The Photosensitized Decomposition of Methane Adsorbed on Porous Vycor Glasses Coated with Metal Oxides at 77°K

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As has been reported previously, it has been found that various types of methyl radicals have been trapped at 77°K on the surface of porous Vycor glass (PVG).[1,2] We were interested in the influence of the metal oxides coated on the surface of PVG on the photodecomposition mechanisms of methane, and so we studied the photolysis of methane at 77°K on various PVG surfaces (abbreviated PVG(V_2O_5) and so on) by the technique of ESR spectroscopy.[1] We have found an interesting new effect of these metal oxides; that is, the photosensitivity of these metal oxides for the formation of methyl radicals at 77°K was quite different from one metal oxide to the other.

Though some of these metal oxides are catalytically active for the oxidation of organics,[3] their photosensitivities have not yet been revealed.

In this communication we will report briefly some results on the photosensitivities of various oxides coated on the PVG for the formation of the methyl radical at 77°K.

Oxide-coated PVG samples were prepared as follows: after the leaching of a PVG rod (Corning ♯7930, 4 mmϕ, 1 cm in length, 38 m^2/sample) with concentrated nitric acid, an appropriate metal salt, for example, ammonium meta-vanadate (NH_4VO_3) for vanadium oxide, was absorbed from an aqueous solution in an amount sufficient for a coverage of $\theta=0.01$—0.001%; the PVG thus treated was ignited at 500—600°C in air to convert the salt into an oxide.

A tenth of the monolayer amount of methane was then introduced at room temperature, followed by repeated oxidation and degassing at 500—600°C in a quartz sample tube. Irradiation of the sample tube was carried out at 77°K directly in a Dewar vessel inserted in the cavity of an ESR apparatus with a filtered light of an ultra-high-pressure mercury lamp (USH-500D, Ushio Electric Co., Ltd.).

Some representative results on the wavelength characteristics of the oxide-coated PVGs for the methyl radical formation at 77°K are shown in Fig. 1.

On these oxide-coated PVGs, the CH_3(II) or CD_3(II), the so-called abnormal methyl radical ($g=2.002$, $A^{\rm H}_{\rm CH_3}=19.3$ G, $A^{\rm D}_{\rm CD_3}=3.0$ G),[1] was observed preferentially by the photolysis at 77°K; this methyl radical showed the characteristic linewidth alternation with a sharper line in the lower magnetic field.

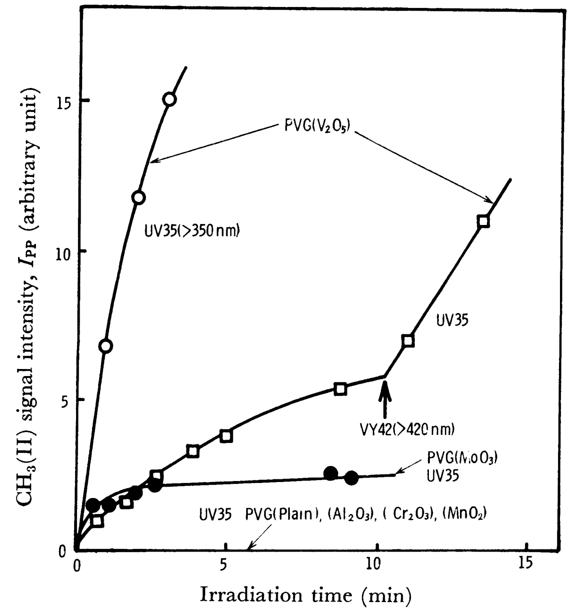

Fig. 1. Photosensitized formation of CH_3(II) radical on metal oxide coated PVGs.

The second hf line from the lower field ($m_{\rm I}=-1/2$) with the largest peak-to-peak intensity, $I_{\rm pp}$, was used as a monitor for the CH_3(II) radical concentration; its change with the irradiation time is plotted in Fig. 1.

The largest photosensitization was observed on the PVG(V_2O_5), and even a visible light larger than 420 nm showed a relatively large photosensitizing effect on the radical formation. Although the PVG(MoO_3) also showed the photosensitizing activity, its activity was less than that of the PVG(V_2O_5). On the PVG(plain) and PVG(Al_2O_3), no photosensitization was observed, and the CH_3(II) radical was observed only with the full light of a low-pressure mercury lamp. Here, it is very interesting that, on the PVG(MnO_2) and PVG(Cr_2O_3), a "photodesensitization" was clearly observed, and that, in these cases, none of the methyl radical could be observed even with the full light of a low-pressure mercury lamp.

It may be worthy of note here that the oxides showing the "photodesensitization" are well known active oxidation catalysts, while, on the other hand, V_2O_5 and MoO_3 are considered to be weak oxidizing catalysts for the complete oxidation of methane.[4] Therefore, one can deduce that there is a reverse correlation between the radical trapping efficiencies and the oxidizing abilities of the oxide-coated PVGs.

When a trace of oxygen was present in the PVG(V_2O_5)-CH_4 system, a large signal of a peroxyradical ($g_1=2.002$, $g_2=2.01$, $g_3=2.03$) was observed in place of the CH_3(II).

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