

Selective oxidation of methanol on iron molybdate catalysts and the effects of surface reduction

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Abstract

The reaction and reduction of an iron molybdate catalyst (Mo:Fe = 2.2:1) with methanol was studied with a pulsed-flow reactor, temperature-programmed desorption (TPD), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The first pulse of methanol under anaerobic conditions shows similar conversion and selectivity to formaldehyde as in aerobic conditions, indicating that gaseous oxygen is not directly involved in the reaction but is used instead to reoxidize the catalyst surface. With further reduction at low temperature (under 250 °C) under anaerobic conditions, conversion of the catalyst drops to zero, due to the loss of a significant amount of surface oxygen. In contrast, at elevated temperatures (at or above 250 °C) oxygen migration occurs through the catalyst so that oxidative products are still formed, and many monolayer equivalents of lattice oxygen are used. The process of oxygen migration leads to the formation of new phases of α -FeMoO₄, MoO₂, and Mo₄O₁₁. The selectivity of the catalyst during reduction is initially changed toward CO, but, rather surprisingly, with further reduction above 300 °C it shifts toward CO₂, which indicates the appearance of iron oxide at the catalyst surface.

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1. Introduction

An excellent review covering various aspects of methanol oxidation on iron molybdates was recently published by Soares et al. [1]; the reader is directed there for a comprehensive review of this system. It is estimated that formalin production is around 20 Mton a year (when measured as 37 wt% formaldehyde in water), and two main processes are currently used. The older method is through dehydrogenation of methanol over a silver catalyst. The more recent process, originally discovered by Adkins in 1931 [2], involves the oxidative dehydrogenation of methanol over an iron molybdate catalyst.

The mechanism of formaldehyde production is believed to follow that of Mars and van Krevelen, with the role of gaseous oxygen thought to be to reoxidize the catalyst surface after its reduction by oxidizing the methanol [3,4]. Bowker et al. studied

the selective oxidation of methanol to formaldehyde on Fe₂O₃, MoO₃, and an industrial iron molybdate catalyst [5]. In TPD, the molybdenum-containing compounds showed formaldehyde as the only carbon-containing compound, arising from the decomposition of a surface methoxy species. In contrast, Fe₂O₃ was a combustor of methanol, yielding only CO₂ and H₂, indicating the presence of a formate species as the major surface intermediate. Pulsed-flow reactor studies showed that methanol conversion for the industrial catalyst was >90% by 240 °C and that formaldehyde selectivity was >80%. The iron molybdate catalyst was more active than molybdenite alone, with conversion beginning at 150 °C for the former and at 270 °C for the latter. This work led to a proposed energy profile for the reaction showing an energy barrier of 132 kJ mol⁻¹ to the rate-determining step of hydrogen abstraction from the adsorbed methoxy species.

The main objective of this work was to study the process of the reduction of iron molybdate catalysts as the anaerobic reaction proceeds, and to determine the extent of reduction and its temperature dependence.

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2. Experimental

A mixed-phase catalyst of iron molybdate with an excess of molybdenite (25.9% by weight) was prepared by acidification of a solution of ammonium heptamolybdate (BDH, $\geq 99\%$) to pH 2 using nitric acid (Fisher, laboratory grade), before the dropwise addition of iron nitrate (BDH, $\geq 98\%$) with stirring at 60 °C. This led to the formation of a canary yellow precipitate, which was then heated to near dryness at 90 °C. The resulting solid was dried at 120 °C overnight before being calcined in air at 500 °C for 48 h. As shown by XRD and reported in more detail below, the catalyst comprised two phases, ferric molybdate and molybdenite, as could be expected from the stoichiometry of the catalyst, which was Mo:Fe 2.2:1, compared with ferric molybdate at 1.5:1.

The pulsed-flow microreactor allows for the examination of industrially important catalytic reactions on a small scale and can provide kinetic and mechanistic data, and has been described in detail elsewhere [6,7]. The reactor consists of a stainless steel U-tube (6 mm o.d., 4 mm i.d.) mounted vertically in a GC oven that can be held at constant temperature or ramped between two temperatures at a constant rate before product monitoring on a mass spectrometer. First, 0.5 g of catalyst is loaded into the tube. Several gases may be passed over the catalyst bed; for example, two gases, a diluent gas (helium) and a dosing gas, can be flowed continuously, and a third gas can be introduced by means of a pulsing valve. Further gases or liquids (in this case methanol) can be injected through a septum assembly, and continuous flow conditions can be introduced here by means of a syringe pump.

All gases were supplied by BOC Ltd with a purity of $\geq 99.5\%$ and were passed through Puritubes (Phase Separation Ltd.) filled with 5 Å molecular sieves to remove carbon dioxide and water. Gas flows were controlled by mass flow controllers (Brookes 5850TR series), allowing flow rates of the gases to be controlled within 0.1 mL min⁻¹, and were calibrated using a bubble flow meter. After flowing over the catalyst bed, the reactants and products flowed down a heated capillary line. The flow of gas to the capillary line was controlled by a needle valve, with most of the gas then vented by a rotary pump, allowing a small fraction to be bled into the UHV chamber containing the mass spectrometer (Hiden Analytical quadrupole Hal 201), which was computer-controlled and displayed results in real time. To account for sensitivity drift within the mass spectrometer, pulses of methanol were passed through the bypass before each run. Reagent conversions and product selectivities were calculated from the product distributions. To accurately measure the temperature, a thermocouple was inserted into the catalyst bed.

Catalysts were subjected to pulsed reduction at various temperatures while the activity and selectivity were monitored. To establish the aerobic ability of the catalyst, 1- μ L injections of liquid methanol were passed over the catalyst every 2 min, in a flow of 30 mL min⁻¹ 10% O₂/He, while the temperature was ramped to ~ 400 °C at a rate of 8 °C min⁻¹. For the reduction experiments, the catalysts were held isothermally with 1- μ L liquid methanol injections every 2 min in a flow of 30 mL min⁻¹

He, except in the case of extended reduction, in which 3- μ L injections were made every 2 min. The TPD experiments were made by saturating the surface with methanol injections at room temperature in a flow of 30 mL min⁻¹ He before the catalyst temperature was ramped at a rate of 12 °C min⁻¹.

In the TPD data displayed here, the contributions to the 30-amu formaldehyde signal by methanol was corrected for methanol cracking and reaction on the mass spectrometer filament. Similarly, the 44-amu signal for carbon dioxide was corrected for the combustion of methanol and formaldehyde on the filament, and the 28-amu signal of carbon monoxide was corrected for methanol and formaldehyde cracking and reaction, as well as CO₂ cracking. The levels of these contributions were estimated by a series of calibrations in which pure gas, or vaporized liquid in the case of formaldehyde, was passed over the catalyst bypass. A similar procedure was followed for determining the conversion–selectivity plots.

The oxygen removed from the catalyst was calculated from the total yield of all products, making use of the number of oxygen atoms removed for each product molecule as follows: H₂, 0; H₂O, 1; CO, 0; H₂CO, 0; CO₂, 1; and CH₃OCH₃, -1. Oxygen removal was calculated by multiplying the amount of a product formed by the amount of oxygen required to form it and totalling these values. The resulting value was converted into a percentage of the total oxygen by assuming that all of the iron in the catalyst formed Fe₂(MoO₄)₃, whereas the excess molybdenum formed MoO₃. The monolayers of oxygen removed were calculated by assuming each monolayer contained 10¹⁹ m⁻² of oxygen atoms, which is a typical value for surface adatom concentrations.

The XRD spectra were obtained using a Enraf Nonus FR590 diffractometer fitted with a hemispherical analyzer, using CuK α radiation ($\lambda = 1.540598$ Å), with a voltage of 40 kV and a current of 30 mA. The XPS spectra were obtained using an ESCALAB 220 spectrometer equipped with AlK α and MgK α sources and fitted with a fast entry lock for easy sample loading. For this study, AlK α (1486.6 eV) irradiation was used, so that the Fe Auger peaks would not overlap with the Fe 2p_{1/2} and Fe 2p_{3/2} peaks.

The surface area of the catalyst was measured using a Micromeritics Gemini 2360 instrument and was found to be 6.7 (± 1) m² g⁻¹.

3. Results and discussion

3.1. Selective oxidative dehydrogenation of methanol

Fig. 1 shows a temperature-programmed pulsed-flow reaction profile for the iron molybdate catalyst in 10% O₂/He; a wider temperature range is shown in supplementary data Fig. S1. Such raw data were obtained for other experiments in this paper but usually are not given for the sake of brevity and clarity. Clearly, formaldehyde selectivity was always high; for instance, as shown in Fig. 1, after 48 min at 250 °C, methanol conversion was close to 100%; note the near-zero 31-amu signal, compared with the high (30-amu) formaldehyde signal. The reaction started below 150 °C, with methanol conversion

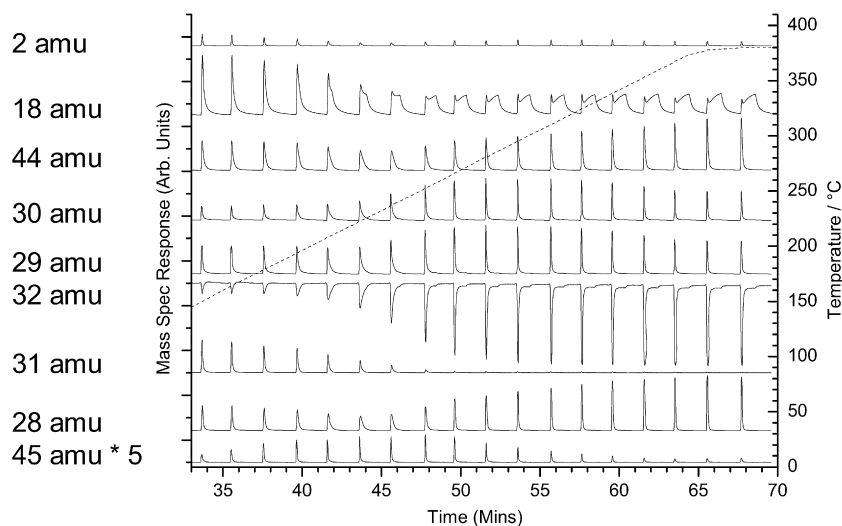


Fig. 1. Temperature-programmed pulsed-flow reaction of methanol and oxygen over the mixed phase catalyst. The data lines are the masses and the dashed line is temperature ($^{\circ}\text{C}$).

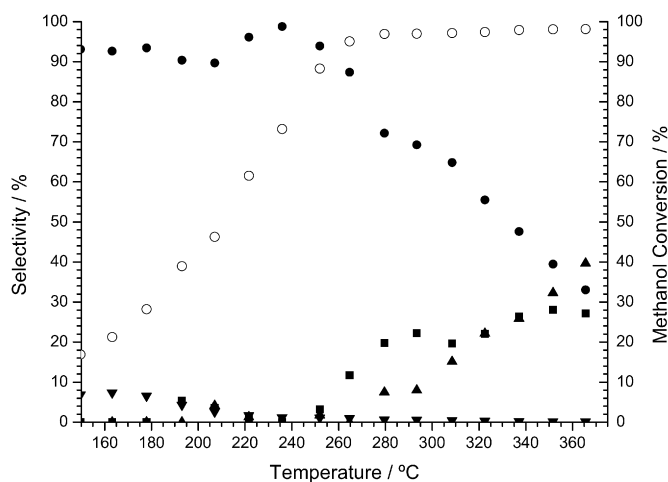


Fig. 2. Selectivity and conversion of methanol over the mixed phase catalyst in a flow of 10% O_2/He . (●) Formaldehyde, (■) carbon monoxide, (▲) carbon dioxide, (▼) dimethyl ether, and (○) methanol conversion.

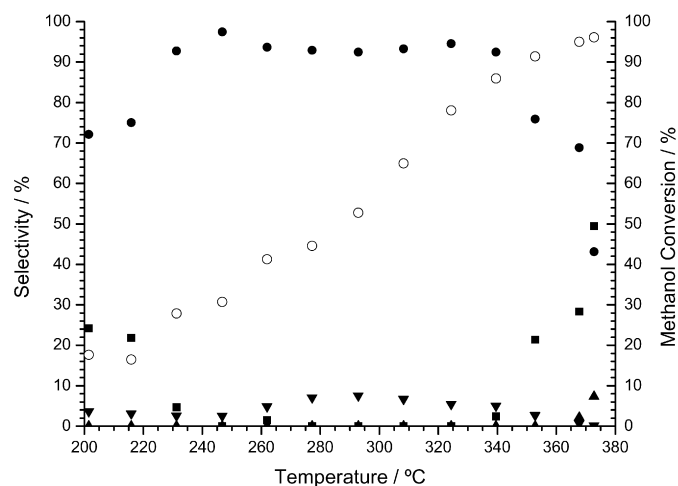


Fig. 3. Selectivity and conversion of methanol over the mixed phase catalyst in a flow of He. Symbols as in Fig. 2.

complete by 270°C ; the formaldehyde selectivity was high ($>90\%$) up to about 260°C (Fig. 2). CO production began at around 250°C and reached an approximate 25% selectivity by 370°C . CO_2 production began at around 270°C and reached $>40\%$ selectivity by 370°C . Dimethyl ether was a minor product that occurred in the greatest quantities at low temperatures; at 180°C , selectivity to dimethyl ether was $\sim 7\%$, whereas the conversion of methanol was 20%. Thus, this catalyst shows high selectivity for formaldehyde up to very high conversions. In what follows, we report the behavior of the catalyst in the absence of oxygen to gain insight into how the removal of surface oxygen from the oxide affects the reactive properties of these methanol oxidation catalysts.

3.2. Anaerobic oxidation of methanol

3.2.1. Pulsed flow reactor measurements

The pulsed-flow TPR profile for the catalyst in methanol/He alone is shown in supplementary data Fig. S2. The activity of

the catalyst decreased from 100% conversion at 250°C in aerobic conditions (Fig. 1) to ca. 40%, even though the formaldehyde selectivity remained high throughout the course of the reaction. There was a much higher yield of the minor product dimethyl ether that peaked at higher temperatures. The conversion/selectivity plot in Fig. 3 shows the decreased catalyst activity more clearly, with 50% conversion reached at 290°C and 90% conversion achieved by 350°C . The dominant product throughout was formaldehyde, with $>80\%$ selectivity up to 350°C . The selectivity to carbon monoxide was negligible up to 340°C , after which it rose rapidly to around 50% by 375°C . The selectivity to dimethyl ether rose from 5% at 230°C to a peak of 9% at 290°C .

When the mixed-phase catalyst was subjected to pulses of methanol in anaerobic and isothermal conditions at 200°C (not shown), the first pulse produced formaldehyde with a selectivity of close to 100% with methanol conversion of ca. 30%. The methanol conversion rapidly decreased, and after 5 μL of

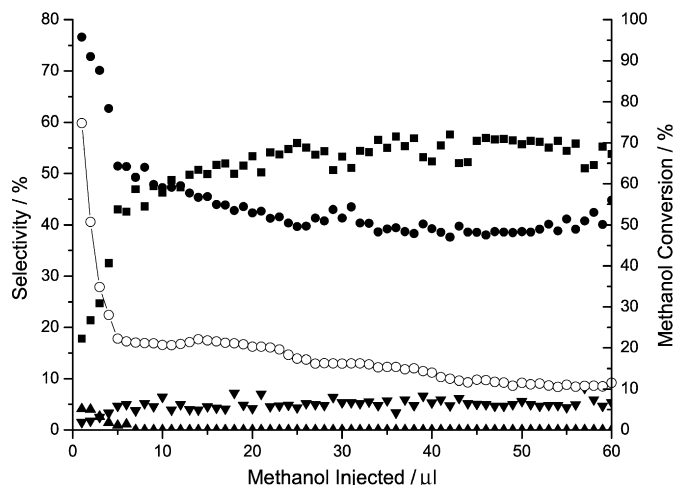


Fig. 4. Selectivity and conversion of methanol over the mixed phase catalyst in a flow of He at 250 °C. Symbols as in Fig. 2.

methanol was passed over the surface, the catalyst showed no activity for methanol conversion.

At 250 °C (Fig. 4), the catalyst activity dropped rapidly, with conversion decreasing from ca. 70% for the first injection to ca. 20% after the sixth pulse. Methanol conversion continued to drop slowly, reaching around 10% after 60 μL of methanol was passed over the surface; nonetheless, the catalyst continued to oxidize methanol for a long time. The selectivity of the catalyst to formaldehyde decreased from ~80% in the first pulse to around 40% after 15 injections, after which it remained reasonably stable. The drop in formaldehyde selectivity was mirrored by the rise in CO production, from ~15% in the first injection to around 50% after 15 pulses. Dimethyl ether selectivity rose from around 2% to around 5% over the first five injections. A small amount of CO₂ was produced initially (around 3% selectivity), but this declined, so that after the fifth injection, no CO₂ was produced. Fig. 5 shows the profile for water evolution, which continually diminished during the course of the experiment as the conversion decreased.

Analogous experiments performed at 275, 300, 330, and 350 °C are described in the supplementary data (Figs. S2a–S2d). These figures have the same general features. Methanol conversion first decreased, but then increased with further reduction, except at the highest temperatures (330 and 350 °C), where conversion remained near 100% throughout. At the lower temperatures, there was a continuous decrease in formaldehyde production, with an increase in CO. At the higher temperatures, CO₂ was formed as the reduction proceeded, at the expense of CO production.

Comparing the first pulse under anaerobic conditions with those under aerobic conditions demonstrates somewhat reduced activity with generally increased selectivity (Table 1). The changes were small and were likely caused by the loss of O at the surface, which is not replaced during the pulse duration. This slight difference compares well with what would be expected, because small injections (0.1 μL) at room temperature have demonstrated that the mixed-phase catalyst is capable of adsorbing 0.73 μL of methanol, equivalent to about

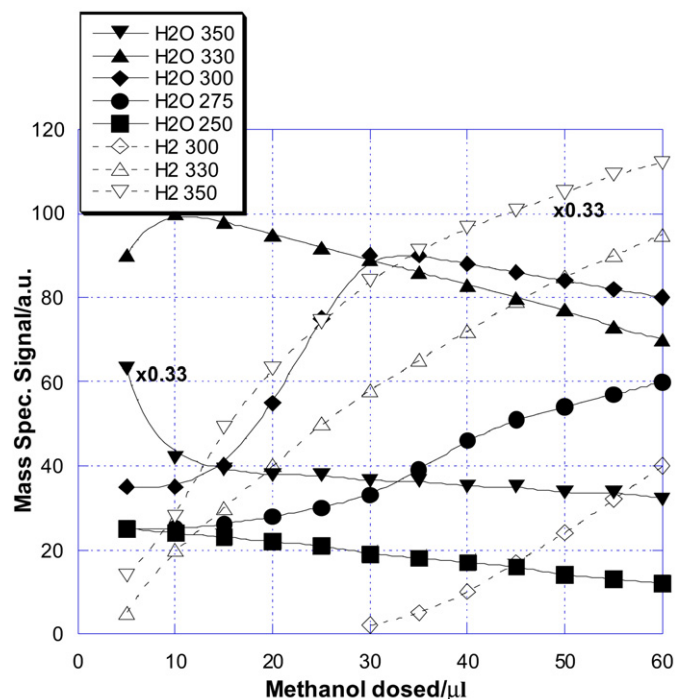


Fig. 5. The evolution of water and hydrogen during the course of the reactions in Fig. 3. All are on the same scale, except for the data at 350 °C, which involves larger doses of 3 μL of methanol per pulse, and so, to fit the data on scale the y-axis is divided by 3, and the x-axis is divided by 6 (that is, 60 μL is actually 360 μL). Data are not shown for H₂ evolution below 300 °C, since very little hydrogen was evolved.

Table 1

Activity and selectivity of catalyst in temperature programmed aerobic conditions compared those for temperature programmed anaerobic conditions and to the first pulse isothermal anaerobic conditions

		Temperature (°C)				
		200	250	275	300	330
Temperature programmed Aerobic	Conversion (%)	40	88	97	97	98
	Selectivity (%)	77	90	71	66	50
Temperature programmed Anaerobic	Conversion (%)	17	32	45	58	81
	Selectivity (%)	70	90	82	82	85
Isothermal Anaerobic	Conversion (%)	27	75	90	95	89
	Selectivity (%)	96	84	83	87	57

0.5 monolayers of surface atoms. TPR under anaerobic conditions showed a considerable reduction in conversion compared with aerobic conditions, and, as a result, an increased selectivity at high temperatures. These differences also are likely caused by surface oxygen availability, because the aerobic TPR experiment can use gas-phase oxygen to replace that lost from the surface. The increase in selectivity to formaldehyde under aerobic conditions (for the first few pulses) can be linked to the high oxygen demand of the unselective products CO and CO₂.

3.2.2. Temperature-programmed desorption

The TPD profile from the mixed-phase catalyst (Fig. 6A) shows a broad low-temperature methanol desorption centered at 130 °C, followed by a large formaldehyde desorption peak centered at 175 °C. A double peak in water desorption can

be seen at 90 and 190 °C. When TPD was carried out on the catalyst reduced at 330 °C by 60 μ L of methanol (Fig. 6B), a very broad methanol desorption feature occurred, peaking at ca. 90 °C. The formaldehyde peak shifted to a higher temperature of around 200 °C and was reduced in intensity. There was now a large CO desorption peak at 250 °C, together with near-coincident hydrogen and CO₂ peaks at about 295 °C. The water trace again exhibited a double peak, first at 90 °C and then at 240 °C. These TPD data suggest the presence of methoxy species on the catalyst (yielding the formaldehyde peak at 175 °C) and a combination of methoxy and formate species (with the latter responsible for CO₂/H₂ production [5]) on the reduced catalyst. The methoxy species, yielding only formaldehyde, were also observed on MoO₃ [5,8,9], whereas formate species, yielding only CO₂ and H₂, could be seen on

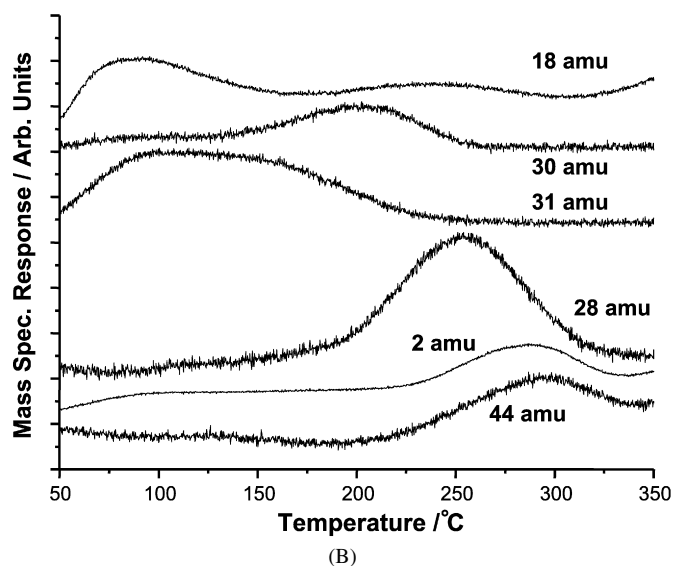
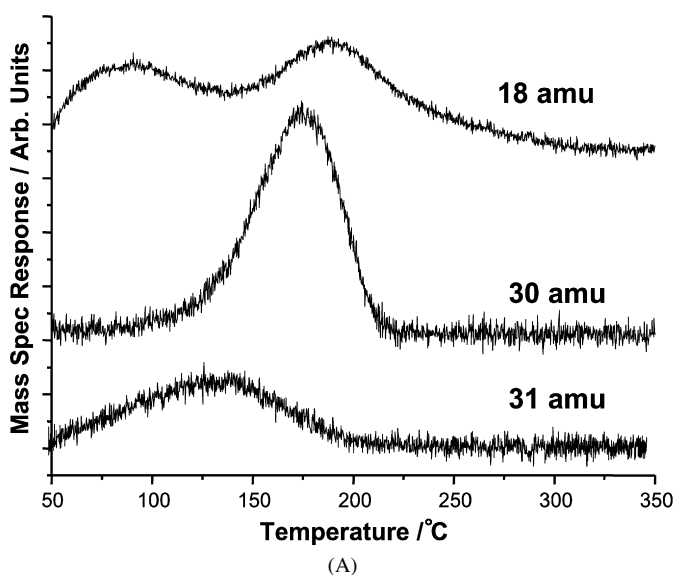


Fig. 6. (A) Temperature-programmed desorption from fresh mixed phase catalyst: (a) mass 18 water $\times 0.2$, (b) mass 30 formaldehyde, (c) mass 31 methanol. (B) Temperature-programmed desorption from mixed phase catalyst reduced with 60 μ L methanol at 330 °C. Labels as in (A), except (d) mass 28 carbon monoxide, (e) mass 2 hydrogen $\times 0.2$, and (f) mass 44 carbon dioxide.

Fe₂O₃ [5]. The methoxy may be rate-limited in its decomposition by dehydrogenation at the methyl group; this step is often cited as the rate-limiting step in formaldehyde synthesis. The source of CO after reduction is likely one of the reduced phases that may be formed (see below). Indeed, preliminary experiments with MoO₂ samples have revealed predominately CO production with little evidence of formaldehyde in TPD. It is not yet clear which kind of species (methoxy or formate) is the source of CO, but we believe that it may be a methoxy associated with isolated Mo sites.

3.2.3. X-ray diffraction measurements

Fig. 7a shows the X-ray diffractogram of the prereactor catalyst, which demonstrates that the synthesized catalyst contained only phases of molybdenite [10] and ferric molybdate (Fe₂(MoO₄)₃) [11], as reported elsewhere [12]. After methanol reaction at 200 °C, no significant bulk change occurred, whereas at 250 °C and above (Fig. 7b), reduction of the bulk occurred. At 250 °C, the pattern remained similar to that at lower temperatures, but a significant change in the diffraction features occurred at $\sim 26^\circ$, indicating the appearance of a new phase, MoO₂ [13]; however, the XRD was still dominated by Fe₂(MoO₄)₃ and MoO₃. Reduction at 300 °C produced a dramatic change (Fig. 7c); the diffractogram showed significantly reduced amounts of MoO₃ (near absence of the peak at $\sim 12.5^\circ$) and was now dominated by MoO₂. There was also a new phase of α -FeMoO₄ [14], together with Mo₄O₁₁ [15]. When the reduction occurred at 330 °C (Fig. 7d), MoO₂, Mo₄O₁₁ and α -FeMoO₄ were the main phases, but some ferric molybdate and MoO₃ were also present. With extended reduction at 350 °C (Fig. 7e), MoO₃ and Fe₂(MoO₄)₃ phases were no longer present; instead, the XRD was dominated by MoO₂, with α -FeMoO₄ and Mo₄O₁₁ also present.

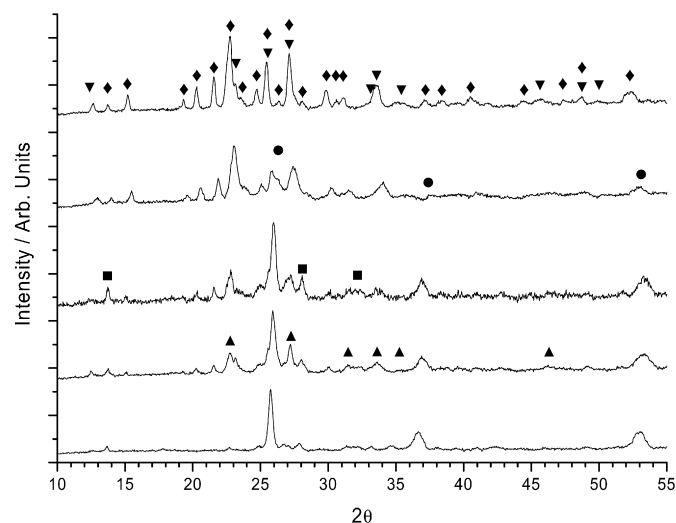


Fig. 7. XRD of fresh mixed phase catalyst. The symbols for the phases are: (▼) MoO₃ and (◆) Fe₂(MoO₄)₃. (b) after reduction at 250 °C by 60 μ L methanol. The symbols for the phases are as (a), except (●) MoO₂. (c) after reduction at 300 °C by 60 μ L methanol. The symbols for the phases are as (a) and (b) except (■) α -FeMoO₄ and (▲) Mo₄O₁₁. (d) after reduction at 330 °C by 60 μ L methanol. (e) after reduction at 350 °C by 321 μ L methanol.

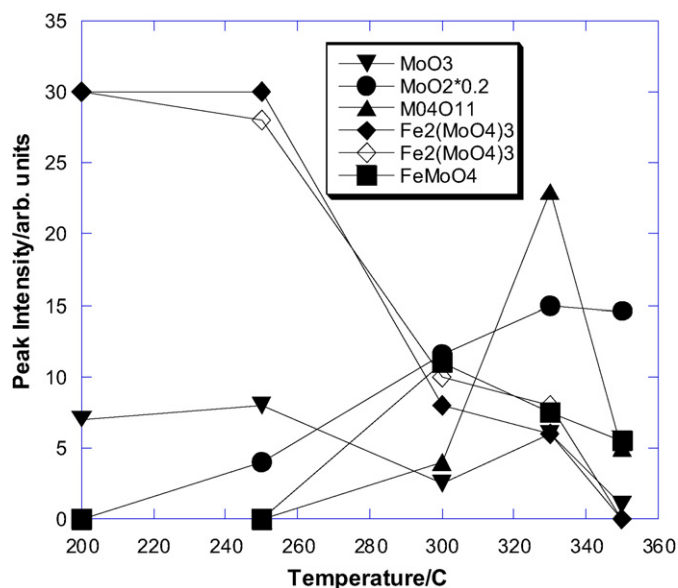


Fig. 8. A plot of the variation of the phases in the catalyst as a function of reaction temperature, determined from the XRD data of Fig. 6. The data point at 200 °C is the same as at ambient temperature is for an unreacted catalyst, whereas the other data are for reaction with 60 μL methanol, except for 350 °C which is for more extensive reaction (321 μL).

These changes are summarized in Fig. 8, which shows the intensity of the major peaks for the significant phases and demonstrates the reduction of the starting phases of molybdenite and ferric molybdate, beginning at ~ 250 °C. This plot provides qualitative information on the phase changes occurring with reduction, but quantification is difficult due to possible changes in sample morphology/agglomeration from pattern to pattern. From these data, it appears that only MoO_2 was produced at this stage. Mo_4O_{11} occurred at 300 °C, together with ferrous molybdate, coincident with the apparent loss of MoO_3 . Apparently, the Mo_4O_{11} phase was not a precursor to MoO_2 , and FeMoO_4 formed during the major loss of $\text{Fe}_2(\text{MoO}_4)_3$ at 300 °C. This transformation must result in the ejection of Mo species from the lattice. It is not clear whether Mo_4O_{11} was formed directly from the initial MoO_3 by reduction or from the matter ejected from the ferric molybdate lattice in forming ferrous molybdate, but it must be noted that Ressler et al. [16,17] proposed that Mo_4O_{11} is an intermediate material formed by reaction between MoO_3 and MoO_2 . This would then explain why a maximum in Mo_4O_{11} was seen at 330 °C, because the amount of MoO_3 was very low at 350 °C, and so it was difficult to make Mo_4O_{11} .

These different observed phase changes at different temperatures demonstrate that at 200 °C, reduction occurred only at the catalyst surface, with no bulk oxygen migration, because only about half a monolayer of oxygen was used (Table 2), but at the higher temperatures, bulk oxygen was able to diffuse through the lattice and was removed as well. Notably, at 250 °C and above, the catalyst was still being reduced, even after the experiment was terminated, so even more oxygen was removable. The catalyst reduction also led to a color change; the fresh mixed phase catalyst was light green, whereas after reduction, the catalyst was black. The only catalyst that did not turn black

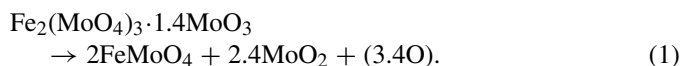
Table 2
Oxygen removed from reduction of the mixed phase catalyst

Temperature of reduction (°C)	Amount of methanol used in reduction (μL)	O removed from the sample (%)	Monolayer equivalent of O
200	60	0.3	0.5
250	60	2.5	3.8
275	60	6.7	10.0
300	60	12.4	18.5
330	60	15.2	22.7
350	321	49.1	73.1

was that reduced at 200 °C, which changed to dark green/gray. Studying the catalyst which was heavily reduced with 321 μL of methanol at 350 °C revealed that the catalyst was reduced to such an extent that the initial phases of $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 were minor components; however, further catalyst reduction occurred even after this change, so the phases seen may not be the final reduction products.

It should be noted that many of these changes are similar to those reported by Zhang et al. [18] but occurred at significantly lower temperature than those authors found using hydrogen as the reductant. Presumably this was due to the greater reducing power of methanol, as well as the difficulty in dissociating hydrogen on such oxides at low temperature. Similar phases were produced, including ferrous molybdate, MoO_2 , and Mo_4O_{11} .

The oxygen loss from the catalyst can be calculated from the product distribution and can be seen to vary considerably depending on the temperature of reduction (Table 2). Even if the catalyst were completely reduced to FeMoO_4 and MoO_2 through Eq. (1), then the oxygen loss would be 21%; however, in the case of the ferric molybdate/molybdenite catalyst held at 350 °C, we were able to remove considerably more than that (i.e., 49%), assuming that no reoxidation reactions occurred (effectively bimolecular reactions of methanol, producing DME and CO_2 ; see below). Thus, we can assume that the catalyst was further reduced to phases that are either too small or too amorphous to be detected by XRD, or that the catalyst was reoxidized to some extent once exposed to air to record the XRD spectra. It is likely that separate iron oxide phases are present but are not detected:



3.2.4. XPS

Integration of the XPS peaks for Mo and Fe (Figs. 9A and 9B) gave a molybdenum-to-iron ratio of 2.7 (± 0.3):1 at the surface, indicating some possible enhancement of Mo in the surface region compared with the stoichiometric composition ($\text{Mo}:\text{Fe} = 2.2$). This enhanced molybdenite may be due to the previously suggested structure, with a monolayer of MoO_3 forming on the catalyst surface [19]. The effect of catalyst reduction temperature broadly followed that identified in the XRD measurements reported earlier; that is, some reduced states appeared at high temperature. We must remember, however, that the catalysts were exposed to air before XPS, and thus it is likely that at least the topmost surface layer was reoxi-

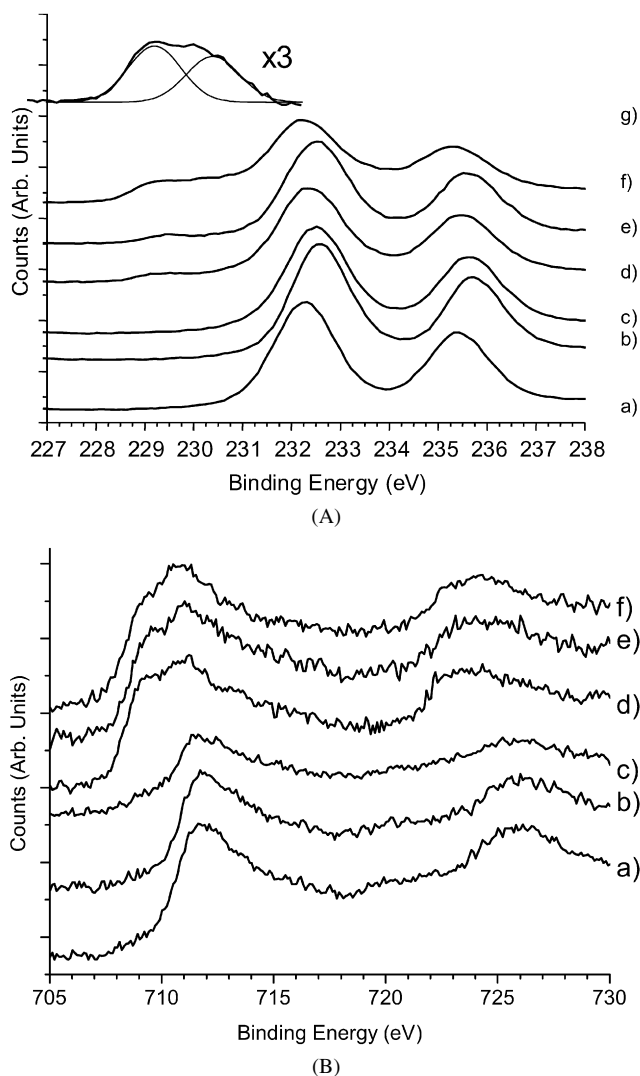


Fig. 9. (A) X-ray photoelectron spectra of the Mo 3d peaks in (a) mixed phase catalyst, (b) catalyst reduced at 200 °C by 60 μ L methanol, (c) catalyst reduced at 250 °C by 60 μ L methanol, (d) catalyst reduced at 300 °C by 60 μ L methanol, and (e) catalyst reduced at 330 °C by 60 μ L methanol, and (f) extended reduction at 350 °C with an insert (g) showing the peak fitting of the reduced Mo peaks, obtained by subtraction of the 6^+ component. (B) X-ray photoelectron spectra of the Fe 2p peaks for the experiments in (A).

dized during that period. Before reduction, the catalyst surface contained only Mo^{6+} and Fe^{3+} cations, but after reduction at 300 °C and above, Fe^{2+} was clearly seen in the iron spectra (peak at ~ 709.5 eV), presumably due to FeMoO_4 formation as shown by XRD and described above; only a very small amount of reduced Mo was seen at this stage (binding energy ~ 229.4 eV). The reduced iron peak may be present to a very small degree after reduction at 250 °C, evidenced by the increase in the low binding energy shoulder. After the extended reduction period at 350 °C, definite evidence was available for the formation of a carbide (at least in the surface region); XPS showed a C 1s peak at ~ 282 eV. The Mo peak now showed a significant, broad, low-binding energy component at ~ 229 – 231 eV, indicating formation of the 4^+ and 5^+ states after extensive reduction; this is presumably associated with the formation of MoO_2 and Mo_4O_{11} , as identified previously on XRD.

The Mo 3d spectrum of the reduced Mo states was isolated by subtracting the scaled Mo 3d spectrum of the fresh catalyst (pure Mo^{6+}) from the composite Mo 3d spectrum observed after extended reduction (Fig. 9A, inset). The difference spectrum could be fitted as shown, with 4^+ and 5^+ peaks at 229.2 and 230.5 eV, giving a ratio of $4^+ : 5^+ : 6^+$ of 0.14:0.12:0.74 at the surface. The overall ratio between molybdenum and iron in the surface layers did not undergo a major change despite the TPD evidence suggesting some iron enrichment of the surface. (The fresh catalyst produced formaldehyde and water as the major products, whereas the reduced catalyst also showed some CO, CO_2 and H_2 .) It has been shown previously that methanol TPD from Fe_2O_3 produces CO_2 and H_2 at the same temperatures as those observed here [5], and that CO_2 is the major product of methanol oxidation on that catalyst. Thus, it is somewhat surprising that the ratio did not change, but this may be due to compensatory changes of the relative amounts of iron molybdates (ferric decreasing with reduction, while ferrous increasing) and Mo oxides, which may mask the appearance of isolated iron oxide at the surface.

3.2.5. General discussion

The differing levels of conversion on the catalysts demonstrates that whereas surface oxygen is used in the mechanism [20], bulk oxygen diffuses to the surface and becomes active at a significant rate above 250 °C. In relation to the phases formed during reduction, Zhang et al. obtained a TPR profile of an iron molybdate catalyst with excess molybdenite demonstrating five peaks at 853, 910, 952, 1014, and 1233 K [18]. The first three of these peaks were assigned to the transformation of $\text{Fe}_2(\text{MoO}_3)_4$ to $\beta\text{-FeMoO}_4$ and Mo_4O_{11} (853 K), MoO_3 to MoO_2 (910 K), and Mo_4O_{11} to MoO_2 and most of the $\beta\text{-FeMoO}_4$ to $\text{Fe}_2\text{Mo}_3\text{O}_8$ and Fe_3O_4 (952 K). The fourth peak (1014 K) was assigned to the complete reduction of $\beta\text{-FeMoO}_4$, whereas the fifth peak was due to the reduction of all of the remaining metal oxide species, producing an Fe_3Mo alloy and metallic molybdenum.

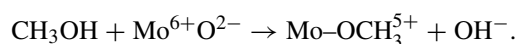
In situ Raman studies have shown that reduction of catalysts with an excess of molybdenum led to the formation of $\beta\text{-FeMoO}_4$ and $\text{Fe}_2(\text{MoO}_4)_3$, but the possibility that $\alpha\text{-FeMoO}_4$ was also formed could not be eliminated [21]. In situ SEM under reactions conditions using CH_3OH , $\text{CH}_3\text{OH-O}_2$, and H_2 has shown that ferric molybdates were reduced by two or possibly three reaction routes simultaneously [22]. These occurred by the formation of $\beta\text{-FeMoO}_4$ and $\alpha\text{-Fe}_2\text{O}_3$ (and/or a spinel of $\text{Fe}_2\text{MoO}_4/\text{Fe}_3\text{O}_4$). However, the reduction was limited by the presence of gaseous oxygen. The level of oxygen use by anaerobic pulsed reduction of toluene by Fe–Mo–O catalysts (with an Fe–Mo ratio of 1:1) 350 °C was found to be much greater for ultrafine particles produced by a sol–gel method than for larger particles produced by co-precipitation [23]. It is notable in our work that in the presence of methanol, reduction could be achieved at lower temperatures than were previously considered. Fig. 8 shows that most of the sample was reduced before 300 °C.

The reduction of MoO_3 by methanol in the absence of oxygen at 200 °C has been shown to form a bronze of composition

H_xMoO_3 in the first few layers [24], although in our study no new phases were seen at this low temperature (Fig. 8). This bronze also has been observed on exposure of MoO_3 to H atoms generated by a hot tungsten filament in a hydrogen pressure of 10^{-8} Torr. Mo bronze formation occurs during the dissociative chemisorption of methanol, but these studies were unable to eliminate the possibility of formation also occurring during hydrogen abstraction from the methoxy group. Hydrogen reduction of bulk MoO_3 at atmospheric pressure has been shown to form a bifunctional $MoO_2(H_x)_{ac}$ phase on the surface of MoO_2 at 350–400 °C [25]. However, little or no H_2 is present during the course of aerobic methanol oxidation.

The ease of reducibility of the single and mixed oxides has been shown to be in the order $Fe_2O_3 > Fe_2(MoO_4)_3 > MoO_3$, leading to the suggestion that the mobility of the oxygen ions within the oxides follows the same order with the highest mobility in Fe_2O_3 and lowest in MoO_3 [26]. The reduction of an iron molybdate catalyst at 350 °C has been shown to lead to the formation of only β - $FeMoO_4$ with methanol and of β - $FeMoO_4$ and MoO_2 during reduction with 1-butene in nitrogen environments [27].

Although the diffusion of bulk oxygen maintained the catalyst activity, the selectivity diminished, likely due to a partial reduction of the surface, which in turn demonstrates the importance of high oxidation states of the surface metals in maintaining selective products. High oxidation states are probably required due to the heterolytic nature of the methanol dissociation process, which requires acid–base catalysis at the acidic proton of the methanol molecule, thereby reducing the surface oxide to hydroxide. This in turn requires electron donation to the Mo-methoxy complex, effectively converting Mo to the lower 5^+ oxidation state (though the electron transfer may include the methoxy species to which it is bonded, which thus may be partly ionic). This can be written as



Methanol is capable of reacting through oxidative processes (e.g., $CH_3OH + O_s \rightarrow H_2CO + H_2O$) or nonoxidative processes (e.g., $CH_3OH \rightarrow CO + 2H_2$). In the present work, the former processes are favored. However, when no oxygen is present in the flow, these reactions cannot continue ad infinitum. An interesting avenue for future work would be to investigate how much oxygen can be removed before the nonoxidative processes begin to dominate. Even for the most extreme methanol dosing experiments carried out here, oxidative products (CO_2 and H_2O) were still formed. As was shown by XPS for the extended run at 350 °C, when the surface becomes extremely reduced, it likely will carbide; this may occur through the Boudouard reaction of CO disproportionation, but will more likely result from cleavage of the C–O bond in methanol, which is significantly weaker than that in CO.

The decrease in selectivity with reduction is due mainly to the formation of CO (Fig. 4 and supplementary data Figs. S3a–S3c), which appears to result from overoxidation of formaldehyde. This in turn seems to correlate with catalyst reduction and MoO_2 and $FeMoO_4$ formation demonstrated on postreaction XRD. This can be confirmed by replotting the data presented

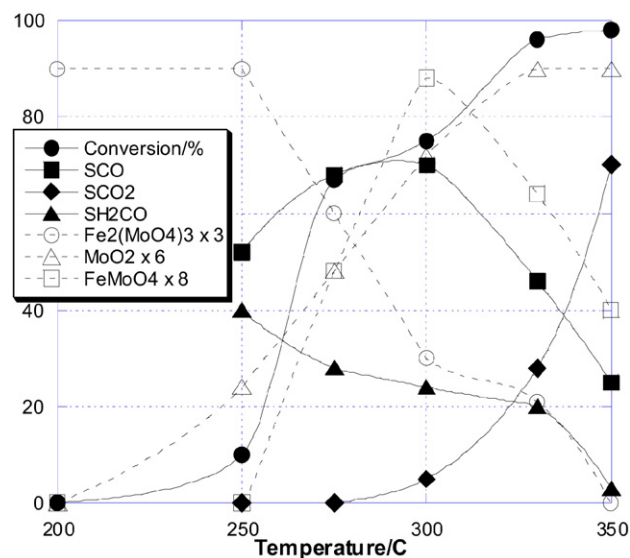


Fig. 10. Correlation between the final catalyst performance (conversion and selectivity, filled data points and full lines) as a function of reaction temperature, and the structures observed in XRD (open data points and dashed lines).

earlier on a single graph showing the final catalyst performance and the XRD structures observed (Fig. 10). There seems to be a clear relationship between CO_x production and the amount of $FeMoO_4$ present, with a maximum for both occurring at around 300 °C. However, it also must be noted that experiments with MoO_2 alone demonstrate mainly CO production in TPD and in reactor experiments [28].

The increased selectivity of the catalyst toward CO_2 for the elevated temperature reactions is in contrast to what might be expected as the catalyst is reduced (i.e. reduced products). This is likely due to the increased iron availability at the surface, because Fe_2O_3 is known to direct methanol toward combustion products [5]. This increased iron at the surface may be due either to reduced iron passing through the catalyst bulk to the surface or to the loss of molybdenum from the surface, which is known to occur over a period of months under industrial oxidizing conditions [4]. Note that Mo also must be removed from the lattice when forming the ferrous molybdate seen in XRD, and that ferrous molybdate itself has a higher Fe ratio, at least in the bulk. When the catalyst that was reduced at 330 °C was reoxidized with sufficient pulses of oxygen to saturate the catalyst, XRD showed that it reformed the bulk phases of $Fe_2(MoO_4)_3$ and MoO_3 , while the surface ratios in XPS again remained unchanged. TPD data from the reoxidized catalyst showed methanol, formaldehyde, and water as the major products in the same profile as before reduction. The major selective intermediate is likely to be the surface methoxy (which decomposes at 170 °C in TPD), which dominates the surface of molybdena and the molybdate catalysts over much of the temperature range of the reaction. CO appears to be a secondary product of formaldehyde reaction with the surface, but it is significantly enhanced by changes in the oxidation state of the surface due to reduction. CO itself can then undergo secondary reactions to produce CO_2 , but extensive reduction results in the appearance of iron oxide-like phases in the catalyst that favor overoxidation of methanol to formate, which then decomposes to produce CO_2 and H_2 .

4. Conclusion

From this work, we have gained insight into the process of oxygen removal and reduction of an iron molybdate catalyst, demonstrating that large amounts of oxygen can be removed from the catalyst sample in the presence of methanol at temperatures above ca. 250 °C. Lattice oxygen becomes readily available at higher temperatures and plays a role in both selective and nonselective processes. The reaction is astonishingly efficient, with 100% conversion of methanol throughout the reduction process at 330 °C, even though oxygen must be delivered to the surface from deep within the catalyst particle. When significant amounts of lattice oxygen are removed, the bulk phases convert from a mix of $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 , to MoO_2 , Mo_4O_{11} and $\alpha\text{-FeMoO}_4$. This results in reduced selectivity of the catalysts toward formaldehyde production and increased production of CO and CO_2 . Such data reinforce the idea that oxygen levels must be maintained reasonably high at the end of the bed for industrial processes, because otherwise deleterious changes occur in the catalyst, resulting in reduced formaldehyde yields.

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Supplementary data

The online version of this article contains additional supplementary data.

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