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ROOM TEMPERATURE PHOTO-ACTIVATION OF METHANE ON TiO_2 SUPPORTED MOLYBDENA

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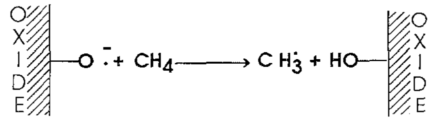
Methane is activated at room temperature and atmospheric pressure on TiO_2, supported molybdena catalyst excited by band gap illumination. With pure TiO_2, complete oxidation to CO_2 is observed in the presence of oxygen. The deposition of 4% molybdena has a pronounced effect on methane activation, partial oxidation to CO becoming a competing pathway. CO is the major oxidation product if TiO_2 loaded with both MoO_3 and $H_4SiW_{12}O_{40}$ is used as a catalyst. MoO_3 used alone or in conjunction with Al_2O_3 or SiO_2 as carriers exhibits poor activity in the photoactivation of methane.

1. Introduction

The primary step of methane activation on oxide materials frequently involves reaction with surface O^- radical ions:



(1)

For example, methane activation by Li-doped MgO possessing O^--centers is presently under active investigation [1]. Here, the methyl radical produced via the hydrogen abstraction reaction undergoes mainly dimerization to ethane. The thermal generation of the O^- surface radical ions on these catalysts requires high temperatures ($T > 800$ K). It is desirable to achieve methane activation under less demanding conditions. Substantial reduction in reaction temperature is obtained when MoO_3 is used as a catalyst in conjunction with N_2O as an oxidant [2]. In this case, the O^- species are formed by reaction of N_2O with reduced molybdena, e.g.

$$Mo^{5+} + N_2O \rightarrow N_2 + O^- + Mo^{6+}. \qquad (2)$$

Another very attractive possibility explored in the present study is to activate the catalyst by light excitation. Most of the transition metal oxides are semiconductors with a fundamental absorption edge in the blue or near UV region. The reactive O^- radical ion corresponds to a surface trapped hole state which can be readily generated by band gap excitation. From the work of Kazansky et al. [3], it

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is known that O^- radical ion sites in early transition metal oxides such as TiO_2, V_2O_5, MO_3 and WO_3 rapidly abstract hydrogen from methane even below room temperature. The present report deals with TiO_2 based catalysts which are examined with respect to their ability to induce methane oxidation under room temperature conditions.

2. Experimental

Titanium dioxide was obtained from Degussa, FRG (P25, a mixture of ca. 70% anatase and 30% rutile, surface area 55 $m^2\ g^{-1}$). Loading with MoO_3 was carried out by mixing the TiO_2 powder with an aqueous solution containing the required amount of $(NH_4)_5Mo_7O_{24} \cdot 4H_2O$ (Fluka) to form a slurry. After solvent removal in a rotavap, the material was dried for 12 h at 120 ° C. Subsequently, it was crushed to a fine powder and calcined at 450 ° C for 10 h in air. For codeposition of $H_4SiW_{12}O_{40}$, required amounts of $H_4SiW_{12}O_4 \cdot H_2O$ (Merck) were added initially along with the ammonium heptomolybdate. To determine the carbon contamination of the catalyst, blank irradiations were carried out with excess O_2 in the absence of methane. Very small amounts of CO_2 (8–15 μl (STP) CO_2 for 200 mg catalyst on prolonged irradiation) corresponding to a carbon level of at most 0.003% were formed and no CO was obtained.

The catalyst (200 mg) was spread over the bottom of a flat pyrex cell (volume 20–24 ml) equipped with side arms and septum for admission and withdrawal of gas samples. Prior to experiments, the catalyst was heated to 120 ° C in flowing Ar for 2 hours. After cooling in Ar, the desired amounts of CH_4 and O_2 were injected into the cell. (It was checked that all gases used were free of CO, CO_2 and other hydrocarbons.) The mixture was then illuminated in a solar simulator (Hanau, sun test) with a total output of 80 mW/cm^2. The temperature was invariably 42 ° C. For experiments requiring higher temperatures, the cell was placed horizontally in a tubular furnace. Light activation was carried out by a 450 W Xe lamp whose beam was reflected into the furnace by a mirror. Periodic gas analysis was carried out using a gas chromatograph with a TC detector. For CO analysis, a molecular sieve (5 Å) column and for CH_4, CO_2, HCHO, CH_3OH and other hydrocarbons a Carbosieve or a Poropak column were used. Carrier gas was He. For experiments measuring O_2 consumption, Ar was replaced by He as the diluent gas of the reaction vessel.

3. Results and discussion

Fig. 1 illustrates the adsorption behavior of methane on the TiO_2 catalyst at 42 ° C. On TiO_2-P25 alone, reversible physisorption occurs. Saturation is reached at 2.08 moles/g TiO_2 (curve 1) corresponding to 44 $Å^2$ surface area per methane

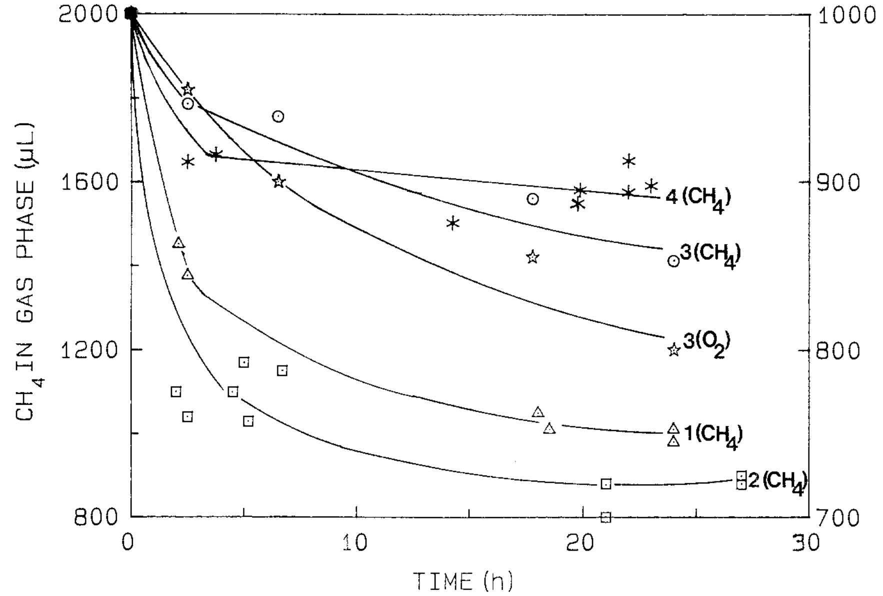

Fig. 1. Plots showing the adsorption behavior of (1) CH_4 on P25 in the dark in the absence of O_2; (2) CH_4 on P25 under light in the absence of O_2; (3) CH_4 and O_2 on P25 in the dark when both are present together; (4) CH_4 on 4% Mo/P25 in the dark in the presence of O_2. For the runs 200 mg powder, 2 ml CH_4 and 1 ml O_2 were used. $T = 42°C$.

molecule, i.e. less than monolayer coverage. Band gap excitation of TiO_2 enhances the adsorption although the effect is small (curve 2). A similar observation has recently been made with dehydrated MoO_3 surfaces [4]. Here, photo enhancement of methane adsorption was more pronounced since no dark uptake was observed. Curve 3 in Fig. 1 shows that oxygen retards the dark adsorption of CH_4 indicating competition for the same adsorption sites, presumably surface titanium ions. This inhibition is also observed with MoO_3-loaded TiO_3 (curve 4).

Although methane and O_2 are co-adsorbed at 42°C on TiO_2/MoO_3, no chemical reaction proceeds in the dark. However, upon light excitation of the catalyst by the solar simulator, methane and oxygen disappear irreversibly and a mixture of CO and CO_2 in about equal amounts is formed, fig. 2. The reaction stops after ca. 10 to 20 hours when all the O_2 initially injected has been consumed and 200–250 µl each of CO and CO_2 have been formed [5]. Upon renewing the supply of oxygen, methane photooxidation continues.

The quantum yield of methane photoactivation can be estimated as follows: the total UV output (300–400 nm) of the solar simulator is ca. 4 mW/cm^2 and the irradiated area of the reactor is 12.5 cm^2. Taking 3.5 eV as the average photon energy, the incident light flux is 5.3×10^{-4} Einstein/h. The absorbed flux is smaller since only part of the reactor is covered with the catalyst and there are losses through reflection and scattering. A lower limit for the quantum yield is derived by assuming that all the incoming UV photons are absorbed by the

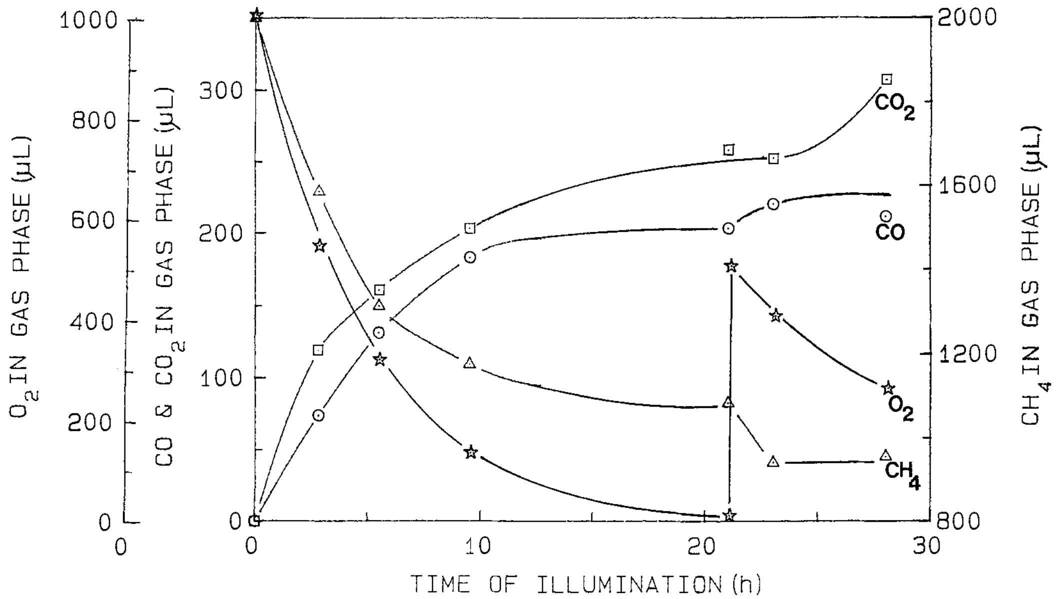

Fig. 2. Production of CO and CO_2 and consumption of CH_4 and O_2 vs time on 200 mg 4% Mo/P25 catalyst kept under illumination at 42° C. $CH_4/O_2 = 2/1$ (ml/ml).

TiO_2/MoO_3 catalyst. In fig. 2, the combined production rate of CO and CO_2 is 4.3×10^{-6} moles/h. Hence, $\phi > 0.81\%$.

Increasing the temperature to 290° C leads to a marked acceleration in the TiO_2/MoO_3 catalyzed photooxidation of methane while there is still no dark activation perceptible. Figure 3 shows that both CO and CO_2 rapidly grow during the initial phase of the reaction. However, whereas the CO concentration reaches soon a maximum and declines thereafter, the CO_2 level continues to increase. With a TiO_2/MoO_3 catalyst heated to 400° C, dark oxidation of methane is observed. Interestingly, this reaction leads directly to the formation of CO_2 without intermediate appearance of CO.

The photoactivation of methane requires radiation from the near-UV region of the spectrum where the semiconducting oxides have their fundamental absorption edge. Methane photooxidation was suppressed when a 450 nm cut-off filter was placed in the light beam. This indicates that the blue Mo^{5+} and Ti^{3+} centers formed under illumination do not exhibit a sensitizing action.

The following control experiments were performed to discriminate the individual roles of TiO_2 and MoO_3 in the photoactivation of methane. Illumination of TiO_2 alone under the same conditions as in fig. 2 leads to complete oxidation of CH_4, CO_2 being the only product observed. The amount of CO_2 produced after 10 h of irradiation is 300 μl. In the absence of methane, only 15 μl CO_2 are formed indicating that methane and not an organic contaminant is the source of practically all the CO_2 generated. Carbon dioxide in very small quantity was also the only product observed when pure MoO_3 was used as a photocatalyst.

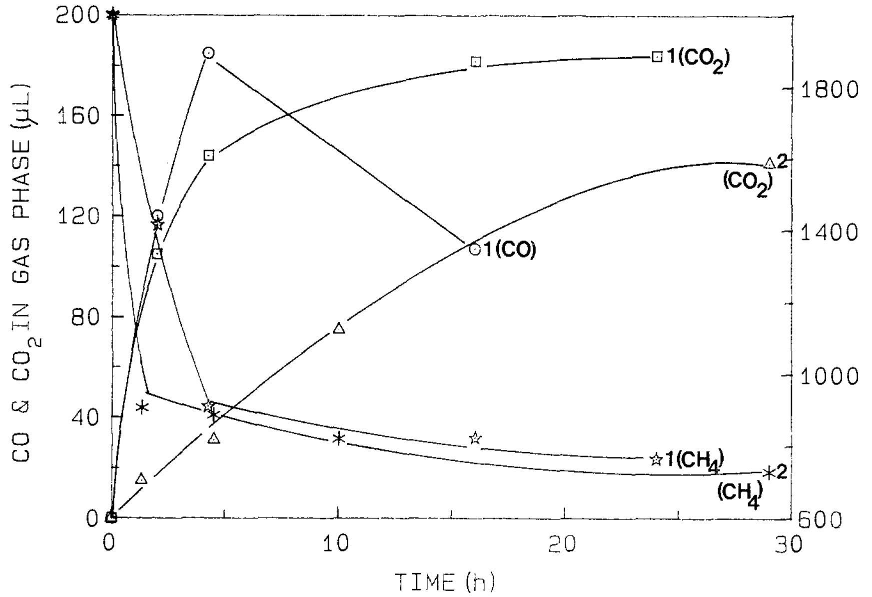

Fig. 3. Production of CO and CO_2 and consumption of CH_4 vs time on 200 mg 4% Mo/P25 catalyst kept under (1) illumination at 290 °C, and (2) in the dark at 400 °C. $CH_4/O_2 = 2/1$ (ml/ml).

Dispersing the MoO_3 onto alumina and silica increased its activity which remained however a factor of three below that of pure TiO_2 under the conditions used in fig. 2, i.e. 42 °C and partial pressures of CH_4 and O_2 of 0.1 and 0.05 atm, respectively.

From these results a synergistic interaction between the TiO_2 and MoO_3 components of the catalyst can be inferred leading to improved activity and selectivity in the methane photooxidation process. Since we have observed a similar effect with TiO_2 supported $H_4SiW_{12}O_{40}$ catalysts [6], it was of interest to check whether the codeposition of both MoO_3 and $H_4SiW_{12}O_{40}$ onto the TiO_2 carrier would further improve the catalyst. In particular, it is desirable to arrest the photooxidation of methane at an intermediate level such as CO before it goes to completion. This idea is born out by the results presented in fig. 4. Conditions employed were again a CH_4/O_2 volume ratio of 2 at a partial pressure of methane of 0.1 atm and a temperature of 42 °C. The addition of $H_4SiW_{12}O_{40}$ affords a significant increase in the CO formation rate and a decrease for that of CO_2. As a consequence, CO remains the major reaction product during the entire reaction, the selectivity for CO formation being remarkable ($> 70\%$) during the first hours of the photolysis.

These observations are rationalized in terms of band gap excitation of the TiO_2 support producing electron-hole pairs:

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^-_{cb}, h^+_{vb}). \qquad (3)$$

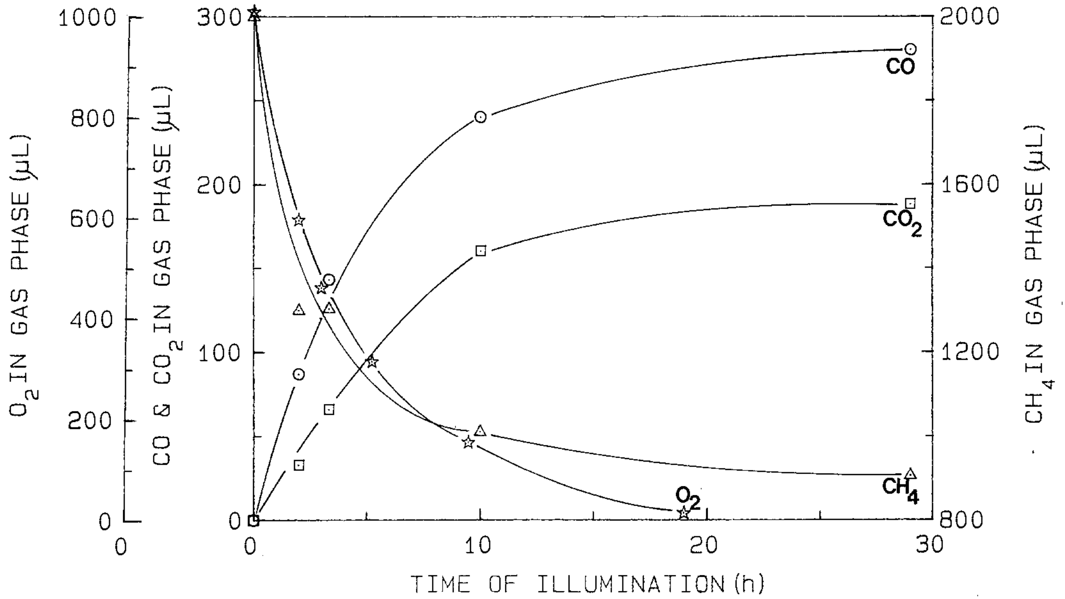

Fig. 4. Production of CO and CO_2 and consumption of CH_4 and O_2 vs time on 200 mg 4% Mo + 15% $SiW_{12}O_{40}$/P25 catalyst kept under illumination at 42° C. $CH_4/O_2 = 2/1$ (ml/ml).

In the case of the MoO_3 loaded titania, the electrons are likely to be transferred to the conduction band of molybdena. The band gap of MoO_3 is several hundred mV smaller than that of TiO_2 and this is expected to lower its conduction band edge [7]. This is confirmed by the intensively blue coloration the catalyst assumes under illumination indicating the formation of Mo^{5+}-centers. Interparticle electron transfer of a similar type has been observed to occur with other mixtures of semiconductors, e.g. CdS/TiO_2 [8,9]. Such processes assist the local separation of the positive from the negative charge carriers preventing their recombination. This could explain the higher yields observed with the mixed TiO_2/MoO_3 catalyst as compared to the pure compounds. The conduction band electrons are removed from the catalyst by reaction with oxygen resulting in the formation of adsorbed superoxide anion radicals or their conjugated acid:

$$e_{cb}^-(MoO_3) + O_2 \rightarrow (O_2^-)_{ads} \overset{H_2O}{\rightleftarrows} {}^{\cdot}HO_2 + OH^- . \qquad (4)$$

The persistence of some blue coloration upon exposing an illuminated catalyst to air indicates nevertheless the presence of trapped electrons, probably Mo^{5+} on lattice defect sites whose reaction with O_2 occurs very slowly.

The valence band holes undergo migration to the titania surface where they are trapped by surface hydroxide groups forming the oxygen anion radicals which react with methane under abstraction of hydrogen, eq. (1). The methyl radicals could either depart as a gas phase molecule or remain adsorbed. The formation of gas phase CH_3 radicals has been observed previously but completeness of the desorption was not assessed [10]. On MoO_3 the desorption energy of CH_4 is ca. 0.4 eV [1] suggesting that the radicals could be mobile on the anion-covered basal plane surface. If during surface migration an O_2^- or O^- center is encountered. $CH_3^{\bullet}$ would be scavenged producing methanol or formaldehyde:

$$CH_3^{\bullet} + HO_2^{\bullet} \rightarrow CH_3OOH \rightarrow H_2CO + H_2O \qquad (5)$$

$$CH_3^{\bullet} + O^- \rightarrow CH_3O^- \xrightarrow{H_2O} CH_3OH + OH^-. \qquad (6)$$

At lom temperature these products remain adsorbed to the catalyst and hence are accessible to further oxidation resulting in the formation of CO and CO_2. A likely oxidant is the photogenerated valence band hole, although reactions with surface bound peroxide or superoxide could also occur.

$$2h^+ + H_2CO \rightarrow 2H^+ + CO \qquad (7)$$

$$4h^+ + CH_3OH \rightarrow CO + 4H^+ \qquad (8)$$

$$CO + H_2O + 2h^+ \rightarrow CO_2 + 2H^+. \qquad (9)$$

The overall reaction corresponds to the partial or complete oxidation of methane:

$$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O \qquad (10)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \qquad (11)$$

The mass balance observed is in accord with the stoichiometric predictions of these equations. For example, in fig. 4, after 29 h of photolysis 285 μl (STP) of CO and 200 μl of CO_2 were formed. Taking into account the adsorbed CO_2 [5], the amount of CO_2 is approximately 235 μl. The quantity of O_2 necessary to form these products is 900 μl. In fig. 4, 1000 μl of O_2 were consumed during the photoreaction. In view of the fact that some peroxide formed during the photo-uptake of O_2 may be left on the catalyst, the agreement is good.

In conclusion, partial oxidation of methane has been shown to occur efficiently over light-activated MoO_3/TiO_2 catalysts under surprisingly mild conditions. The TiO_2 based catalysts thus show promising properties for further development which will be directed towards selective production of compounds such as C_2H_6, and CH_3OH which can serve as a chemical feedstock.

Acknowledgement

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References

[1] a) T. Ho and J.H. Lunsford, Nature (London) 314 (1985) 721;
b) D.J. Driscoll, W. Martin, J.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 58;
c) T. Ho, J.-W. Wang, C.-H. Lin and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 5062.

[2] R. Pitchai and K. Klier, Cat. Rev.-Sci. Eng. 28 (1986) 13.

[3] a) V.A. Shvets, V.M. Vorotyntsev and V.B. Kazansky, Kinet. Katal. 10 (1969) 356;
b) V.B. Kazansky, Kinet. Katal. 18 (1977) 43;
c) N.I. Lipatkina, V.A. Shvets and V.B. Kazansky, Kinet. Katal. 19 (1978) 979;
d) S.L. Kaliaguine, B.N. Shelimov and V.B. Kazansky, J. Catal. 55 (1978) 384.

[4] W. Hill, B.N. Shelimov and V.B. Kazansky, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 2381–2389.

[5] The adsorption of CO and CO_2 on TiO_2/MoO_3 (4%) was examined by exposing 200 mg catalyst, pretreated in the reactor at 120 ° C for 2 h in flowing He, to a mixture of 1 ml CO and 1 ml CO_2. Reaction temperature was 42 ° C. After 18 h in the dark, 980 μl of CO and 856 μl of CO_2 were left in the gas phase. Thus, CO absorption is negligible while that of CO_2 is appreciable. Illumination for 7.5 h in the solar reactor at 42 ° C reduced the amount of CO to 650 μl while that of CO_2 increased to 1136 μl. Thus, light induced disproportionation of CO, i.e. the Boudart reaction $2CO \rightarrow CO_2 + C$, appears to occur on this catalyst.

[6] M. Grützel, K.R. Thampi and J. Kiwi, J. Phys. Chem., submitted.

[7] M.A. Butler and D.S. Ginley, J. Mat. Sci. 15 (1980) 1.

[8] N. Serpone, E. Borgarello and M. Grätzel, J. Chem. Soc., Chem. Comm. (1983) 342.

[9] L. Spankel, H. Weller and A. Henglein, J. Am. Chem. Soc. 109 (1987) 6632.

[10] D.J. Driscal and J.H. Lundsford, J. Phys. Chem. 89 (1985) 4415.

[11] S.P. Mehandru, A.B. Anderson, J.F. Brazdil and R.K. Graselli, J. Phys. Chem. 91 (1987) 2930.