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Contrasting the Behaviour of MoO_3 and MoO_2 for the Oxidation of Methanol

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Abstract The oxidation of methanol has been measured on MoO_3 and MoO_2. The properties of these two materials are interchangeable, depending upon the conditions in which the reaction is run. MoO_3 produces high yields of formaldehyde, but MoO_2 does not, due to the importance of the Mo^{6+} state for the selective reaction. However, if the MoO_3 material is run in anaerobic conditions it behaves in a very similar way to MoO_2, due to the presence of Mo^{4+} in the surface layers. In complement to this MoO_2 converts to high yield behaviour when run in aerobic conditions, due to the conversion of the material to Mo^{6+} at the surface, and, ultimately to MoO_3 in the bulk. In TPD experiments MoO_3 yields formaldehyde, whereas MoO_2 yields CO. In both materials oxygen transport within the lattice becomes appreciable above 300 °C, and the reaction proceeds via the Mars-van Krevelen mechanism.

Keywords Molybdenum oxide catalyst · Methanol selective oxidation · Formaldehyde · MoO_2 · MoO_3 · Redox

1 Introduction

The selective oxidation of methanol to formaldehyde takes place on Ag and on mixed oxide catalysts, the latter based on ferric molybdate. There is still much discussion regarding the nature of the active site for this reaction, see for instance the recent review article by Soares et al. [1], though it appears that Mo plays the major role in the catalysis [see, for example, 2–5]. In a recent article Ressler et al examined the catalytic nature of molybdenum trioxide in the oxidation of propene [6], and concluded that the reaction begins at about the same time as reduction of the material begins. The exact nature of the oxidation state of the surface *during* the reaction is of great interest, and so, in the present paper we have examined the efficacy of MoO_2 and MoO_3 for the industrially important methanol oxidation reaction, and show that the two materials behave quite differently, with a poor formaldehyde yield from MoO_2.

The reduction of MoO_3 by methanol in the absence of oxygen at 200 °C has been shown to result in the production of a bronze of H_xMoO_3 in the first few layers [7]. The bronze forms during the dissociative chemisorption of the methanol, but the possibility of formation also occurring during hydrogen abstraction from the methoxy group was not eliminated. This bronze also forms with hydrogen reduction, and on the (0 1 0) face it forms topotactically, aligned along the ‹203› direction [8]. With further heating in H_2, the bronze is consumed to form nucleation sites for MoO_2 formation, before the growth of MoO_2 occurs.

The level of reduction of a MoO_3 sample helps dictate the activity and selectivity of MoO_3 in reaction with 2-butanol [9]. Where reduction is stabilised through the formation of bulk Mo sub oxide phases (MoO_3 with shear planes), the oxygen exchangeability is impaired, so dehydration of the 2-butanol is observed (i.e., oxygen is not transferred to the hydrocarbon via the Mars and van Krevelen mechanism). When only the surface is reduced, however, exchangeability of lattice oxygen in the surface layer is enhanced, with total oxidation to CO_2 and water observed.

With MoO_3 it is thought that below ~327 °C, participation of O from the bulk is negligible in such redox processes, while between ~327 and 427 °C O vacancy

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diffusion makes the redox mechanism possible, with partially reduced MoO_3 observed under reaction conditions with propene [10]. At temperatures above ~427 °C there is sufficiently fast O diffusion from the lattice combined with rapid formation and destruction of crystallographic shear planes that considerable lattice O can be used for partial oxidation.

Mo_4O_{11} is observed from the reduction of MoO_3 in the presence of 5 vol% H_2 at 500 °C [11]. Most notably, Mo_4O_{11} forms after MoO_2 is observed, as it is not directly formed from the reduction of MoO_3, but is instead thought to be formed from the solid state reaction between MoO_3 and MoO_2.

The objective of the work here was to directly compare, for the first time, the behaviour of the Mo(VI) and Mo(IV) oxides for the selective oxidation of methanol, in order to (i) ascertain the efficacy of each for formaldehyde production, and (ii) to assess the ability of oxygen to exchange with the gas phase by reaction within each lattice, thus allowing redox switching between (VI) and (IV) states.

2 Experimental

The MoO_3 (BDH, ≥99.5%) and MoO_2 (Alfa Aesar, 99.95%) were commercial samples. The catalytic experiments were carried out in a pulsed flow reactor described elsewhere [12] and 0.5 g. of sample was used in all the experiments. The catalysts were run either aerobically in 10% O_2 in He, or anaerobically in He alone. Liquid methanol (usually 1 μl) was injected periodically (usually every 2 min) into the gas flow via a septum upstream from the reactor. The surface areas of the samples were measured by the BET method to be 3.6 $m^2\ g^{-1}$ for MoO_2 and ~1 $m^2\ g^{-1}$ for MoO_3. XRD patterns were recorded on an Enraf Nonus FR590 diffractometer, employing Cu Kα radiation with a voltage of 40 kV and a current of 30 mA.

3 Results and Discussion

3.1 The Behaviour of MoO_3

As shown in Fig. 1a, molybdenum trioxide is very selective for methanol oxidation to formaldehyde; all methanol used is converted to products. The selectivity is very high up to high conversion, being, for instance, 95% selective at 80% conversion. Due to the low surface area of the molybdena, given above, 100% conversion could not be achieved in this temperature range. The only other products seen in the reaction are small amounts of dimethyl ether, appearing at low temperature and low conversion (at ~10% maximum selectivity, and hence the selectivity to formaldehyde is <100% in this range), and small amounts of CO_2, reaching ~8% at 360 °C. The X-ray diffraction pattern for the MoO_3 is characteristic of α-MoO_3 [13], as shown in Fig. 2

If the catalyst is run in the absence of oxygen (Fig. 1b) the catalyst is still selective at low conversions, but it is apparently a little less active (at 320 °C methanol conversion is 40%, compared with 60% in the presence of gas phase oxygen) and selectivity seriously declines at high temperature due to the formation of CO as a major product, together with smaller amounts of CO_2. The CO production is associated with an increase of hydrogen, indicating that this is due to dehydrogenation of the methanol, and occurs due to reduction of the surface layers as the temperature increases and water continues to be produced. Clearly, however, the surface can still enable selective oxidation to formaldehyde at low temperature, with water production obviously coming from the lattice oxygen at the surface. The reduced activity in the anaerobic situation is due to the reduced availability of oxygen. In fact, the effect is less than might have been imagined considering the lack of gas phase oxygen. This is because lattice oxygen is supplied by diffusion to the surface from the bulk lattice and this supply

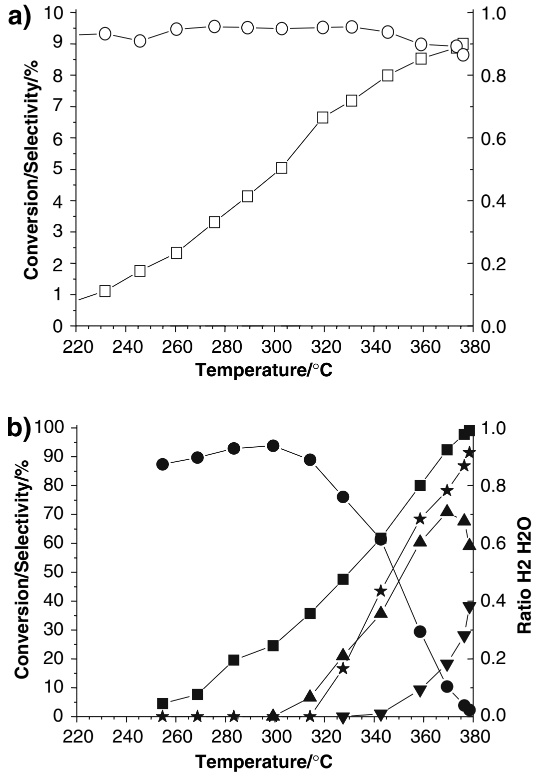

Fig. 1 (**a**). Catalytic performance of MoO_3 for the oxidation of methanol in oxygen. Conversion (squares), selectivity to formaldehyde (circles). (**b**). Catalytic performance of MoO_3 in the absence of oxygen. Conversion (squares), selectivity to formaldehyde (circles), CO (triangles), CO_2 (inverse triangles). The stars refer to the ratio of H_2 to H_2O formed in the anaerobic reaction. Note that no H_2 is formed in the aerobic reaction

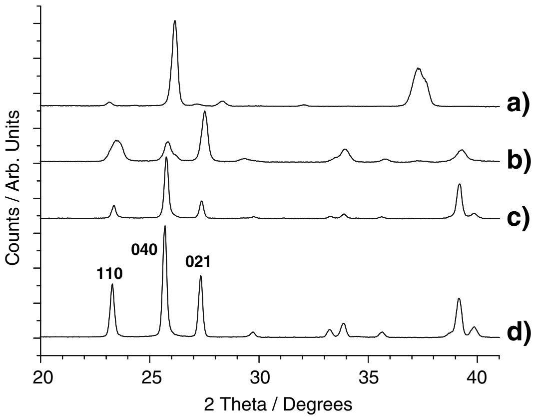

Fig. 2 X-ray diffractograms of (a) Fresh MoO_2, (b) Post Reactor MoO_2, (c) post reactor MoO_3 and (d) fresh MoO_3

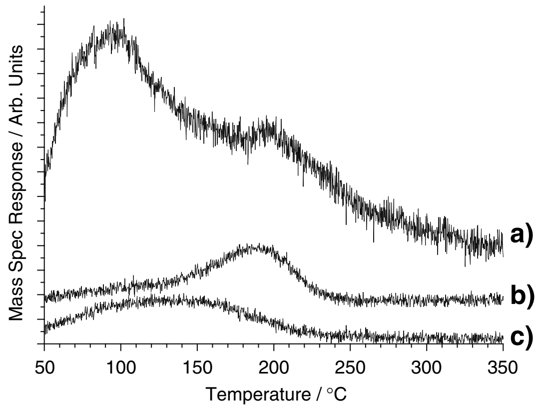

Fig. 3 TPD for MoO_3 saturated with methanol at room temperature. (a) Water, (b) Formaldehyde, and (c) Methanol. There is no CO evolution from MoO_3

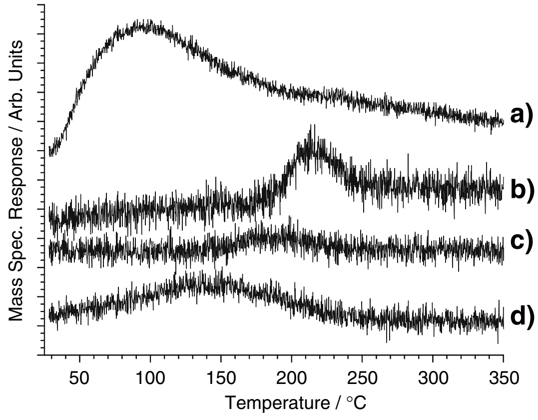

Fig. 4 TPD for MoO_3, after an anaerobic reaction run, saturated with methanol at room temperature. (a) Water, (b) Carbon monoxide (c) Formaldehyde, and (d) Methanol

is limited at low temperature, as shown elsewhere [10]. As the supply increases at higher temperature, so the bulk molybdena lattice becomes reduced. Thus the change of selectivity seen in the anaerobic experiment in Fig. 1 is probably due to the formation of Mo^{4+}, and this is supported by experiments with MoO_2 itself, as described below. The post-reactor XRD shows little change in the bulk structure, which is presumably due to the limited loss of oxygen in the anaerobic run. With propene reduction Ressler et al [11] showed that the bulk can be reduced to MoO_2 above about 400 °C though the reduction was shown to be much slower at that temperature than at 450 °C. In the present case the oxygen removal is calculated to be $\sim$1.3% of the oxygen present within the sample, or approximately 16 monolayers equivalent, if we assume that the oxygen concentration at the surface is 10^{19} m^{-2}, and increases with increasing temperature in Fig. 1. Post reaction XPS shows the presence of small amounts of Mo^{4+} and Mo^{5+} in the surface region. Note that due to the rapid solid-state oxygen supply at high temperature, the activity is similar to that in the presence of oxygen.

It is instructive to examine TPD spectra from the sample before and after such treatments, Figs. 3 and 4. Here it can be seen that if MoO_3 is dosed with methanol to saturation at room temperature, the only products to evolve during TPD are formaldehyde and water, the formaldehyde evolves in a very specific peak at 190 °C. This is very similar to the TPD reported earlier by Farneth et al [14, 15] and from our own laboratory [16], and is similar to that from industrial type iron molybdate catalysts [16]. The TPD is 100% selective, with no evidence of other products. However, after anaerobic reaction (Fig. 4), we now see CO desorption, peaking at 220 °C, and it is the dominant product. We believe this CO is due to the presence of reduced Mo species, probably Mo^{4+}, in the surface layers. Note that formaldehyde production occurs at lower temperature than for CO, that is, it is an easier reaction, as might be expected, since there is less bond disruption involved in the process.

3.2 The Behaviour of MoO_2

The reactor results for molybdenum dioxide are shown in Fig. 5, which shows data for the first and second runs over the catalysts, both in aerobic conditions, and they are particularly revealing. We can see that, like molybdenum trioxide above, the sample is selective to formaldehyde at low conversion, and indeed, it appears to be significantly more active than molybdenum trioxide (conversion at 260 °C is 70%, versus only 25% on MoO_3, and conversion reaches close to 100% by 320 °C). This is mainly due to the difference in surface area between the two samples, MoO_2 being 3.6 m^2 g^{-1}, while MoO_3 is only $\sim$1 m^2 g^{-1}, and the conversion difference at 240 °C of about a factor of four supports this view. However, the selectivity drops

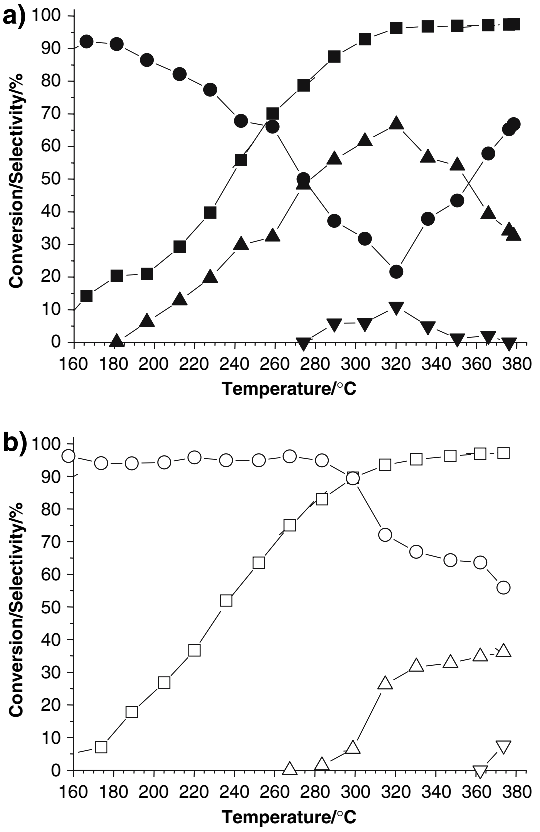

Fig. 5 (**a**) Performance of the MoO_2 catalyst for methanol oxidation during the 1st run, Symbols as in Fig. 1 above. (**b**) Performance of the MoO_2 catalyst for methanol oxidation during the 2nd run, Symbols as in Fig. 1 above

markedly at moderate temperatures, the main other product at 260 °C being CO, and it is the dominant product at 320 °C. CO_2 begins to be formed in small amounts above 280 °C. There is then a remarkable change in behaviour at 320 °C, with an increase in the yield of formaldehyde again, together with a drop in the yield of CO and CO_2. This agrees well with the temperature at which Ressler et al [11] found oxidation of the MoO_2 lattice to proceed fast. Indeed, if a second run is then carried out in our reactor, starting from low temperature, the catalyst is now much more selective across the whole range, showing very similar selectivity for formaldehyde to MoO_3 at the same conversion. At the highest temperature there is some loss of formaldehyde selectivity and CO production. The behaviour in the first run is due to the conversion of MoO_2 to MoO_3, with a large *additional* uptake of oxygen beginning at $\sim$280 °C and continuing to the end of the run. This oxidation behaviour is supported by the post-reaction XRD which shows the pattern of MoO_2 [17] in Fig. 2 before reaction, whereas after reaction it has almost completely transformed to MoO_3 (there is a small peak at $\sim$37° scattering angle, and a shoulder at $\sim$26°, indicating a very small amount of remaining MoO_2). Note the broadening of the diffraction peaks for oxidised MoO_2 compared with MoO_3, which may be due to the higher surface area of the former, and perhaps due also to some disorder in the lattice. There is also a different distribution in the peaks, with [021], being dominant in the diffractogram, compared with [040], [110] for MoO_3. This is a sign that the morphology of the MoO_3 from MoO_2 oxidation is quite different, possibly existing as small needles, similar to those seen by Arruano and Wanke in SEM for real catalysts [18]. XPS analysis of the MoO_2 surface after reaction also shows that it has completely converted to the 6+ state. It is somewhat surprising that the methanol conversion appears to be unaffected by the oxidation state of the catalyst, perhaps implying that the only important requirement for the activity is the presence of cation/anion pairs at the surface, independent of their oxidation state, which act to dissociate the methanol to methoxy and hydroxyl groups at the surface as shown in step 1 below.

In TPD, Fig. 6, the main product is CO, appearing in a similar position to that for reduced MoO_3 in Fig. 4, again supporting the fact that it is a characteristic of Mo^{4+}.

The reactor results for the various samples are summarised in the selectivity-conversion plots shown in Fig. 7. These again confirm the importance of the presence of the Mo^{6+} state for selective catalysis, since both MoO_3 and MoO_2 after oxidation in the first run have excellent selectivity at high methanol conversion. This is crucial for industrial catalysis where yields are in the 90% region. The MoO_2 catalyst, notwithstanding the fact that at low temperature it is highly selective to formaldehyde, is a poor catalyst, since it gives a low maximum yield of formaldehyde. The MoO_2 and reduced MoO_3 show very similar selectivity-conversion profiles in Fig. 7, presumably due to the presence of Mo^{4+} in the surface layers of both.

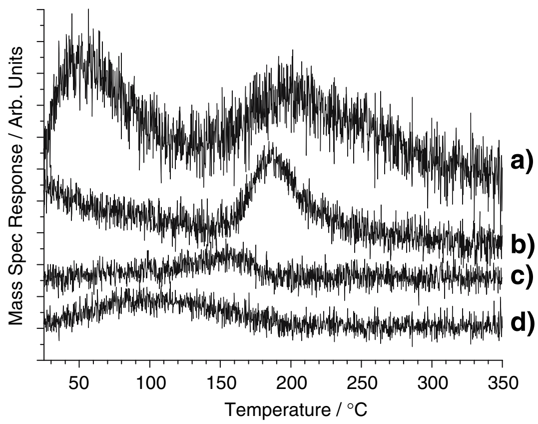

Fig. 6 TPD for MoO_2 saturated with methanol at room temperature. (a) Water, (b) Carbon monoxide (c) Formaldehyde, and (d) Methanol

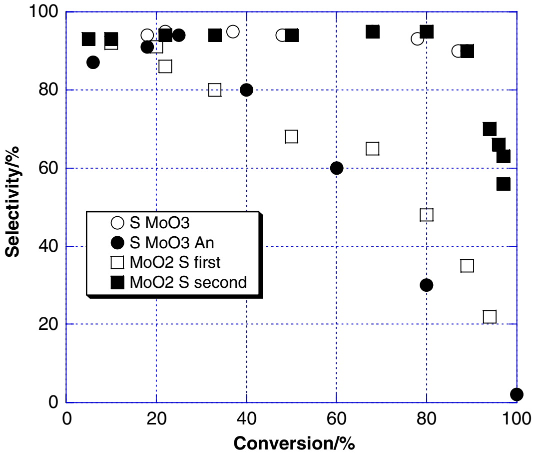

Fig. 7 Selectivity-conversion plots for the samples studied in this work, showing results for MoO_3 in aerobic and anaerobic conditions, together with data for MoO_2 from the first and second runs. Note that the behaviour of MoO_2 after a methanol oxidation run becomes very similar to that of MoO_3, while MoO_3 run in anaerobic conditions behaves very similarly to MoO_2 during the first run up to the point of lattice oxidation

It is quite clear that MoO_3 is a highly successful material for the selective oxidation of formaldehyde and that Mo^{6+} is not only involved in the catalysis, it is the crucial component for selective performance and high formaldehyde yield. As proposed by ourselves [16] and others (see, for example, [19–21]) it is likely that the first step in the catalysis is methanol adsorption, followed by hydrogen abstraction by surface oxygen anions to form surface methoxy species, as also identified by IR measurements [22]. We can write the latter step as follows; based on a two Mo site mechanism -

$$Mo^{6+}O^{2-}Mo^{6+} + CH_3OH \rightarrow (MoOCH_3)^{5+} + (MoOH)^{5+}$$

here proton abstraction occurs at the basic anion site, with methoxy binding to the Mo site. This parallels the work of McCarron et al who prepared bulk compounds of Mo-methoxy-oxides (e.g., $Mo_2O_5(OCH_3)_2$) and showed methoxy binding to the Mo centre [23]. The binding probably first occurs by interaction of the methanol non-bonding lone pairs with the cation sites, followed by the proton abstraction. Formaldehyde is then produced by dehydrogenation in the following manner, where Vo refers to an anion vacancy. Again it must be noted that for the solid state Mo-methoxy oxide, McCarron et al found formaldehyde as a product of thermal decomposition [23]

$$(MoOCH_3)^{5+} + (MoOH)^{5+} \rightarrow 2Mo^{5+} + Vo + H_2CO + H_2O$$

The molybdenum can then be re-oxidised in the normal way via the Mars-van Krevelen mechanism

$$4Mo^{5+} + O_2 \rightarrow 2(Mo^{6+}O^{2-}Mo^{6+})$$

Thus the sample is always predominantly in the 6+ state in aerobic conditions, providing the $CH_3OH{:}O_2$ ratio is appropriate. If, however, oxygen is absent from the gas phase, the surface can be further reduced by methanol

$$Mo^{5+}O^{2-} + CH_3OH \rightarrow (MoOCH_3)^{4+} + OH^-$$

At this point of lower Mo oxidation state, the surface is more reactive and is able to strip off further hydrogen atoms from the methoxy group (or from readsorbing formaldehyde) to yield CO

$$(MoOCH_3)^{4+} \rightarrow CO + Mo^{4+} + 3H$$

The fate of the liberated hydrogen is to react with surface oxygen to produce water and form more vacancies and probably form other low oxidation state Mo species. After significant reduction of the surface layer molecular hydrogen can also be produced, as shown in Fig. 1. The presence of oxidation state 4 and 5 is seen in post reaction XPS measurements.

In conclusion, we have shown that the oxidation state of molybdena is crucial for the selective oxidation of methanol to formaldehyde. It is essential that the surface is in it's highest oxidation state of 6+, though the selective state at the active site probably cycles between 5+ and 6+. It is important to note that molybdenum is the central species involved in selective oxidation catalysis in industrial catalysts of this type.

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