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Catalysis, Structure & Reactivity

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Michael Bowker[*1,2], **Matthew House**[1], **Abdulmohsen Alshehri**[1], **Catherine Brookes**[1,2], **Emma K. Gibson**[2] **and Peter P. Wells**[2]

[1]Cardiff Catalysis Institute, School of Chemistry, Cardiff CF10 3AT, UK
[2]Rutherford Appleton Laboratory, UK Catalysis Hub, Research Complex at Harwell (RCaH), Harwell, Oxon OX11 0FA, UK

Abstract Evolution of the IRAS spectrum with temperature after adsorbing methanol at room temperature. The bands at 2930 and 2820 cm^{-1} are due to the methoxy species C–H stretches, while that at 2870 is due to the formate.

Here, we report a simple, quantitative model to describe the behaviour of bi-cationic oxide catalysts, in terms of selectivity variation as a function of increased loading of one cation into a sample of the other. We consider its application to a particular catalytic system, namely the selective oxidation of methanol, which proceeds with three main C1 products, namely CO_2, CO, and H_2CO. The product selectivity varies in this order as Mo is added in increasing amounts to an iron oxide catalyst, and the product selectivity is determined by the distribution of dual sites and single sites of each species.

Keywords Methanol oxidation, Oxide catalysis, Iron oxide, Molybdenum oxide, Reaction modelling, Selectivity, Formaldehyde

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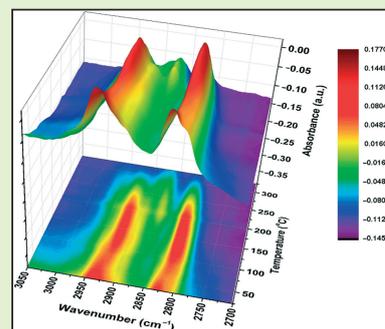
Introduction

A number of catalyst systems are based on oxidic materials with two or more cations present in the active phase, and these are often applied in selective oxidation reactions. Commercial examples include the oxidation and ammoxidation of propene to acrolein and acrylonitrile,[1] where mixed oxides of Bi and Mo or Fe and Sb were originally used, butane conversion to maleic anhydride[2] and methanol oxidation to formaldehyde.[3]

The latter reaction is carried out on either Ag or iron molybdate catalysts, and for the latter case it has been found that there is a very strong dependence of the product selectivity on the cation ratio in the bulk.[3,4] In turn, these changes are then because of changes in that ratio in the top layer, which is the active layer for reaction with the gas phase. This has lead to a few studies where researchers have made surface doped materials in the hope of learning what is the active configuration and what it is that makes that special for high selectivity to formaldehyde.[5–10] Coverages of $<6\,nm^{-2}$ (*ca.* 70% coverage) of MoO_3 appear to be supported as a monolayer, whereas at higher amounts

aggregation of oxide particles was observed.[5–7] These studies all show that with molybdenum present, improved selectivity towards formaldehyde is achieved for methanol oxidation. An increase in methanol oxidation turn-over frequency was observed with increasing molybdenum oxide coverage on the surface (up to $\sim6\,Mo\,nm^{-2}$), and this was proposed to be because of the necessity for adjacent molybdenum sites for the selective reaction (one for methanol adsorption, and one for hydrogen abstraction from the methoxy).[5] The structure of the monolayer was seen to be similar to that of bulk $Fe_2(MoO_4)_3$, with good methanol conversion and formaldehyde selectivity, though we only took conversion up to 60%.

Similar catalysts have also been created by simply heating a mixture of MoO_3 with Fe_2O_3[6] In that case, the dispersion capacity was calculated to be about $5\,nm^{-2}$ after calcination at 420°C. Calcination at higher temperatures lead to the reaction of MoO_3 with the bulk oxide to produce ferric molybdate. This $Fe_2(MoO_4)_3$ remained at the surface, effectively encapsulating the Fe_2O_3 inside. Similarly, Huang *et al.* made a material consisting of iron oxide and molybdenum ground together, and calcined to various temperatures;[7] they reported high selectivity performance, though again conversion was only taken to $\sim70\%$.

*Corresponding author, email bowkerm@cardiff.ac.uk.

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In our laboratories, we have put some considerable effort into the understanding of selective oxidation reactions and especially methanol oxidation. Our main conclusion is that it is Mo, which is the most important component in ferric molybdate catalysts for high selectivity; it has very high selectivity on its own to formaldehyde, and is proposed to be present in commercial catalysts as an active Mo monolayer on top of ferric molybdate.[8–12]

Here, we examine how the selectivity of such catalysts is affected by the relative surface compositions of different cations that have intrinsically different properties from one another.

Experimental

The experimental methods used have been described in detail previously.[9,13,14] To summarise, the reactor was a tubular reactor, 1/4″ OD, operating in TPD (temperature programmed desorption) mode with a continuous flow of helium at a flow-rate of 30 mL min^{-1}, with a usual loading of 0.5 g of catalyst. Methanol was dosed onto the surface before heating by manual injection. Part of this flow was taken into an on-line mass spectrometer (Hiden Hiden Analytical quadrupole Hal 201) and the gas products were analysed as the catalyst was heated by ramping the temperature of the fan oven in which it was housed, typically at 12°C min^{-1}. The thermocouple measuring the temperature was placed directly in the catalyst bed. In reaction mode, the methanol was injected periodically (typically every 2 min) into a continuous flow of 10% oxygen in helium while ramping the temperature.

Site Distribution, general considerations

It is imagined that a catalyst consists of two components A and B, and further that these two components have a novel property when intimately mixed. That is, when like atoms are beside each other, then the reactivity is different from when they are isolated. So pure component A has the property of yielding product X, pure component B gives Y, while the mixed material yields product Z from isolated sites. It is assumed that these properties are then purely a function of the nature of *dual sites* in the system, then the following applies for random site occupation, for a catalytic surface which is changing from pure A to pure B:

- Fraction dual sites A–A, AA $= N_A^2/N$
- Fraction dual sites B–B, BB $= N_B^2/N$
- Fraction isolated sites A and B, AB $= 1-$AA$-$BB

where $N_{A,B}$ are the number of A and B sites out of the total sites N, and adsorption of B results in loss of an A site (that is, A + B = 1)

By way of example, Fig. 1 shows three extremes of such behaviour for a dilute layer of B in A, a dilute layer of A mixed in mostly B, while approximately equal amount of both is shown in the middle panel. In a mixed layer then, the fraction of isolated sites is maximised at half coverage of A and B on the surface.

More explicitly, the result of this is shown in Fig. 2, which shows the variation in the distribution of homogeneous double sites, and of isolated sites as a function of increasing fraction of B in the mixed surface of A and B sites. There are parabolic declines in A, and rises in B double sites with increasing B

coverage, and during this process the occurrence of sites which do not have a like neighbour shows a broad maximum at 1/2 a monolayer coverage, when there are 50% of such sites, and 50% of sites with like neighbours. Thus, if there is a specific product Z from the mixed surface, then it is expected that product will be maximised in the intermediate coverage range.

Site distribution, a specific example

We have examined the oxidation of methanol on iron molybdate catalysts and a major conclusion from this is that the surface of such catalysts is completely dominated by Mo.[4,8–10] This is the main reason that they are so selective, since we[4,13,15] and others[16] have shown that MoO_3 itself is highly selective for this reaction. However, what is of somewhat more interest to us is the effect of going to lower Mo:Fe ratios than that which is used commercially (typically 1.6:1–2.2:1) and lower than the stoichiometric ratio of 1.5:1 for ferric molybdate [$Fe_2(MoO_4)_3$] itself.

Figure 3 shows a result to indicate the kinds of reaction profile which we see as a function of temperature for methanol oxidation on ferric molybdate (in this case Mo:Fe 2.2:1). Here, is seen that conversion begins at ∼160°C, and there is some evolution of dimethyl ether at very low conversion. When conversion becomes significant, then formaldehyde is seen as the major product, being formed at very high peak yield (∼95%), while at higher temperatures and conversion CO dominates. At very high conversion and temperature CO_2 is seen, and can become dominant, but is likely to be because of secondary CO oxidation. This behaviour is similar to what is observed for 1.5:1 Mo:Fe catalysts, and for MoO_3 itself, which are highly selective to formaldehyde over a wide temperature range,[4,8,13] though the conversion for MoO_3 itself is much lower than for iron molybdate and only reaches 100% at much higher temperatures.[4,13] Data for iron oxide are in contrast to those in Fig. 3, since it is a complete combustor of methanol to CO_2 and H_2O[4,13]. For a catalyst with a sub-stoichiometric loading of Mo, as in Fig. 4, for example, the major product is CO, very different from the results of the individual oxides and the iron molybdate catalyst shown in Fig. 3.

It is useful to examine the results of TPD experiments on such materials, since TPD often gives very clear results, relating to the presence and nature of surface intermediates. They also relate closely to the reactor results in flowing oxygen and methanol. Figure 5 shows the TPD for these materials, again contrasting the behaviour of the different types. Iron oxide gives only CO_2 as the carbon product, while MoO_3 gives only formaldehyde. The full catalyst behaves very similarly to MoO_3 alone, yielding only formaldehyde, but with a slightly lower peak temperature, perhaps indicative of a slightly lower activation energy for methoxy dehydrogenation. However, a low Mo:Fe ratio catalyst gives CO as a major product, as shown in Fig. 6.

The important point here is that as the Mo concentration in molybdate catalysts increases, so the selectivity changes from combustion to selective oxidation, as follows

Low Mo loadings
$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$$

Intermediate Mo loadings
$$CH_3OH + O_2 \rightarrow CO + 2H_2O$$
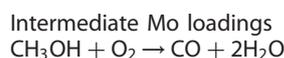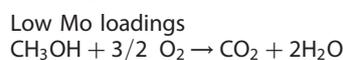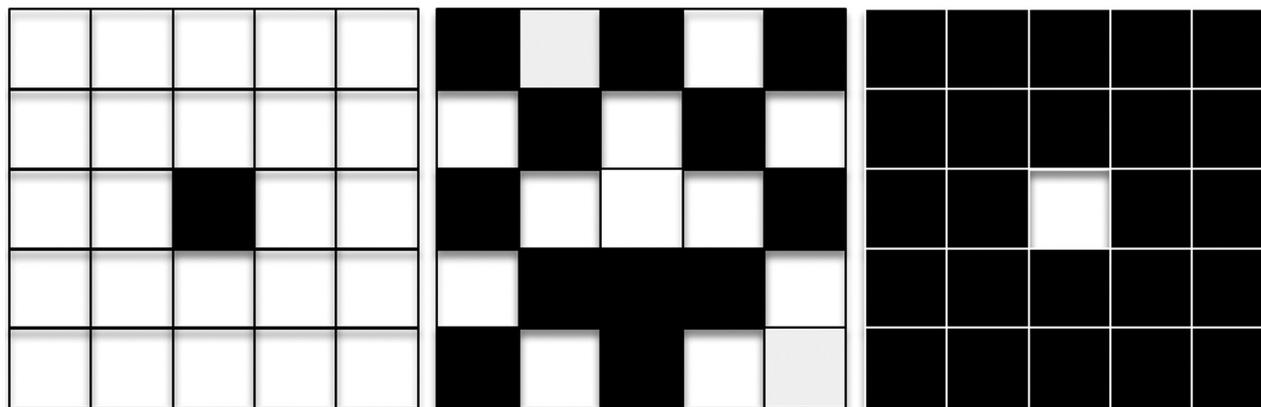
Figure 1 Schematic diagrams of site distribution as type B (black squares) is added to a lattice of sites A (white squares). Left low B coverage, middle ∼ half a monolayer of type B, right near saturation of B.
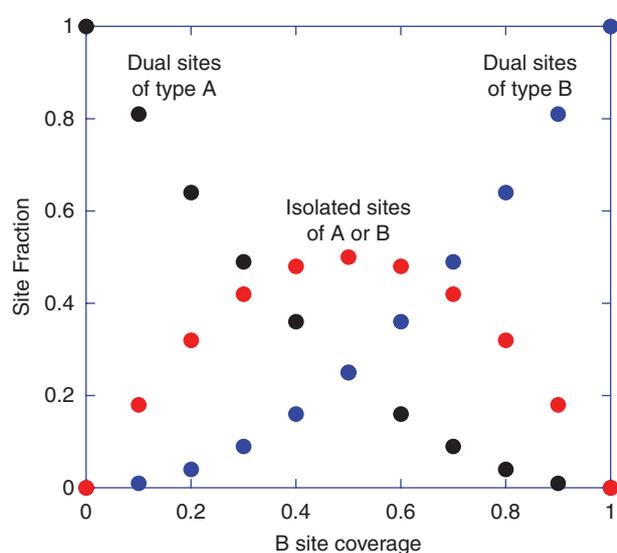
Figure 2 The variation of dual sites and single sites as a function of coverage of type B on the surface, assuming a randomised distribution model
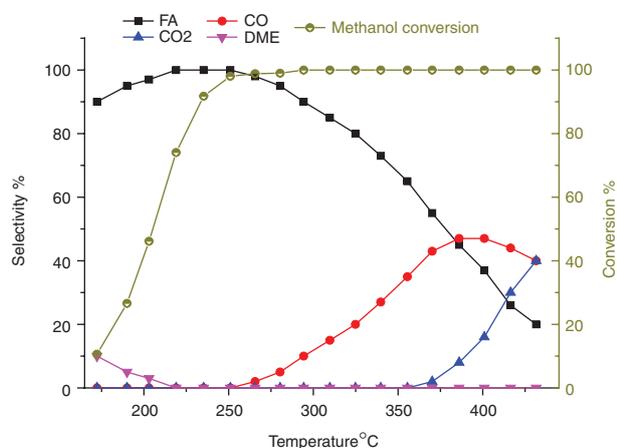
Figure 3 The temperature dependence of selectivity and conversion for $Fe_2(MoO_4)_3$. FA – formaldehyde, DME – dimethyl ether
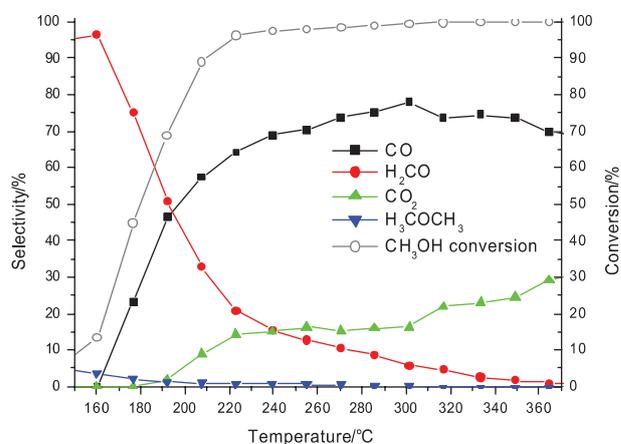
Figure 4 Product selectivity and conversion for a Mo:Fe ratio of 0.5, showing the dominance of CO production
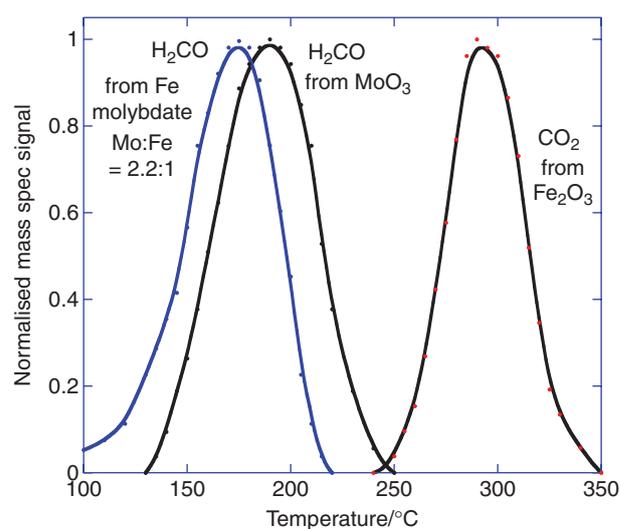
Figure 5 Normalised TPD spectra from MoO_3, ferric molybdate with Mo:Fe = 2.2:1, and Fe_2O_3. The latter shows predominantly carbon dioxide as the methanol oxidation product, whereas the former two materials give only formaldehyde

High Mo loadings

$$CH_3OH + 1/2\ O_2 \rightarrow H_2CO + H_2O$$
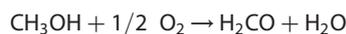
In connection with the considerations in section 3 above, the results for product yield from iron oxide as the level of Mo doping varies from 0 to the stoichiometric material ferric molybdate, and this variation is shown in Fig. 7. It is apparent that, as shown above, CO_2 is dominant at high Fe levels, while H_2CO is dominant at low Fe. However, over a wide range of the intermediate concentrations, CO is the dominant product, and this behaviour is somewhat similar to that in Fig. 2 above. The question is, what exactly is it that dictates the shape of the curve in Fig. 7? It is our contention that double sites here are important for the selective reaction, as has already been proposed for Mo sites and formaldehyde production by others,[5,17,18] and as discussed further below.
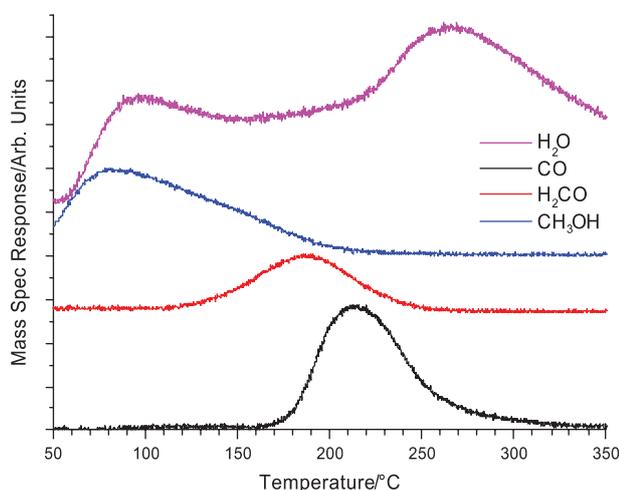
Figure 6 TPD from iron molybdate catalyst with a Mo:Fe ratio of 0.5. For such a sample, CO is a major product
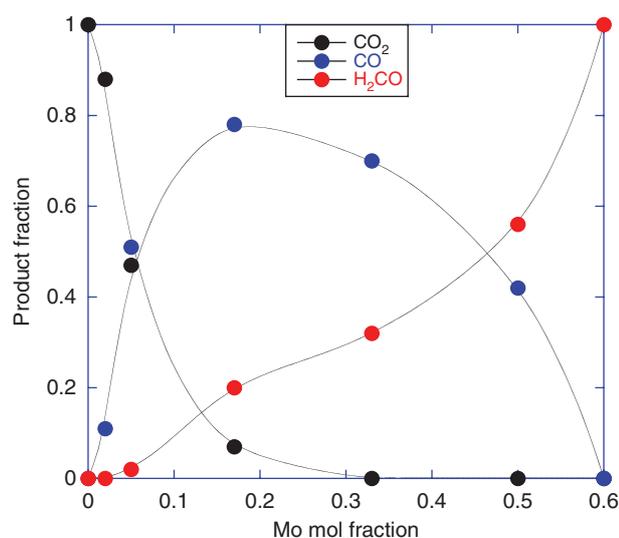
Figure 7 The yields of the three main products of methanol oxidation seen in TPD, as a function of the amount of Mo in the catalyst, note that a mole fraction of 0.6 corresponds with the stoichiometric materials Fe$_2$(MoO$_4$)$_3$

Although the data of Fig. 7 are broadly similar to those in Fig. 2, the results are not presented in the same way, so cannot be accurately compared. Figure 2 presents products as a function of *surface loading*, whereas Fig. 7 is a function of *bulk loading* and we do not at this point know if the latter is the same as the surface concentration of Mo. Indeed, we[4,8,10] and others[5–7,11,12] have shown that there is a strong tendency of Mo to segregate to the surface of these materials, that is, the surface concentration is higher than the bulk concentration. This may especially be important for the very low mole fraction of Mo in Fig. 7, where a very dramatic effect of low bulk loadings of Mo on knocking out CO_2 production in TPD. By only 0.28 of stoichiometry in the bulk, the CO_2 production has been reduced by a factor of 20. Further 100% selectivity to formaldehyde has been achieved at a mole fraction of 0.6, the stoichiometry of compound ferric molybdate.

We have some evidence related to this from XPS. For very low bulk loadings of Mo (Mo:Fe, 0.02 : 0.05) in Fig. 7 above, the surface ratio by XPS is higher (at 0.09 and 0.13, respectively), whereas at high Mo ratios, the XPS value is similar to that for the bulk loading. Thus, this would shift the low Mo level data points a little higher along the abscissa. However, this would not really have a dramatic effect on the shape of the curve; it would still show a severe decline in CO_2 at low Mo loadings. We must also remember that XPS measures the surface *region* (~ 5 layers), and does not give the top surface layer concentration. Studies with doping Mo onto the surface[9,10] shows that it tends to remain there and does not diffuse into the bulk. Indeed, if the reverse is attempted (Fe doping onto the surface of MoO_3), then Fe diffuses away from the surface into the bulk.[9]

There is another likely reason for the difference between Figs. 2 and 7, and that relates to the assumption that two sites are needed for methanol combustion and selective oxidation to formaldehyde, whereas one is needed for CO production. That two Mo sites are needed for formaldehyde production has been proposed earlier by a number of authors.[5,17,18] But when it comes to the combustion of methanol, albeit thermodynamically favoured, it is clearly a rather more complex reaction than selective oxidation, since it proceeds via a number of steps, such as

$$CH_3OH + O_s \rightarrow CH_3O + OH_s$$

$$CH_3O + 3O_s \rightarrow HCOO + 2OH_s + O_v$$

$$HCOO + 3OH_s \rightarrow CO_2 + 2H_2O + O_s + 3O_v$$

$$Overall:\quad CH_3OH + 3O_s \rightarrow CO_2 + 2H_2O + 3O_v$$
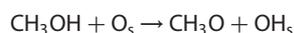
where O_s is a surface lattice oxygen and O_v is an anion vacancy at the surface.

Thus, it is not difficult to envisage that at least one of these steps may require a bigger ensemble than just two sites. The most stable intermediate in this sequence is the formate, and the presence of both methoxy and formate is shown by *in situ* IRAS (Fig. 8). Here, the methoxy (bands at 2820, 2930 cm^{-1}) dominates in the temperature range between 100 and 230°C, but it converts to formate (2870 cm^{-1}) above that temperature, which in turn is reduced as surface decomposition occurs. As shown above, the decomposition of this intermediate may require the involvement of three
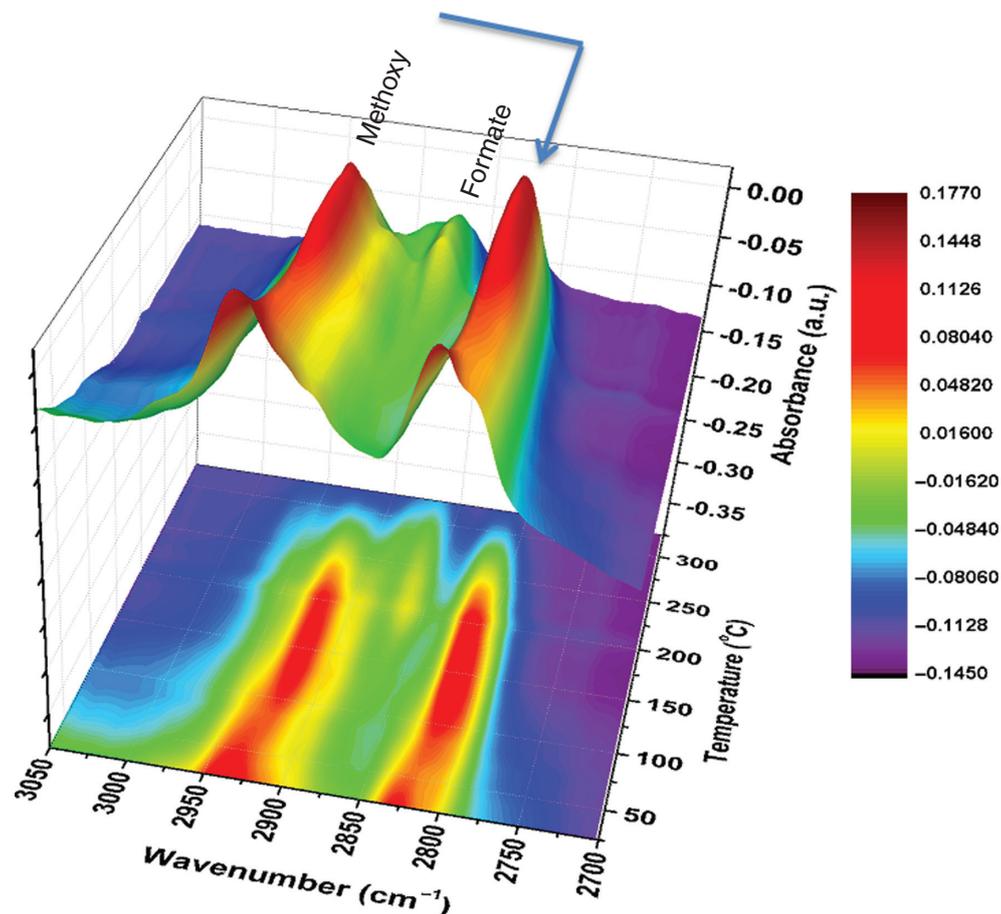
Figure 8   Evolution of the IRAS spectrum with temperature after adsorbing methanol at room temperature. The bands at 2930 and 2820 cm^{-1} are because of the methoxy species C–H stretches, while that at 2870 is because of the formate

oxygen functions, and the adsorbed system may require a large number of Fe sites for the hydroxyls and bidentate formate. If such large ensembles are required, then this could explain why the CO$_2$ yield goes down so quickly with increasing bulk loading of Mo. For instance, a model with the requirement for a larger ensemble adjacent Fe sites to be required, rather than dual sites, has just this effect, as shown in Fig. 9, and shows much closer agreement with the data of Fig. 7. It is interesting to note that in another selective oxidation reaction, namely the oxidation of ethylene to ethylene oxide, it has long been considered that CO$_2$ production is more `demanding' than selective oxygen insertion to ethene, and that the role of Cl in hugely improving selectivity of Ag catalysts for this reaction is to restrict the size of sites available.[19] It is considered that the active site for combustion requires many more sites in the ensemble than does the selective oxidation. Thus, the plot in Fig. 8 would appear to be a reasonable approach to the methanol oxidation problem and we believe that this model gives a general description of the behaviour of such materials.

What may be a little more contentious is the single site hypothesis for CO production, and even if that hypothesis is true, there are two different single sites to be considered, namely Mo and Fe single sites. It would be difficult to imagine that such single sites have the exactly same chemistry or stability for the intermediate (probably methoxy), which produces it. Indeed, if we examine the desorption of CO in particular, as the Mo loading is varied (Fig. 10), this peak shifts
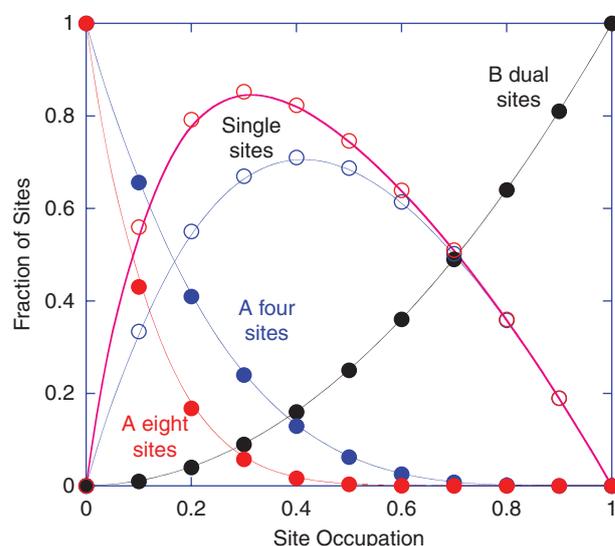
Figure 9   The distribution of surface sites with higher ensemble knock-out of species A sites by the adsorption of species B. In the specific case here, A are iron sites and B are Mo sites. If eight sites, for instance, were required for combustion, then they are affected as shown by the red curve, full red data points

significantly with increasing Mo coverage, from ~260°C at 0.05 to 215°C at 0.5 Mo:Fe ratio. This is in complete contrast to formaldehyde production and the formate decomposition, which stay at fixed decomposition temperatures.
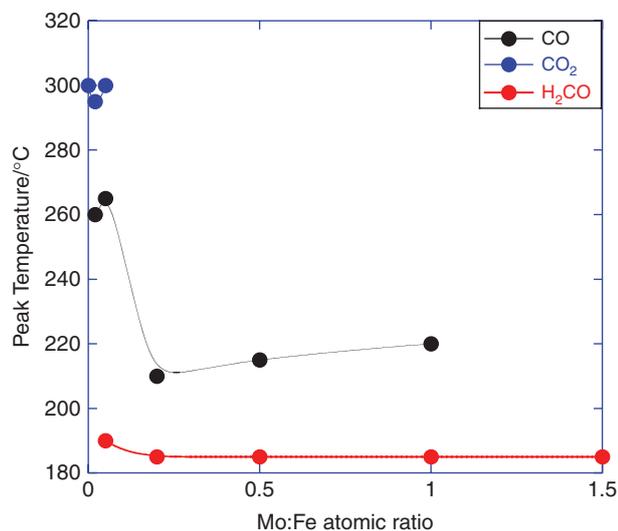
Figure 10 **The variation in peak temperatures for CO_2, CO, and H_2CO desorption from catalysts with varying ratios of Mo:Fe. There is little variation for CO_2 and H_2CO, but a significant shift for CO at low Mo loadings**

Figure 11 **Model of the active sites on the Fe−Mo oxide materials used in this work, showing the variation in products from different site ensembles**

Of course, these considerations then relate in an important way to the industrial catalyst typically used, which consists of iron molybdate with super-stoichiometric amounts of Mo present. The stoichiometry of ferric molybdate [$Fe_2(MoO_4)_3$] is Mo:Fe = 1.5, whereas industrial catalysts usually have the ratio in the range 1.7–2.2. In terms of our discussion above, it is clearly unwise to have any Fe in the surface layer of such catalysts. There would be a danger of that being the case if pure ferric molybdate were used because of two reasons: (i) possibilities from batch to batch of being slightly sub-stoichiometric and (ii) loss of Mo during time on stream, which certainly occurs over a long period under reaction conditions. Thus, high ratios of Mo:Fe compensate for any possible sub-stoichiometry and maintain the surface layers of the catalyst as purely Mo oxide.

Thus, we envisage this model pictorially, as shown in Fig. 11, which shows sites for CO, formaldehyde and carbon dioxide production.

In conclusion, we have shown that methanol reaction with iron oxide loaded with increasing amounts of surface Mo changes from combustion, to selective oxidation to CO, to selective oxidation to formaldehyde in sequence. Over a wide range of Mo loading CO is the dominant product and we propose that this is because of a requirement for a different site ensemble, requiring only one cation to be involved in the rate determining step. For formaldehyde, two Mo sites are required and it is likely that an even bigger ensemble is required for combustion on iron oxide via the formate intermediate. A simple ensemble model appears to show the general trend of behaviour observed and may well be applicable to a range of catalytic reactions and to other bi-cationic materials.

Acknowledgements

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