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Partial Oxidation of Methanol to Formaldehyde over Molybdenum Oxide on Silica

TSONG-JEN YANG AND JACK H. LUNSFORD

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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Molybdenum oxide supported on high surface area silica was found to be an active, though not a particularly selective catalyst for the partial oxidation of methanol to formaldehyde. Both the activity and selectivity with N_2O as the oxidant were considerably less than with O_2. This observation suggests that O^- ions, derived from N_2O, are not involved in the activation of CH_3OH, but they may be important in the oxidation of HCHO and CO. The initial activity was greater with the catalyst in a partially reduced state, which lends support to the role of Mo^{IV}, as well as Mo^{V} and Mo^{VI} in the redox cycle. Similarly, it was found that among several unsupported oxides and an oxyhydroxide, Mo_2O_5 had the greatest activity for the formation of formaldehyde. Kinetic isotope effect studies confirm an earlier observation that the breaking of C—H bonds in the methyl group is the slow step in a catalytic cycle. © 1987 Academic Press, Inc.

INTRODUCTION

Formaldehyde, which is used mainly in the production of phenolic resins, is an important industrial chemical (*1*). In 1931 Adkins and Peterson (*2*) discovered the high catalytic activity of mixed Fe–Mo oxides for methanol oxidation to formaldehyde, but the related industrial process was developed only after 1950. Recently a new process using a fluidized catalyst bed has been reported (*3*). At virtually total methanol conversion (98%) catalyst selectivities from 90 to 98% have been achieved, depending upon the weight fraction of the iron–molybdenum compound in the catalyst. The catalyst contained up to 1.7 wt% iron–molybdenum oxide on microspheroidal silica.

Fundamental studies dealing with the role of oxide composition (*4–6*), as well as the nature of the active sites (*6–12*), have provided insight into this important catalytic process. In a series of papers Sleight and co-workers (*6, 13–15*), using MoO_3 as a model compound, have explored the surface chemistry and dynamics of the methanol oxidation process. They have proposed a mechanism which involves the dissociative adsorption of CH_3OH to form surface methoxide ions. The slow step in the catalytic cycle is the abstraction of a methyl hydrogen by a surface oxygen. This is followed by a rapid intramolecular rearrangement and the desorption of formaldehyde.

Results from our laboratory have demonstrated that molybdenum oxide supported on silica is a reasonably active and selective catalyst for the oxidation of ethane to ethylene (*16, 17*) and acetaldehyde (*18*), and the oxidation of methane to methanol and formaldehyde (*19*), provided N_2O is employed as the oxidant. In each of these cases the alkane is believed to be activated by surface O^- ions which are derived from nitrous oxide. One of the purposes of the present study was to determine whether this particular oxygen ion may be effective in the conversion of methanol to formaldehyde; however, the following results indicate that such is not the case.

In addition to exploring the role of O^-, we were interested in providing more information on the mechanism of the supported metal oxide system with emphasis on the redox cycle of the molybdenum. Niwa *et al.* (*11*) have argued that with SnO_2–MoO_3 catalysts the Mo^{IV}/Mo^{V} couple is involved;

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whereas, Novakova *et al.* (*7*) and more recently Sleight *et al.* (*14*) conclude that with MoO_3 the completely oxidized molybdate surfaces are the most active and selective for formaldehyde production. Clearly, additional data is needed to understand this important part of the catalytic cycle.

EXPERIMENTAL

Reagents. Methanol (98.8%) was obtained from MCB and was used without purification. Deuterated methanol (CH_3OD, 99.5% D and CD_3OD, 99.5% D) was obtained from Aldrich. Extra-dry oxygen (99.6%), nitrous oxide (99%), and carbon monoxide (99.8%) were obtained from Matheson.

Catalyst preparation and pretreatment. Supported catalysts containing 3.2 to 13.8 wt% Mo were prepared by evaporating to dryness a slurry of 5 g silica gel (Davison Grade 578, 20–40 mesh) and the appropriate amount of ammonium heptamolybdate (Climax Molybdenum) in a 50-ml solution of 0.1 M HNO_3–0.1 M NH_4NO_3 (pH = 2) with slow stirring at 100°C. One catalyst sample was prepared by adding 4.0 g silica gel to a 50-ml solution of 0.1 M NH_4OH–0.1 M NH_4NO_3 (pH = 11) which contained 0.5 g ammonium heptamolybdate. The catalysts were dried in air at 110°C for 1 h and then heated for 16 h at 500°C to decompose the ammonium heptamolybdate. These catalysts were further heated at 480°C in O_2 for 1.5 h and then degassed *in vacuo* at the same temperature.

Unsupported molybdenyl hydroxide, $MoO(OH)_3$, and molybdenum pentoxide, Mo_2O_5, were prepared according to the method of Palmer (*20*). The dried materials were ground to a powder (20–40 mesh) and heated to the reaction temperatures over a period of 30 min in a stream of He.

Catalytic studies. Kinetic data for the oxidation of methanol was carried out under atmospheric pressure, utilizing a single-pass flow reactor. The reactor, which was constructed of 18-mm-o.d. Pyrex tubing, typically was loaded with a 3.1-g sample of Mo/SiO_2 or about 0.5 g of unsupported catalyst. A thermocouple was positioned in a well, just below the catalyst bed. A gas mixture of O_2 (or N_2O) and He flowed through a gas dispersion tube in the methanol saturator and then into the reactor. The saturator was kept in a water bath at a temperature which would give the desired partial pressure of methanol. The entire system, except the saturator and the reactor, was maintained at 70°C.

The effluent was sampled using an in-line loop and analyzed with a Carle AGC-311 gas chromatograph. The column packings were 16 ft. of 10% Carbowax 1500 on Chromosorb W-AW (60–80 mesh) for the separation of formaldehyde, methyl formate, and methanol; 6 ft. of Porapak Q for the separation of CH_4, CO_2, and N_2O; and 6 ft. of 5A molecular sieve for the separation of O_2, N_2, and CO. All materials were packed in 0.25-in-o.d. stainless-steel tubing. The temperature was 50°C for the Carbowax and Porapak Q columns and 25°C for the molecular sieve column.

A pulse flow system was used to study the relationship between reactivity and oxidation state. During the pretreatment 0.5 g Mo/SiO_2 (5.3% Mo) was reduced with CO, and the resulting CO_2 was collected in a cold trap. The amount of CO_2, subsequently analyzed by gas chromatography, was used to calculate the extent of reduction using the reduction parameter χ, where

$$\chi = \frac{(CO_2)\text{ produced}}{(O)\text{ total}} \times 3.$$

Thus, the stoichiometry of the oxide may be expressed as $MoO_{3-\chi}$. The value of O_{total} is the amount of oxygen in the original, fully oxidized molybdena.

Spectroscopic studies. For X-ray photoelectron spectroscopy (XPS) fresh or used catalysts were degassed at 190°C to less than 1×10^{-5} Torr, and the samples were then transferred under nitrogen, in a glovebox, to a HP5950A spectrometer. Typical collection times were 3 h for Mo 3*d* lines, 1.5 h for the Si 2*p* line, and 1.5 h for the

O 2*p* line. Binding energies were referenced to a gold spot which was deposited on the sample. The Au $4f_{7/2}$ line was assigned a binding energy of 84.0 eV. The Si 2*s* line from SiO_2 at 154.0 eV was used as a secondary standard. Binding energies for the Mo 3*d* lines were reproducible to ±0.2 eV.

Electron paramagnetic resonance (EPR) spectra were obtained using a Varian E-6S X-band spectrometer. After carrying out a pretreatment or reaction in a catalytic reactor, the catalyst was transferred to a 4-mm-o.d. sidearm and cooled to −196°C. The *g* values are reported relative to a DPPH standard at 2.0036.

RESULTS

Comparison of N_2O and O_2 as oxidants. The catalytic activities and selectivities as a function of temperature are compared in Figs. 1 and 2, respectively, when either N_2O or O_2 was employed as the oxidant. The catalyst was 5.3% Mo/SiO_2 (3.1 g) which was prepared under acidic conditions. The reactant mixture contained 318 Torr of oxidant, 62 Torr CH_3OH and 380 Torr He and a value of $W/F = 5.3 \times 10^{-2}$ g · min · ml^{-1} was adopted. All experimental data was taken under steady-state conditions which were achieved after 1 h on stream at a given temperature. In a blank experiment the conversion over silica gel was found to be negligible in the temperature range of interest. The selectivity, for example, to formaldehyde, is defined as (moles HCHO)/[(moles HCHO) + 2 (moles $HCOOCH_3$) + 2 (moles CH_3OCH_3) + (moles CO) + moles (CO_2)]. The mass balance for carbon was approximately 97%.

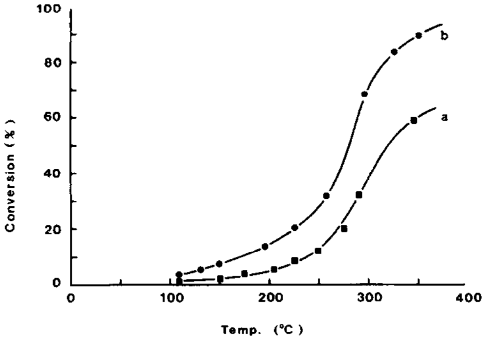


FIG. 1. Effect of temperature on methanol conversion with (a) 318 Torr N_2O or (b) 318 Torr O_2 as the oxidant: 62 Torr CH_3OH, 380 Torr He, $W/F = 5.3 \times 10^{-2}$ g · min · ml^{-1}, 5.3% Mo/SiO_2.

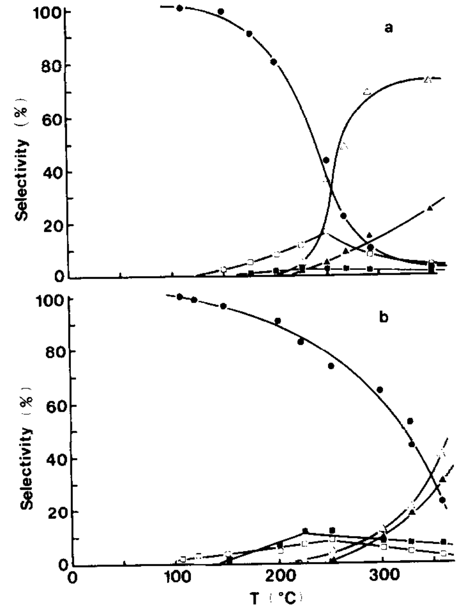


FIG. 2. Variation of selectivities as a function of temperature with (a) 318 Torr N_2O or (b) 318 Torr O_2 as the oxidant (62 Torr CH_3OH and 380 Torr He at $W/F = 5.3 \times 10^{-2}$ g · min · ml^{-1} over 5.3% Mo/SiO_2): (●) HCHO, (□) CH_3OCH_3, (■) $HCOOCH_3$, (▲) CO, (△) CO_2.

It is evident from Fig. 1 that over the entire temperature range the activity with O_2 was greater than that observed with N_2O. This is in contrast with the oxidative dehydrogenation of C_2H_6, for which it was found that N_2O was the more active oxidant (*17*). The activation energies, determined at low conversions, were 22 ± 1 kcal/mol with N_2O and 18.3 ± 0.2 kcal/mol with O_2.

The differences between the two oxidants are even more striking when one also considers the selectivities which are depicted in Fig. 2. For example, when the conversion was 50% the selectivity to HCHO was 5% with N_2O and 70% with O_2 as the oxidant. The sharp decrease in the HCHO selectivity at ca. 250°C was accom-

TABLE 1

The Inhibition Effect of Water[a]

Amount of water added (Torr)	Amount of water produced[b] (Torr)	Rate $\left(\frac{\mu\text{mol HCHO}}{\text{min}\cdot\text{g Mo}}\right)$	Conversion (%)	Selectivity to HCHO (%)
0	8.2	242	20.0	89
4.0	7.7	227	18.5	90
8.2	7.4	217	17.6	91
16.6	6.1	181	14.2	94
27.1	5.0	147	11.3	96

[a] Reaction conditions: $P_{He} = 358$ to 331 Torr, $P_{CH_3OH} = 46$ Torr, $P_{O_2} = 356$ Torr, $T = 203°C$.

[b] Calculation based upon the reaction

$$CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O.$$

panied by a corresponding increase in the CO_2 selectivity, which suggests that N_2O is promoting the further oxidation of HCHO. It is significant that Mo/SiO_2 is an effective catalyst for the oxidation of CO when N_2O is the oxidant (*21*). With O_2 only a small selectivity to CO_2 was found at 250°C, and at higher temperatures the selectivities for CO and CO_2 were comparable.

From log–log plots of methanol consumption rate versus reactant partial pressure it was determined that the reaction orders were 0.64 and 0.13 with respect to N_2O and CH_3OH and were 0.49 and 0.50 with respect to O_2 and CH_3OH. The inhibiting effect of water on the reaction rate was studied and the results are summarized in Table 1. The addition of water vapor suppressed the rate of formaldehyde formation, and, as expected, the selectivity to formaldehyde increased. The EPR spectrum of Mo^V indicated that the water coordinated with these surface ions.

Kinetic isotope effects. The kinetic isotope effect (KIE) using CH_3OD and CD_3OD are shown in Table 2, along with similar results obtained by Machiels and Sleight (*13*) for unsupported MoO_3 over a different temperature range. As previously observed (*13*) the KIE due to the methyl proton is much more pronounced than that of hydroxyl protons. The breaking of the C—H bond is believed to be the slow step in the reaction scheme (see below). The observed primary KIE is in good agreement with that calculated using Eq. (2 · 12) of Melander (*22*) and the vibrational frequencies of surface methoxide ions reported by Groff (*23*).

TABLE 2

Ratios of Rate Constant from Kinetic Isotope Effect

T (°C)	k_{CH_3OH}/k_{CH_3OD}	k_{CH_3OH}/k_{CD_3OD}	$(k_{CH_3OH}/k_{CD_3OD})_{\text{theor.}}$[a]	Ref.
108	1.06	7.3	7.5	This work
121	1.05	6.4	6.8	This work
135	1.04	5.3	6.3	This work
265	1.15[b]	6.7[b]	3.4	(*13*)
300	1.04[b]	3.2[b]	3.0	(*13*)
335	1.07[b]	2.7[b]	2.7	(*13*)

[a] Calculated using Eq. (2 · 12) of Ref. (*22*).

[b] Data obtained for unsupported MoO_3.

TABLE 3

Activities of Catalysts Prepared from Solutions of Different pH Values[a]

pH	Conversion (%)	Selectivity to HCHO (%)	(μmol HCHO/ min · g Mo)
2	14.5	77	207
11	8.1	84	127

[a] Reaction conditions: $P_{O_2} = 71$ Torr, $P_{CH_3OH} = 93$ Torr, $P_{He} = 596$ Torr, $T = 190°C$, total flow rate = 58 ml/min, 5.3% Mo.

The calculated values also are listed in Table 2. It should be pointed out, however, that there are various ways to calculate kinetic isotope effects. Thus, the agreement between observed and calculated values found in this paper may well be fortuitous. The apparent activation energies for the oxidation of CH_3OD and CD_3OD were 18.6 ± 0.2 and 20.8 ± 0.3 kcal/mol, respectively.

Effect of Mo loading and catalyst preparation. As the Mo loading was varied from 3.2 to 13.8 wt% the activities and selectivities of the catalysts varied as shown in Fig. 3. A broad maximum in activity was observed at 9.7% Mo, but the selectivity decreased continuously as the loading increased. The latter result was surprising as unsupported MoO_3 is a selective catalyst, and one would expect that the catalysts having higher loadings would more closely approximate this unsupported state.

The state of dispersion can be modified somewhat by altering the pH of the impregnating solution. According to Eq. (1), more mononuclear molybdate ions should be present in more basic solutions.

$$7MoO_4^{-2} + 8H^+ \rightleftarrows Mo_7O_{24}^{6+} + 4H_2O \quad (1)$$

The results shown in Table 3 were observed with catalysts impregnated at pH = 2 and pH = 11. Clearly, the activity of the catalyst having more polymolybdate ions (low pH) is greater than the activity of the catalyst which is believed to have greater dispersion. In this case it is not possible to determine whether the greater selectivity observed for the catalyst prepared at pH = 11 is the result of lower conversion or if there is an intrinsic difference in the catalyst.

Unsupported molybdenum oxides and an oxyhydroxide. For comparison purposes the activities and selectivities of several unsupported molybdenum oxides and an oxyhydroxide were determined and the results are summarized in Table 4. At the conversion levels achieved the selectivities were uniformly high, but the activities varied greatly among the several oxides and the hydroxide, with Mo_2O_5 being the most active catalyst. It is significant that the specific activity of this catalyst was about threefold greater than that of MoO_3. On a mass basis the Mo_2O_5 catalyst was comparable in activity to the 5.3% Mo/SiO_2 catalyst, and if one assumes a reasonable dispersion of the MoO_x on SiO_2, the specific activity (based on exposed Mo) of the Mo_2O_5 would be even greater than that found with the supported catalyst.

Activities determined by pulse experiments. A 0.5-g sample of supported catalyst containing 5.3% Mo/SiO_2 was used for the partial oxidation of methanol in the pulse-flow system. The catalyst was fully oxidized with O_2 at 450°C before the first pulse was added. Pulses which contained 52.4 μmol CH_3OH and 7.6 μmol O_2 were added successively to the catalyst at 191°C. The amount of HCHO produced following the

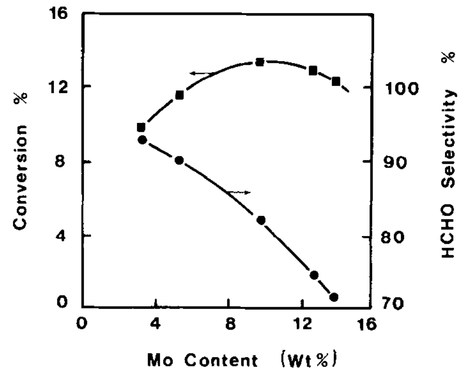


FIG. 3. Effect of Mo loading on conversion and selectivity: 124 Torr O_2, 96 Torr CH_3OH, and 546 Torr He; $W/F = 5.3 \times 10^{-2}$ g · min · ml^{-1}; $T = 191°C$.

TABLE 4

Catalytic Activities of Molybdenum Oxides and Hydroxide[a]

Compounds[b]	Surface area (m^2/g)	Selectivity to HCHO (%)	Conversion (%)	Rate $\left(\frac{\mu\text{mol HCHO}}{\text{g Mo} \cdot \text{min}}\right)$
MoO_3	9.0 ± 0.4	93	5.4	44
Mo_2O_5	9.8 ± 0.4	92	21	159
$MoO(OH)_3$	16.8 ± 0.8	98	0.7	7
MoO_2	17.8 ± 0.8	90	7.0	25
5.3% Mo/SiO_2	238 ± 12	91	17	273

[a] Reaction conditions: $P_{He} = 596$ Torr, $P_{CH_3OH} = 93.5$ Torr, $P_{O_2} = 70.5$ Torr, total flow rate = 58 ml/min, $T = 191°C$.

[b] Weight used for reaction: 1.04 g MoO_2; 3.1 g supported catalyst with 5.3% Mo by weight; 0.5 g MoO_3, Mo_2O_5 or $MoO(OH)_3$.

reaction of each pulse is shown in Fig. 4. The production of formaldehyde increased very much during the first five pulses, but thereafter the activity was essentially constant. Meanwhile, the color of the molybdena catalyst turned from an initial yellow color to blue–black, and the concentration of Mo^V progressively increased as indicated in the figure. With the first pulse approximately 2.8 μmol of H_2O was formed, and the amount of water produced decreased with each successive pulse to a final level of 0.8 μmol.

In a separate experiment pulses of the effluent gases from a conventional flow reactor were passed either through an open tube or through the pulse reactor with the catalyst present. It was found that 96.4% of the HCHO passed through the pulse reactor at 140°C, which suggests that the adsorption and desorption rates must be rapid at 191°C. These results are consistent with the recent temperature-programmed reaction study of Farneth *et al.* (*15*), who demonstrated that formaldehyde exhibited a desorption peak at 220°C, but even at 191°C considerable formation and desorption of formaldehyde occurred.

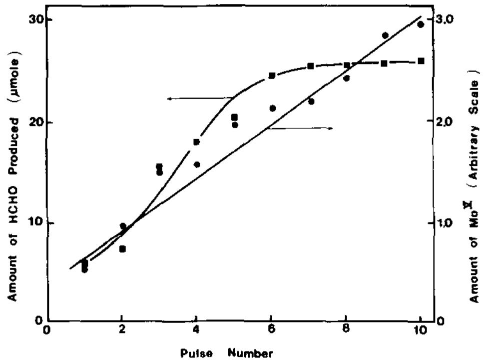


FIG. 4. Formation of HCHO and Mo^V in pulse-flow reactions at 191°C. Each pulse contained 52.4 μmol CH_3OH and 7.6 μmol O_2 over 0.5 g of 5.3% Mo/SiO_2.

Another blank experiment carried out at 192°C demonstrated that with 0.47 g of pure silica in the reactor about 50% of a first pulse of 24 μmol of CH_3OH was adsorbed, but for the next seven pulses only 25% of the CH_3OH was adsorbed per pulse. It is doubtful, therefore, that the results of Fig. 4 could be explained by extensive adsorption of the reactant on silica during the first two pulses.

Pretreatment of the catalyst with CO caused the reduction of supported MoO_3. Following reduction of a 0.5-g sample containing 5.3% Mo a pulse of gas containing 70.8 μmol CH_3OH in helium (no O_2) was introduced to the catalyst at 190°C. As shown in Fig. 5 the amount of HCHO production increased as the extent of reduction increased. At $\chi = 0.5$ ($MoO_{2.5}$), the amount of HCHO formation was comparable to that which resulted from pulse 10 of Fig. 4.

XPS studies. In the XPS experiments the

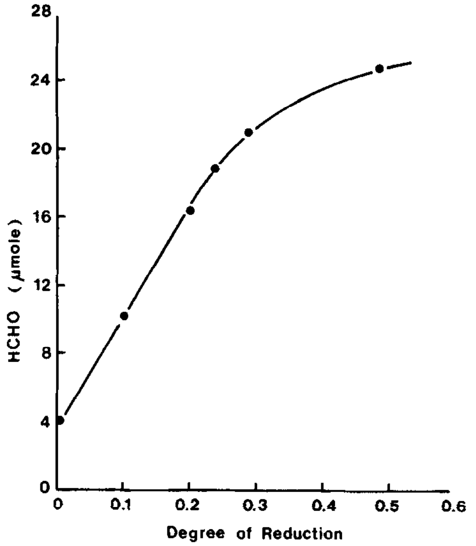


FIG. 5. Relationship between catalyst activity at 190°C and the degree of catalyst reduction. Each pulse contained 70.8 μmol CH_3OH over 0.5 g of 5.3% Mo/SiO_2.

relative concentrations of Mo^{IV}, Mo^{V}, and Mo^{VI} on the surface were investigated both before and after the catalytic reaction. A gas mixture of 383 Torr He, 315 Torr O_2, and 63 Torr CH_3OH was passed over the catalyst at 190°C for about 2 h. After evacuating the gas phase, the sample was pressed under N_2 into the form of a pellet suitable for XPS analysis.

The experimental and deconvoluted spectra for the 5.3% Mo/SiO_2 catalyst are depicted in Fig. 6. In order to perform the deconvolution the following conditions were assumed:

1. The full width at half maximum (FWHM) of each peak in the doublets was assumed to be the same; and
2. The $3d_{5/2}$ and $3d_{3/2}$ binding energies were 232.1 and 235.3 eV for Mo^{VI}, 230.8 and 234.0 eV for Mo^{V}, and 228.8 and 232.0 eV for Mo^{IV}.

The sets of binding energies used by Ward *et al.* (*16*) for Mo/SiO_2 were 232.4 and 235.5 eV for Mo^{VI}, 230.9 and 234.0 eV for Mo^{V}, and 229.1 and 232.2 eV for Mo^{IV}. Cimino and De Angelis (*24*) reported binding energies of $3d_{5/2}$ and $3d_{3/2}$ as 231.6 and 234.8 eV for Mo^{VI}, 230.1–230.6 and 233.3–233.8 eV for Mo^{V}, and 228.3 and 231.5 eV for Mo^{IV}.

The results of Fig. 6a indicate that the oxidized Mo/SiO_2 sample contained, as expected, a large excess of Mo^{VI} (88% Mo^{VI} and 12% Mo^{V}). It is evident from the spectrum that the Mo^{V} peak was not resolved, and the actual percentage of this species could have been less. After reaction, even in excess O_2, the amount of Mo^{V} significantly increased (57% Mo^{VI}, 43% Mo^{V}) with approximately equivalent amounts of Mo^{V} and Mo^{VI} being present on the surface.

The XPS spectra of Mo_2O_5 (not shown) revealed that this compound had a mixture of oxidation states (59% Mo^{VI}, 19% Mo^{V}, 22% Mo^{IV}) which was essentially the same after outgassing under vacuum and after the catalytic reaction. It is significant to note, however, that the surface of this very active catalyst contained an appreciable amount of Mo in a reduced state.

DISCUSSION

The smaller rates observed with N_2O as the oxidant (Fig. 1) provide convincing evidence that O^- is not an important intermediate in the conversion of CH_3OH to HCHO; however, the lower selectivities observed with N_2O suggest that the O^- ion may be important in the further oxidation of

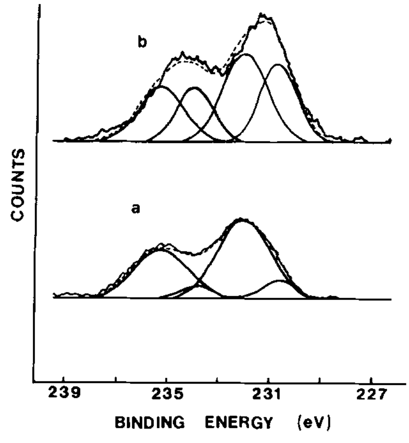


FIG. 6. XPS spectra and deconvoluted spectra of Mo/SiO_2 (a) before and (b) after the steady-state catalytic oxidation of methanol.

HCHO and CO to CO_2. It is known that CO reacts with O^- to form CO_2^- (*21*), and this ion is believed to be an intermediate in the oxidation process at elevated temperatures. The smaller rates obtained with N_2O may reflect a slower rate of incorporation of oxygen ions into the lattice relative to O_2. These results, therefore, suggest a more classical Mars–van Krevelen-type mechanism (*25*) in which methanol is first oxidized by the molybdenum oxide and the latter, in turn is reoxidized either by N_2O or O_2. Support for this mechanism also is found in the pulse data of Fig. 5, which shows that even in the absence of gas phase oxidant the oxidation of CH_3OH occurs.

The activation energies observed with N_2O and O_2 are within the range of those reported previously for O_2 (*6, 9*). The order of the reaction with respect to the oxidation has been reported from zero to $\frac{1}{2}$, although values near $\frac{1}{2}$ are common (*6, 9, 11*). It is tempting to attribute the $\frac{1}{2}$ order to an equilibrium step in the mechanism

$$O_2 \rightleftarrows 2O \qquad (2)$$

This, however, may be an oversimplification since the order with respect to N_2O also was near $\frac{1}{2}$ and it is difficult to imagine a comparable equilibrium for this molecule. Moreover, there is no evidence that the reverse reaction of Eq. (2) occurs with supported molybdenum oxide; i.e., that the oxide can be reduced simply by heating it under vacuum at the temperatures of interest here. It seems more likely that the order of reaction with respect to the oxidant is the result of a complicated series of reactions in which the O_2 or N_2O dissociates on the surface and then is incorporated into the oxide, eventually reaching the active site.

The KIE listed in Table 2 nicely extend the observations of Machiels and Sleight (*13*) and confirm that the breaking of the C—H bond, probably in the methoxide group, is the slow step in the catalytic cycle for MoO_3/SiO_2 as well as for unsupported MoO_3.

Differences between the supported and unsupported catalysts begin to appear when one considers the effect of reduction on catalytic activity. As noted previously (*14*) it was found in pulse studies that the most oxidized iron–molybdate surfaces were the most active; whereas, with supported molybdenum a catalyst which was reduced to an average oxidation state of about 5 was the most active (Fig. 5). Moreover, among the unsupported oxides listed in Table 4, Mo_2O_5 was the most active. These results support the conclusion of Niwa *et al.* (*11*) that with SnO_2–MoO_3, TiO_2–MoO_3, and MoO_3–SiO_2 catalysts the important redox cycle is Mo^{IV}/Mo^{V}, rather than Mo^{V}/Mo^{VI}.

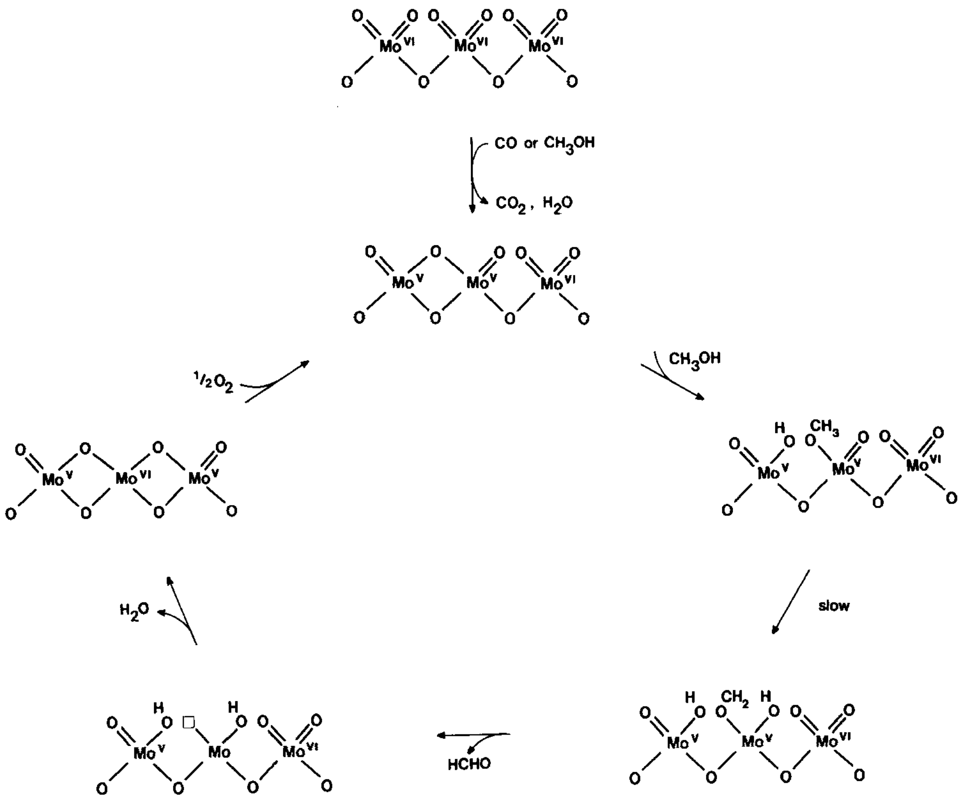
We favor, however, the mechanism depicted in Scheme 1 in which both redox couples are involved. Under the experimental conditions used to obtain the XPS data of Fig. 6 the reoxidation step must have been rapid as no MO^{IV} was detected for the supported catalyst, but it was observed with Mo_2O_5. This mechanism emphasizes the importance of the polymolybdate phase in contrast to isolated Mo ions. Evidence for the importance of this phase is found in the data of Table 3.

The negative effect of H_2O on activity (Table 1) is probably the result of three factors: (1) the dehydroxylation step noted in scheme 1 is inhibited, (2) water competes with methanol for the available coordination sites, and (3) water rapidly reacts with methoxide ions to form methanol. The latter reaction was demonstrated to be an important step in the partial oxidation of methane to methanol (*19*).

CONCLUSIONS

1. Molybdena supported on high surface area silica is an active catalyst for methanol oxidation to formaldehyde, but at high conversions the selectivity is considerably less than that reported for commercial catalysts.

2. When compared with O_2, N_2O is a less active and selective oxidant. This is taken as evidence that O^- ions do not play a di-



SCHEME 1

rect role in the activation of CH_3OH, but these ions may be involved in the further oxidation of HCHO and CO.

3. The supported molybdenum oxide catalysts are more active in a partially reduced state. Molybdenum IV, V, and VI all may be involved in the catalytic cycle.

ACKNOWLEDGMENT

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