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Photoinduced Methanol Conversion to Hydrocarbons on Supported MoO_3 Catalysts

Photocatalysis by powdered semiconductors has received much attention from the standpoint of photochemistry of solid surfaces as well as the utilization of solar energy (*1–3*). Although it is well established that surface ions in low coordination play a significant role in heterogeneous catalysis, their role is still unclear in photocatalysis (*2*). It seems to be important to clarify the role of surface ions at positions of coordinative unsaturation in photoinduced surface reactions, especially in the primary processes and the excited states of the catalysts. In connection with these problems we have recently investigated the photoluminescence of metal oxides as well as making ESR measurements of the transient intermediate species together with analyses of the photoreaction products (*4*). In previous papers, we have reported that the charge transfer excited state, $[Me^{(n-1)+}—O^-]^*$, plays a significant role in photoreactions on supported transition metal oxides; the O^- species with trapped holes as well as the $Me^{(n-1)+}$ ions with trapped electrons are closely associated with the key species of the photoinduced surface reactions (*4*).

In the present work similar studies have been extended to the photoinduced decomposition of methanol on supported MoO_3 catalysts. It has been found that the reaction leads to the formation of hydrocarbons similar to those obtained in the methanol conversion reaction on shape-selective zeolite catalysts such as ZSM-5 (*5*).

The gases used were of 99.5% purity (Takachiho Kogyo Co.) and were used after purification by low-temperature fractional distillation. CH_3OH (99.5% purity; E. Merk Darmstadt) was purified by distillation. MoO_3 supported on porous Vycor glass (PVG) was prepared by impregnation of PVG (Corning No. 746686-7930, BET surface area; 160 m^2/g, 1.0-mm-thick sheet, major composition; $SiO_2 > 95\%$) with an aqueous solution of $(NH_4)_6Mo_7O_{24}$. The catalysts were dried at 350 K and heated in oxygen at 773 K followed by evacuation at 523 K. The content of supported MoO_3 was determined to be 0.07 wt% by atomic absorption and/or colorimetry. Details of the apparatus and the measurements of photoluminescence and ESR spectra have been described previously (*4, 6*). The UV absorption spectra of the catalysts were determined with a Shimadzu VU-210 A Type spectrophotometer by measuring transmission through the catalysts. The reaction products were analyzed by gas chromatography. Details of the experimental procedures have been described elsewhere (*4, 6*).

MoO_3/PVG exhibits photoluminescence with two peaks at around 437 and 340 nm when it is excited by light corresponding to the charge transfer bands of the MoO_3 surface complex. As described previously (*4*), they are assigned to phosphorescence (437-nm peak) decaying from the charge transfer excited triplet states and fluorescence (340-nm peak) from the excited singlet state, respectively. Figure 1 shows the effect of the addition of CH_3OH on the photoluminescence of MoO_3/PVG at 300 K. It is clear that the phosphorescence alone is quenched at first, but after a long time of adsorption both emissions are quenched, the quenching extent being much larger for phosphorescence than for fluorescence.

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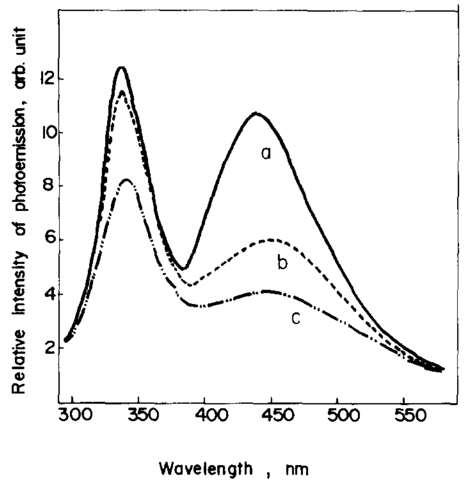


FIG. 1. Effect of the addition of CH_3OH on the photoluminescence of MoO_3/PVG at 300 K. (a) Before introduction of CH_3OH, (b) after 5 min of introduction of CH_3OH (15.6×10^{-6} mol), (c) after 5.0 h of introduction of CH_3OH. A slow and small change was observed for 2–3 h after the introduction of CH_3OH onto the catalyst at 300 K. Excitation wavelength, 280 ± 10 nm; slitwidth of emission, 7.5 nm.

The results clearly indicate that the added CH_3OH easily interacts with the charge transfer excited triplet states of MoO_3 in a manner similar to that with other molecules as described in the previous papers (*4*). The decrease in the intensity of fluorescence is to be attributed to the change of coordination of surface ions of MoO_3/PVG from tetrahedral to octahedral rather than a simple interaction of CH_3OH with the excited states of MoO_3, since the adsorption of CH_3OH onto the catalysts brings about a red shift in the absorption band due to charge transfer in the MoO_3 surface complex (*7*). As suggested by Gritskov *et al.* (*8*), this change arises from the fact that the vacancies in the first coordination sphere of the surface Mo^{6+} ions are occupied by the adsorbed CH_3OH molecules. This has been confirmed by the fact that no change in the absorption spectra is observed with bulk metal oxides such as MoO_3, V_2O_5, etc. This conclusion is in agreement with the results reported by Iwasawa and Ogasawara (*9*), who have concluded that the photoluminescence around 437 nm is closely associated with Mo^{6+} ions located in tetrahedral coordination on SiO_2. This is also supported by the results obtained with highly dispersed Mo oxide grafted onto SiO_2 (*10*).

There seem to be two types of dark adsorption of CH_3OH onto MoO_3/PVG, since 13% of the total amount of adsorbed CH_3OH (15.6×10^{-6} mol) after 6 h of adsorption time was not removed on desorption at 300 K. The remaining strong adsorption appears to be attributed to the chemisorption of methanol onto the MoO_3 catalyst, i.e., to the formation of methoxy species. As shown in Table 1, the CH_3OH adsorbed underwent photoreactions, in addition to its photoadsorption. Figure 2 also shows the yield of the photoformed products as a function of the time of UV irradiation at 77 K. It is seen that the major photoformed products are CH_4, C_2H_4, C_2H_6, C_3H_6, and CH_3OCH_3. CH_3CHO and $CH_2{=}CHCHO$ were detected as minor products.

ESR studies have provided detailed information on the interaction of the CH_3OH with the charge transfer excited states of MoO_3/PVG. UV irradiation of MoO_3/PVG at 77 K in the presence of CH_3OH led to the appearance of an ESR spectrum comprised of two different kinds of signal (Fig. 3). A relatively small signal consists of four lines with intensity ratio of roughly 1 : 3 : 3 : 1 and hyperfine splitting of $a_H = 23.8$ G, which is in good agreement with those of CH_3 radicals reported by Katsu *et al.* (*11*), who in-

TABLE 1

Yields of Photoformed Products in the Reaction of CH_3OH on Supported MoO_3 Catalyst at 300 K (10^{-9} mol)

CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	CH_3OCH_3
3.60	14.0	0.98	21.8	1.51	56.50

Note. Amount of adsorbed CH_3OH; 5.8×10^{-6} mol. UV irradiation ($\lambda > 290$ nm) time; 4.0 h with 75-W Hg lamp. Amount of used catalyst, 0.3 g (Mo wt%; 0.07). Conversion 1.86%. Minor products, CH_3CHO, $CH_2{=}CHCHO$.

vestigated the ESR signals of alkyl radicals formed from the photolysis of R-I compounds on PVG coated with V_2O_5 and MoO_3. The other strong signal consists of three lines, two of them being rather broad and not symmetrical. This signal has a hyperfine splitting of a_H = 20.6 G and g = 2.0031 at 77 K. Its shape and ESR parameters are in good agreement with $\dot{C}H_2$—O— radicals on various metal oxides obtained by Melamud *et al.* (*12*). Kubota *et al.* (*13*), who investigated the photodecomposition of methoxy groups formed on various oxide surfaces, have found that the magnitude of the hyperfine splitting of CH_2 protons in the $\dot{C}H_2$—O—Me radicals is closely related to the electronegativity of the metal ions (Me) constituting the oxide. The hyperfine splitting observed with the $\dot{C}H_2$—O— radicals in the present work, namely 20.6 G, is in good agreement with what is expected from the binding of the radicals to Mo ions. Thus, the appearance of $\dot{C}H_3$ radicals and $\dot{C}H_2$—O—Mo radicals under UV irradiation is confirmed. In addition to these radicals, UV irradiation led to the formation of

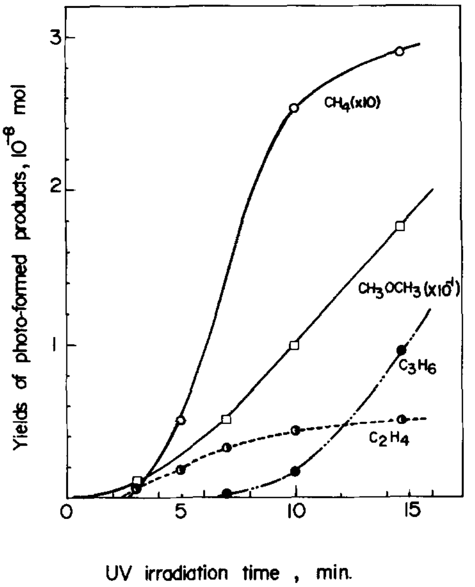


FIG. 2. Yield of photoformed products as a function of UV irradiation time of MoO_3/PVG at 77 K in the presence of CH_3OH. (UV irradiation was carried out in the ESR cavity with a 500-W Hg lamp, λ > 290 nm; amount of CH_3OH = 15.6×10^{-6} mol. Desorption of photoformed products was carried out at 323 K.)

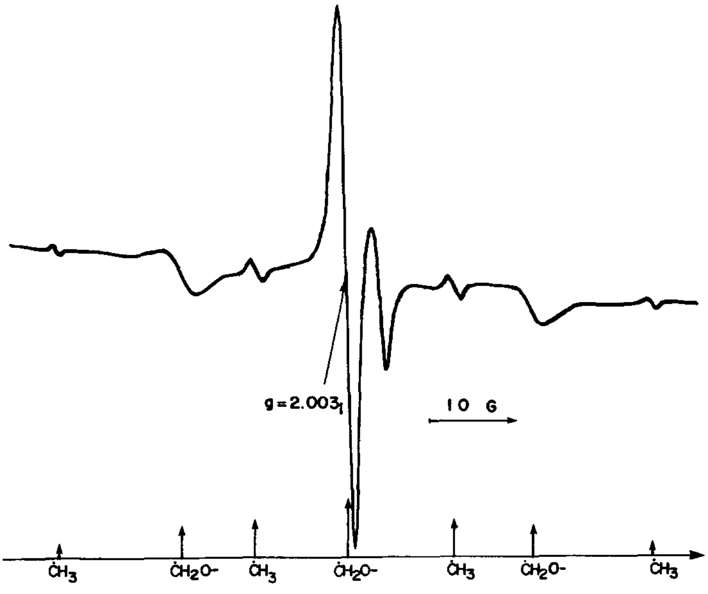


FIG. 3. ESR spectrum of photoformed $\dot{C}H_3$ and $\dot{C}H_2$—O—Mo radicals on MoO_3/PVG at 77 K. (UV irradiation was carried out at 77 K with a 500-W Hg lamp, λ > 290 nm. Amount of photoformed $\dot{C}H_2$—O—Mo radicals = 5.03×10^{-7} mol.)

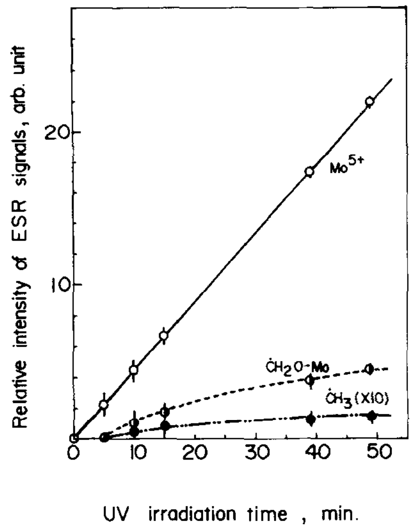
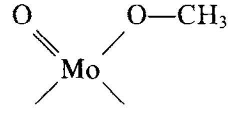


FIG. 4. Relative yield of photoformed Mo^{5+} ions, $\dot{C}H_3$ radicals, and $\dot{C}H_2$—O—Mo radicals as a function of UV irradiation time of MoO_3/PVG at 77 K. (UV irradiation was carried out with a 500-W Hg lamp, $\lambda >$ 290 nm. Amount of CH_3OH = 15.6×10^{-6} mol.)

Mo^{5+} ions, as shown in Fig. 4. The formation of Mo^{5+} would be attributed to formation of methoxy groups



arising from the interaction of CH_3OH with the $[Mo^{5+}—O^{-}]^*$ excited complex. The occurrence of such a process is expected from the efficiency of O^- species toward hydrogen abstraction (*14*). It has already been mentioned that formation of the methoxy groups is enhanced by UV irradiation of MoO_3/PVG.

Figure 4 shows formation of $\dot{C}H_3$ and $\dot{C}H_2$—O—Mo radicals as well as Mo^{5+} ions as a function of time of UV irradiation at 77 K. It is seen that Mo^{5+} ions are produced prior to the formation of those radicals, suggesting that the photoformed methoxy species undergo photoreactions. Under UV irradiation they will decompose to form $\dot{C}H_3$ radicals and to regenerate Mo=O groups and also undergo hydrogen abstraction by O^- species to form $\dot{C}H_2$—O—Mo radicals. The $\dot{C}H_3$ radicals will lead to CH_4 formation. The presence of CH_3—O— groups would explain the formation of CH_3OCH_3 in view of the results of the catalytic decomposition of alcohol reported by many workers (*5*). Although the nature of C—C bond formation resulting in the formation of C_2H_4 (and C_2H_6) as well as C_3H_6 (and C_3H_8) is unclear, it appears that the interaction of $\dot{C}H_2$—O—Mo radicals with CH_3OH under UV irradiation would result in insertion of CH_2 into CH_3OH and regeneration of Mo=O species. The occurrence of such an insertion reaction appears to explain the formation of C_2H_4 and C_3H_6 as well as the existence of the induction period (Fig. 2) for their information. Further study is necessary to clarify the mechanism of the C_2H_4 and C_3H_6 formation.

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