JOURNAL OF CATALYSIS **114**, 398–410 (1988)

Mechanism of Partial Oxidation of Methanol over MoO_3

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Received December 22, 1987; revised July 18, 1988

The partial oxidation of methanol was carried out over molybdenum oxide at low temperatures, where high-order products (dimethyl ether, dimethoxymethane, and methyl formate) were formed in small amounts. Both the electronic and the geometric states of the catalysts were observed by techniques such as transient experiments, volumetric adsorption, and *in situ* infrared observation of methoxy group and Mo–O structural bands. Correlation of activity data with data on the surface state makes it possible to suggest a reaction mechanism for the partial oxidation of methanol over molybdenum oxide. The reaction can be represented by a mechanism involving methoxy intermediates chemisorbed on oxygen vacancy sites. Formaldehyde and CO are mainly produced from methoxy on terminal oxygen (Mo=O) vacancy sites while bridged oxygen (Mo–O–Mo) vacancy sites are responsible for the production of dimethyl ether, dimethoxymethane, and methyl formate. The bond strength of chemisorbed methoxy is greatly affected by the electronic state of the oxygen vacancy. Reduced oxygen vacancy sites weaken the CH bond but strengthen the CO and chemisorption bonds in the methoxy, resulting in the formation of more hydrogen-abstracted products. The decrease in the formation of high-order products (dimethyl ether, dimethoxymethane, and methyl formate) at high reaction temperatures is caused by the decrease in the concentration of bridged oxygen vacancy sites by formation of shear planes in the surface layers. © 1988 Academic Press, Inc.

INTRODUCTION

The selective oxidation of methanol on molybdenum oxide and its mixtures with other oxides has been extensively studied by a number of authors since the early sixties (*1–11*). Although there is a growing realization of the importance of structural factors (*12*) and the role of Mo=O (*9, 13*) for the oxidation activity of methanol, the nature of the active sites and the way in which they are involved in the formation of products is not clear.

There is some agreement that the methoxy group is an important intermediate (*8–11*). However, the presence of the methoxy had not been confirmed by infrared spectroscopy since the surface area of conventionally made MoO_3 or molybdate is very low (<5 m^2/g). By using finely divided high-surface-area (27 m^2/g) MoO_3, Chung *et al.* (*14, 15*) have succeeded in confirming the presence of methoxy as well as other chemisorbed species and have observed that a terminal oxygen vacancy with one electron trapped is an active site for the formation of formaldehyde (FA).

In this work we report activities and selectivities for methanol oxidation reactions at low temperatures where small amounts of high-order products (dimethyl ether (DME), dimethoxymethane (DMM), methyl formate (MF)) are formed. This is combined with other measurements such as the estimation via infrared spectroscopy of the structural losses of Mo–O bands, volumetric adsorption, and transient techniques in order to understand the reaction mechanism for the oxidation of methanol over molybdenum oxide.

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EXPERIMENTAL

Preparation of Catalyst

The same finely divided molybdenum oxide described in the previous paper (*14*) was used. The orthorhombic MoO_3 structure was stabilized by extensive exposure to pure oxygen at 400°C. Individual particles are rod-shaped when observed in the electron microscope (TEM). The BET surface area is 27 m^2/g and this value agrees with the average particle size of 450 Å, measured by X-ray line broadening. The original molybdenum oxide sample is transformed into Mo_9O_{26} by treating with purified helium for 2 h at 350°C. The monoclinic structure of Mo_9O_{26} is confirmed by X-ray diffraction analysis. The color of MoO_3 is yellowish white and that of Mo_9O_{26} is gray-blue.

Experimental System

The experimental system consists of the feed system, the infrared system with the infrared cell, the reactor, and the mass spectrometer with a minicomputer. A gas manifold system permits various prepurified gas mixtures to be directed to the infrared cell or to the reactor so that step functions or pulses of concentration can be studied (*16*). The stainless-steel differential reactor of 1 ml capacity can be used either in the differential mode or in the recycle mode. The grain size of the pressed catalyst particles is between 60 and 100 mesh. The analysis of gases is made with an on-line magnetic-sector-type (12-in. radius analyzer) Nuclide mass spectrometer. The mass spectrometer is controlled by a DEC MINC computer to follow up three peaks per second in a peak-stepping mode. Data collection and manipulation are automated so that concentrations of all the components as a function of time can be plotted by a Calcomp plotter.

The infrared spectra have been obtained on a Spex double-beam instrument using a Hg–CdTe detector and a lock-in amplifier. The cell configuration and optical path have been described previously (*14, 15*). The cell has low volume and short path length, and the cell window is cooled to permit spectra to be taken up to 350°C. The cell window used is usually CaF_2 of 1 mm thickness. However, ZnS of 2 mm thickness is used in the low-frequency region of less than 1100 cm^{-1}.

Activity and Selectivity Measurements

Experiments at steady state (Figs. 1–3) are obtained in the recycle mode. From 10 to 110 mg of the pressed catalyst is loaded in the reactor and a gas flow rate of 20 to 40 ml/min is used. After steady state is attained the outlet is sampled for at least 10 min and then the temperature is raised. An average of 100 samples per peak is taken as a data point. After reaching 400°C, the system is cooled down stepwise and new measurements are done at each temperature. About 1 h is needed to attain a steady state and to avoid hysteresis effects after a temperature change. Transient and adsorption experiments are done in the once-through differential mode. In order to calculate the amount of methanol adsorbed during the step input of gaseous methanol, a tracer component, Ar, in the gas mixture is used to produce a standard curve for the response of the reactor system to a step change. After the concentration of Ar is set equal to that of methanol, the difference in the response curves for the adsorbate and that for Ar is used to calculate the amount of methanol adsorbed.

Infrared Measurements

The infrared spectrum of adsorbed methanol is observed in the same way as in the previous paper (*14*). The optical density of infrared bands is obtained by calculating the area which contains all the CH stretching bands.

The structural bands of Mo=O and Mo–O–Mo are observed by measuring the emission spectrum. With a transmission spectrum it is difficult to get the optical density, because the existence of a series of structural bands below 1000 cm^{-1} makes it impossible to find a proper background. The emission band at 1140 cm^{-1}, an overtone or combination of MO–O–Mo bands, is used to observe the structural losses of Mo–O–Mo during reaction. Similarly, the well-known band at 970 cm^{-1} is used to measure the loss of Mo=O during reaction. The intensity of each band was converted into concentration according to the Beer–Lambert law,

$$C = k \ln(I_s/I),$$

where k depends on the weight of the catalyst charged, die pressure applied to make the catalyst disk, and reaction temperature. In order to eliminate catalyst mass and pressure effects, percentage loss is defined as

$$\% \text{ loss} = [(C_o - C_r)/C_o] \times 100,$$

where the subscripts r and o represent a reduced and a fully oxidized sample of molybdenum oxide, respectively. By using MoO_3 as a fully oxidized reference, and Mo_9O_{26} as a 3.4% reduced reference, the degree of reduction of the structural bands is obtained for a particular partly reduced sample. The two reference samples are of course in a uniform degree of reduction through their bulk. However, we shall present evidence that the samples which have been partly reduced by exposure to methanol/oxygen mixtures at varying temperatures exhibit a variation in degree of reduction from the surface towards the interior of the particles. The degree of reduction observed by infrared spectroscopy based on the structural bands is much higher than the reduction observed by weight loss, for example, which is the average reduction of whole particle. This behavior seems to be consistent with the scattered transmission through the particles (*17*) and will be discussed further later.

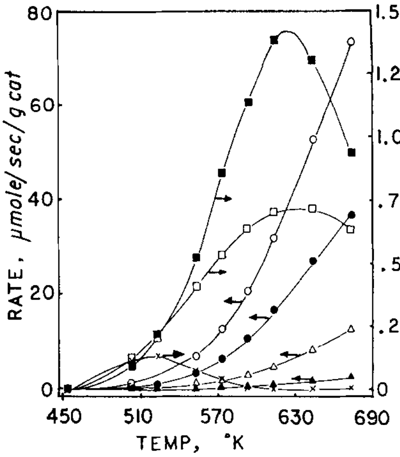


FIG. 1. Steady-state oxidation of methanol on molybdenum oxide: 3.6% methanol and 5% oxygen in helium with flow rate of 0.0013 mol/min; 10 mg of MoO_3; ○, water; ●, formaldehyde; ▲, CO; △, CO_2; □, methyl formate; ■, dimethyl ether; ×, dimethoxymethane.

RESULTS

Figure 1 shows an example of the reaction carried out at steady state for methanol and oxygen concentrations of 3.6 and 5%, respectively, using 10 mg of molybdenum oxide and a flow rate of 0.0013 mol/min. It should be noted that when using a differential reactor (not in the recycle mode) the yield of CO_2 is always less than that of CO. During the reaction the main products are water, formaldehyde, and CO. At low temperatures, dimethyl ether, dimethoxymethane, and methyl formate are also produced in small amounts. It is interesting to observe that the high-order products, although small in amount, show a maximum in the yield as a function of reaction temperature. The activation energy at temperatures of 443–713 K is equal to 9.6 kcal/mol, and the reaction order is almost zero with respect to oxygen concentrations from 3 to 10% in the reaction mixture.

Figure 2 presents the effect of oxygen concentration in the feed on the selectivities of the main products, and Fig. 3 does the same for the high-order products. Although not shown in the above figures methanol concentration also affects the selectivity in exactly the opposite direction from oxygen. From Fig. 2 it can be observed that the selectivity of formaldehyde

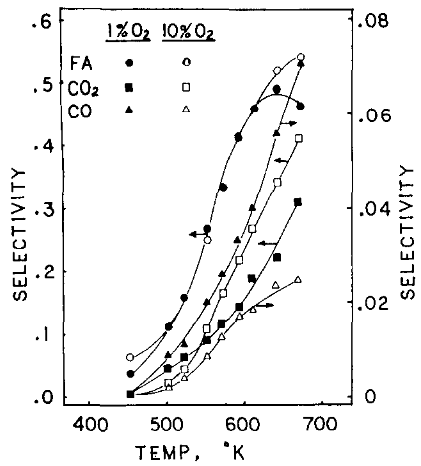


FIG. 2. Selectivities with respect to formaldehyde, CO, and CO_2: the reaction conditions are the same as in Fig. 1 except for changes in the oxygen concentration.

is relatively insensitive to the oxygen concentration except at high reaction temperatures (>350°C) and at low oxygen concentrations (<1%). Other products show some dependence on oxygen concentration. However, the selectivity toward methyl formate is increased abruptly at oxygen concentrations of less than 1%. For the high-order products there is a maximum in the selectivity. The maximum is observed at temperatures of around 270°C for DMM and at around 360°C for DME and MF. Generally more formaldehyde and CO_2 are produced with a less reduced catalyst (higher oxygen or lower methanol concentration) while the formation of CO and the high-order products is increased with a more reduced catalyst (lower oxygen or higher methanol concentration).

Figure 4 shows transient responses of some products to step changes of reactant composition at 300°C, in which a period of partial reduction of MoO_3 with methanol/helium is followed by oxidation with 10% oxygen/helium and by reduction with methanol/10% oxygen/helium. The last section was a switch to methanol/helium again. In the absence of oxygen in the reaction mixture, concentrations of formaldehyde, CO_2,

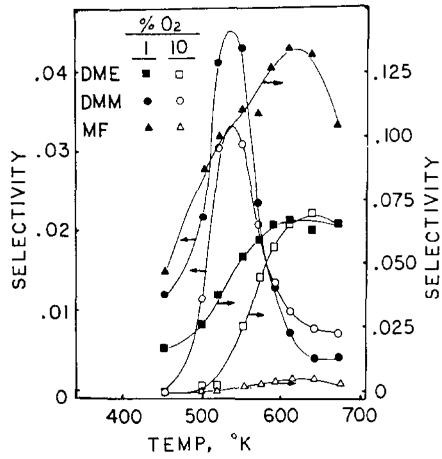


FIG. 3. Selectivities with respect to dimethyl ether, dimethoxymethane, and methyl formate: reaction conditions are the same as in Fig. 1 except for changes in oxygen concentration.

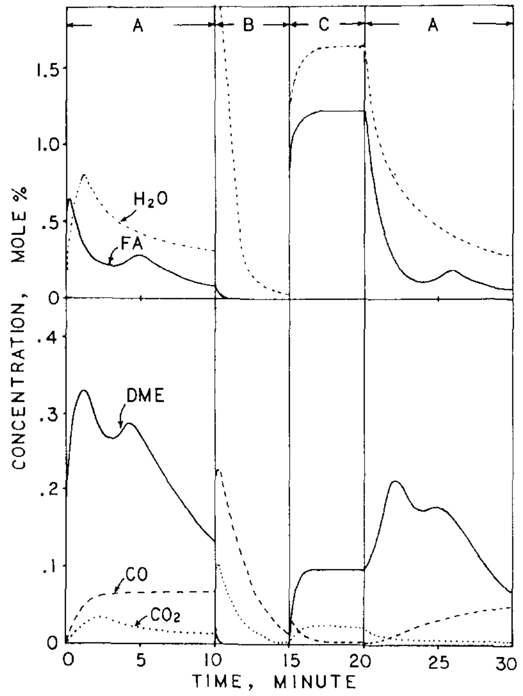


FIG. 4. Transient response of product concentration to step changes of reactant composition: catalyst, 50 mg of MoO_3; reaction temperature; 300°C; flow rate, 40 ml/min (NTP); A, 3.6% methanol/helium; B, 10% oxygen/helium; C, 3.6% methanol/10% oxygen/helium.

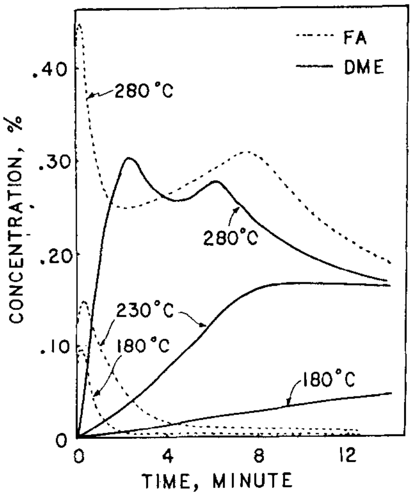


FIG. 5. First minutes of reduction of fully oxidized molybdenum oxide with 3.6% methanol/helium as a function of reduction temperature: catalyst, 50 mg; flow rate, 40 ml/min (NTP).

and dimethyl ether keep decreasing as reduction proceeds because of the consumption of oxygen available on the surface. Oxygen in the reaction mixture not only increases total conversion of methanol but also enhances the selectivity toward formaldehyde. An interesting feature of the response curve in a reducing atmosphere is the presence of a second peak for FA and DME.

The same reductions as those done in the last section of Fig. 4 were done at lower temperatures. The result in Fig. 5 shows that the second peak can appear only when the temperature is higher than 230°C. The activation energies for the low-reduction and the high-reduction peaks (here reduction activity is taken as a synonym of methanol oxidation rate) are 8.2 and 20.2 kcal/mol, respectively. The appearance of double peaks must result from a change in the surface state of catalyst while two different phenomena compete: the removal of labile surface oxygen and the restructuring of molybdenum oxide to accommodate the oxygen loss. The first peaks for both FA and DME conversions correspond to the surface reduction and the second, to the restructuring of the reduced catalyst. Gai *et al.* (*18*), upon reduction of MoO_3 with propylene and hydrogen, have observed the formation of dislocations at the surface at low temperatures. Up to 380°C the surface domains grow in size and extend into the bulk as temperature increases. At about 400°C crystallographic shear planes are formed by switching from corner to edge sharing. Formation of shear planes will promote diffusion of bulk oxygen to the surface and will increase the yields of FA and DME. Thus the second peak, which corresponds to the restructuring, requires higher activation energy than the first, the surface reduction, and extends to a lower height than the first. The difference in the peak position between FA and DME implies that FA and DME are produced by different sites. This will be discussed later.

In order to study the sites responsible for the production of products, losses of the MoO_3 structural bands with respect to those of the fully oxidized state after various treatments of catalyst were observed by infrared spectroscopy, and results are shown in Fig. 6. The reaction was carried out by feeding 3.6% methanol in oxygen, followed by a purge with helium, followed by treatment in pure oxygen at each temperature. Each data point was obtained 30 min after a change in treatment condition. The results show several features. After introduction of methanol over MoO_3 at temperatures below 100°C, there is no loss of bridged oxygen in Mo–O–Mo. The appreciable loss of terminal oxygen in Mo=O when methanol is introduced and the recovery of the initial loss after a switch to helium agree with the previous observation (*14*) that methanol chemisorbs dissociatively and reversibly on terminal oxygen at low temperatures. The loss of bridged oxygen begins at 100°C and generation of oxygen vacancies increases sharply at temperatures above 150°C.

After a switch from methanol mixture to helium there are appreciable recoveries in both Mo=O and Mo–O–Mo bands. The re-

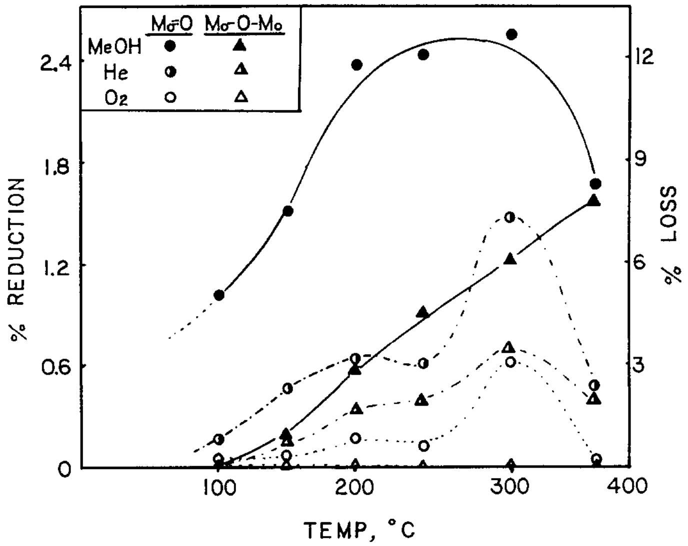


FIG. 6. The losses in structural bands of MoO_3: ●, ▲, during reaction of 3.6% methanol/oxygen; ◑, ▲, after a switch to helium; ○, △, after a switch to oxygen. Exposure time to each gas was 30 min.

covery of structural bands is also evidenced by the change of color from light yellow to yellowish-white at high temperature after the switch from methanol mixture to helium during the infrared measurements. In order to explain the results two preconditions may be needed. First the catalyst particle is reduced in a shallow depth during the reaction with methanol in oxygen. Second the Mo–O infrared bands represent the surface or subsurface properties of molybdenum oxide particles rather than the average of the whole particles. It has been shown (*17*) that the penetration depth of infrared radiation into a catalyst particle increases with frequency and that even at high frequency the penetration depth into individual molybdenum oxide particles is only a few subsurface layers when infrared radiation passes through 10 mg of the catalyst disk (order of 130 μm thickness). This is because in scattered transmission infrared radiation loses most of its intensity by the processes of Rayleigh scattering and absorption. A possible explanation for the existence of a gradient of reduction in the catalyst particle during the reaction is that methanol and oxygen do not chemisorb on the same faces of molybdenum oxide. Thus oxygen could diffuse into a particle through one face and then diffuse toward a different reactive face. Tatibouet and Germain (*12*) observed that the (010) faces of MoO_3 are responsible for the production of formaldehyde, the principal consumer of oxygen. If we assume that sites for oxygen adsorption and entrance into the lattice are on the other faces, then transport of oxygen through the crystal to the (010) faces would always require a gradient of degree of reduction. Therefore the reduced layers will be reoxidized by the diffusion of oxygen from the bulk if reactants are removed from the surface by helium.

If the catalyst is reduced in a shallow depth during the reaction the average degree of reduction based on the whole catalyst particle must be lower than the degree of surface reduction measured by structural bands. This is shown in Table 1. The average degree of reduction based either on the weight change or on the oxygen titration of reduced catalyst is substantially lower than the reduction based on Mo–O structural bands. Guidot and Germain (19) did *in situ* measurements of the X-ray diffraction

TABLE 1

Reduction State of MoO_3 after Reaction with 3.6% Methanol Mixtures for 30 min

Temp (°C)	% O_2	% Reduction based on structural bands of		% Reduction based on	
		Mo=O	Mo–O–Mo	weight change[c]	oxygen titration[d]
250	0[a]	—[e]	—	0.8	—
250	5	5.3	4.2	0.1	—
310	0[b]	—	—	2.3	—
310	5	6.8	6.4	0.24	0.28
310	18	3.7	3.0	0.12	0.14
370	5	12.7	13.8	0.42	0.5
370	18	3.6	3.6	0.15	0.16

[a,b] After being reduced for 15 and 5 min, respectively.

[c] Did not compensate for possible chemisorbed species on the catalyst during the reaction.

[d] Oxygen was titrated by introduction of oxygen pulses at 450°C. The reduced catalyst was purged with helium for 5 min at reaction temperature before temperature was raised to 450°C.

[e] —, not measured.

pattern of MoO_3 during oxidation with 3.6% methanol/18% oxygen at 380°C. They found that there was no change in the bulk structure. From the results in Table 1 the surface reduction is about 4%, but the bulk reduction is less than 0.2%. The Mo_9O_{26} reference whose structure is detectable by X-ray is in a uniform degree of reduction of 3.4% and shows gray–blue color. Therefore, for the partly reduced sample the surface reduction of 4% will show blue color, but X-ray diffraction pattern does not show any change in the bulk structure because the average reduction of 0.2% is far less than the 3.4%.

From Fig. 6 we see that at 370°C a switch from the somewhat reducing reaction mixture of 3.6% methanol in oxygen to helium results in reoxidation, as the reduction of the surface falls from 1.6 to 0.4%. The color changes from light yellow to yellowish-white (from blue to light yellow when 3.6% methanol/18% oxygen/helium is employed during the reaction). However, during this process there is no weight change. Therefore, the working catalyst was reduced principally in the surface layers, and when the reaction was quenched, oxygen diffused from the interior to reoxidize the surface to a large degree. The catalyst which had been reacted and then purged with helium was finally subjected to an oxygen environment. As shown in Fig. 6, the lost sites of Mo–O–Mo are recovered almost completely, but the lost sites of Mo=O cannot be oxidized easily until the temperature goes up to 380°C. In general the oxygen vacancies of Mo–O–Mo are oxidized more easily than those of Mo=O when molybdenum oxide is reduced in a small degree without any kind of restructuring or formation of slip planes. The catalyst in Fig. 6 was reduced with a high concentration of oxygen (3.8% methanol plus the balance as oxygen) in the reaction mixture. If, however, the oxygen concentration used is 18% during the reaction, the reoxidation of reduced sites of Mo–O–Mo is not always easier than those of Mo=O especially if restructuring has occurred during the reaction. This is shown in Fig. 7 at temperatures between 170 and 220°C. Thus the peak for the reduced sites of Mo–O–Mo does not correspond to the individual oxygen vacancies but to the loss of the oxygen vacancy by the restructuring. Dislocations or changes from corner to edge sharing will

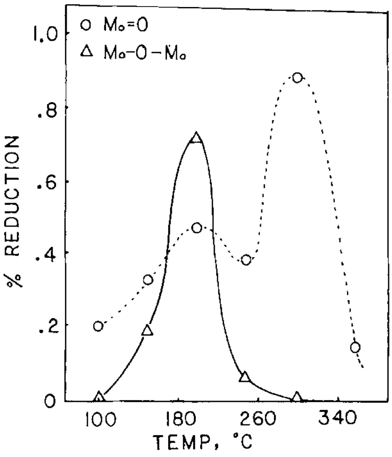


FIG. 7. The losses which remain in structural bands of MoO_3 after a switch to oxygen: before the switch to oxygen the catalyst was reacted with 3.6% methanol/10% oxygen/helium, followed by a purge with helium. Exposure time to each gas was 30 min.

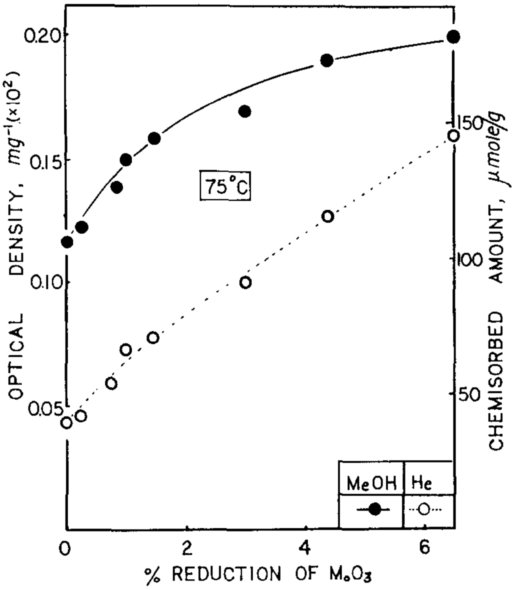


FIG. 8. Effect of reduction state of MoO_3 on chemisorption of methanol at 75°C: ●, adsorption after exposure to 3.6% methanol in helium; ○, remaining adsorption of methanol after a helium purge of 10 min.

occur along the oxygen vacancies of Mo–O–Mo. The oxygen vacancies of Mo═O are at protruding positions and will not be lost by minor changes in structure. Here the change in the structure should be limited at the surface because the results in Fig. 5 have shown that restructuring into the bulk occurs at temperatures higher than 230°C. After there is once a change in the structure, oxidation of the collapsed defects (the loss of Mo–O–Mo band) requires higher activation energy than oxidation of individual oxygen vacancies of Mo═O. Reoxidation of the collapsed defects occurs at temperatures higher than 220°C.

The effect of catalyst reduction on the amount of chemisorbed methanol is studied at 75°C as shown in Fig. 8. At this temperature there is no generation of oxidized products by reaction between adsorbed methanol and lattice oxygen (*14, 20, 21*). The reduced molybdenum oxide is obtained by repeated reduction with methanol in helium which is followed by a helium purge at 250°C. Then the sample is cooled down quickly to 75°C for the chemisorption experiment. The results show that the chemisorption of methanol is greatly affected by the electronic state of the catalyst surface. As the reduction of MoO_3 increases, the fraction of irreversibly held methanol increases while that held reversibly decreases.

DISCUSSION

Infrared study (*14, 15*) has revealed methoxy groups chemisorbed on two different types of oxygen vacancy; one is a terminal oxygen vacancy in Mo═O (V_t) and the other is a bridged oxygen vacancy in Mo–O–Mo (V_b). Each vacancy (V_t and V_b) can be divided into three different types depending on the electronic state of the surface,

$$V \xrightarrow{+e} V^- \xrightarrow{+e} V^{2-}.$$

A high degree of reduction favors the formation of a reduced vacancy with more electrons trapped because of a narrower band gap between the conduction band and the Fermi energy level.

For methoxy chemisorbed on an oxygen vacancy, there are three types of bond: bonds between C and H, between C and O, and between O and V. Here V represents the oxygen vacancy site, either V_t or V_b. Previous study (*15*) has shown that the bond strength of C–H decreases with the reduction of the vacancy (with more trapped electrons or more acidic vacancy). It was not possible to measure the bond strength of C–O because, during infrared measurement, there was severe interference in the CO stretching bands from structural bands of molybdenum oxide. The data in Table 2 show the frequencies of the CO stretching bands of methoxy groups which have been observed on other oxides. The ϕ in the table was defined previously (*15*) and it represents the acidity of metal cation (oxygen vacancy with less trapped electrons). The data in Table 2 show generally the strengthening of the C–O bond with decreased ϕ, although there is a large devia-

TABLE 2

Observed Frequencies of the CO Stretching Band of Methoxy on Metal Oxides

Metal oxide	ϕ	cm^{-1}	Reference
MgO	0.11	1080	(*22*)
Cr_2O_3	0.45	1085	(*23*)
γ-Al_2O_3	0.67	1030	(*24*)
TiO_2	0.82	1060	(*25*)
$Ge(OCH_3)_4$	1.51	(1040)[a]	(*26*)

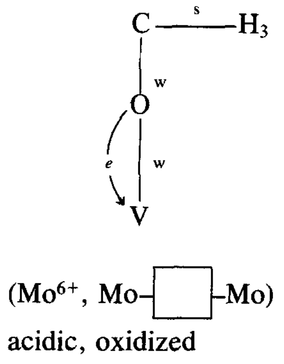
Note. The ϕ was defined previously (*15*); $\phi = (I_p)(Z^2/R^3)^{3/4}/1000$, where Z is the cation charge, I_p is the ionization potential (in volts), and R is the radius (Å) of the metal ion with cation charge Z.

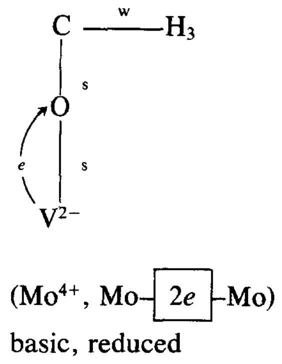
[a] For methoxide compound.

tion with alumina which is known to be an active catalyst for the dehydration reaction (C–O bond breaking). Thus more reduced vacancies will make the C–O bond of methoxy on molybdenum oxide stronger.

During chemisorption of methanol there may be an electron transfer between the methoxy group and the catalyst. We monitored the intensity of infrared background transmission through molybdenum oxide during the chemisorption measurements in order to observe any change in the electronic state of the catalyst. Recently there have been indications that, upon adsorption or reaction on semiconductor oxides, the intensity change of infrared background transmission is related to the change in the concentration of free electrons in the conduction band of the oxide (*28, 29*). For example, increased free electrons of a reduced *n*-type oxide absorb infrared radiation and reduce the intensity of background transmission. But a *p*-type oxide behaves in the opposite way; formation of free holes after reduction increases the intensity of background transmission. Figure 9 shows the intensity change of the background transmission upon adsorption of methanol on molybdenum oxide. The frequency at 2500 cm^{-1} was chosen as a level where there was no specific absorption band from either chemisorbed methanol or the MoO_3 structural bands. On the full oxidized MoO_3 the adsorption of methanol decreases the background intensity. This shows us that when methanol is adsorbed there is a donor type of electron transfer from adsorbed methanol to *n*-type MoO_3. However, adsorptions on partially reduced catalysts show an acceptor type of electron transfer from the catalyst to methanol.

With results discussed so far we can compare the relative strength of each bond and direction of electron flow when methanol is adsorbed on the two extreme sites of oxygen vacancies,

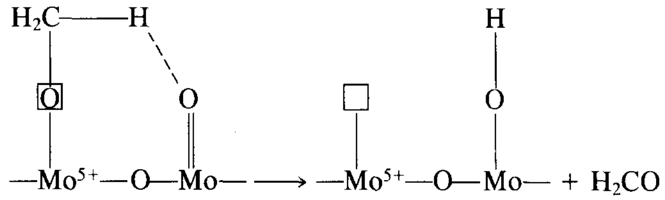




Here the symbol "s" means strong bond and "w" means weak bond in a relative scale. The arrow indicates the direction of electron flow. The CO bonding in methoxy chemisorbed on Mo^{6+} is not actually weak enough to produce dehydration products owing to the weak bonding of VO. This is supported by the fact that methoxy on

Mo^{6+} desorbs as methanol with a peak maximum at 110°C (*14*) during the temperature-programmed desorption, while methoxy groups on other oxides (*24, 27, 30*) remain even at 250–400°C.

The methoxy on less acidic Mo^{5+} (V_t^-) produces formaldehyde owing to the moderate bond strength in the VO and CH, and the previous study (*15*) shows that the most abundant species at reaction temperatures above 150°C is methoxy chemisorbed on Mo^{5+}, a terminal oxygen vacancy in Mo=O with one electron trapped. The methoxy now requires oxygen to produce formaldehyde. This oxygen can be provided by terminal oxygen in Mo=O,



$$-\mathrm{Mo}^{5+}-\mathrm{O}-\mathrm{Mo}- \longrightarrow -\mathrm{Mo}^{5+}-\mathrm{O}-\mathrm{Mo}- + \mathrm{H_2CO}$$

Therefore multifunctionality of both acidic (oxygen vacancy) and basic (oxygen) sites is required to produce formaldehyde.

There is a high probability of CO production by the methoxy on the most reduced Mo^{4+} because of the weak CH bond and the strong chemisorption bond. A catalyst after about 1 month of everyday use, in an oxygen-poor atmosphere (1–3%) and with incomplete oxidation, was identified as mostly MoO$_2$ by X-ray diffraction analysis.

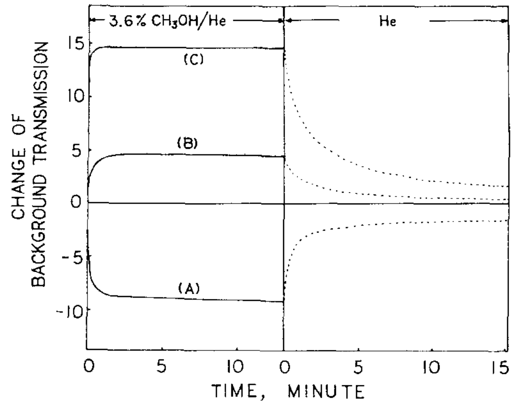
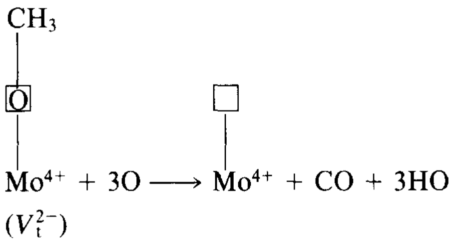


Fig. 9. Effect of the initial reduction state of MoO$_3$ on the change in the background transmission upon adsorption and desorption of methanol on molybdenum oxide at 75°C: (A) fully oxidized MoO$_3$, (B) 1.8% reduced, (C) 3.3% reduced. The zero point on the ordinate refers to the conditions of (A), (B), or (C) just before exposure to the 3.6% methanol in helium. The unit of background intensity has an arbitrary scale.

Activity measurements with the catalyst showed good activity but poor selectivity. The major products were CO and CO$_2$ at test temperatures of 523–553 K,

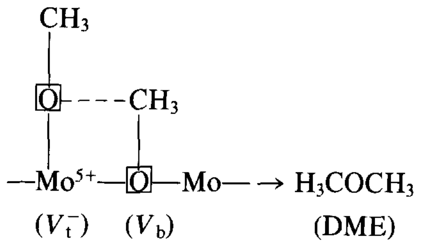


$$\mathrm{Mo}^{4+} + 3\mathrm{O} \longrightarrow \mathrm{Mo}^{4+} + \mathrm{CO} + 3\mathrm{HO}$$

(V_t^{2-})

If we consider geometric effects near the oxygen vacancy, the formation of the high-order products may proceed with the methoxy on bridged oxygen vacancies in Mo–O–Mo. When methanol chemisorbs on the V_b sites, neighboring oxygen on V_t is at such a position that it interacts easily with the carbon in the methoxy on V_b. This weakens the CH bond and enhances breaking of the CO bond in the methoxy on V_b. The production of higher order products can be achieved when the methoxy on V_b is combined with that on V_t in a specific configuration.

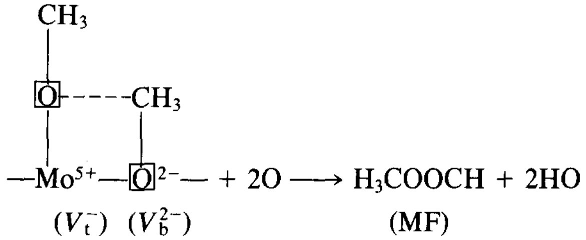
The electronic state on a bridged oxygen vacancy will affect the chemisorption of methoxy in a manner similar to that for a terminal oxygen vacancy. The methoxy on an oxidized V_b has a relatively stronger CH bond than that on a reduced V_b and will produce less hydrogen-abstracted product (for example, dimethyl ether) after combination with the methoxy on V_t,



$$\underset{(V_t^-)}{-\mathrm{Mo}^{5+}}-\underset{(V_b)}{\boxed{\mathrm{O}}}-\mathrm{Mo}- \rightarrow \underset{(\mathrm{DME})}{\mathrm{H_3COCH_3}}$$

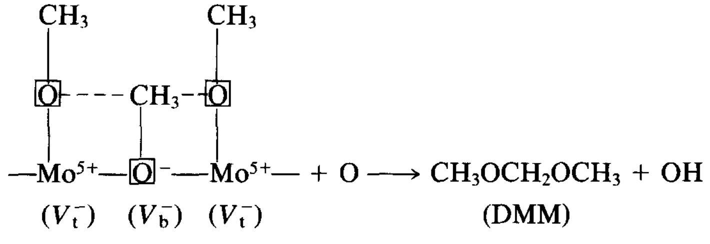
Now we can explain the results in Fig. 5. At the beginning of reduction the terminal oxygen vacancies are generated from the labile surface oxygen in Mo=O, and these vacancies produce formaldehyde. This is followed by the generation of bridged oxygen vacancies, as reduction proceeds, to produce dimethyl ether. The production of both formaldehyde and dimethyl ether will decrease as the surface oxygen decreases. Further reduction of the surface will develop crystallographic shear planes into the bulk. The process facilitates the diffusion of oxygen from the bulk, showing the appearance of the second peaks. Further reduction results in the structural change from corner to edge sharing. The change removes individual bridged oxygen vacancies, and the formation of dimethyl ether must decrease to show the second peak in Fig. 5. Oxygens still available from the bulk increase the formation of formaldehyde after the disappearance of dimethyl ether, showing the second peak for formaldehyde right after that for dimethyl ether.

Methyl formate will be produced by the most basic site of V_b^{2-} on which the CH bond in methoxy becomes weakest and the CO bond is strongest to yield methylene (HCO–). This is why the selectivity of methyl formate is appreciable only when the catalyst is severely reduced as shown in Fig. 3. The chemisorption bond of methylene (HCO) on V_b^{2-} is very strong, and the previous study (*21*) shows that the chemisorbed methylene remains on the surface even at 400°C after a purge with helium,



$$\underset{(V_t^-)}{-\mathrm{Mo}^{5+}}-\underset{(V_b^{2-})}{\boxed{\mathrm{O}}^{2-}}- + 2\mathrm{O} \longrightarrow \underset{(\mathrm{MF})}{\mathrm{H_3COOCH}} + 2\mathrm{HO}$$

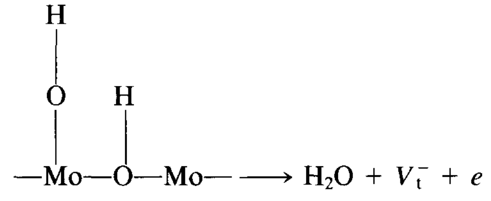
The formation of dimethoxymethane requires a combination of methoxy on V_b with two methoxy groups on V_t. It is difficult to obtain this kind of specific configuration unless methoxy on V_t^- exists abundantly in the neighborhood of the methoxy on V_b^-. This is probably the reason why the selectivity of DMM in Fig. 3 shows a maximum at much lower temperatures than those of DME or MF,



$$\underset{(V_t^-)}{-\mathrm{Mo}^{5+}}-\underset{(V_b^-)}{\boxed{\mathrm{O}}^-}-\underset{(V_t^-)}{\mathrm{Mo}^{5+}}- + \mathrm{O} \longrightarrow \underset{(\mathrm{DMM})}{\mathrm{CH_3OCH_2OCH_3}} + \mathrm{OH}$$

This model agrees with the result in Fig. 3 where the formation of high-order products shows a maximum as a function of reaction temperature since the generation of shear planes at high temperatures reduces the concentration of oxygen vacancy sites of Mo–O–Mo. The oxygen vacancy sites of Mo=O are hardly affected by the restructuring because they are at protruding terminal positions. Therefore, as shown in Fig. 2, the formation of formaldehyde, CO, or CO_2 does not show any maximum in selectivity as a function of temperature because they are not produced from the methoxy on V_b but from that on V_t. The effect of the electronic state of the oxygen vacancy is tested by poisoning experiments done with pyridine and formic acid. Molybdenum oxide poisoned by pyridine showed an increased selectivity to the formation of formaldehyde and a decreased selectivity to the formation of dimethyl ether, while the catalyst poisoned by formic acid showed opposite effects on the selectivities to the formation of formaldehyde and dimethyl ether. Pyridine will poison the most acidic sites such as oxidized V_t or V_b diminishing the formation of dimethyl ether on V_b, while formic acid will poison basic (less acidic) sites such as V_t^- and V_b^- diminishing the formation of formaldehyde on V_t^-.

For the production of water, we suggest that it proceeds by the combination of surface hydroxyl groups which are formed by the abstraction of hydrogen from chemisorbed methanol. It is known that a hydroxyl group chemisorbed on V_b is much stronger than that on V_t (*14*). Thus desorption of water will generate the vacancy V_t, rather than V_b,



$$\text{—Mo—}\overset{\overset{\displaystyle H}{|}}{\underset{}{O}}\text{—}\overset{\overset{\displaystyle H}{|}}{O}\text{—Mo—} \longrightarrow H_2O + V_t^- + e$$

The oxygen vacancy V_t^- is reoxidized by gas-phase oxygen or by the diffusion of lattice oxygen on V_b, probably the latter being a more favorable process since a bridged oxygen vacancy is oxidized more easily than a terminal oxygen vacancy,

$$Mo^{5+}(V_t^-) + OV_b + e \rightarrow Mo{=}O + V_b^{2-}$$

Gas-phase oxygen oxidizes the reduced oxygen vacancy, V_b^{2-},

$$V_b^{2-} + \tfrac{1}{2}O_2 \rightarrow OV_b$$

Therefore the combination of V_t^-/V_b^{2-} may be called a reduction–oxidation couple for the methanol oxidation reaction on molybdenum oxide which occurs by the typical redox mechanism. The type of oxygen which participates in the reaction is not clear. Oxygen isotopic experiments for the reaction have proved the participation of lattice oxygen from the bulk (*30*). The present study shows that only the shallow surface layers are reduced with a large unreduced core at steady state. This indicates that the catalyst faces where methanol chemisorbs are different from the faces where oxygen chemisorbs.

CONCLUSIONS

The oxidation of methanol on molybdenum oxide can be represented by a mechanism involving methoxy as reaction intermediate and oxygen vacancies as active sites. The chemisorption of methoxy on an oxygen vacancy is greatly influenced by geometric and electronic factors. Formaldehyde and CO are produced mainly from methoxy on terminal oxygen vacancy sites. Bridged oxygen vacancy sites are responsible for the formation of high-order products (dimethyl ether, dimethoxymethane, and methyl formate). Reduced oxygen vacancy sites weaken the CH bond but strengthen the CO and chemisorption bonds in chemisorbed methoxy, and this results in the formation of more hydrogen-abstracted products. During the reaction, the terminal oxygen vacancy is more abundant than the bridged oxygen vacancy because the bridged oxygen vacancy is reoxidized more easily than the terminal oxygen vacancy.

Thus high oxygen concentrations in the feed or the formation of shear planes along bridged oxygen vacancies at high temperatures reduces the formation of the high-order products.

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