Direct Evidence for the Participation of Extrinsic Surface Sites in the Enhancement of Photocatalytic Activity of Luminescent Zinc Sulphide Catalysts

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The extrinsic surface states due to sulphur clusters injected by mechanical grinding of a luminescent ZnS catalyst, acting as photo-produced hole-trapping sites, play a decisive role in the photocatalytic activity of ZnS for *cis–trans* isomerization reactions of but-2-ene.

Photocatalysis with powdered semiconductor catalysts has received much attention from the standpoint of photochemistry of solid surfaces as well as potential utilization of solar energy. However, there seem to be few studies on the primary processes or on the excited states of catalysts. For a complete understanding of photocatalysis, we need to know the detailed fate of electrons and holes injected into the catalysts by u.v. and/or visible light, and the chemical nature of these electrons and holes leading to chemical reactions. Although it is well established that extrinsic surface sites or defects (or co-ordinatively unsaturated surface sites) play a significant role in heterogeneous catalysis, the role of such surface sites or defects in photocatalysis is still unclear.[1,2] To investigate this problem, luminescent ZnS powders can be used, since photoluminescence not only can be used as a probe of electron–hole surface processes but also is very sensitive to changes in the environment of surface active sites.[3—6]

Luminescent ZnS powder samples were obtained from Nakarai Chemical Co. *X*-Ray diffraction measurements showed that all the samples used had purely cubic crystal structures with good crystallinity. Prior to the experiments, the catalysts were evacuated at 573 K for 1 h. *cis*-But-2-ene (0.67 kPa, 5 Torr) was introduced onto the catalyst which was spread over a quartz window with a surface area of about 23 cm^2. The photocatalysed isomerization was carried out by using a high pressure mercury lamp (Toshiba, SHL-100 UV) without a colour filter in an ice–water bath. U.v. diffusion reflectance and photoluminescence spectra of the catalysts were measured with a Shimadzu UV-210 A double-beam digital spectrophotometer at 298 K and a Shimadzu RF-501 spectrofluorophotometer, equipped with colour filters, at 298 and 77 K, respectively. E.s.r. spectra were measured at 77 K using a JES-ME-1 (X-band) spectrometer. Mn^{2+} impurity in the ZnS catalysts was used as an internal standard for determining the relative concentration of radical species and *g*-values. The surface area of the catalysts was measured by the adsorption of N_2 at 77 K, after the catalyst had been degassed at 298 K for 2.5 h. There was no direct correlation between photocatalytic activity and surface area. Details of the experiments have been described elsewhere.[2,6,7]

As shown in Figure 1, the pre-ground original ZnS catalyst (a) exhibits an absorption band at *ca.* 390—410 nm, and a photoluminescence spectrum at *ca.* 420—470 nm with high efficiency. This photoluminescence spectrum is similar to the blue luminescence which was attributed by Bard *et al.* to the radiative recombination of photo-produced holes and electrons supplied from sulphur vacancies in ZnS, generating localized electron donor sites.[8] It was found that the intensity of the photoluminescence spectrum of the ZnS catalyst changes by mechanical grinding in an agate mortar. As shown in Figure 1, the efficiency of the photoluminescence decreases with increasing grinding. Simultaneously, the absorption band of the ZnS catalyst gradually shifts towards longer wavelengths with a tail in the long wavelength region, as shown in Figure 1. These changes clearly imply that some extrinsic surface energy levels are created in the band structure of the ZnS catalyst caused by damage due to grinding, the extent increasing with longer grinding times.

The pre-ground original ZnS catalyst exhibited a weak e.s.r. signal having *g*-values of $g_1 = 2.0063$, $g_2 = 2.0021$, and $g_3 = 2.000$. In addition to this signal, new e.s.r. signals having *g* values of 2.016—2.024 were observed with the ground ZnS

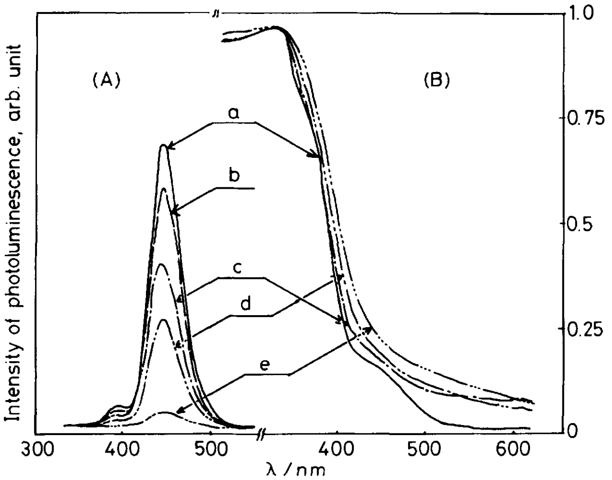

Figure 1. (A) Photoluminescence and (B) absorption spectra of ZnS catalyst and effect of grinding (298 K; excitation wavelength, 285 ± 15 nm); (a) pre-ground original ZnS, no. of grindings 0; (b) no. of grindings 50; (c) 250; (d) 1250; (3) 6250.

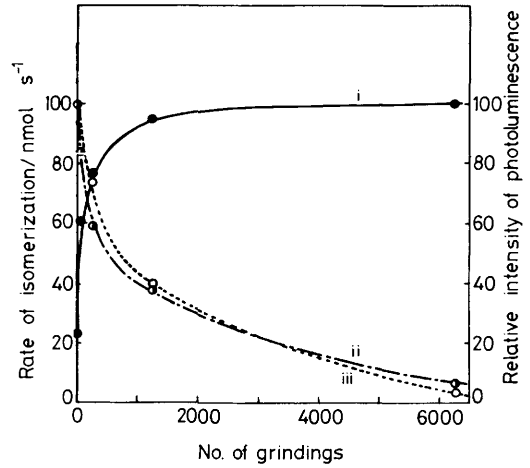

Figure 2. Effect of grinding upon (i) the rate of photoisomerization of *cis*-but-2-ene and the yield of photoluminescence (ii) at 298 K and (iii) at 77 K for the ZnS catalyst (0.6 g); Brunauer–Emmett–Teller (B.E.T.) surface area of catalysts (a)—(e) of Figure 1: (a), 0.5; (b) 0.5; (c) 0.6; (d) 0.9; (e) 2.3 m^2/g.

catalysts. According to the literature,[5,9—11] e.s.r. signals having g-values in the region 2.002—2.024 with sulphide catalysts can be attributed to radical-like sulphur species such as $\cdot S_n$ involving S_3^- and/or sulphur cluster species. The concentration of these species was found to increase drastically with increasing grinding of the ZnS catalyst. Although it is known that mechanical damage causes the appearance of some surface energy levels in the band structure of semiconductors,[12,13] these spectroscopic data clearly and directly provide evidence that the extrinsic surface energy states due to radical-like sulphur and/or sulphur cluster species are produced by grinding between the valence and conduction band structure of ZnS.

The *cis–trans* isomerization of but-2-ene was found to proceed catalytically on the ZnS catalyst under u.v. irradiation, in agreement with previous work.[7,9,14] The initial rate of the isomerization on the pre-ground original ZnS catalyst was rather low, but it increased with increasing grinding. As seen in Figure 2, the effect of grinding the ZnS catalyst upon the efficiency of the photocatalysed isomerization is opposite to the effect upon the efficiency of photoluminescence of the catalyst.

These results indicate that the extrinsic surface energy states due to sulphur cluster species and/or radical-like sulphur species produced on the surfaces by grinding play a decisive role in trapping photo-formed holes. This results in a suppression of photoluminescence arising from recombination of photo-formed holes and electrons supplied from sulphur vacancies.[8] Simultaneously, this results in an enhancement of photocatalytic activity of ZnS for *cis–trans* isomerization reactions, since according to work by Yanagida *et al.*[9] and Kodama *et al.*,[7] trapped holes at surface sites, *i.e.* sulphur radicals arising from interstitial sulphur on surfaces, play a decisive role in the photocatalysed *cis–trans* isomerization of alkenes on sulphides. Thus, the extrinsic surface energy states play a significant role in determining the fate of photo-produced holes (and/or electrons), *i.e.*, the efficiency of photocatalytic activity as well as photoluminescence of the catalyst.

Received, 9th February 1987; Com. 174

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