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PHOTODECOMPOSITION OF ISOPROPOXIDE ADSORBED ON POROUS VYCOR GLASS

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Photoenhancement of the propene formation from the isopropoxide on porous Vycor glass is attributed to O^- hole centers formed by the charge transfer process at low co-ordination sites, which gives rise to the absorption around 250 nm as well as the emission at 400 nm.

As for the photocatalysis on metal oxides, there have been a few studies made on insulators as compared to extensive studies on semiconductors such as ZnO and TiO_2. Information on how the energy of photons is absorbed into insulators is important for understanding of its photocatalysis. For this purpose porous Vycor glass (PVG) appears to be one of the most appropriate materials, because of its high transparency. Accordingly, in continuation of the previous work,[1] we have investigated the correlation between the absorption as well as the photoemission spectra of PVG and its activity towards photodecomposition of surface isopropoxide.

PVG (Corning, 749303-7930) was used. In the previous paper,[1] it was denoted by PVG-B. The PVG with presorbed propan-2-ol was heated at 493 K for 2 hr to form surface isopropoxide. This isopropoxide was irradiated in the wavelength region between 220 and 440 nm, using a high pressure mercury arc (Toshiba) or a monochromater (Shimadzu). Absorption spectrum of PVG was measured with a Hitachi EPS-3T-spectrophotometer measuring the transmission through the sample. Its photoluminescence was measured at room temperature using a Shimadzu RF-501 spectrofluorometer with filters to eliminate scattered light.

Dashed lines in Fig.1 show the absorption spectra of PVG-B outgassed at various temperatures for 7 hr. A broad absorption having a maximum around 250 nm appears above 673 K, its intensity increasing with increasing degassing temperature. Simultaneously, the PVG exhibited an emission band at 400 nm with an excitation band at

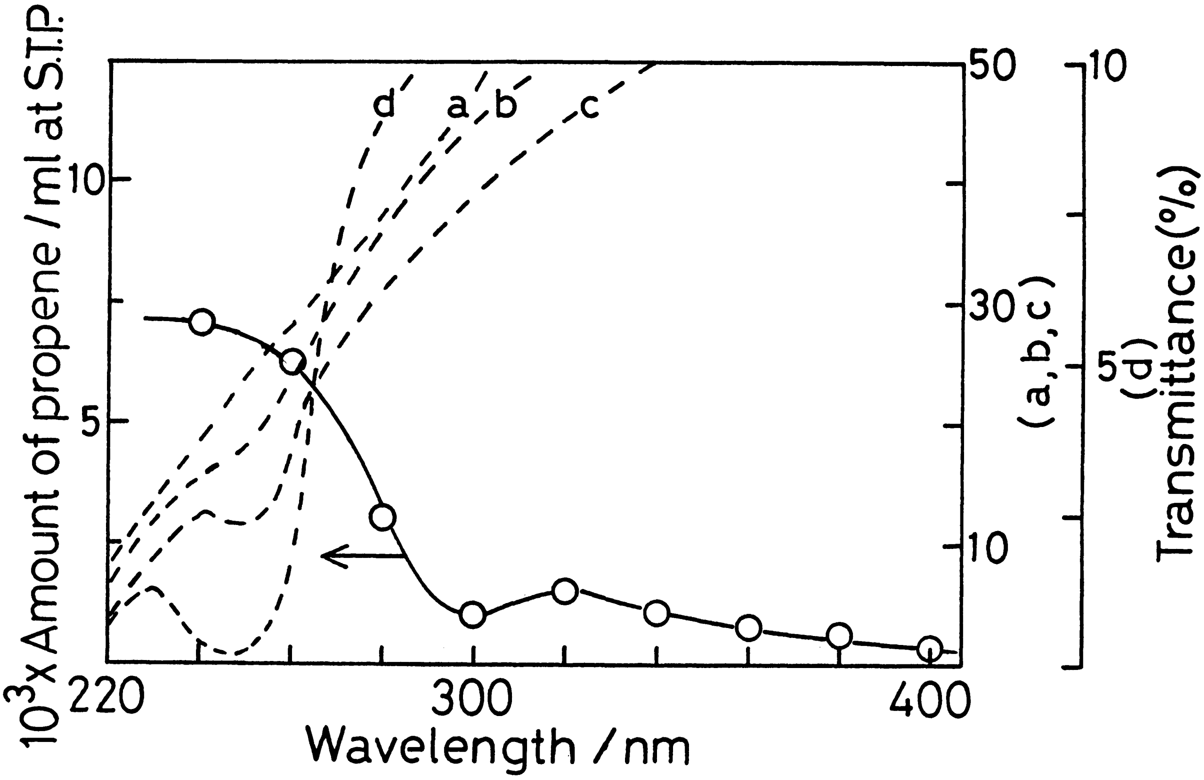

Fig. 1. Absorption spectra of PVG and action spectra of propene formation Dashed lines, Absorption spectra : a, 523 K ; b, 673 K ; c, 973 K ; d, 1100 k. Solid line, Propene formation. Amount of isopropoxide, 0.200 ml g^{-1}, S.T.P. Irradiation time , 120 min (monochromater, band width ; ±9 nm). The propene formation was measured with the PVG outgassed at 973 K.

255 nm. The emission increased in intensity with increasing degassing temperature.

Tench et al.[2] have shown that less energy is required for the charge transfer process at low co-ordination sites on the surface of high surface area oxides outgassed at high temperatures, e.g., MgO (band gap ; 8.7 eV) shows the absorption at 260 nm as well as the emission at 400 nm with an excitation band at 280 nm. A similar situation would be expected for PVG. Specific sites of low co-ordination appear to be responsible for the absorption as well as the emission of PVG. Morikawa et al.[3] have also attributed the photocatalytic activity of PVG to the presence of Si ions in very low co-ordination such as Si^{3+}.

The photoproducts from the isopropoxide were found to be propan-2-ol and propene as described previously.[1] In the case of PVG-B, formation of propene was found to be much larger as compared to that of propan-2-ol. A marked photoenhancement of propene

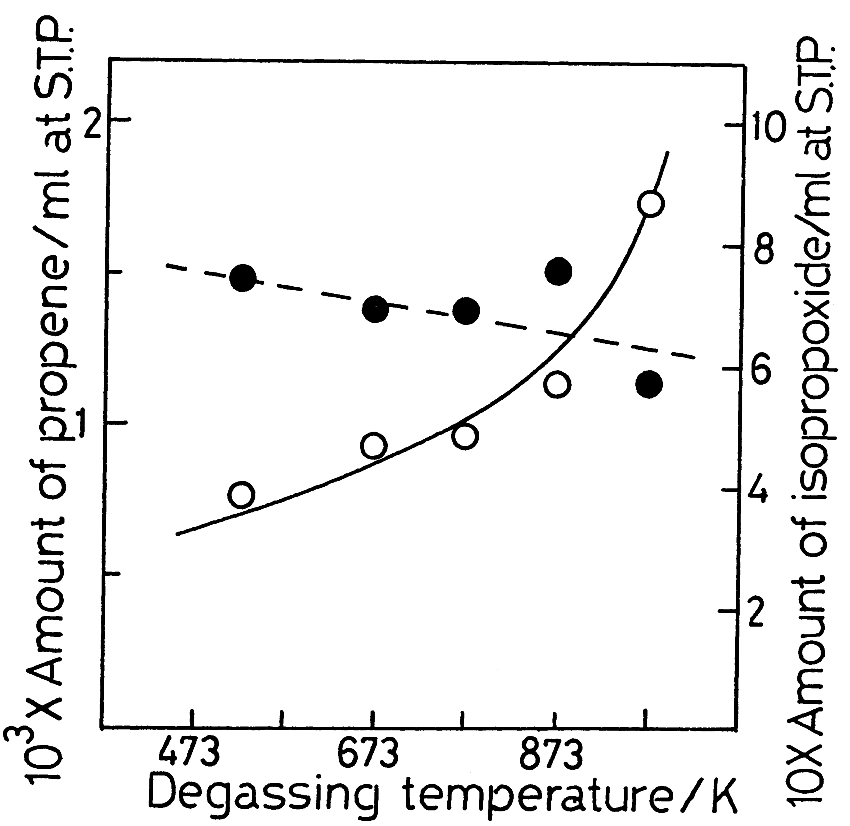

Fig. 2. Effects of degassing temperature upon the yield of propene and the amount of isopropoxide. --●--, Isopropoxide ; —○— , Propene formation. Irradiation time, 120 min. (high pressure mercury arc)

formation is observed in the range where the absorption spectrum shows a maximum. (Solid line in Fig. 1) Below the range of 240 nm, the light intensity available for the reaction decreases markedly because of light scattering of PVG, resulting in a very small rate of the propene formation. The absence of the rate maximum might be attributed to such a small rate of formation, which makes it impossible to carry out accurate rate measurements. Accordingly, it is concluded that the propene formation is closely associated with the absorption around 250 nm. As expected from this conclusion, the propene formation increased with increasing degassing temperature, in a similar manner to that observed with the intensity of the absorption as well as the emission. Little or no change in the amount of isopropoxide formed on PVG was observed on increasing degassing temperature. (Fig.2)

The correlation between the absorption as well as the emission of PVG and its activity towards photo-induced surface reactions may be given from the following considerations. The charge transfer process, $\left[M^{n+}O^{2-}\right] \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} \left[M^{(n-1)+}O^{-}\right]$, results in formation of O^- anion radicals. Since Kazansky et al.[4] have shown that O^- anion radicals exhibit the high reactivity in many systems, it seems likely that photoenhancement of the propene formation is associated with formation of O^- radicals due to the charge transfer process. We have also studied the effect of addition of an electron scavenger such as O_2 or N_2O upon the propene formation, since it is expected that

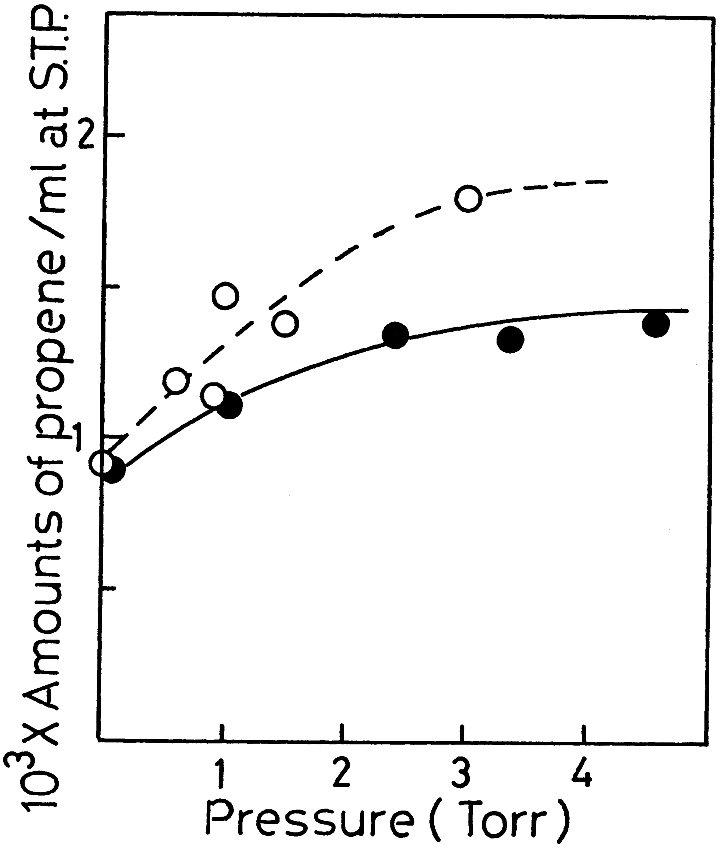

Fig. 3. Effects of added gases upon the yield of propene.
– –○– –, Oxygen ; ——●——, Nitrous oxide.
Irradiation conditions are the same as Fig. 2. (1 Torr = 133.3 Pa)

trapping of electrons by O_2 or N_2O depresses recombination of hole centers O^- with electrons, leading to enhancement of photoreaction. In fact, the increase in the propene formation has been observed. (Fig. 3) It would be very difficult, however, to determine the contribution of such an increase in the lifetime of hole centers O^- to the overall increase in the propene formation, since enhancement of the propene formation is attributable to the increase in the lifetime of hole centers as well as to hydrogen abstraction by O_2^- or O^- formed by trapping of electrons. The propene formation appears to proceed via hydrogen abstraction by O^- radicals and scission of the C-O bond of isopropoxide as proposed for the dehydration of alkoxides on Al_2O_3.[5]

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