Photohydrogenation of Acetylene and Ethylene by Pt and Rh supported on CdS Semiconductor Particles

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Hydrogenation of acetylene and ethylene in aqueous sulphide solution occurs during the illumination of semiconducting CdS particles loaded with Pt or Rh catalysts; the product distribution of the hydrogenation reaction depends on both the pH of the solution and the identity of the transition metal catalyst.

Photocatalytic studies of semiconducting particles have attracted considerable interest recently because of their potential application to the synthesis of fuels and useful chemicals and the removal of industrial pollutants.[1] The hydrogenation of unsaturated carbon structures has been of special interest to us. The light-induced hydrogen reduction of acetylene (C_2H_2) and ethylene (C_2H_4) in homogeneous aqueous media consisting of a sensitizer, Ru(2,2′-bipyridine)$_3{}^{2+}$; an electron relay, methyl viologen; a sacrificial electron donor, ethylenediaminetetra-acetic acid; and transition metal catalysts has been reported.[2]

In this article, we discuss the utilization of semiconducting CdS powders [E(bandgap) 2.4 eV; λ 517 nm] charged with Pt or Rh catalysts for the photohydrogenation of C_2H_2 and C_2H_4 and the concomitant oxidation of sulphide, a frequent industrial pollutant. The CdS particles were loaded with either a Pt or a Rh catalyst (2% w/w). Platinized CdS particles were prepared by illumination of 144.5 mg of CdS dispersed in an argon-purged aqueous solution (10 ml) of 2×10^{-3} M K_2PtCl_4 with a 1000 W halogen-quartz lamp ($\lambda > 400$ nm) for 2 h.[3] Rhodium was deposited onto CdS powder by irradiation of 144.5 mg of CdS in a deaerated aqueous solution (10 ml) of 2×10^{-3} M $RhCl_3$ with a 150 W xenon-arc lamp ($\lambda > 400$ nm) for 4 h. The samples for photohydrogenation experiments consisted of 30 mg of metallized CdS powder dispersed in deaerated aqueous solutions (10 ml) with 3.4×10^{-2} M Na_2S bubbled to saturation with C_2H_2 or C_2H_4. The light source was a 1000 W halogen-quartz lamp ($\lambda > 400$ nm). Aliquots of the photolysed samples were removed at frequent intervals for gas chromatographic analysis. The hydrocarbon products and H_2 were separated, respectively, on a Poropak N column at 40 °C and a 5 Å molecular sieve column at 50 °C.

Figure 1 summarizes the effect of different catalysts and pH on the hydrogenation of C_2H_2 and C_2H_4. Figure 1(a) shows ethane production from ethylene at pH 10.3 in the Pt–CdS system; no H_2 was detected in either the absence or the presence of ethylene. In the former case, argon was substituted for ethylene. The ratios of $C_2H_4 : C_2H_6$ were determined after 135 min illumination. At pH 10.3, ethylene and ethane were produced from acetylene in illuminated Pt–CdS suspensions with a $C_2H_4 : C_2H_6$ product ratio of 2.6 : 1 [Figures 1(b) and 1(c)]. At pH 7.2 (phosphate buffer), the ratio of $C_2H_4 : C_2H_6$ is 1.25 : 1, indicating a change in the product distribution for the photo-induced hydrogenation of C_2H_2 [Figures 1(f) and 1(g)]. No H_2 was detected in the presence of C_2H_2, although it was observed when argon was substituted for C_2H_2 [Figure 1(h)]. Figure 1(i) depicts the calculated equivalent amount of H_2 expected based on the conversion of C_2H_2 into C_2H_4 and C_2H_6. A comparison of Figures 1(h) and 1(i) reveals that the hydrogenation reaction consumes hydrogen more efficiently than the H_2 evolution reaction.

Figures 1(d) and 1(e) show the photogeneration of ethylene and ethane from acetylene in the Rh–CdS system. The yield of C_2H_4 and C_2H_6 is much lower with the Rh catalyst compared with the Pt catalyst. Also the product ratio of $C_2H_4 : C_2H_6$ (2 : 1), after 135 min illumination, suggests that ethane formation is more favoured with Rh than with Pt.

The net photocatalytic hydrogenations of acetylene and ethylene are summarized in equations (1) and (2), where the protons originate from water. These reactions are thermo-

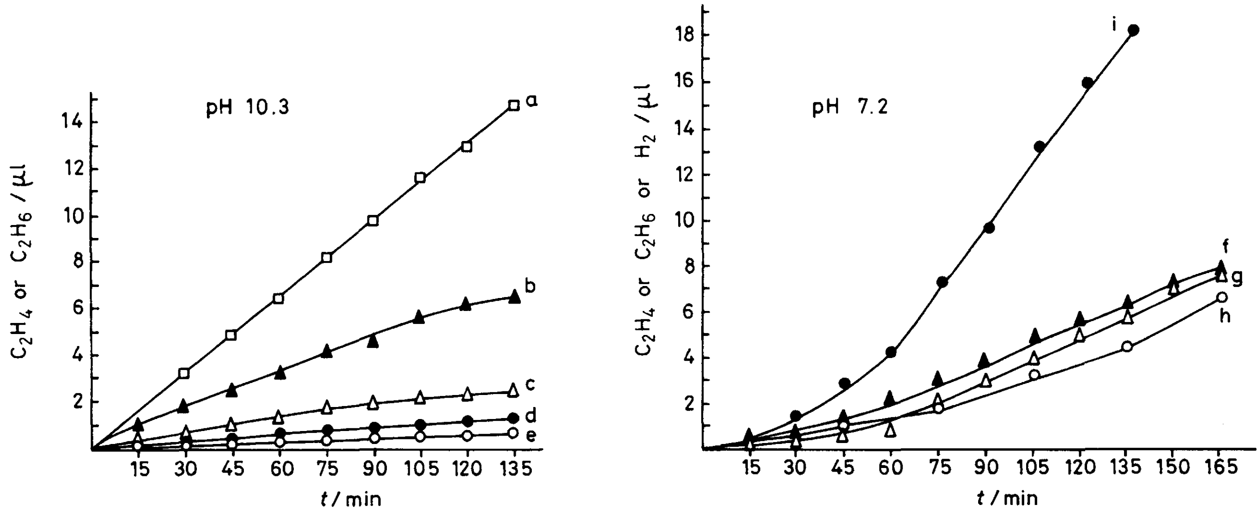

Figure 1. Hydrogenation products and H_2-evolution by metal supported CdS powder. (a) Pt–CdS, C_2H_6 production from C_2H_4; (b) Pt–CdS, C_2H_4 from C_2H_2; (c) Pt–CdS, C_2H_6 from C_2H_2; (d) Rh–CdS, C_2H_4 from C_2H_2; (e) Rh–CdS, C_2H_6 from C_2H_2; (f) Pt–CdS, C_2H_4 from C_2H_2; (g) Pt–CdS, C_2H_6 from C_2H_2; (h) Pt–CdS, H_2 evolution; (i) estimated H_2 evolution equivalents based on hydrogenation products ($C_2H_4 + 2 \times C_2H_6$).

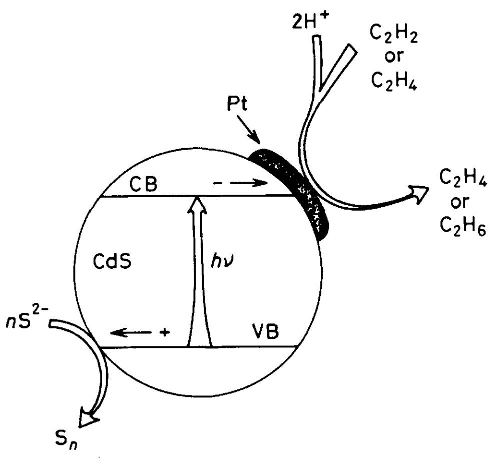

Figure 2. Photohydrogenation of acetylene or ethylene by Pt–CdS semiconductor particles.

$$C_2H_2 + 2H^+ + S^{2-} \xrightarrow[\text{cat.}]{h\nu} C_2H_4 + S \quad (1)$$

$$C_2H_4 + 2H^+ + S^{2-} \xrightarrow[\text{cat.}]{h\nu} C_2H_6 + S \quad (2)$$

dynamically downhill by *ca.* -25.8 and -16.2 kcal mol^{-1} (1 kcal = 4.184 kJ), respectively, although no C_2H_4 and C_2H_6 are formed in the dark. Thus, these reactions should be considered as photocatalysed processes. In both neutral and basic solutions, the hydrogenation reactions inhibit H_2 evolution. Since the calculated amount of H_2 produced based on the hydrogenation reaction [Figure 1(i)] is considerably larger than the actual amount of H_2 evolved in the absence of C_2H_2 [Figure 1(h)], by a factor of ~4 after 135 min illumination, the hydrogenation must predominate over H_2 evolution. Also we conclude that H_2 production competes less effectively than valence-band holes of CdS for Pt-bound hydrogen. The photohydrogenation reactions thus allow a larger fraction of valence-band holes to react with and oxidize sulphide (Figure 2). The oxidation of sulphide by means of the photohydrogenation of unsaturated substrates may be of practical importance for the desulphurization of waste materials such as in petroleum-based industries.

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