Partial Oxidation of Methane by Nitrous Oxide over Molybdenum on Silica

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Abstract: Molybdenum supported on silica is a catalyst for the selective oxidation of methane to methanol and formaldehyde when nitrous oxide is the oxidant and steam is present in the system. At a conversion level of 3% the combined selectivity to CH_3OH and HCHO is 78%, with CO being the principal other product. Spectroscopic evidence indicates that the reaction is initiated by the formation of reactive O^- ions which are coordinated to Mo^{VI} at the surface. The O^- ions are capable of hydrogen atom abstraction from CH_4, and the resulting methyl radicals rapidly react with the surface to form methoxide complexes. The methoxide may decompose to form HCHO or it may react with water to form CH_3OH. In this cycle molybdenum begins and ends in the V oxidation state. The nonselective oxidation of methane occurs (a) when $Mo^{VI}O^{2-}$ is formed or (b) when the products CH_3OH and HCHO are more fully oxidized. The rate law resulting from this mechanistic scheme is consistent with the observation that the reaction is first order with respect to N_2O and zero order with respect to CH_4. Over the range of H_2O partial pressures from 50 to 260 torr the conversion did not vary; however, the presence of H_2O greatly enhanced the selectivity of HCHO and CH_3OH.

The partial oxidation of methane is one of the most challenging problems in heterogeneous catalysis. Although the patent literature contains numerous references to this subject, very little fundamental work has been reported.[1,2] Results from this laboratory have demonstrated that molybdenum supported on silica is an effective catalyst for the partial oxidation of methane to methanol and formaldehyde when nitrous oxide is present as the oxidant;[3] however, we have not been able to reproduce the combination of selectivities and activities which were reported previously.

Using EPR spectroscopy we and others have shown that N_2O reacts with surface Mo^V ions to form O^- ions[4,5] which are capable of hydrogen atom abstraction from CH_4, even at −196 °C.[3,6] The resulting $CH_3\cdot$ radicals are thought to react with molybdenum oxide, forming methoxide ions, and a subsequent reaction with water yields methanol. Formaldehyde may be formed both by the decomposition of methoxide and as a secondary product of methanol oxidation.

In this paper kinetic data are presented to show how the selective oxidation mechanism fits into an overall reaction scheme. Moreover, in support of this selective mechanism spectroscopic evidence is given for the formation of methyl radicals and methoxide ions on the surface.

Experimental Section

Catalytic Experiments. The gases used in this study included CH_4 (99.99%), N_2O (99%), and CO (99.8%) having the indicated levels of purity. No additional purification was attempted.

The supported molybdenum oxide catalysts were prepared by adding 16 g of Cab-O-Sil M-5 silica (lot no. 1B260) to 150 mL of a solution which contained 0.51 g of ammonium heptamolybdate. The pH of the solution was adjusted to 11 by adding about 50 mL of $NH_4OH(aq)$ prior to the addition of the Cab-O-Sil. The slurry was mixed in a Rotavapor for 2 h at 25 °C and for 6 h at 80 °C. Another 50 mL of NH_4OH was added to the slurry, and mixing was continued while the liquid phase was evaporated with the aid of an aspirator (ca. 0.5 h). The partially dried material was heated in air at 120 °C for 2 h and at 600 °C for 24 h. The resulting catalyst, which initially contained 1.7% Mo by weight, normally was sieved to 20–40 mesh size.

The catalytic experiments were carried out in a fixed-bed reactor which was operated at a total pressure of 1 atm. The reactor consisted of a fused quartz tube (23 mm o.d. x 120 mm) which was connected to capillary quartz tubing (2 mm i.d. x 60 mm) so that the products CH_3OH and HCHO could be rapidly removed from the heated zone. In a typical experiment the reactor contained 1 g of catalyst which occupied a volume of 4 mL. A bed of quartz chips 50 mm in depth was placed above the catalyst to preheat the reactants.

The catalysts were further pretreated in the reactor by heating 1 h in vacuo at 500 °C and reducing in 100 torr of CO for 30 min at 500 °C. After the temperature was lowered to 400 °C, the reacting gas mixture was introduced at a flow rate of 1.33 mL s^{-1}, and the catalyst was raised to the desired temperature. Helium was used as a diluent to achieve a total pressure of 760 torr. Water was admitted from a syringe pump through a preheated region. Care was taken to assure that the addition of water did not cause pressure fluctuations in the system. All effluent lines were heated to 100 °C in order to prevent liquid condensation.

A dark film formed on the reactor wall below the heated zone, indicating loss of molybdenum from the catalyst; therefore, a fresh catalyst sample was employed in each experiment. The molybdenum remaining on the catalyst after a reaction was 1.6% by weight. Since steady-state activity was achieved after 4 h of reaction, it is assumed that no further loss of molybdenum occurred after this period.

All of the gases except HCHO were analyzed by gas chromatography. The column packings were Porapak Q (3 m) for the separation of CH_4, CO_2, N_2O, C_2H_4, and C_2H_6; Carbowax 600 (4 m) for the separation of CH_3OH and H_2O; and a 5-A molecular sieve (1 m) for the separation of N_2, CO, and O_2. The Porapak Q and Carbowax 600 columns were operated at 80 °C; the 5-A sieve column was operated at 40 °C. The formaldehyde was analyzed by means of an iodometric titration. The effluent from the reactor could either be diverted through an in-line sample loop for GC analysis or through two water scrubbers for a period of 1 h in order to collect the formaldehyde. In some cases cold traps were substituted for the water scrubbers. Satisfactory precision in the analysis is indicated by the fact that a 90% carbon mass balance was achieved.

Spectroscopic Experiments. Variations in the Mo^V concentrations as a function of N_2O and CH_4 partial pressures were determined at −196 °C by EPR spectroscopy using a Varian E6-S spectrometer. The reactor for this study consisted of a fused quartz U-tube (10 mm o.d.) with a side arm (4 mm o.d.). Catalyst samples were activated as described previously and exposed to reaction mixtures under flow conditions in the large part of the reactor. After a set time the gases were evacuated, the reactor was rapidly quenched to 0 °C, the gases were evacuated at 25 °C to 10^{-3} torr, and the catalyst was transferred to the side arm for EPR analysis.

Experiments designed to detect surface methoxide ions by infrared and methyl radicals by EPR were carried out on Cab-O-Sil silica which has better infrared transmission properties. The catalyst was prepared as previously described except that after drying the solid was calcined at 600 °C in air for 24 h, heated under vacuum at 500 °C for 0.5 h, reduced in 100 torr of CO at 600 °C for 1 h, and finally evacuated at 600 °C for 0.5 h. In the EPR experiments powdered samples were transferred to a quartz side arm prior to recording the spectra. EPR spectra were recorded at −196 °C. The *g* values and spin concentrations were determined by using a phosphorus doped silicon standard. In the infrared experiments self-supporting wafers (6–9 mg cm^{-2}) were treated in situ in a fused quartz infrared cell. Infrared spectra were recorded with a

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(1) Imre, L.; Nassenstein, H. W. German Offen. 2404738: Dowden, D. P.; Walker, G. T. British Patent 1244001.

(2) McConkey, B. H.; Wilkenson, P. R. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 437.

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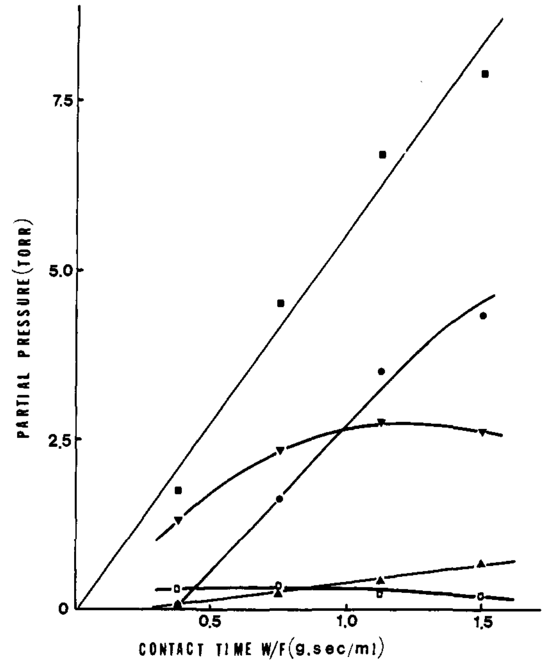

Figure 1. Methane conversion and product distribution as a function of contact time: ■, CH_4 reacted; □, CH_3OH; ▼, HCHO; ● CO; ▲, CO_2. $P_{CH_4} = 70$ torr, $P_{N_2O} = 280$ torr, $P_{H_2O} = 260$ torr, $T = 580$ °C, $F = 1.33$ mL/s.

Perkin-Elmer Model 580B spectrophotometer linked to a microcomputer. The spectra reported in the region 3200–2600 cm^{-1} were obtained after averaging the results of 10–30 scans.

Preparation of $MoO(OCH_3)_4$. As a model compound for studying the reaction between a molybdenum methoxide compound with water, $MoO(OCH_3)_4$ was prepared from $MoOCl_4$. The latter compound was synthesized by refluxing MoO_3 with $SOCl_2$ as described by Colton et al.[7] Under a nitrogen atmosphere 0.58 g of Na metal (25.2 mmol) was added slowly to 20 mL of anhydrous methanol over a period of 10 min. After the sodium was reacted to form the soluble methoxide, 1.60 g (6.28 mmol) of $MoOCl_4$ crystals were added slowly to the solution. After the NaCl precipitate was filtered out, the remaining orange filtrate was evacuated to dryness, leaving an orange solid.

By elemental analysis the Mo:C:H ratio of the solid was found to be 8.9:3.8:1.0 as compared with a theoretical ratio of 8.0:4.0:1.0 for $MoO(OCH_3)_4$. Attempts to obtain reasonable size crystals for X-ray diffraction were unsuccessful since the compound decomposed under vacuum before it sublimed. The ^1H NMR spectrum of the orange solid dissolved in Me_2SO-d_6 had a single resonance at δ 4.00 relative to Me_4Si. This chemical shift is characteristic of a metal methoxide group.

Results

Kinetic Experiments. The conversion of methane to the various products as a function of the pseudocontact time, W/F, is depicted in Figure 1. Here W is the mass of catalyst and F is the flow rate, evaluated at 25 °C. In this series of experiments the value of W/F was varied by changing the mass of catalyst and holding the flow rate constant. Blank experiments over silica were carried out at a W/F value of 1.5 s mL^{-1}, and the conversion of CH_4 was 1% of that observed with the Mo/SiO_2 catalyst.

It is apparent from the amounts of CH_3OH and HCHO formed that selectivities to these partial oxidation products were favored by short contact times. As the contact time increased, the selectivities, for secondary products CO and CO_2 increased. Even at moderately high levels of conversion, for example 7.5%, CO is strongly favored over CO_2 as a product. This selectivity to CO may be important in a practical problem where one might want to use the remaining gases as a fuel after recovering the methanol and formaldehyde.

The effect of temperature on methane conversion and selectivities to the several products is shown in Table I. An Arrhenius plot of the rate of conversion of CH_4 vs. the reciprocal of the absolute temperature gave rise to an activation energy of 42 ± 2 kcal/mol. The conversions, which were recorded for a random sequence of temperatures over a period of 12 h, all fell on a straight line when plotted as a function of $1/T$, indicating that the catalyst was stable with respect to time over the temperature range 550–594 °C.

Table I. Conversion and Selectivity during Methane Oxidation[a]

T, °C	convn, %	selectivity, % HCHO	CH_3OH	CO	CO_2
550	1.6	79.5	20.5		
560	1.9	80.1	19.9		
570	2.9	64.3	13.8	19.1	2.8
580	4.0	58.8	10.0	27.7	3.4
594	6.0	49.5	7.8	38.1	4.6

[a] 1.0 g of Mo/Cab-O-Sil, $P_{CH_4} = 75$ torr, $P_{N_2O} = 280$ torr, $P_{H_2O} = 260$ torr, $F = 1.33$ mL/s.

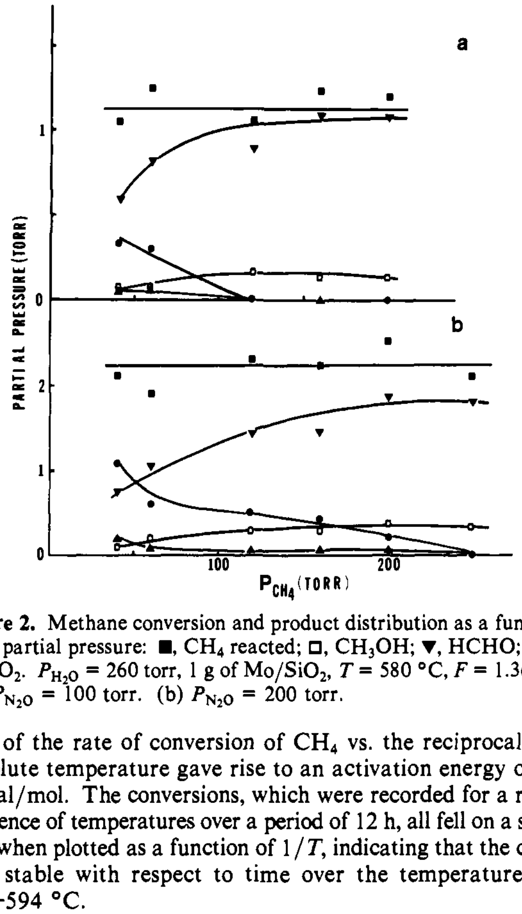

Figure 2. Methane conversion and product distribution as a function of CH_4 partial pressure: ■, CH_4 reacted; □, CH_3OH; ▼, HCHO; ●, CO; ▲, CO_2. $P_{H_2O} = 260$ torr, 1 g of Mo/SiO_2, $T = 580$ °C, $F = 1.36$ mL/s. (a) $P_{N_2O} = 100$ torr. (b) $P_{N_2O} = 200$ torr.

In order to determine a rate law for the reaction and to understand the mechanism more fully the activity and product distributions were determined as a function of the partial pressures of CH_4, N_2O, and H_2O. These results are shown in Figures 2 and 3. From a plot of the CH_4 conversion rate under differential conditions vs. the partial pressure of CH_4 and N_2O the order of the reaction was determined. The rate equation may be best described by

$$d[CH_4]/dt = -k[N_2O]^1[CH_4]^0 \qquad (1)$$

over the range of partial pressures $P_{N_2O} = 80$–200 torr and $P_{CH_4} = 40$–250 torr. At $P_{N_2O} < 80$ torr the rate increased linearly with respect to P_{N_2O} (Figure 3), but with a distinctly smaller rate constant. This transition pressure also corresponds to a transition in selectivity: for $P_{N_2O} < 80$ torr the combined selectivity to HCHO and CH_3OH was approximately 100%, whereas at higher N_2O pressures both CO and CO_2 were detected in the reaction products. A similar selectivity variation is apparent in Figure 2; only in this case the combined selectivity approaches 100% above some critical partial pressure of CH_4, or more correctly, a P_{CH_4}/P_{N_2O} ratio of 1.2 at 580 °C.

As pointed out previously, water vapor is essential for the selective formation of methanol, but the results of Figure 4 show that H_2O does not inhibit the rate of CH_4 conversion. In fact, at P_{H_2O} pressures up to 50 torr H_2O enhanced the conversion. Over the range of partial pressure studied the conversion to methanol

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[7] Colton, R.; Tomkins, J. B.; Wilson, P. W. *Aust. J. Chem.* **1964**, *17*, 496.

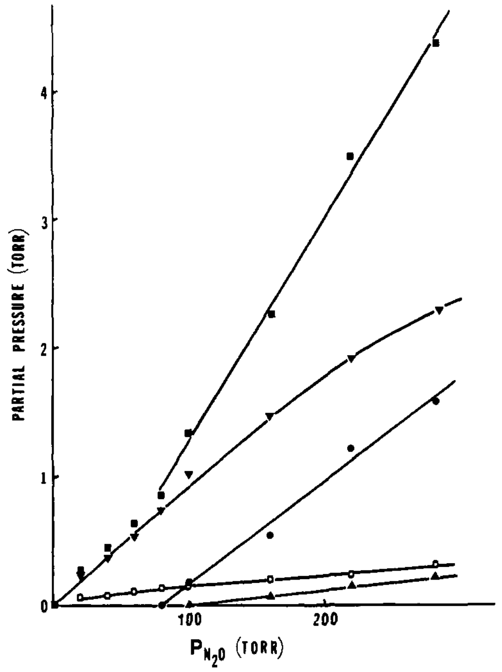

Figure 3. Methane conversion and product distribution as a function of N_2O partial pressure: ■, CH_4 reacted; □, CH_3OH; ▼, HCHO; ●, CO; ▲, CO_2. P_{CH_4} = 75 torr, P_{H_2O} = 266 torr, 1 g of Mo/SiO_2, T = 580 °C, F = 1.33 mL/s.

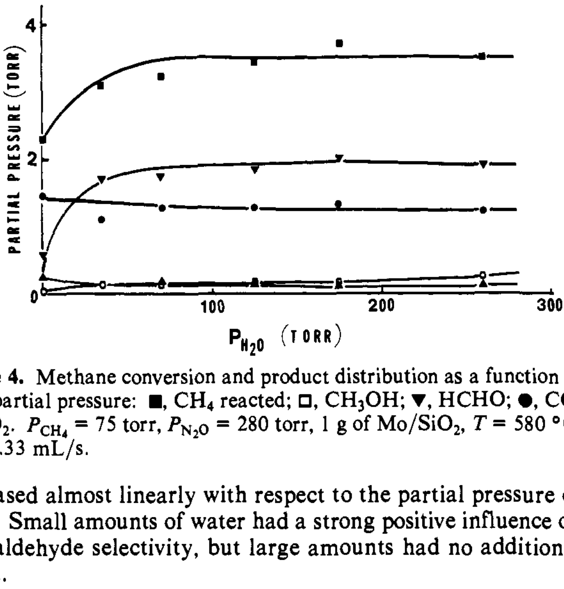

Figure 4. Methane conversion and product distribution as a function of H_2O partial pressure: ■, CH_4 reacted; □, CH_3OH; ▼, HCHO; ●, CO; ▲, CO_2. P_{CH_4} = 75 torr, P_{N_2O} = 280 torr, 1 g of Mo/SiO_2, T = 580 °C, F = 1.33 mL/s.

increased almost linearly with respect to the partial pressure of H_2O. Small amounts of water had a strong positive influence on formaldehyde selectivity, but large amounts had no additional effect.

In the mechanistic scheme which follows, the *nonselective* reduction of Mo^{IV} by CH_4 and oxidation by N_2O will play an important role. In order to determine the concentration of Mo^V, we carried out reactions at 560 °C under flow conditions in a mixture of CH_4, N_2O, and He. After the reaction had reached steady state at this temperature, the catalyst was rapidly quenched to 0 °C and the EPR spectrum of Mo^V was recorded. The concentration of Mo^V varied with the gas composition, but at a maximum level it was only 0.2% of the total molybdenum present in the sample. The results shown in Figure 5 demonstrate that at N_2O or CH_4 pressures greater than ca. 80 torr the steady-state concentration of Mo^V was zero order with respect to either gas.

Spectroscopic Experiments. Since the partial oxidation of methane is believed to occur via methyl radical and methoxide ion intermediates, an attempt was made to verify the presence of these species, albeit not under reaction conditions. The molybdenum on Cab-O-Sil was active and selective for the oxidation reaction.

The methyl radicals formed on the surface of Mo^V/SiO_2 are highly reactive, even at −196 °C, and therefore are difficult to detect. Following the reduction of Mo^{VI} at 600 °C an EPR spectrum of Mo^V was observed which corresponded to 2×10^{18} spins g^{-1}. Upon the introduction of 100 torr N_2O at 150 °C and equilibration for 4 h, the spectrum of Mo^V almost completely disappeared, and a large O^- spectrum which corresponded to 1.4×10^{18} spins g^{-1} was detected. After brief evacuation and upon the addition of 1×10^{19} molecules g^{-1} of CH_4 to the catalyst at −196 °C the O^- signal diminished significantly immediately and slowly thereafter. Two peaks, indicated in spectrum a of Figure 6, having the intensity ratio of ca. 3:1 and separated by 22 G were observed on the high-field side of the O^- spectrum. These peaks are consistent with the high-field components of the $CH_3\cdot$ spectrum. The low-field components are masked by the O^- spectrum.

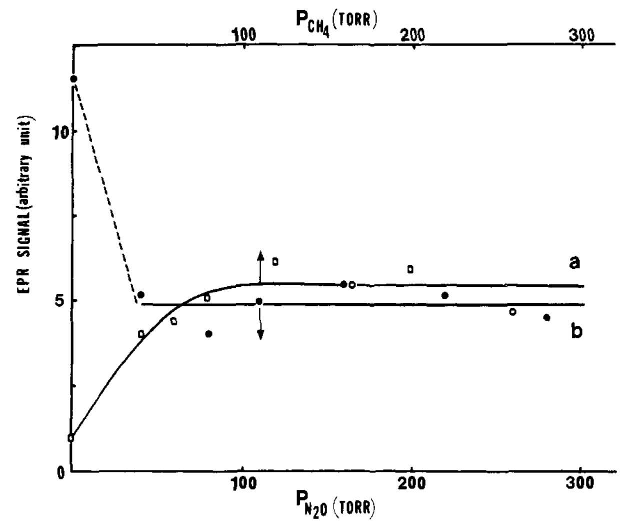

Figure 5. Concentration of molybdenum at steady state as a function of (a) CH_4 partial pressure, P_{N_2O} = 100 torr, and (b) N_2O partial pressure, P_{CH_4} = 75 torr. T = 560 °C, W/F = 0.4 g·s/mL.

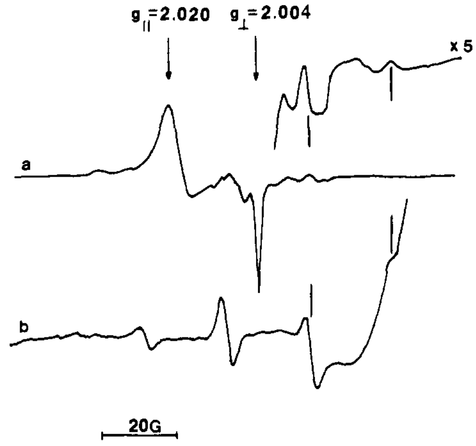

Figure 6. EPR spectra of methyl radicals: (a) after reaction of CH_4 with O^- on Mo/SiO_2; (b) after UV irradiation of oxidized Mo/SiO_2 in the presence of CH_4. Reactions were carried out and spectra recorded with the sample at −196 °C.

As previously reported by Lipatkina et al.,[6] methyl radicals also may be generated by UV irradiation of Mo^{VI}/SiO_2 in the presence of CH_4. Similarly, irradiation in the presence of H_2 leads to the formation of surface hydrogen atoms.[8] The methyl radicals are believed to be formed by the reactions

$$Mo^{VI}O^{2-} \xrightarrow{h\nu} Mo^VO^- \qquad (2)$$

$$Mo^VO^- + CH_4 \rightarrow Mo^VOH^- + CH_3\cdot \qquad (3)$$

This technique has been used to generate the methyl radical spectrum of Figure 6b, in which the four hyperfine lines may be

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[8] Balistreri, S.; Howe, R. F. in "Magnetic Resonance in Colloid and Interface Science"; Fraissard, J. P., Resing, H. A., Eds.; D. Reidel: Boston, 1980; pp 489–494.

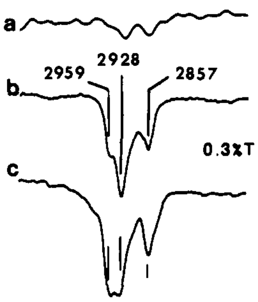


Figure 7. Infrared spectra of methoxide ions on Mo/SiO_2: (a) background after reduction of catalyst in CO, followed by adsorption of N_2O and evacuation; (b) after subsequent adsorption of CH_4 and evacuation; (c) after adsorption of CH_3OH and evacuation.

observed since there is no interfering O^- spectrum. It should be noted that the concentration of the observed methyl radicals is substantially less than the concentration of Mo^V on the surface. Moreover, the observed $CH_3\cdot$ radicals are separated by a distance of more than 10 Å from the paramagnetic Mo^V centers. This suggests that of the total number of $CH_3\cdot$ radicals formed by reaction 3 only a fraction diffuse to the silica where they survive other reactions.

Evidence for the formation of methoxide ions was obtained by using infrared spectroscopy. The catalyst wafer was reduced in CO and exposed to N_2O after which the gas phase was evacuated briefly. Methane was added at 25 °C, the sample was allowed to stand for 30 min, and excess CH_4 was removed. The spectrum (Figure 7b) exhibited two sharp peaks at 2928 and 2857 cm^{-1} with a shoulder at 2959 cm^{-1}. These peaks remained unchanged upon heating the catalyst at 300 °C for 30 min, but they were greatly diminished in intensity when the sample was treated with 50 torr of H_2O at 300 °C and heated under vacuum. No peaks in this region, above background (Figure 7a), were observed before the addition of CH_4 on the N_2O-treated sample or upon addition of CH_4 to the reduced catalyst before exposure to N_2O.

A reduced Mo/Cab-O-Sil wafer was exposed to about 0.1 torr of CH_3OH at 25 °C, and the excess gas phase was evacuated. The three peaks shown in Figure 7c were observed at 2958, 2935, and 2858 cm^{-1}. Depending on the phase, the infrared spectrum of methanol consists of a very strong band in the region 2973–2934 cm^{-1} due to the CH_3 asymmetric stretching mode and a band in the region 2944–2821 cm^{-1} due to the CH_3 symmetric stretch.[9] The CO stretching mode appears in the 1034–1029-cm^{-1} region. In the catalyst samples there was no transmission in the region around 1030 cm^{-1}.

These results provide evidence that methoxide ions are formed when CH_4 reacts with O^- ions on the surface of the catalyst. The differences in the infrared spectra of methoxide ion formed from CH_4 and from CH_3OH may be understood if one accepts that CH_4 largely results in the formation of molybdenum methoxide, whereas CH_3OH leads to the formation of methoxide ions mainly on the silica.

Reaction of $MoO(OCH_3)_4$. Although the reactions of alkoxide ions with water are well-known, we could not find an example in the literature where the reaction $MoO(OCH_3)_4$ had been studied. When small amounts of water were added to $MoO(OCH_3)_4$ dissolved in Me_2SO-d_6, the resonance at δ 4.00 decreased in intensity, and a new resonance appeared at δ 3.33 which is characteristic of CH_3OH. Moreover, upon the addition of 45 mL of water to the 1.80 g (7.37 mmol) of the orange $MoO(OCH_3)_4$ solid, the solid turned blue and the liquid phase, after distillation, was found to contain 22 mmol of CH_3OH. Thus, the facile reaction of molybdenum methoxide with water to form methanol was established.

Discussion

The oxidation of methane may be understood in terms of nonselective redox reactions and a selective reaction cycle. The nonselective reduction and oxidation may be described by the stoichiometric reactions

$$8Mo^{VI} + 4O^{2-} + CH_4 \xrightarrow{k_1} 8Mo^{V} + 2H_2O + CO_2 \tag{4}$$

$$2Mo^{V} + N_2O \xrightarrow{k_2} 2Mo^{VI} + N_2 + O^{2-} \tag{5}$$

The rate of Mo^V formation is given by

$$d[Mo^{V}]/dt = k_1[Mo^{VI}][CH_4]^n - k_2[Mo^{V}][N_2O]^m \tag{6}$$

From the evaluation of relative Mo^V concentrations at steady state it was determined that $m = 0$ and $n = 0$. An important aspect of this nonselective oxidation cycle is the two-electron transfer to N_2O which results in the formation of oxide ions, rather than the more reactive O^- species.

The selective cycle may be described by the reactions

$$Mo^{V} + N_2O \xrightarrow{k_3} Mo^{VI}O^- + N_2 \tag{7}$$

$$Mo^{VI}O^- + CH_4 \xrightarrow{k_4} Mo^{VI}OH^- + CH_3\cdot \tag{8}$$

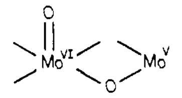
$$Mo^{VI}O^{2-} + CH_3\cdot \xrightarrow{k_5} Mo^{V}OCH_3^- \tag{9}$$

$$Mo^{V}OCH_3^- + H_2O \xrightarrow{k_6} Mo^{V}OH^- + CH_3OH \tag{10}$$

$$Mo^{VI}OH^- + Mo^{V}OH^- \xrightarrow{k_7} Mo^{V} + Mo^{VI}O^{2-} + H_2O \tag{11}$$

Here it is important to note that the reactive surface species Mo^V may be regenerated many times until the two-electron transfer (reaction 5) occurs. Every step in this cycle occurs rapidly at 600 °C relative to reactions 4 and 5.

The active site for partial oxidation is believed to be a highly dispersed form of molybdenum on silica as indicated by the observation that at comparable conversions smaller concentrations of molybdenum results in a greater selectivity for methanol.[3] The site may consist of molybdenum which is coordinated to oxygen ions of silica in the form



where this particular complex represents the molybdenum species on the right hand side of reaction 11. If this complex were further reduced before reaction with N_2O, then the situation would be suitable for the undesirable two-electron transfer described in reaction 5. Otherwise, the cycle described by reactions 7–11 could be repeated. Apparently the chain length for this cycle is long provided the CH_4/N_2O ratio is sufficiently large and the conversion is small. If these conditions do not prevail, the molybdenum will be oxidized to Mo^{VI} (reaction 5) and HCHO or CH_3OH will compete with CH_4 in reaction 4.

The intermediates $Mo^{VI}O^-$, $CH_3\cdot$, and OCH_3^- have now been identified on this catalyst, although not under reaction conditions. Moreover, reaction 10 has been verified independently, both by the reaction of the pure compound and the reaction of supported methoxide ions with water.

Formaldehyde, which is the other selective oxidation product, may be formed both by the direct decomposition of methoxide ions and by the secondary reaction of methanol. Iron molybdates are known to be selective catalysts for the oxidation of methanol to formaldehyde, and we have demonstrated in a separate study that Mo/SiO_2 is also an effective catalyst for this reaction.[10–12]

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(9) Falk, M.; Whalley, E. *J. Chem. Phys.* **1961**, *34*, 1554.

(10) Pernicone, N.; Lasserin, F.; Liberti, G.; Lanzavecchia, G. *J. Catal.* **1969**, *14*, 293.

(11) Yang, Y. P.; Lunsford, J. H., unpublished results.

(12) Machiels, C. J.; Sleight, A. W. In "Proceedings of the 4th International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, D. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; pp 411–414.

Even in this case the methoxide ion is considered to be an important intermediate. These and subsequent oxidation reactions may be described by the equations

$$Mo^VOCH_3^- + Mo^{VI}O^{2-} \xrightarrow{k_8} Mo^{IV} + Mo^VOH^- + HCHO \quad (12)$$

$$CH_3OH + N_2O \xrightarrow[Mo/SiO_2]{k_9} HCHO, CO, CO_2, N_2 \quad (13)$$

Methyl formate, a known byproduct in the partial oxidation of methanol to formaldehyde, was also detected in this study.

On the basis of this mechanism the overall rate equation for the conversion of methane may be derived. Making the usual steady-state approximation for $d[Mo^V]/dt$, $d[O^-]/dt$, and $d[CH_3\cdot]/dt$, and recognizing that $[Mo^V] \ll [Mo]_{total}$ enables one to obtain the rate equation for the disappearance of methane

$$-\frac{d[CH_4]}{dt} = \left(1 + \frac{k_3}{k_2}[N_2O]\right)k_1[Mo]_{total} \quad (14)$$

Since reaction 7 occurs at 25 °C and reaction 5 at much higher temperatures[5]

$$\frac{k_3}{k_2}[N_2O] \gg 1 \quad (15)$$

eq 14 becomes

$$\frac{d[CH_4]}{dt} = -\frac{k_1k_3}{k_2}[N_2O][Mo]_{total} \quad (16)$$

which is in agreement with the experimental rate equation with respect to the gas-phase reactants. The order of the reaction with respect to $[Mo]_{total}$ has not been tested; however, a simple first-order relationship is unlikely because of the various phases of Mo which might exist on the surface; i.e., the form of Mo which appears in eq 16 is probably a subset of the actual total amount of Mo.

Conclusions

The selective oxidation of methane to methanol and formaldehyde occurs over a supported molybdenum via a catalytic cycle in which O^- is the reactive form of oxygen. This ion initiates a reaction sequence in which methyl radicals and then methoxide ions are formed. The methoxide ions may decompose directly to formaldehyde or they may react with water to form methanol. The reaction of N_2O to O^{2-} rather than O^- results in the nonselective oxidation.

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Registry No. Mo, 7439-98-7; N_2O, 10024-97-2; methane, 74-82-8.

Mechanism of One-Electron Electrochemical Reductive Cleavage Reactions of Sulfonium Salts

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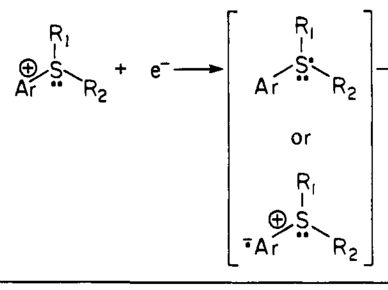
Abstract: Irreversible one-electron reduction potentials (E_p) were measured for 12 arylmethyl(substituted-alkyl)sulfonium salts (aryl = phenyl and 1-naphthyl). One-electron reduction produced homolytic sulfur-carbon σ-bond cleavage in each of the sulfonium salts studied, providing the observed irreversible electrochemical behavior. The E_p values were extremely sensitive to the electronegativity of the fragmenting radical, suggesting that the electrochemical one-electron reductive cleavage reaction of sulfonium salts occurs by a concerted or nearly concerted mechanism in which bond breaking is concomitant with electron acceptance.

One-electron electrochemical or chemical reduction of sulfonium salts is generally irreversible, as a consequence of carbon-sulfur σ-bond cleavage, providing a sulfide and a carbon radical.[1-3] The rate-determining step for fragmentation has been attributed to the formation of an intermediate sulfuranyl radical[1] via direct addition of an electron to sulfur or an intermediate π-ligand radical-anion sulfonium cation[3] preceding homolytic cleavage of a σ carbon-sulfur bond.



The proposed two-step mechanism for reductive cleavage of sulfonium salts can be compared to the one-electron reduction of aryl halides with an electron-withdrawing substituent such as nitro or cyano.[4] These systems produce dehalogenation, i.e., heterolytic σ-bond cleavage, after initial formation of an anion radical. The dehalogenation has been viewed as an intramolecular electron-transfer reaction whereby the electron initially added to the π system of the aryl ring is transferred in a second step to the C-X σ bond to form X^- and a carbon-centered radical.[4] The delay in the electron transfer has been attributed to the lack of overlap between the π system and the σ bond.

In contrast to the two-step fragmentation via an intermediate ion radical, there are several systems, e.g., reduction of alkyl halides, oxidation of carboxylates, and reduction of diaroyl peroxides, that are thought to occur by a synchronous electron-transfer/bond-cleavage reaction.[5] The sulfuranyl radical postulated to be the intermediate in the reductive cleavage process contains the 9-S-3 system, by the classification scheme proposed by Perkins et al.,[6] where nine valence-shell electrons are associated

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