activation

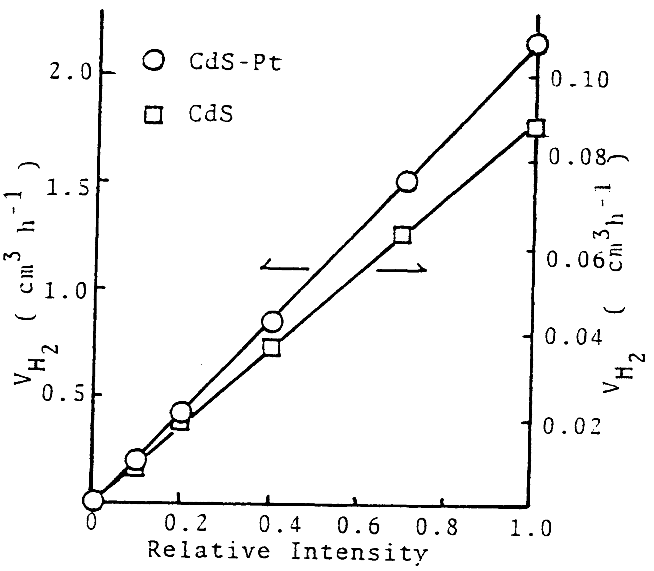

Fig. 2.

Dependence of the rate of H_2 evolution upon the light intensity of the suspension of CdS and CdS-Pt catalysts (in 1 m aq-Na_2SO_3 solution) energies of the reaction over CdS and CdS-Pt catalysts were determined by putting a bottom opened furnace around the reactor. The results in Fig. 3 demonstrate that there exist some temperature dependent slow step like desorption of hydrogen in the reaction over CdS alone, whose activation energy is rather high (12.7 kcal/mol). But, by adding platinum, the activation energy was lowered considerably (2.4 kcal/mol), suggesting an important role of platinum as an active center for hydrogen evolution.

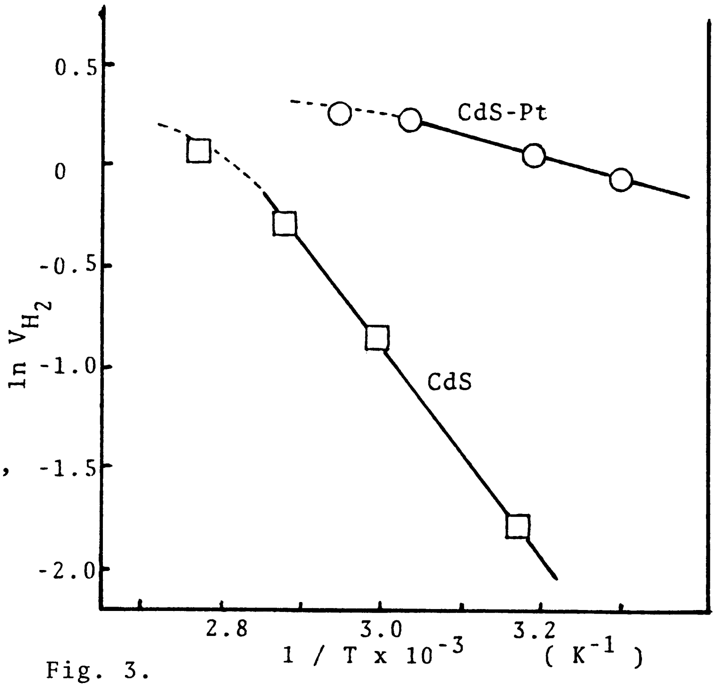

Fig. 3.
Arrhenius plots of the rate of H_2 evolution by the suspension of CdS and CdS-Pt catalysts in 1 M aq-Na_2SO_3 solution under illumination.

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