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The surface of iron molybdate catalysts used for the selective oxidation of methanol.

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Abstract

The oxidation of methanol to formaldehyde is a major chemical process carried out catalytically and iron molybdate is one of the major catalysts for this process. In this paper we explore the nature of the active and selective surface of iron molybdate catalysts and show that the effective catalysts comprise molybdenum rich surfaces. We conclude that it is therefore important to maximise the surface area of these active catalysts and to this end we have studied using a new physical grinding method with oxalic acid. For super-stoichiometric materials (Fe:Mo =1:2.2) the reaction data show that physical mixing produces effective catalysts, possibly offering an improvement over the conventional co-precipitation method.

Keywords: methanol, formaldehyde, selective oxidation

1. Introduction

Iron molybdate catalysts have been used for the industrial production of formaldehyde from methanol oxidation for many years. They are robust catalysts which are generally used in an unsupported form, and which operate in an oxygen rich environment. Interest in these materials has increased as the volume of formaldehyde production has increased, now reaching over 52 MT p.a. with an annual growth rate of 5% expected for the foreseeable future.

Two Industrial processes for the production of formaldehyde have been used; i) the dehydrogenation of methanol over a supported silver based catalyst [1-3] or ii) the partial oxidation of methanol over mixed metal oxide catalysts such as iron molybdate [4-6]. The dehydrogenation reaction uses a high concentration of methanol in the feed (90%) and relatively high temperatures (600 °C), whereas the partial oxidation reaction uses a lower methanol concentration (< 10%) at a lower temperature (300 °C). The lower operating temperature and robust nature of the mixed metal oxide catalyst has made the partial oxidation process more economically viable compared to the silver based catalytic system [7].

Iron molybdate has been established as an effective methanol partial oxidation catalyst since it was reported in 1931 [8]. The industrial catalysts are composed of two phases; $\text{Fe}_2(\text{MoO}_4)_3$ with an excess of MoO_3 [5]. The excess MoO_3 has recently been found to have a dual function. First it increases the selectivity towards formaldehyde production by aiding the dispersion of iron sites over the surface of the catalyst [9]. These iron sites have been conclusively shown to be detrimental towards the selective partial oxidation of methanol, by increasing selectivity towards carbon oxide products [10-12]. Secondly, whilst an excess of MoO_3 helps maintain high selectivity, it also extends the catalyst lifetime, as deactivation can occur by the loss of MoO_3 *via* sublimation. The loss of MoO_3 has been determined to lead to deactivation *via* the formation of iron oxide centres [4-6 and 13].

Many studies have focussed on the synthesis of iron molybdate catalysts using co-precipitation [6,11,14-16]. These catalysts have been successful in the production of formaldehyde from methanol achieving high yields [14]. Synthesising iron molybdate catalysts in this way produces large volumes of aqueous waste containing unprecipitated iron and molybdenum and can result in phases containing only iron or molybdenum that do not contribute to the catalytic activity [9]. These factors, along with low active surface area of these materials, leads to a decreased catalytic performance as reoxidation of the catalyst is limited [17].

Alternative preparations of iron molybdates have been investigated, such as sol-gel methods [18] or supported iron on molybdenum nanorods [19]. These synthetic strategies aimed to achieve higher

surface area materials with the aim of decreasing the propensity of iron-dense regions responsible for total oxidation.

In recent years we have particularly been interested in the nature of the active surface of this material, that is, what is the surface composition and structure [9,11,12,14,16, 20-25]? In addition, we are exploring novel ways of making such catalysts, and in making it in different morphologies [19].

More recently, the production of iron molybdate nanoparticles using oxalic acid has been reported [26]. The solid state reaction, by grinding the salts together with oxalic acid, provides a cheaper and greener alternative, by eradicating the need for a solvent in the catalyst preparation procedure. These potential catalysts for the conversion of methanol to formaldehyde have been reported to exhibit a significant increase in the overall surface area compared to a conventional co-precipitation method.

In this study we investigate two features of this important catalyst. First, we report on the nature of the active surface of iron molybdate catalysts. From this it is clear that high surface area catalysts are required in which the surface is dominated by molybdenum. Secondly we investigate the new oxalic acid method of preparation to achieve materials with enhance surface area. In particular we investigate the effect of varying the Fe:Mo, ratio (1:1.5, 1:2.2 and 1:3), and assess the catalytic performance for the selective oxidation of methanol to formaldehyde. The performance of the oxalate solid state ground catalysts are compared with a conventional coprecipitation catalyst.

2. The nature of the surface in iron molybdate catalysts.

We have examined the surface of iron molybdate catalysts that are active for selective methanol conversion by a range of techniques. The conclusions of this work are i) it is critically important that the surface is dominated by Mo, ii) Mo tends to segregate to the surface, even when present in the catalyst at very low levels. The performance of the catalyst is critically dependent on this surface level of Mo [9,23], as shown in figure 1. Here we have made catalysts of varying molar ratio of Mo by co-precipitation [23], and have measured the products from the surface after adsorbing methanol at ambient temperature. We see a particular pattern of behaviour with increasing Mo level. At very low bulk loadings CO₂ is the main product since iron oxide is a combustor, and converts adsorbed methoxy through to formate as the intermediate in the combustion pathway. Figure 2 shows DRIFTS identification of the presence of methoxy on the catalyst surface [9], which converts to formate upon heating, coinciding with CO₂ evolution in TPD. As the Mo loading increases this combustion is

reduced very quickly, so that by only 0.05 mol ratio of Mo the CO₂ has been reduced to only 50% selectivity. The major product at the intermediate loadings of Mo is CO, though formaldehyde begins to be made even at low loadings. Finally, as we approach stoichiometry of Mo:Fe 1.5 (mol fraction 0.6) for ferric molybdate, then CO is diminished and very high selectivity for formaldehyde is achieved.

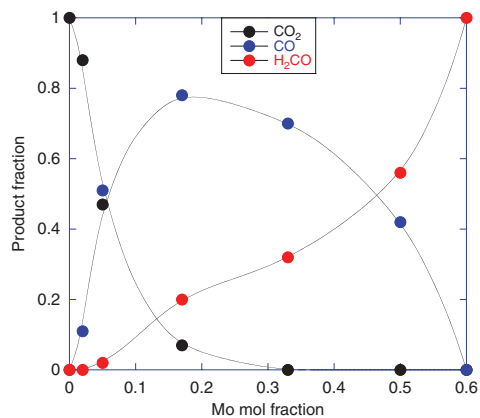


Figure 1. The dependence of relative product yields in TPD upon the bulk loading of Mo in the oxide with Fe.

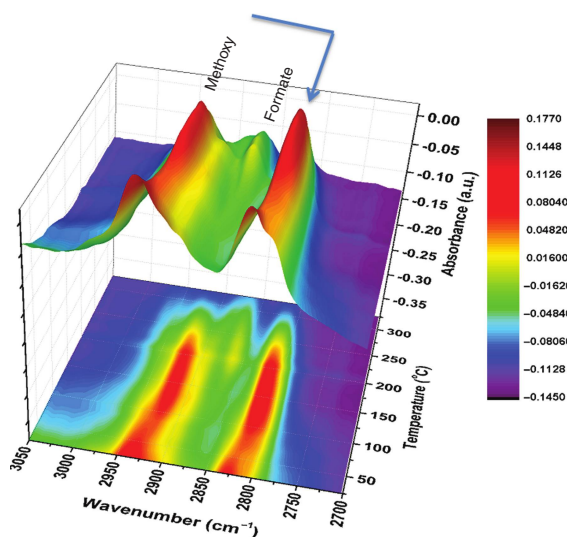


Figure 2. Stacked temperature-programmed DRIFTS spectra for methanol adsorbed on an iron oxide surface

So why do we have this distribution of products? We have very recently proposed that this is due to the nature of the ensembles on the surface [9]. If we imagine that the products are determined by pairs of Fe sites (which only produce CO₂) and pairs of Mo sites (which are required for formaldehyde, as is proposed by a number of authors [27-29]), and that single sites of each produce CO, then the result of such a simple model, with a random statistical distribution is seen in figure 3.

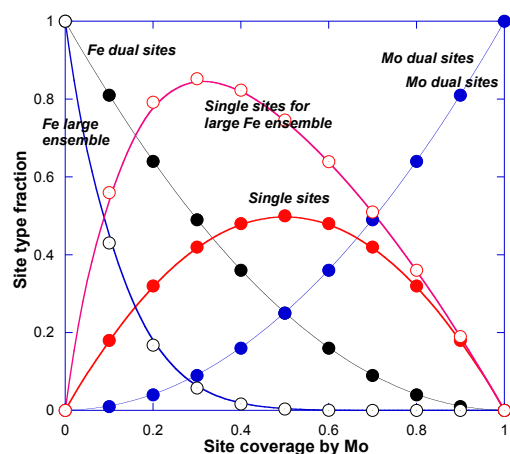
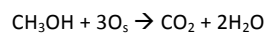


Figure 3. The distribution of single and pair sites on a surface within a random distribution of Mo model (solid data points). The open points are for the situation with larger ensembles of eight Fe atoms required for the combustion reaction, showing then the more severe effect on combustion sites.

This gives broadly the distribution shown in figure 1, except that is totally symmetric with respect to Mo coverage, and especially the CO₂ level does not decrease fast enough with increasing Mo loading. However, in principle, combustion of methanol is a much more demanding reaction than selective oxidation, in the sense of surface oxygen (O_s) demand, as illustrated by the equations below –



Thus we can easily imagine that a number of Fe sites in an ensemble might be needed to facilitate the complete combustion process, and so figure 3 shows another ensemble size requirement and it can be seen that increasing this requirement has a positive effect on quickly diminishing CO₂ production at low Mo levels. Of course figures 1 and 3 are not directly comparable, in the sense that the latter is for surface Mo, whereas figure 3 is for bulk ratios. We know from a variety of experiments that Mo segregates to the surface, as shown in figure 4 for a ferric molybdate particle [14,22]. Here the use of aberration-corrected STEM and EELS analysis clearly shows enhancement of Mo and depletion of Fe in the surface region. If we carefully make iron oxide particles surface doped with Mo, that Mo stays there even after calcination at high temperature [12,24,25]. Such layers show excellent activity for the conversion, and high selectivity, though the maximum yield is a little lower than for the stoichiometric material. In the reverse material, Fe doped at the surface of MoO₃, then the Fe disappears into the bulk upon calcination [12].

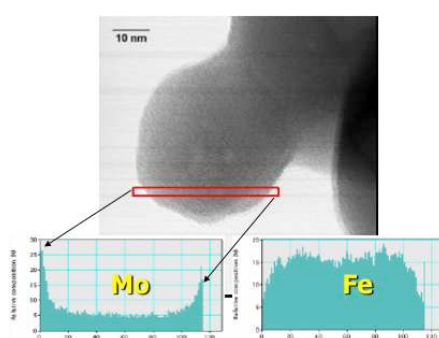


Figure 4. acSTEM image of a ferric molybdate nanoparticle and the results of EELS analysis using a 1nm electron beam probe. Mo is preferentially segregated to the surface.

Returning then to figure 1, it could be that the surface Mo is higher than the bulk value. This is undoubtedly the case [12, 23], but the level of segregation is insufficient to explain the asymmetry in the curves (e.g. the surface region Mo by XPS for the bulk loading of 0.05 is 0.13 [23]). Thus we believe the ensemble description of figure 3 is indeed a reasonable approach to describe the behaviour seen. So, we consider that the selective surface is one which has no Fe present in the surface layer, which is totally dominated by Mo. However, we don't yet know the EXACT nature of the active site. Recent experiments with XAS on monolayer catalyst have shown that the surface layer of Mo is of distorted octahedral structure (as it is in MoO₃), whereas ferric molybdate itself is tetrahedral, see figure 5. When several layers of molybdenum are added in the preparation, then

after calcination, several layers of ferric molybdate underlie the overlayer of octahedral Mo, which in turn stay near the surface as overlayers on the core Fe_2O_3 .

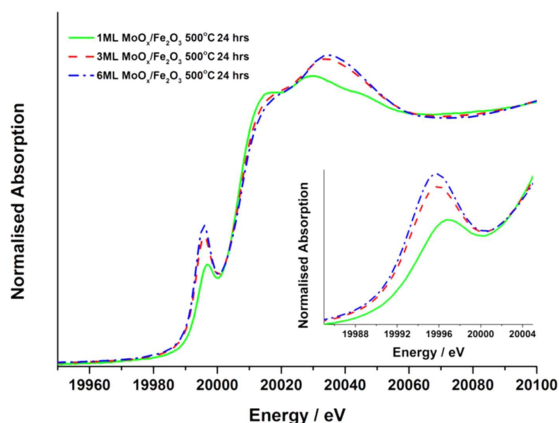


Figure 5. XAS for the Mo K edge of core-shell catalysts with a core of haematite and shell of molybdena with three different coverages [M].

We have made some attempts to make models of such catalysts which can then be imaged by STM at the atomic level [30]. When we dose Mo onto the surface of single crystal iron oxide then we observe the nature of the monolayer Mo. It is in the 6+ oxidation state, which is the selective oxidation state for formaldehyde formation [21], but it is adsorbed on the surface in a particular form, as shown in figure 6, as it adsorbs as a Mo_3O_9 -like trimer. It may be that such clusters are of the type which are important for the oxidation process, and Raman shows monolayer species of the 'polymeric' type on powdered catalysts, as described further below. These structures are shown in figure 6 and locally cover the iron oxide surface in a 2x2 structure, though there are bare patches of iron oxide which are also exposed. So far we have not been able to obtain TPD data for such surfaces which have high selectivity to formaldehyde – we observe all three products shown in fig 1.

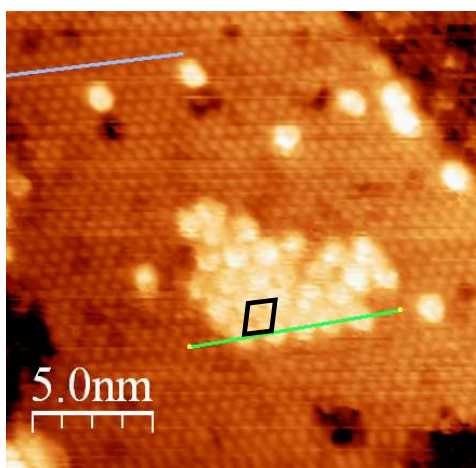


Figure 6. A scanning tunnelling microscopy image of the $\text{Fe}_3\text{O}_4(111)$ surface, showing atomic resolution of the Fe cations, with Mo oxide deposited onto it (the bright features). The unit cell of the bright features has twice the periodicity of the underlying lattice.

3. Alternative synthetic strategies

Based on the knowledge gained from our studies on the surface of the active and selective iron molybdate catalysts we have investigated synthetic methods to try to produce more active catalysts.

3.1 Catalyst preparation

The preparation of the iron molybdate catalysts with Fe:Mo ratios of 1:1.5, 1:2.2 and 1:3 were carried out using a procedure described previously [20]. Iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ (molar ratios = 1/0.21/10, 1/0.31/10 and 1/0.42/10) were physically ground using a pestle and mortar for 10 min inducing a solid state reaction. The solid oxalic precursors were then heated on a hotplate at $160\text{ }^\circ\text{C}$ for 3 h. The catalyst oxalate precursors were calcined under flowing air (20 ml min^{-1}) in a tubular furnace ($500\text{ }^\circ\text{C}$, 2 h, $10\text{ }^\circ\text{C min}^{-1}$) resulting in the final catalysts.

A catalyst was also prepared using a conventional coprecipitation method [15]. A solution of ammonium heptamolybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, (9.71 g in 150 ml distilled water) was acidified to pH 2 using conc. HNO_3 (70 %). A solution of iron nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (10.1g in 150 ml distilled water) was added dropwise with vigorous stirring. The suspension was aged at $80\text{ }^\circ\text{C}$ for 3 h, and the solution was cooled to room temperature and the precipitate recovered by

Mike Bowker 12/6/2015 11:40

Comment [1]: How do you know there's a 'solid state reaction' – the reviewer will almost certainly ask. How does grinding mix at the atomic scale

filtration, dried at 120 °C for 16 h and calcined in flowing air at (500 °C, 2 h, 10 °C min⁻¹, 20 ml min⁻¹) resulting in the final iron molybdate catalyst with Fe:Mo 1:2.2.

3.2 Catalyst characterisation

X-Ray powder diffraction patterns (XRPD) were attained using an X'Pert PANalytical diffractometer operating at 40 kV and 40 mA selecting the Cu-K α radiation. Analysis of the patterns were carried out using X'Pert HighScore Plus software and phases were assigned using the ICDD database. BET surface areas were determined by N₂ adsorption at – 196 °C using a Quantachrome Quadrasorb-evo instrument. The samples were prepared for analysis by removing physisorbed water at 120 °C for 2 h under vacuum. Raman measurements were carried out using a Renishaw Raman microscope with a 514.5 nm laser power over a wavenumber range of 100– 1200 cm⁻¹. Typical measurements used a 1 % laser power, with 10 accumulations at 5 s exposure time for each catalyst. SEM micrographs of the iron molybdate catalysts were obtained using a Carl-Ziess Evo-40 microscope which has combined facilities for both SEM and EDX. The samples were mounted onto Carbon Lite adhesive disks attached to aluminium studs.

3.3 Catalyst performance

The catalytic performance of the iron molybdate catalysts were evaluated for the partial oxidation of methanol to formaldehyde in a laboratory plug flow microreactor. The catalyst was pressed and sieved between 400-600 μ m. Typically, 0.3g of the catalysts were placed in a quartz reactor tube (8 mm i.d) held between plugs of quartz wool. The reactor was placed in a tubular furnace (carbolite) and temperature monitored using a k-type thermocouple at the centre of the catalyst bed. Helium was delivered to a saturator containing methanol (99.5 % Sigma Aldrich) which was maintained at 5.2 °C in a thermostatically controlled water bath. The methanol/helium and oxygen were introduced using mass flow controllers (Bronkhorst) to give a total flow rate of 60 ml/min (MeOH:O₂:He = 5:10:85). Both Inlet and outlet lines were heated at 130 °C to prevent condensation. The data was collected and analysed using an on-line gas chromatograph (Agilent 7820A) equipped with a Porapak Q (1 m) column and Molsieve 13 X (80-100) column for separation and a methanizer to convert the separated products to methane, in order to overcome detection limitations, *via* an FID.

3.4 Characterisation of the synthesised catalysts

Figure 7 shows the powder X-ray diffraction patterns for calcined iron molybdate catalysts prepared by solid state grinding, indicating they contained both MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$ phases. The reflections observed at 12.8° (452 \AA) and 33.8° (138 \AA) relate to the lattice planes (200) and (111) of the MoO_3 phase. The peaks at 20.5° (410 \AA), 21.8° (395 \AA), 23.0° (202 \AA) and 31.4° (143 \AA) correspond to the lattice planes (120), (214), (220), (032) and correspond to the $\text{Fe}_2(\text{MoO}_4)_3$ phase [31].

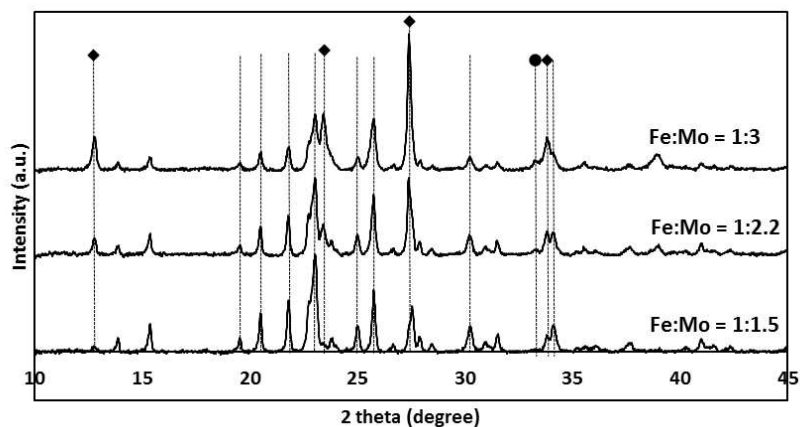


Figure 7. XRPD of the iron molybdate fresh catalysts A-C. Phases present: black dotted lines = $\text{Fe}_2(\text{MoO}_4)_3$; dotted diamond lines = MoO_3 ; dotted circle line = Fe_2O_3 .

An excess of MoO_3 is present in catalyst Fe:Mo = 1:1.5, even though it was made with the stoichiometric amount of Fe:Mo. This suggests that upon grinding the solid precursors did not intimately mix and therefore phase segregation occurred producing a non-homogenous catalyst. However, we could not identify a separate iron oxide phase to compensate for the MoO_3 formed. As the molybdenum content was increased the reflection indicative of excess molybdenum trioxide increased (12.8°). The increase in iron oxide present observed with increasing molybdenum content is counterintuitive, excess molybdenum should promote the formation of the iron molybdate phase *via* the dilution of the iron within the sample [32]. This suggests that there is localised iron and molybdenum oxide regions within the catalyst sample, as a result of poor mixing from the grinding stage.

Raman spectra (Figure 8) were also obtained for the fresh iron molybdate catalysts. Raman spectroscopy shows that with increasing molybdenum content, from 1:1.5 to 1:3, the bands characteristic for molybdenum oxide stretching modes in MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$ increased. A weak Raman band (667 cm^{-1}) is observed for catalyst with the stoichiometric amount of iron to

molybdenum which complements the data attained from XRPD, suggesting isolated regions of molybdenum. Molybdenum trioxide bands appeared at 996 cm^{-1} and 667 cm^{-1} . The bands at 996 cm^{-1} and 971 cm^{-1} are from the $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases respectively. These arise from the Mo=O terminal stretching modes. The bands at 785 cm^{-1} and 817 cm^{-1} are the Mo-O-Mo vibrations within the $\text{Fe}_2(\text{MoO}_4)_3$ phase and the MoO_3 phase respectively [33].

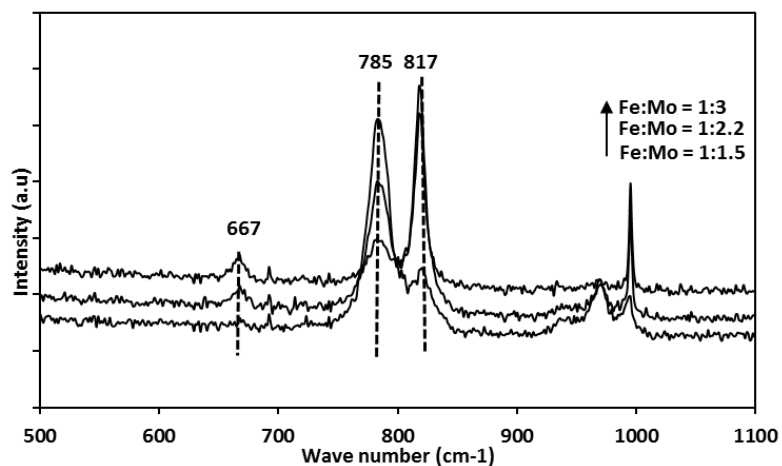


Figure 8. Raman spectroscopy of catalysts prepared by physical grinding with oxalic acid after calcination with flowing air ($500\text{ }^{\circ}\text{C}$, 2 h , $10\text{ }^{\circ}\text{C min}^{-1}$, 20 ml min^{-1}). Lines from bottom to top are the catalysts with Fe:Mo = 1:1.5, 1:2.2 and 1:3.

Table 1: BET surface area analysis and maximum yield of formaldehyde production of the iron molybdate catalysts.

Catalyst	BET Surface Area ($\text{m}^2\text{ g}^{-1}$)	Max Yield (%) (Temp $^{\circ}\text{C}$)
Fe:Mo = 1:1.5	$4.4 (\pm 0.1)$	76.8 (260)
Fe:Mo = 1:2.2	$4.6 (\pm 0.1)$	92.6 (320)
Fe:Mo = 1:2.2 (Coprecipitation)	$3.9 (\pm 0.1)$	90.0 (350)
Fe:Mo = 1:3	$7.0 (\pm 0.1)$	87.1 (320)

Mike Bowker 10/6/2015 17:48

Comment [2]: It's not easy to distinguish these three curves – can we separate them more vertically, or have different colours?

BET results shown in table 1 display that increasing the molybdenum content increased the surface area, which is in contrast to our previous findings for co-precipitated catalysts [14]. The catalyst prepared by co-precipitation and the analogous material prepared using the oxalic acid method, has a lower surface area. This suggests that upon calcination the oxalic organic material decomposes to produce a higher surface area material. SEM images (Figure 9) complements the BET surface area analysis data and shows that the pores formed on the surface by the decomposition of the oxalic acid may produce the voids, as these are not present with co-precipitation catalysts. Increasing the molybdenum to iron ratio increased the number of the pores which coincides with an increase in surface area. The formation of these voids may also indicate the encapsulation of the iron oxalate species by MoO_3 . This is supported by XRPD which indicated an increase in iron oxide with increase molybdenum content of the sample as a greater proportion of the iron oxalate is surrounded. This results in areas of high iron content within the catalyst sample which may be detrimental to the partial oxidation of methanol.

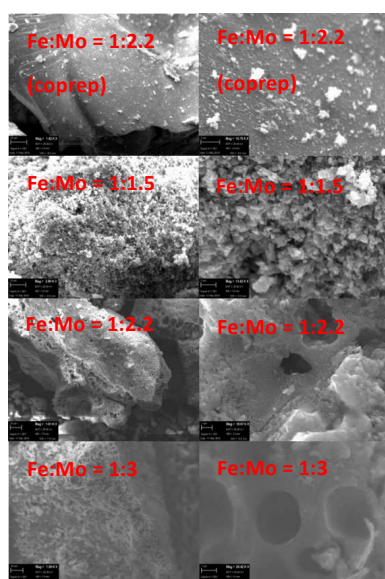


Figure 9. SEM comparison of catalysts A-C and B.

3.5 Catalytic performance of the synthesised catalysts

Figure 10 shows the catalytic performance of the catalysts for methanol partial oxidation at different temperatures. With increasing temperature, the catalysts showed an increase in conversion yielding the primary product formaldehyde. Dimethylether (DME) was produced in low quantities at low

Stuart 4/6/2015 17:05

Comment [3]: Inadequate legend, probably need to annotate figs to show features described in text.

Hutch 8/6/2015 06:22

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temperatures but as the temperature increased CO_x was produced, which was shown in our earlier work using mass spectrometry to be mainly CO [2,3, 12]. The catalysts prepared by physical grinding showed a little higher activity achieving above 90 % conversion at 300 °C, compared to the catalyst prepared by coprecipitation, which only achieved this at 320 °C.

The stoichiometric catalyst (Fe:Mo = 1:1.5) showed a slightly higher selectivity to formaldehyde compared to the catalysts with higher molybdenum ratios. Catalysts with a Fe:Mo = 1:2.2 and 1:3 showed similar performances while the coprecipitated catalyst (Fe:Mo 1.22) resulted in high selectivity to formaldehyde even at high conversions of methanol.

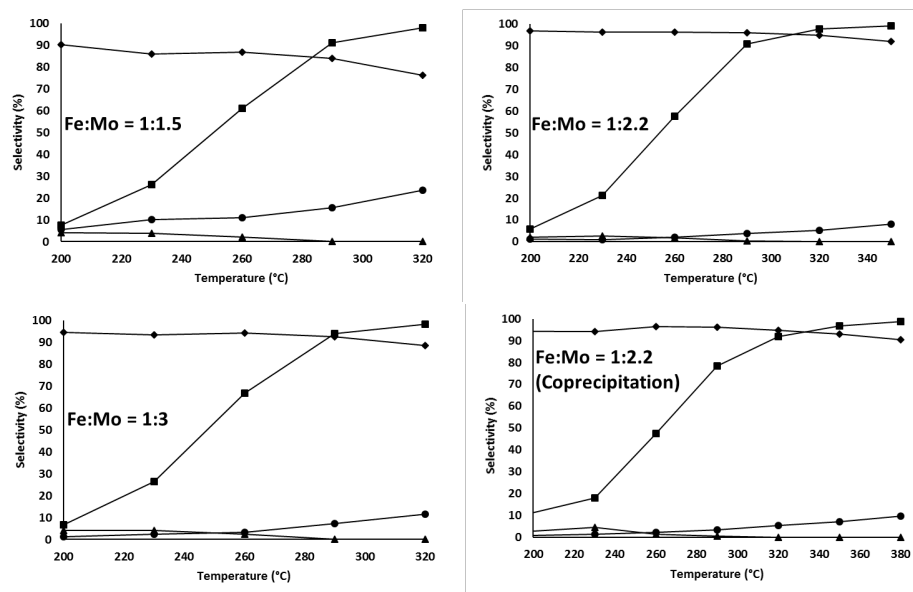


Figure 10. Catalytic performance of catalysts prepared by physical grinding, Fe:Mo 1:1.5, 1.22 and 1 :3, and by coprecipitation (Fe:Mo = 1:2.2). Product selectivity and conversion showing the high selectivity to formaldehyde. COH_2 = diamonds (◆), CO_x = circles (●), DME = triangles (▲), Conversion = squares (■).

A summary shown in Figure 11 and Table 1 compares the performance of all the catalysts. The catalyst with Fe:Mo 1:1.5 produced lower yields of formaldehyde. However, the catalyst was more active at lower temperatures than catalysts with higher Fe:Mo ratios and the catalyst prepared by coprecipitation, which is characteristic of higher iron content iron molybdates [11]. Both catalysts

with Fe:Mo 1:2.2, prepared either by physical grinding with oxalic acid or by co-precipitation, are similar, initially showing higher selectivity towards formaldehyde. Formaldehyde selectivity then decreased steadily and the catalyst prepared by physical grinding showed a higher yield, 2.6 % more than the catalyst prepared by co-precipitation, and with 30 °C lower temperature for the maximum yield. The introduction of voids in the catalyst surface creates a larger surface area shown by BET (Table 1) which may be a cause of the increase in formaldehyde yield. Catalyst with a Fe:Mo = 1:3 showed a decrease in selectivity towards formaldehyde resulting in a lower yield (87.1 %) shown in Table 2. The localisation of high iron centres shown by XRPD (Figure 7), which may reside in the voids, could cause the decrease in selectivity due to the presence of iron oxide species promoting total oxidation [12]. The presence of the iron oxide may be a sign of some poor mixing in the preparation procedure at this ratio. Note, however, that the amount of surface iron oxide must be very low, since iron oxide has been shown to be an active material for methanol combustion [U] as we have discussed in detail earlier in this paper. This is supported by the evidence provided by the SEM images (Figure 9) where more voids are present on the surface of catalyst Fe:Mo 1:3 compared to 1:2.2, even though this catalyst has the lower bulk iron content. Controlling the presence and distribution of these voids is important for the selectivity shown by the catalysts.

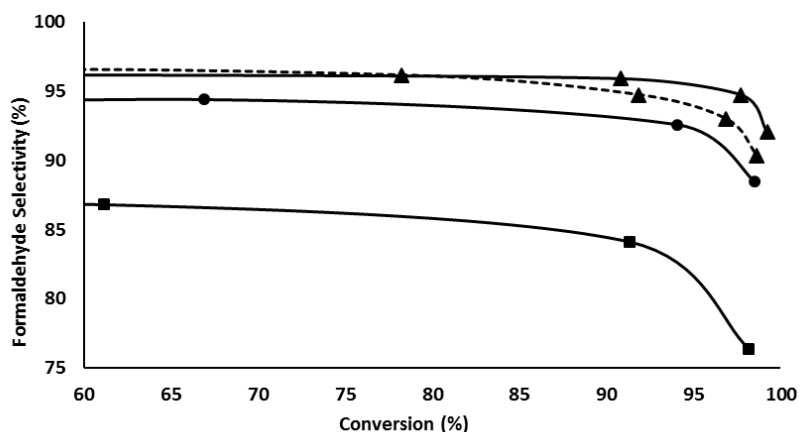


Figure 11. Formaldehyde selectivity and conversion of the catalysts . Coprecipitated (Fe:Mo = 1:2.2) catalyst =black triangles and dotted line(--▲--), Fe:Mo 1:1.5 catalyst = squares and solid line (-■-), Fe:Mo 1:2.2 catalyst = triangles and solid line (-▲-) and Fe:Mo 1:3 catalyst = circles and solid line (-●-)

Stuart 4/6/2015 17:24

Comment [5]: Calculate surface normalised rates to investigate further the effect of SA, best done under differential conditions, <10% methanol conversion. Differences in SA are relatively minor and I think phase composition may be more important.

Benjamin Yeo 6/6/2015 21:41

Comment [6]: I agree, but do we have time for this? I'm also waiting for TEM, this might shine some light on what the phases are in the voids, perhaps this can be done at the revision stage?

Hutch 8/6/2015 06:27

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4. Conclusions

Iron molybdate catalysts can be very selective for the oxidation of methanol to formaldehyde. The detailed study of the surface has shown that it is important to have a molybdenum-rich surface to ensure high selectivity. It is therefore important to maximise the surface area of these active catalysts and this we have studied using a new physical grinding method with oxalic acid. The synthesis of iron molybdate catalysts using this physical mixing method is compared with conventional co-precipitation. Increasing the molybdenum content affected both the structure and performance of the catalysts prepared by the oxalic acid method with the best catalyst having an Fe:Mo ratio of 1:2.2. For super-stoichiometric materials (Fe:Mo =1:2.2) the reaction data showed that physical mixing produced effective catalysts, possibly offering an improvement over the conventional co-precipitation method.

Acknowledgements

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