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Photoformation of $(O_2^-)_{ads}$ Radicals and Their Reactivity on Porous Vycor Glass

As for the photocatalysis on metal oxides, there have been rather few studies made on insulators, in contrast to extensive studies on semiconductors such as ZnO and TiO_2 (*1*). It seems necessary to obtain information on photocatalytic reactions on insulators for understanding the nature of photocatalysis. For this purpose porous Vycor glass (PVG) appears to be one of the most appropriate materials because of its high transparency and high surface area. We have investigated the correlation between the photoluminescence of PVG and its activity toward photoinduced surface reactions (*2*). In the present work we now deal with photoformation of $(O_2^-)_{ads}$ radicals and their reactivity on PVG, since adsorbed oxygen species such as $(O_2^-)_{ads}$ together with lattice oxygen activated by uv irradiation play a significant role in photooxidation and other photocatalytic reactions on oxide catalysts (*1*).

PVG (Corning No. 7930-79303) was used. Prior to the experiments, it was heated in oxygen at 873 K followed by evacuation for 5 hr at 773 K. It has a BET surface area of 160 m^2/g. Its photoluminescence was measured at room temperature using a Shimazu RF-501 spectrofluorophotometer with filters to eliminate scattered light. ESR measurements were carried out at 77 K using a JES-ME-1X. The photoinduced uptake of oxygen was measured at 300 K using a Pirani vacuum gauge.

On evacuation at temperatures above 600 K PVG showed a broad absorption spectrum having a maximum around 240–260 nm. Simultaneously, a photoluminescence with a peak at 400 nm appeared. Coluccia *et al.* (*3*) have shown less energy is required for the charge-transfer process at low-coordination sites on the surface at high surface area oxides outgassed at high temperatures, e.g., MgO (band gap, 8.2 eV) shows an absorption maximum in the region of 220–270 nm as well as the emission at 440 nm with an excitation band at 250 nm. A similar situation would be expected for PVG. Specific sites of very low coordination appear to be responsible for the emission as well as the absorption of PVG (*2*). It seems very difficult to exclude the possibility that specific sites associated with impurities in the PVG, such as boron, are responsible for the emission. Their contribution to the total emission, however, would be very small, since according to the work of Bell *et al.* (*4*) pure silica gel partly reduced exhibits the emission and absorption similar to those with PVG. Similar interpretation favorable to low coordination sites has been proposed by Morikawa *et al.* (*5*), who investigated the photocatalytic activity of PVG.

The PVG which had been outgassed at higher temperatures induced adsorption of oxygen when it was irradiated in the presence of oxygen with the uv light capable of exciting the surface states arising from low coordination sites (<330 nm). The photoadsorption of oxygen as a function of time is shown in Fig. 1. No such photoinduced adsorption was observed for nitrogen, hydrogen, and carbon monoxide. Taking into account the high electron affinity of oxygen, such a photoadsorption of oxygen might be attributed to formation of anion radicals such as $(O_2^-)_{ads}$. ESR studies showed that on the PVG which had photoadsorbed oxygen the ESR signal having $g_1 = 2.0310, g_2 =$

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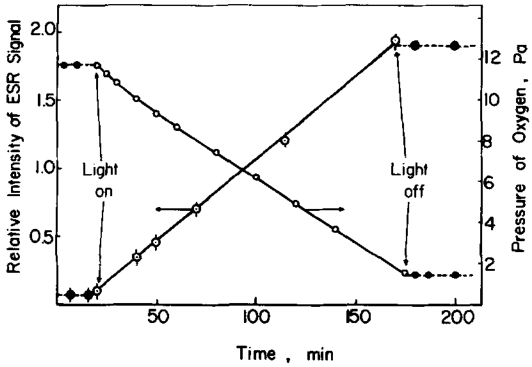

FIG. 1. Effect of irradiation time upon the relative intensity of ESR signal of photo-formed $(O_2^-)_{ads}$ radicals as well as the amount of adsorbed oxygen on PVG surface. Amount of photo-adsorbed oxygen, 3.0 × 10^{-6} mol/g.

2.0109, and g_3 = 2.0053 appeared on the field lower than that for F-center (Fig. 2). The ESR signal intensity as well as the amount of photoadsorbed oxygen increased with increasing time of irradiation (Fig. 1). The signal can be identified as the $(O_2^-)_{ads}$ anion radicals, since their g-values as well as their shape agree well with those obtained by Fujita and Turkevich (*6*), who have established formation of $(O_2^-)_{ads}$ radicals in the photolysis of H_2O_2 and D_2O_2 adsorbed on PVG. With the oxygen adsorption on γ-irradiated silica gel Mikheikin *et al.* (*7*) have found essentially the same signal as that obtained by us and attributed it to $(O_2^-)_{ads}$ anion radical. On increasing degassing temperature of PVG up to 850 K, the photouptake of oxygen as well as the intensity of $(O_2^-)_{ads}$ signal increased. Simultaneously, the intensity of the absorption arising from the surface states described above increased. This suggests that photoformation of $(O_2^-)_{ads}$ radicals is closely associated with the presence of the specific sites in low coordination. After pumping of the PVG at room temperature to 1.33 × 10^{-3} Pa only about 10% of the photoadsorbed oxygen remained on the surface, while no significant decrease in the intensity of the ESR signal was observed. This suggests that about 90% of the photoadsorbed oxygen is a weakly adsorbed species and is not observable by ESR, although its true nature is unknown at present.

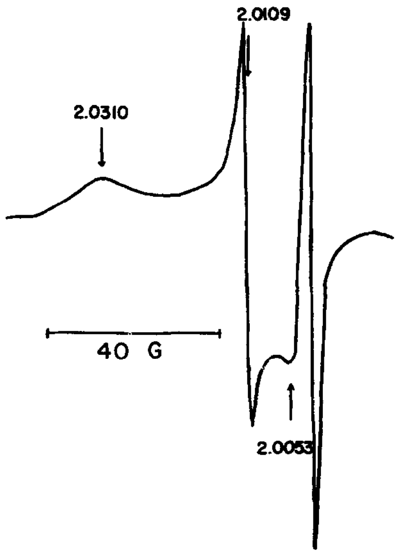

FIG. 2. ESR signal of $(O_2^-)_{ads}$ radicals obtained with PVG at 77 K after evacuation of gaseous oxygen at room temperature. Amount of adsorbed oxygen, 1.0 × 10^{-7} mol/g.

It has been reported that $(O_2^-)_{ads}$ radicals formed on oxide catalysts are much less reactive as compared to $(O^-)_{ads}$ or $(O_3^-)_{ads}$ and can exist even in the temperature range of 370–420 K (*8*). In fact, it was found in this word that the photoformed $(O_2^-)_{ads}$ radicals on PVG were stable up to the evacuation temperature of about 350 K (Fig. 3). As expected from such a behavior, the $(O_2^-)_{ads}$

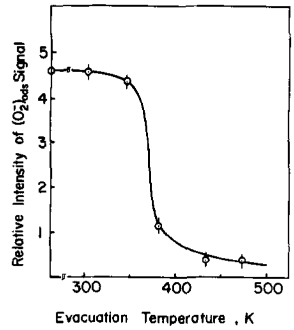

FIG. 3. Thermal stability of $(O_2^-)_{ads}$ radicals on PVG surface A plot of relative surface concentration of $(O_2^-)_{ads}$ radicals against evacuation temperatures.

radicals were stable for more than several days under vacuum or in the presence of oxygen. The ESR signal was removed by contact with 1-C_4H_8 at room temperature but unaffected by C_2H_4. In a separate experiment 1-C_4H_8 was introduced on the PVG having $(O_2^-)_{ads}$ radicals. The major product was found to be 1,3-butadiene, little or no oxygen-containing compounds being formed. It should be noted that uv irradiation of a mixture of oxygen and 1-C_4H_8 over PVG caused formation of various oxygen-containing compounds in a similar manner to that observed with alkane and TiO_2 systems (*9*).

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M. ANPO
C. YUN
Y. KUBOKAWA

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai, Osaka 591, Japan

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