Photoemission of Porous Vycor Glass and its Photodesorption Activity

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Summary The photodesorption activity of porous Vycor glass in the formation of propan-2-ol from surface isopropoxide increases with increasing emission at 345 nm, and arises from the excited state of surface OH groups.

Although the photoluminescence technique has been used[1] to obtain information on the nature of the surface of oxide catalysts, no studies have been made of correlations between the photoemission of an oxide catalyst and its photodesorption activity. We now report the photoreactions of isopropoxide on porous Vycor glass (PVG).

PVG-A (Corning, 746685-7930) and PVG-B (Corning, 749303-7930) were used. The PVG with presorbed propan-2-ol was heated at 493 K for 2 h to form surface isopropoxide species. This isopropoxide was then irradiated by monochromatic light at 300 ± 9 nm, and the photoluminescence of the PVG was measured at room temperature using a Shimadzu RF-501 spectrofluorophotometer with filters to eliminate scattered light.

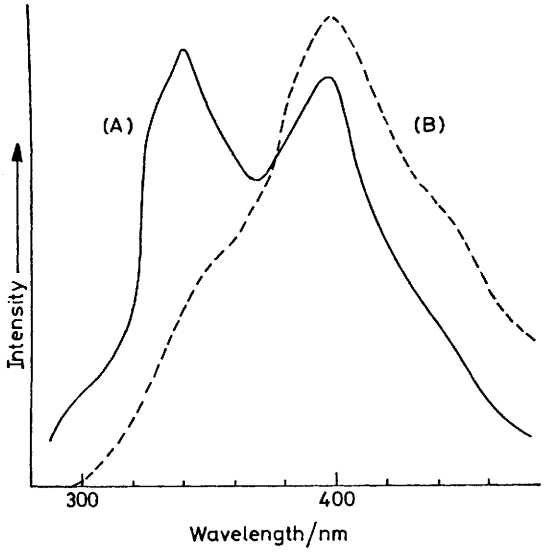

FIGURE 1. Emission spectrum of PVG at 300 K excited at 280 nm. (A) PVG-A; (B) PVG-B.

PVG-A exhibits emission bands at 345 nm and 400 nm, while PVG-B has an emission band at 400 nm with a shoulder at 345 nm (Figure 1). The excitation spectrum shows maxima at 295 and 255 nm for the emission bands at 345 and 400 nm, respectively. The photoproducts from the isopropoxide on both PVG's were found to be propan-2-ol and propene. Although there was no difference in the amounts of propene formed from PVG-A or PVG-B, ten times as much propan-2-ol was formed from PVG-A as from PVG-B.

As seen in Figure 2, with PVG-A the intensity of the emission band at 345 nm as well as the amount of propan-2-ol formed decreases with increasing degassing temperature. Simultaneously, the concentration of surface OH groups decreases. This suggests that the photoemission, as well as formation of propan-2-ol, is associated with the presence of OH groups, *i.e.*, the emission could arise from excited OH groups. It has been reported[2] that aqueous solutions of KOH and OH ions in KBr matrix show an emission band at 310 nm, with an excitation at 255 nm which is different from the emission and excitation frequencies reported here. This difference might be attributed to the difference in the environment of the OH ions, *i.e.*, the specificity of surface OH ions, as suggested by Tench *et al.*[1] It is concluded, therefore, that propan-2-ol is formed from the reaction of isopropoxide species with surface OH groups excited by irradiation. This participation of excited OH groups is supported by the fact that on PVG-A the exchange reaction: $D_2 + OH(surface) \rightarrow HD + OD(surface)$ was feasible at room temperature only under irradiation at 300 nm.

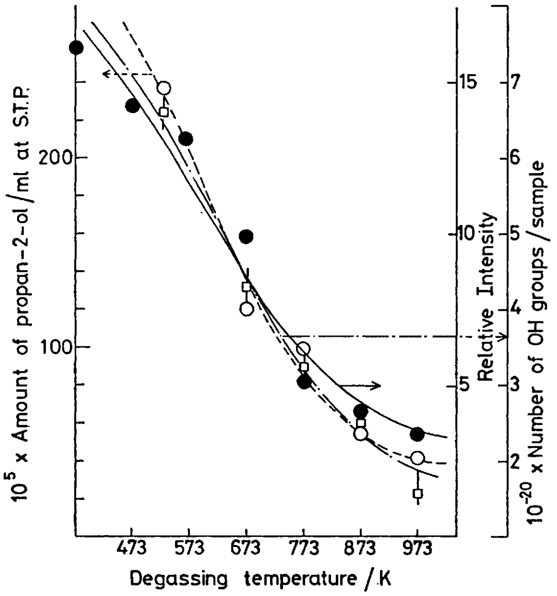

FIGURE 2. Effects of degassing temperature upon the yield of propan-2-ol, intensity of emission at 345 nm, and concentration of OH groups (M. J. D. Low and N. Ramasubramanian, *J. Phys. Chem.*, 1967, **71**, 730) for PVG-A. Amount of isopropoxide formed was 0·200 ml g^{-1}, S.T.P. Irradiation time, 120 min. ○, propan-2-ol; ●, emission; □, OH concentration, with error limits.

The emission at 400 nm is attributable to charge-transfer interaction taking place at low co-ordination sites[1] on the surface. Although no information is available on the nature of the difference in the emission spectra between PVG-A and PVG-B, such a difference might originate from the presence of particular types of OH groups associated with trace metal ions, as has been suggested by Gesser *et al.*[3]

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