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Surface Segregation in Iron Molybdate Catalysts

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Abstract The high selectivity of iron molybdate catalysts for the production of formaldehyde from methanol is somewhat surprising in view of the very different behaviour of the individual oxides of Fe and Mo for this reaction. The former, on its own, is a complete combustor of methanol, whereas the latter is highly selective. Here we use STEM (scanning transmission electron microscopy) at high resolution to image the surface of small particles of the catalyst and to show that this high selectivity is due to the dominance of the surface region by molybdenum oxide.

Keywords Formaldehyde synthesis · Selective oxidation · Methanol oxidation · Iron molybdate · STEM · Surface segregation

1 Introduction

There has been considerable debate about the nature of the surface of selective oxidation catalysts in general, but in particular in this letter, we wish to address the nature of the surface of iron molybdate catalysts. Some discussion on this point is given in the recent review by Soares et al. [1] though it mainly focuses on the bulk properties of iron molybdate and its reactivity. Iron molybdate catalysts are used commercially for the selective oxidation of methanol to formaldehyde in aerobic conditions; they are very successful materials for this purpose, showing selectivities in excess of 90% at greater than 90% conversion [2–4].

It has been proposed by ourselves [3–7], and by others [8–17] that Mo segregates to the surface in such materials, and indeed we have proposed that the surface may be entirely Mo oxide for the $Fe_2(MoO_4)_3$ material [4, 18]. However, until now there was no direct evidence that this is the case. In this note we report STEM measurements of the composition of iron molybdate particles at very high resolution which confirm this proposal.

2 Experimental

In this work the iron molybdate catalyst was prepared by co-precipitation from a solution of iron nitrate (BDH, ≥98%) which was added dropwise to an acidified (~pH 2 with HNO_3) ammonium heptamolybdate (BDH, ≥99%) solution at 60 °C. After precipitate formation the solution was heated to near dryness at 90 °C and then dried at 120 °C, before being calcined at 500 °C for 48 h. The catalyst was made to have the stoichiometry of $Fe_2(MoO_4)_3$, i.e. Mo:Fe 1.5:1. XRD showed that this material was monophasic, consisting of only α-ferric molybdate, and its surface area by the BET method was 6.5 $m^2\ g^{-1}$.

Iron oxide was prepared by the dropwise addition of 50 mL of $Fe(NO_3)_3 \cdot 9H2O$ (BDH >98%) solution to 100 mL of nitric acid solution at pH 2, with stirring, at 60 °C. Water was then evaporated at 90 °C, the sample was dried overnight at 120 °C and was finally calcined at 500 °C for 48 h. This resulted in a material with a surface

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area of 11.8 m^2 g^{-1}, while XRD showed it to be α-Fe_2O_3. The MoO_3 used was a commercial sample (BDH, ≥99.5%) with a surface area of approximately 1 m^2 g^{-1}.

The incipient wetness method was used for the impregnation of Mo onto the surface of the Fe_2O_3 catalyst. Ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, BDH >99%] was made into an aqueous solution and added with stirring until all the support voids were full. The ammonium heptamolybdate solution was made to the appropriate concentration to yield a 60% surface coverage of the surface of the iron oxide, assuming that the Mo was entirely segregated to the support surface. This corresponds with a bulk ratio of Mo:Fe of ∼0.01. The material was dried overnight at 120 °C before calcination of the material at 400 °C for 30 min in situ in the reactor in a flow of 10% O_2/He.

The catalyst was tested for methanol conversion using a pulsed flow reactor in which small injections (1 μL of liquid) were introduced into the gas stream (10% O_2/He, 30 mL min^{-1}) before the catalyst. More details of this equipment and methodology are given elsewhere [3, 4]. While most exhaust gas was vented via a rotary pump, a small fraction was bled into a UHV chamber containing an online mass spectrometer (Hiden Hal 201). Lines in the reactor were kept hot (>120 °C) to allow for vapourisation of the methanol and to prevent formation of paraformaldehyde in the exit lines.

The STEM used here is based at the Superstem facility at Daresbury Laboratory UK and consists of a Vacuum Generators 501 FEGCTEM, aberration-corrected (Nion) scanning TEM. It is capable of operating at ∼1 Å spatial resolution, with chemical analysis using atomic column electron energy loss spectroscopy (EELS). The beam energy is 100 keV with a typical current at the sample of ∼1 mA in the ∼1 Å beam. For more details of this facility see ref. [19].

3 Results and Discussion

When reactor measurements are carried out on catalysts with varying bulk ratios of Fe and Mo, it is at once clear that catalysts with even small amounts of Mo behave quite differently to iron oxide [6, 16–18]. Haematite has been shown previously to produce insignificant amounts of formaldehyde and simply combusts the methanol, whereas molybdena has been shown to give very high selectivity to formaldehyde [3]. However, with very small amounts of Mo are impregnated into the catalyst, it shows much increased conversion (Fig. 1a) and high selectivity to formaldehyde (Fig. 1b), at least at low temperature, as shown in Fig. 1, and it has similar activity to that of iron

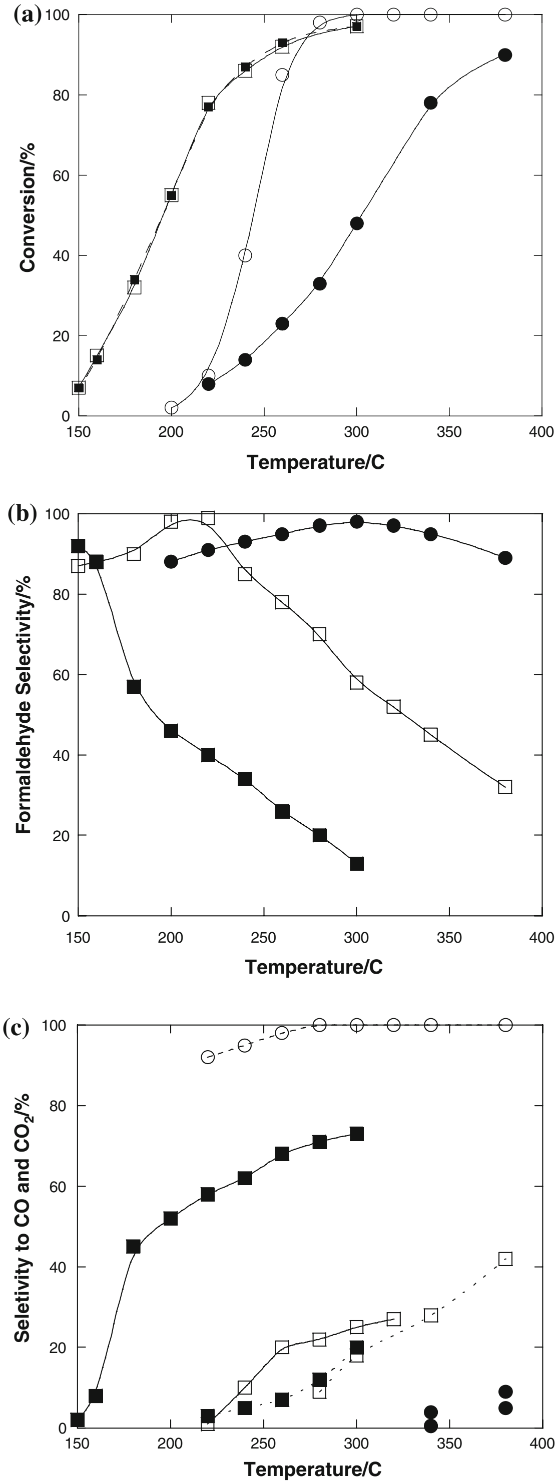

Fig. 1 Showing the activity and selectivity performance of Fe_2O_3, $Fe_2(MoO_4)_3$, MoO_3 and Fe_2O_3 with a small amount of Mo incorporated by impregnation onto the haematite sample. (**a**) Conversion over Fe_2O_3 (◯), $Fe_2(MoO_4)_3$ (□), 60% ML Mo on Fe_2O_3 (■) and MoO_3 (●). (**b**) Formaldehyde selectivity: symbols as in Fig. 1a; note that iron oxide has very little selectivity and so is not shown. (**c**) CO and CO_2 selectivity: symbols as in Fig. 1a, CO, solid lines, CO_2 dashed lines

molybdate. Iron oxide in Fig. 1 is non-selective (Fig. 1b, c) and produces only CO_2 (Fig. 1c) and water, whereas the MoO_3 sample shows very high selectivity (Fig. 1b), but the lowest activity, largely due to its very low surface area (Fig. 1a). The important point about MoO_3 is that high selectivity can be retained up to very high conversion, resulting in an extremely efficient catalyst in terms of formaldehyde yield. The $Fe_2(MoO_4)_3$ catalyst is very active and selective up to very high conversion (giving 95% selectivity at 80% conversion). The sample with a very small amount of molybdenum added by impregnation is less selective than the ferric molybdate (Fig. 1b), producing large amounts of CO above 200 °C (Fig. 1c), but nonetheless it shows very high selectivity to formaldehyde at low conversions. It is also much more active than the haematite alone. This contrast of iron oxide alone with iron oxide incorporating small amounts of molybdenum, leads to the proposal that Mo segregates to the surface in such materials, and indeed that the surface may be entirely Mo oxide for the $Fe_2(MoO_4)_3$ material. This was recently proposed by Briand et al. [14], by others [10, 15], and by ourselves [4, 6, 7, 18] but until now there was little spectroscopic evidence that this is the case. These ideas are confirmed by STEM measurements of the composition of iron molybdate particles, at very high spatial resolution, which show the segregation rather directly, as reported below.

Figure 2a shows STEM images of a particle of the catalyst and Fig. 2b shows the composition profiles of Fe, Mo and oxygen through a section across the sample using the EELS facility on the microscope. Here it is clear that the surface is enriched in Mo and depleted in Fe compared with the bulk composition. Thus surface enrichment is proved. Although this is only one area of the sample generally similar results were obtained from several different areas and on several different particles. It is not certain why the oxygen appear to be depleted in the surface region, but this could be due to a number of causes. It could be due to surface reduction. Surface carbon contamination is often observed in electron microscope images, it was sometimes observed in this work in other experiments, and is often due to the method of sample preparation (grid-cleaning with organic solvents can be one cause). If such contamination is present it can reduce the sample if it gets hot. Another reason for the apparent depletion could be that the very topmost layer is mainly Mo. Since the beam is ~1 nm in size, then the spatial resolution is averaged over that range and so a reduction in oxygen signal would be seen to start when the beam edge actually hits the edge of the sample. Finally, there may be some electron-induced or thermally-induced oxygen desorption from the surface.

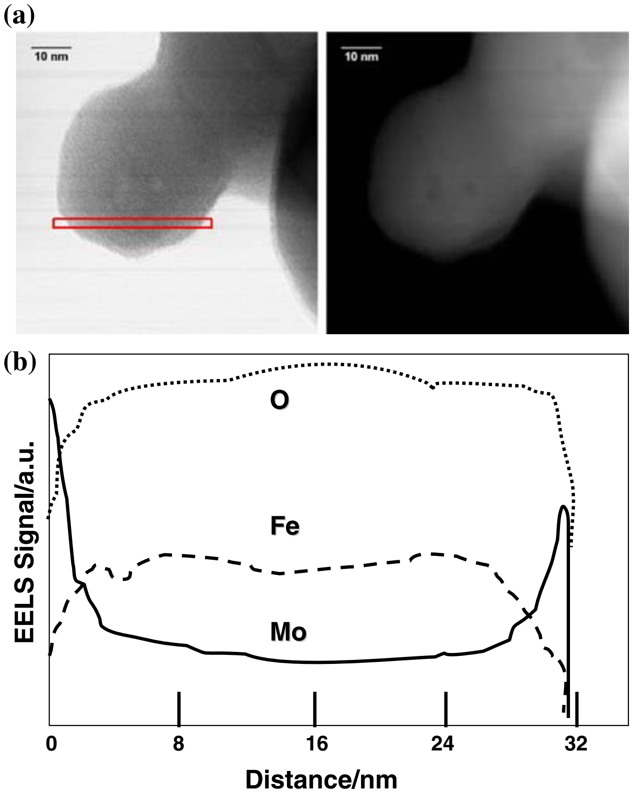

Fig. 2 (**a**) STEM images of an iron molybdate particle in bright field and dark field modes and (**b**) Mo, Fe and O signals across the linescan shown in (**a**)

XPS is a surface-sensitive technique, but not so surface sensitive as the STEM when used in this mode. The XPS of such samples was carried out, and the ratio of Mo:Fe in the surface region of the impregnated catalyst was determined to be 0.16, whereas it was 1.63 for the ferric molybdate sample. If the Mo in the impregnated sample were simply to dissolve in the haematite lattice to form a random mixture, then we would expect to see a very small Mo:Fe ratio of ~0.01 by XPS. This further confirms that the molybdena coats just the surface layer, in agreement with the findings of Dong et al. [20], who physically mixed MoO_3 and Fe_2O_3, and found that, after calcination, no MoO_3 could be identified in XRD below a certain level of MoO_3 in the mix, that level corresponding with the amount needed to form a monolayer on the iron oxide. For the ferric molybdate sample the XPS ratio at the surface is only slightly higher than the expected ratio of 1.5, but the surface layer of molybdenum oxide rests on ferric molybdate, which is the only bulk phase seen in XRD at this ratio. Thus, most of the XPS signal is contributed by the underlying stoichiometric compound and so we would not expect a very much higher Mo:Fe ratio in XPS than the bulk value of 1.5.

To conclude, we have shown that Mo enrichment occurs at the surface of iron molybdate catalysts and that it is this property which is responsible for giving high selectivity and activity to samples with a very low bulk loading of Mo.

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