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PHOTOGENERATION OF HYDROGEN FROM WATER WITH MIXED SEMICONDUCTOR CATALYST

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Alumina-supported mixed semiconductor catalyst, $ZnS \cdot CdS/Al_2O_3$, showed a significant rate of hydrogen generation from water under UV irradiation without an assistance of any noble metals. Singly supported catalyst, ZnS/Al_2O_3 or CdS/Al_2O_3, showed, however, less activity for photogeneration of hydrogen. The activity was not improved by physical mixture of ZnS/Al_2O_3 and CdS/Al_2O_3 although the amount of ZnS and CdS were the same as those in the $ZnS \cdot CdS/Al_2O_3$ catalyst. This indicates that the intimate contacts between ZnS and CdS particles are necessary to photogeneration of hydrogen.

Calchogenide semiconductors have often been used as photocatalysts since the photocorrosion of calchogenides could be improved in the presence of a proper sacrificial reagent such as Na_2S.1) Among the calchogenides ZnS2) and CdS3) have been extensively studied because of a lot of knowledge about their electronic and electrochemical properties. Light absorption is an important step for photogeneration of hydrogen and it takes place over the surface region of a catalyst. Therefore, the light absorption efficiencies of catalysts increase with increasing their surface areas. Hence, much attention has been paid to fine semiconductor particles to improve the activity for hydrogen production from water. Henglein et al.4) studied the changes in the onsets of colloidal ZnS and CdS in the absorption spectra and discussed their activity for hydrogen generation from water. Reber et al.5) have also claimed the enhancement in the rate of hydrogen production from water when colloidal ZnS was employed as a photocatalyst in the presence of Na_2S sacrificial. In this communication it will be presented that the rate of hydrogen generation with alumina-supported ZnS·CdS mixed semiconductor catalyst is ca. 10 times higher than those with singly supported catalysts and this will be explained by intimate contacts between ZnS and CdS particles in the mixed catalyst. The catalysts employed were prepared by a conventional impregnation technique as follows : 1.00 g of Al_2O_3 powder(γ-Al_2O_3 with surface area of 260 m^2/g) was immersed in 50 ml of water containing 2.31 x 10^{-3}mole of $Zn(NO_3)_2 \cdot 6H_2O$, 2.31 x 10^{-3}mole of $Cd(NO_3)_2 \cdot 4H_2O$ or a mixture of 1.65 x 10^{-3}mole of each nitrate. After the Al_2O_3 powder was immersed, the solution was stirred for 2 h and then another 50 ml of water saturated with H_2S was added and the stirring continued for an additional 24 h. The resulting precipitates were filtered and dried in an oven at 110 °C. The fine powder thus obtained was either 24 wt% ZnS/Al_2O_3, 26 wt% CdS/Al_2O_3 or 12 wt% ZnS·13 wt% CdS/Al_2O_3, respectively, as determined by an atomic absorption, neglecting a trace amount of water. A physical mixture of the singly supported catalysts was prepared by mixing the ZnS/Al_2O_3 and CdS/Al_2O_3 with the weight ratio of 1:1. Unsupported ZnS·CdS catalyst was also prepared by coprecipitation method so as the ratio of ZnS and CdS being 12:13 in weight.

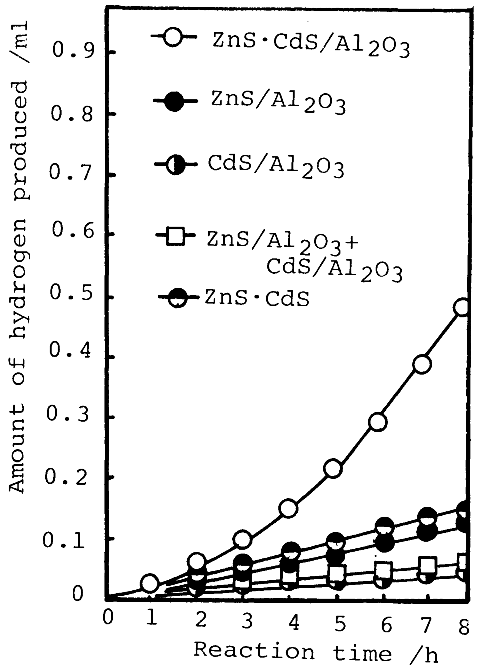

Fig. 1. Amount of hydrogen (S.T.P) produced over various catalyst.

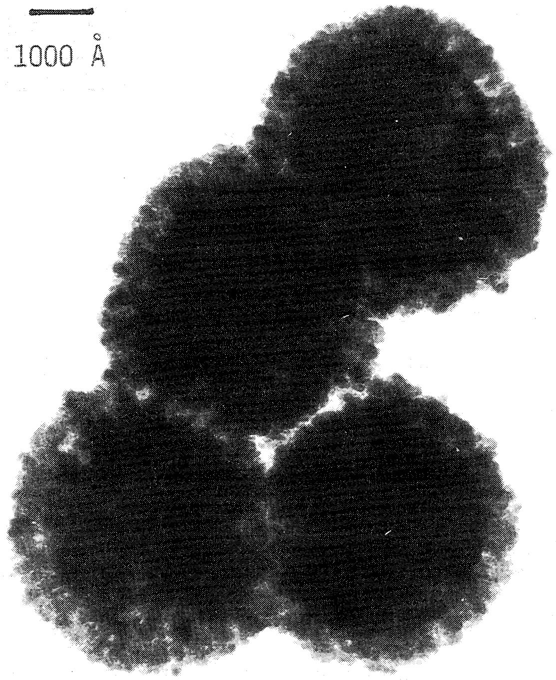

Fig. 2. TEM photograph of particles in the unsupported catalyst.

Photogeneration of hydrogen from water was carried out using a pyrex glass vial whose volume is 20 ml. The catalyst (50 mg) was placed (not suspended) at the bottom of the vial and 10 ml of water containing 0.1 mole of Na_2S was poured into the vial, followed by deaeration assisted by ultrasonication and a purge with N_2. A 450 W Xe lamp was used as a light source to irradiate the catalyst at the bottom of the vial. The top of the vial was sealed with a rubber septum to remove a sample gas into a gas syringe for analysis. The gases produced were analysed by gas chromatography using a column packed with molecular sieve 13X. No gases other than hydrogen and nitrogen were obserbed. In Fig. 1 are shown the amounts of hydrogen produced by UV irradiation over the catalysts. After a couple of hours of induction period, the rate of hydrogen generation becomes constant. Apparently, the rate decreased in the following sequence: $ZnS\cdot CdS/Al_2O_3$ > unsupported $ZnS\cdot CdS$ > ZnS/Al_2O_3 > physical mixture > CdS/Al_2O_3. Although the amounts of ZnS and CdS in the unsupported catalyst were 4 times more than those in the alumina-supported $ZnS\cdot CdS$ catalyst, the rate with the unsupported catalyst was ca. 4 times lower than that with the supported one. This may be due, in part, to the particle sizes of ZnS and CdS in the catalysts. The particle sizes of ZnS and CdS were monitored by a transmission electron microscope (Hitachi H-800), operated at an accelerating voltage of 200 KV with the magnification of 5×10^4. As is shown in Fig. 2 the particles in the unsupported catalyst are larger than 4×10^3 Å, while the particles of ZnS or CdS in the ZnS/Al_2O_3 or CdS/Al_2O_3 are smaller than 100 or 200 Å, respectively (see Figs. 3a and 3b). The particles of ZnS and CdS in the alumina-supported mixed catalyst, $ZnS\cdot CdS/Al_2O_3$, would be sized not so much differently from those in the ZnS/Al_2O_3 and CdS/Al_2O_3 catalysts since the preparation procedures and the conditions were the same in these catalysts. A question, however, will arise why the rates of hydrogen production with the singly supported catalysts and their physical mixture are so much lower than that observed with the supported $ZnS\cdot CdS/Al_2O_3$ catalyst, although the sizes of ZnS and CdS are the same in these catalyst. This might be explained in term of the interaction between ZnS and CdS particles. This kind of interaction should be caused by contacts between particles and the contacts between ZnS and CdS particles in the physically mixed catalyst of ZnS/Al_2O_3 and CdS/Al_2O_3 must be less intimate than those in the mixed $ZnS\cdot CdS/Al_2O_3$ catalyst.

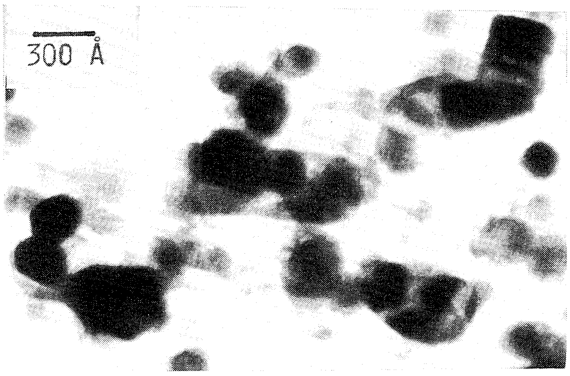

Fig. 3a. TEM photograph of CdS particles in CdS/Al_2O_3 catalyst.

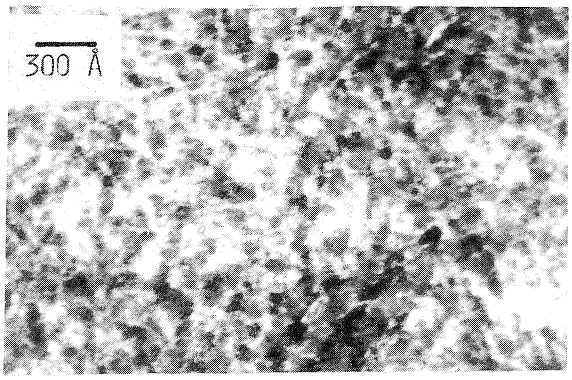

Fig. 3b. TEM photograph of ZnS particles in ZnS/Al_2O_3 catalyst.

Recently, Gratzel et al.$^{6)}$ proposed an inter-particle electron transfer to explain the enhancement in the rate of hydrogen generation with CdS/TiO_2 mixed semiconductor catalyst. Accordingly, in the $ZnS \cdot CdS/Al_2O_3$ system the electron transfer between particles originated from the intimate contacts between the fine ZnS and CdS particles might attribute to the improved rate of hydrogen production from water.

It must be noted that the absorption spectrum of the $ZnS \cdot CdS/Al_2O_3$ catalyst showed two onsets at 320 and 530 nm, which correspond to the onsets of ZnS and CdS, respectively. This means that no solid solution between ZnS and CdS were formed in the $ZnS \cdot CdS/Al_2O_3$ catalyst.

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