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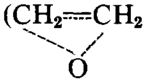
Reaction of C_2H_4 with Photo-Formed O^- Hole Centers on Supported MoO_3

Information on the excited states of metal oxides appears to be important for understanding of the photocatalysis on them. In connection with this problem, Kazansky and co-workers (*1*) have made extensive studies on the structure and reactivity of the transient O^- hole centers formed on supported metal oxides according to the process $(Me^{n+}{=}O^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (Me^{(n-1)+}{-}O^-)$. We have also investigated the excited states of metal oxides as well as the photocatalytic reactions on them and found that in some cases the features of the reactions caused by the photo-formed O^- hole centers are somewhat different from what is expected from the results with the stabilized O^- anion radicals reported by various workers (*2, 3*). It seems important to clarify the difference between the reactivities of both types of O^- species, and to understand the role of the transient photo-formed O^- hole centers in photocatalysis. The characters of the reactions of C_2H_4 with the stabilized O^- anion radicals on oxides surfaces appear to be established according to the works of Kazansky *et al.* (*4, 5*), Che *et al.* (*6*), and Tench *et al.* (*7*), i.e., the O^- anion radicals interact with C_2H_4 to yield a linear type $(CH_2{=}CH_2O)^-$ radicals for MgO and MoO_3/SiO_2 while a bridged type  $(CH_2{=}CH_2)^-$ (bridged by O) radicals for WO_3/SiO_2. Accordingly, the reaction of C_2H_4 with the O^- hole centers photo-formed on MoO_3/PVG by ESR as well as analysis of reaction products have been investigated.

The MoO_3/PVG (0.007 Mo wt%) was prepared by impregnation of PVG with an aqueous solution of $(NH_4)_6Mo_7O_{24}$. It was heated in oxygen at 773 K and evacuated at 613 K. Ultraviolet irradiation was carried out in an ESR cavity using a 500 W Hg lamp with a color (transmitted light >280 nm) and a water filter. The reaction products were analyzed using a gas chromatograph and/or a quadrupole mass spectrometer. ESR measurements were carried out at 77 K using a JES-ME-X (X-band). Mn^{2+} ion in MgO powder was used for *g*-value and sweep calibration. The photoluminescence of MoO_3/PVG was measured as described previously (*8*).

Ultraviolet irradiation of MoO_3/PVG in the presence of ethene was found to induce the formation of propene (Table 1). The propene yield increases with decreasing temperature. As described previously (*2*), it is well known that absorption of light corresponding to the charge transfer band of MoO_3 ($\gamma_{\max.}$ = 295 nm) brings about electron transfer from oxygen to Mo ions, i.e.,

$$(Mo^{6+}{=}O^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (MO^{5+}{-}O^-)^*$$

resulting in formation of a transient of hole center (O^-) and a trapped electron (Mo^{5+}). The phosphorescence associated with the charge transfer process was quenched by

TABLE 1

Photo-Induced Transformation of C_2H_4 to C_3H_6 on MoO_3/PVG at Various Temperatures[a]

Reaction temperature (K)	Yield of photo-formed C_3H_6 (10^{-7} mol)
77	1.22
273[b]	0.16_5
300[b]	0.07_1

[a] Amount of adsorbed C_2H_4, 6.98×10^{-6} mol/0.26 g. Ultraviolet irradiation time, 20 min; photo-formed minor products, 2-C_4H_8, HCHO, and 1-C_4H_8.

[b] Photo-induced uptake of C_2H_4 was observed.

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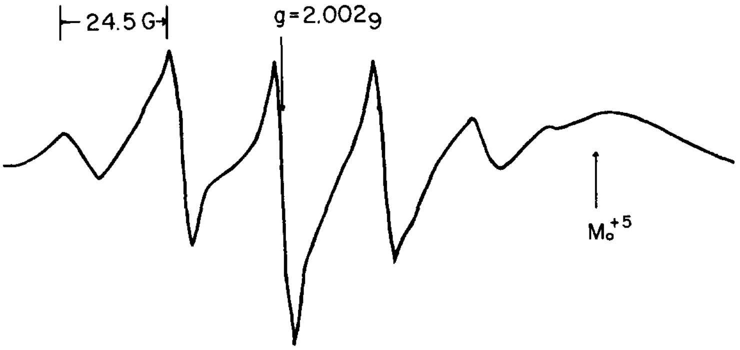
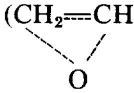


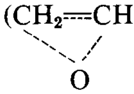
FIG. 1. ESR spectrum of photo-formed bridged type $C_2H_4O^-$ anion radicals on MoO_3/PVG at 77 K (amount of adsorbed C_2H_4: 1.85×10^{-5} mol/g).

added ethene, suggesting that ethene interacts with the excited triplet states $(Mo^{5+}—O^-)^*$. It seems that the excited triplet states are involved in the propene formation and longer lifetimes at lower temperatures may explain the increase in the propene yield with decreasing temperature.

On increasing the temperature of MoO_3/PVG from 290 to 473 K, small amounts of 2-C_4H_8, 1-C_4H_8, and HCHO were found to be desorbed, in addition to C_3H_6 and unreacted C_2H_4. It should be emphasized that no interaction of C_2H_4 with MoO_3/PVG occurred in the absence of uv irradiation, since complete recovery of the C_2H_4 introduced was observed by desorption around 290 K.

ESR studies provided detailed information on the interaction of ethene with the transient charge transfer excited complexes. Ultraviolet irradiation of MoO_3/PVG at 77 K in the presence of ethene led to an appearance of the ESR spectrum with $g = 2.002_9$ (Fig. 1). It consists of five lines with intensity ratio of 1:4:6:4:1 and hyperfine splitting of $a = 24.5 \pm 0.5$ G, being similar to that reported by Kazansky *et al.* (*5*) who investigated the reaction of ethene with the O^- anion radicals formed on reduced WO_3/SiO_2 by adsorption of N_2O, and proposed formation of the bridged type  $(\underset{\diagdown O \diagup}{CH_2{=}CH_2})^-$ species. Accordingly, it is tentatively concluded that the signal shown in the figure is attributed to the same bridged type species. On ceasing uv irradiation, the signal decreased in intensity with line-broadening and disappeared.

O'Neill and Rooney (*9*) found that three ethene molecules are directly transformed to two propene molecules on $Mo(CO)_6/Al_2O_3$ and proposed that the reaction is caused by the methylene formed from splitting of ethene. Accordingly, it appears that methylene formation plays a significant role in the photo-induced formation of propene described above. This conclusion is supported by the fact that when propene is used in place of ethene, metathesis of propene with equimolar formation of C_2H_4 and 2-C_4H_8 takes place very efficiently, which is expected from the formation of methylene (*10*). These results together with those of the ESR experiments suggest that on uv irradiated MoO_3/PVG the formation of methylene from ethene occurs via the bridged type intermediate, resulting in the propene formation. In order to make this conclusion more definite, it seems necessary to investigate the correlation between the propene yield and the concentration of the bridged type radicals.

According to the works of Kazansky *et al.* (*4, 5*) and Tench *et al.* (*7*), the linear $(CH_2{=}CH_2O)^-$ type and bridged  $(\underset{\diagdown O \diagup}{CH_2{=}CH_2})^-$ type complexes, both originating from the O^- species formed thermally, decompose at higher temperature as follows:

$$C_2H_4O^- \rightarrow OH^- + \dot{C}_2H_3.$$

Such a feature is completely different from that with the bridged type complex originating from photo-formed O^- where the C=C bond fission takes place as described above.

It should be noted that there is a source of electrons in the neighborhood of the photo-formed O^- hole center, since it constitutes the charge transfer excited complex $(Me^{(n-1)+}—O^-)^*$. Such a situation is completely different from that with the stabilized O^- species formed thermally. Thus, the reactivity characteristic of the photo-formed O^- hole center would be explicable as follows: The photo-induced increase in electron density in the Mo ions which constitute the excited states $(Mo^{5+}—O^-)^*$ is expected to enhance back-donation of electron to π^* orbital of the bridged type π-complex with consequent easier rupture of the C=C bond, leading to the formation of methylene and HCHO. In other words, the energy produced when electrons and holes recombine is used for the C=C bond fission.

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