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# Methanol oxidation over shell-core $\text{MO}_x/\text{Fe}_2\text{O}_3$ ( $\text{M} = \text{Mo}, \text{V}, \text{Nb}$ ) catalysts

Pip Hellier <sup>a,b</sup>, Peter P. Wells <sup>c,d</sup>, Michael Bowker <sup>a,b,\*</sup>

<sup>a</sup> UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell,

UK <sup>b</sup> School of Chemistry, Cardiff University, Cardiff, UK

<sup>c</sup> School of Chemistry, University of Southampton, Southampton, UK

<sup>d</sup> Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, UK

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ABSTRACT

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Shell-core catalyst

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We present a comparison of Mo, V and Nb oxides as shell materials atop haematite cores used for selective methanol oxidation. While Mo and V both yield high selectivity to formaldehyde, Nb does not. Very different reactivity patterns are seen for Nb, which mainly shows dehydrogenation (to CO) and dehydration (to DME), indicating the lack of a complete shell, while Raman spectroscopy shows that the Mo and V formation process is not followed by  $\text{NbO}_x$ . We suggest this is due to the large differences in mobility within the solid materials during formation,  $\text{NbO}_x$  requiring significantly higher (and deleterious) calcination temperatures to allow sufficient mobility for shell completion.

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## 1. Introduction

Methanol is an important intermediate chemical and fuel, and it may have a significant role in CCU (carbon capture and utilisation) [1]. Thus, renewable electricity from wind and photovoltaic can be used to produce hydrogen, but due to its low energy density we may want to densify it in the form of a liquid fuel such as methanol. A demonstrator plant for such a process is in place in Germany through a European collaboration [2]. Since formaldehyde is a derivative of methanol, we can then envisage a route to 'green' formaldehyde.

In this paper we describe the behaviour of mixed oxide catalysts for this process in which one cation is  $\text{Fe}^{3+}$ , and the other is M, where M is either Mo, V, or Nb. Mo is the cation of choice

and industrial catalysts are composed of ferric molybdate,  $(\text{Fe}_2(\text{MoO}_4)_3)$  [3–5]. This material has very high selectivity at high conversion and hence its industrial significance [6]. Here we compare its behaviour with those of two high oxidation state cations nearby in the periodic table. We also utilise our model shell-core catalysts in which we put a shell of M on top of a haematite core (which forms the oxide shell during calcination) and we have shown that, at least in the case of Mo and V, it remains at the surface [7,8]. The aim of the work is to determine why Mo is the cation of choice for such catalysts by finding out how related cations compare in reactivity. Here we show that although V is good, it is not as effective as Mo in terms of selectivity and yield of formaldehyde, and that Nb differs considerably in reactivity from these two.

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\* Corresponding author. E-mail: bowkerm@cardiff.ac.uk

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## 2. Experimental

### 2.1. Catalyst synthesis

1 ML  $\text{MO}_x/\text{Fe}_2\text{O}_3$  catalysts (where  $M = \text{Mo}, \text{Nb}$ ) were prepared by incipient wetness impregnation, in which the relevant amount of ammonium heptamolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , or ammonium niobate oxalate hydrate,  $\text{C}_{10}\text{H}_5\text{NbO}_{20}\cdot x\text{H}_2\text{O}$  (both Sigma-Aldrich, >99%), to achieve 1 ML coverage was dissolved in water and added dropwise to  $\text{Fe}_2\text{O}_3$  (Sigma-Aldrich, nano-powder, 99%).  $\text{MoO}_3$  and  $\text{Nb}_2\text{O}_5$  references were obtained commercially. 1 ML  $\text{VO}_x/\text{Fe}_2\text{O}_3$  catalysts were prepared by an analogous incipient wetness impregnation method, but with ethanolamine as the solvent and ammonium meta-vanadate,  $\text{NH}_4\text{VO}_3$ , as the precursor.  $\text{V}_2\text{O}_5$  was obtained commercially as a reference material. All reference compounds were calcined at  $500^\circ\text{C}$  for 24 h in air before being used as references. The weight loadings of the second cations on the sample were Mo 2.56%, Nb 2.76% and V 1.62%.

### 2.2. Catalytic testing

TPD and selectivity/conversion analysis data were obtained from a Hiden CATLAB microreactor with online mass spectrometric analysis, consisting of a furnace around the sample through which gas passes. For TPD, methanol was injected in microlitre quantities (5) at room temperature, followed by heating to  $500^\circ\text{C}$  under a He flow; for pulsed flow reactions (to determine selectivity and conversion), microlitre aliquots of methanol were injected every 2 min into a  $30\text{ mL min}^{-1}$  flow of 10%  $\text{O}_2/\text{He}$  during a  $10^\circ\text{C min}^{-1}$  ramp to  $500^\circ\text{C}$ . Products of these processes were monitored by the online Hiden QGA quadrupole mass spectrometer during the temperature ramps. Figures using mass spectra data display processed data, i.e. post removal of spectral overlaps. The reproducibility of data was  $\pm 5\%$  on conversion and on selectivity at any one temperature. The products shown in the figures are the only ones seen and the mass balance was  $100 (\pm 2\%)$ .

### 2.3. Characterisation

Vibrational spectroscopy was primarily used to identify component speciation at different calcination stages and after full calcination at  $500^\circ\text{C}$ . Raman measurements were undertaken using a Renishaw Raman microscope with an 830 nm laser under ambient conditions, with typical measurements ranging between  $300$  and  $1200\text{ cm}^{-1}$  with 1% laser power and 5 accumulations of 20 s each. XPS spectra were obtained using an ESCALAB 220 spectrometer equipped with Al  $K\alpha$  and Mg  $K\alpha$  sources and fitted with a fast entry lock for easy sample loading. For this study, Al  $K\alpha$  ( $1486.6\text{ eV}$ ) irradiation was used, to prevent overlap of the Fe  $2p_{1/2}$  and  $2p_{3/2}$  peaks with Fe Auger peaks.

Particle sizes were between 45 and 60 nm, from TEM measurements (JEOL JEM-2100), and the surface area was  $16\text{ m}^2\text{ g}^{-1}$ .

## 3. Results and discussion

We have made a series of methanol oxidation catalysts by doping 1 monolayer (ML for short) of a transition metal oxide onto a haematite support. We have shown previously that iron oxide itself is a combustor for methanol [5,8]. In TPD it shows only  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{H}_2$  as products, the latter two appearing coincidentally, indicating the presence of a surface intermediate formate species which was confirmed by DRIFTS [9,10]. Similarly in reactivity it is only moderately active ( $T_{50}$  at  $230^\circ\text{C}$ , where  $T_{50}$  is defined as the temperature required for 50% conversion). We have previously shown that dosing Mo onto the surface induces high selectivity to formaldehyde and minimises combustion [8,9]. Here we compare results, under the same conditions for three different TM oxides in order to elucidate what it is that drives selectivity in this reaction.

### 3.1. Molybdenum

As can be seen in Figure 1, a layer with 1 ML of Mo is very selective to formaldehyde. Conversion begins at very low temperature ( $\sim 140^\circ\text{C}$ ), has a  $T_{50}$  of  $\sim 170^\circ\text{C}$  and reaches close to full conversion by  $\sim 250^\circ\text{C}$ . Selectivity to formaldehyde is high; at low temperatures the other product is dimethyl ether (DME), selectivity to formaldehyde reaches a maximum at  $\sim 220^\circ\text{C}$ , and declines after that due mainly to CO production, but  $\text{CO}_2$  is also made at higher temperatures. By  $390^\circ\text{C}$  nearly equal amounts of each are produced and the formaldehyde selectivity has dropped to  $\sim 15\%$ .

Figure 2 shows TPD data after dosing methanol at  $40^\circ\text{C}$ . Here it can be seen that formaldehyde is produced with a peak at  $\sim 160^\circ\text{C}$ , but significant amounts of CO are also produced, peaking at  $205^\circ\text{C}$ . This is in contrast to findings for a bulk iron molybdate catalyst where no CO is produced [6].

In many ways the above techniques are the most useful ones for characterising these catalysts because they are the ultimate in surface sensitivity: they only probe the nature of the top monolayer. The 2D nature of the Mo layer makes it impossible to determine structure by XRD. However, there is some infor-

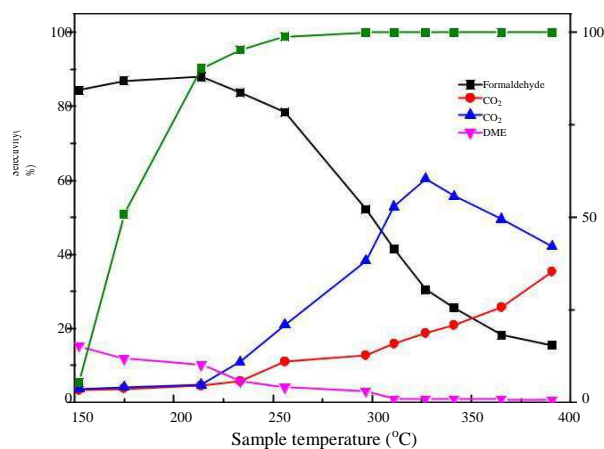
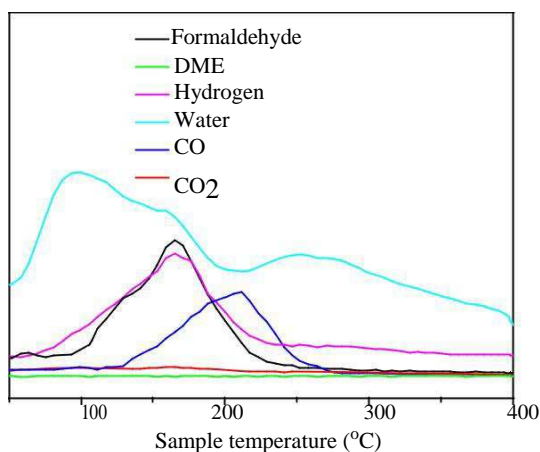


Fig. 1. Selectivity/conversion data for 1 ML  $\text{MoO}_x/\text{Fe}_2\text{O}_3$ : 50% conversion at  $180^\circ\text{C}$ .



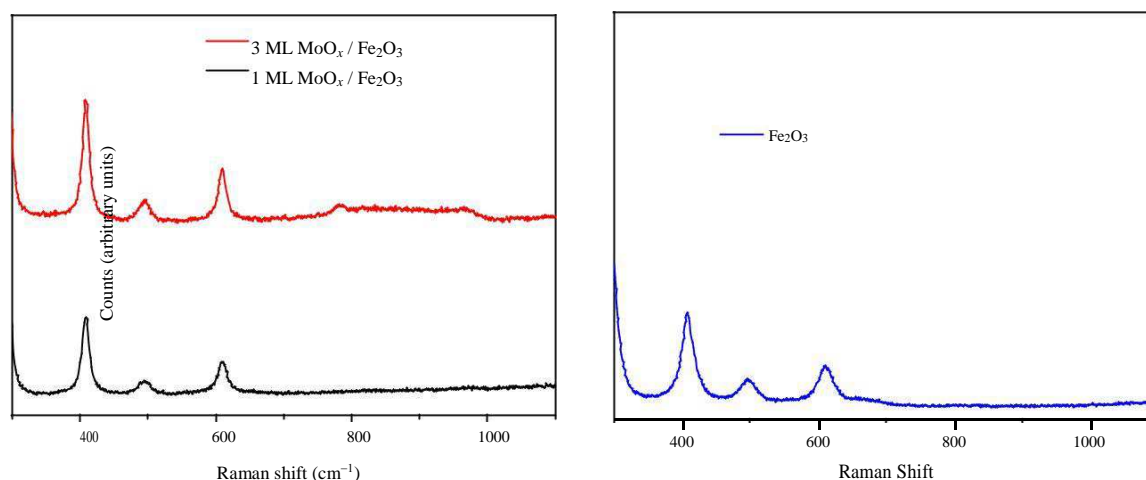
**Fig. 2.** TPD data for 1 ML MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>.

mation from Raman which is sensitive enough to see changes. The limited dimensionality of a 1 ML MoO<sub>x</sub> catalyst does not afford any observable peaks by Raman. A 3 ML MoO<sub>x</sub> catalyst, however, displays Raman peaks resembling iron molybdate which are partially visible (Figure 3). There are additional bands in the region 780–1000 cm<sup>-1</sup> from the Mo layer compared with Fe<sub>2</sub>O<sub>3</sub> alone, but due to the low dimensionality they are very broad. However, they seem to be related to bands seen for Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (780 and 960 cm<sup>-1</sup>), and there may possibly be bands for MoO<sub>3</sub> (820 and 980 cm<sup>-1</sup>) too [8,11]. Note that for 3 ML equivalent, only 1 ML remains at the surface as a MoO<sub>x</sub> layer, while the other two make Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> layers (~ four such layers), so these dominate the spectrum.

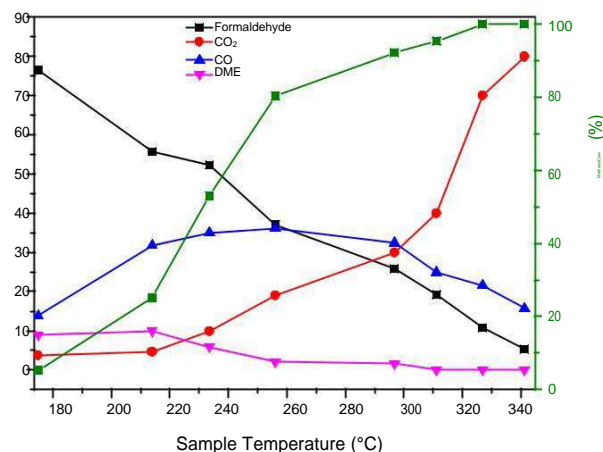
Analysis of XPS data (Figure S1) show Mo to be in its highest oxidation state (Mo<sub>6+</sub>) with Mo 3d<sub>5/2</sub> binding energy (b.e.) of 232.5 eV: XPS does not provide greater insight into the surface speciation [12,13].

### 3.2. Vanadium

When 1 ML of V is applied to a haematite support, the re-



**Fig. 3.** Left: Raman spectra of 1 and 3 ML MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> – limited dimensionality reduces the Mo contribution to the 1 ML sample spectrum, which shows the core haematite spectrum, but iron molybdate is visible in 3 ML at approximately 780 and 960 cm<sup>-1</sup>. Right: Raman spectrum of α-Fe<sub>2</sub>O<sub>3</sub> for comparison.



**Fig. 4.** Selectivity/conversion data for 1 ML VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>: 50% conversion occurs at 230 °C.

sultant VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalyst is selective to formaldehyde, albeit not to the degree observed for Mo (Figure 4). Conversion begins in earnest at approximately 180 °C with T<sub>50</sub> at 230 °C; however, clear differences in product selectivities from Mo are observed. At temperatures up to T<sub>50</sub>, formaldehyde is the major product, with small amounts of DME and CO observed. Above T<sub>50</sub>, however, formaldehyde selectivity decreases rapidly, initially due to increased CO production but then to greater production of CO<sub>2</sub> (rising to 90% CO<sub>2</sub> by 340 °C).

In TPD, 1 ML VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> demonstrates strong selectivity to formaldehyde (Figure 5). Formaldehyde and CO are the significant products observed, and little CO<sub>2</sub> is produced, demonstrating that the haematite core is sufficiently shielded to prevent combustion of the methanol, which requires an ensemble of several Fe sites to be available [9]. The ratio of formaldehyde produced to CO produced is poorer than for the equivalent 1 ML MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalyst, indicating lower selectivity to formaldehyde for VO<sub>x</sub> catalysts: this is to be expected, since Mo is the metal of choice for methanol oxidation catalysts.

Similarly to 1 ML MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>, the low dimensionality of the 1 ML VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalyst renders invisible the peaks which



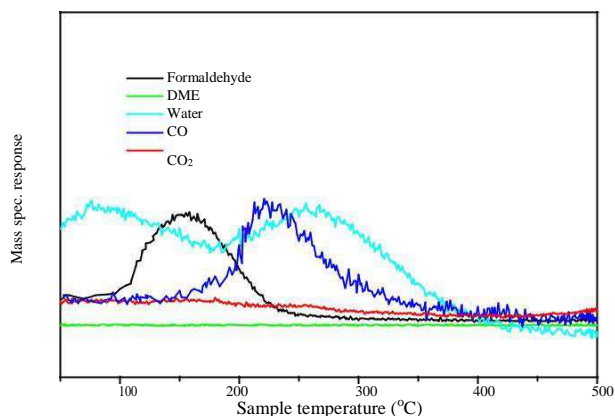


Fig. 5. TPD data for 1 ML  $\text{VO}_x/\text{Fe}_2\text{O}_3$ .

could be expected in its Raman spectrum, namely those of  $\text{V}_2\text{O}_5$  ( $\sim 700$  and  $990\text{ cm}^{-1}$ ) and  $\text{FeVO}_4$  ( $930\text{--}970\text{ cm}^{-1}$ ). However, the Raman peaks of  $\text{FeVO}_4$  can be seen clearly for the 3ML sample due to the greater quantity of shell material present (Figure 6) [7,14]. XPS analysis of 1 ML  $\text{VO}_x/\text{Fe}_2\text{O}_3$  confirms that each element is present in its highest oxidation state, namely  $\text{V}^{5+}$  and  $\text{Fe}^{3+}$  (Figure S2): the  $2p_{3/2}$  peak at  $\sim 517\text{ eV}$  confirms this for V [15].

### 3.3. Niobium

The analogous 1 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$  catalyst displays very significant differences from the other two transition metal cations in both pulsed flow reaction and TPD. Pulsed flow reaction of 1 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$  gives high selectivity to DME at lower temperatures and conversions, which is superseded by  $\text{CO}_2$  production at higher temperatures; however,  $\text{CO}_2$  production becomes significant at lower temperatures than equivalent Mo and V catalysts (commencing  $<200\text{ }^\circ\text{C}$ ). Some formaldehyde selectivity is seen at low conversions, but it decreases rapidly above  $250\text{ }^\circ\text{C}$  and is completely absent above  $350\text{ }^\circ\text{C}$  when conversion is near 100%. The material has much lower reactivity, having a

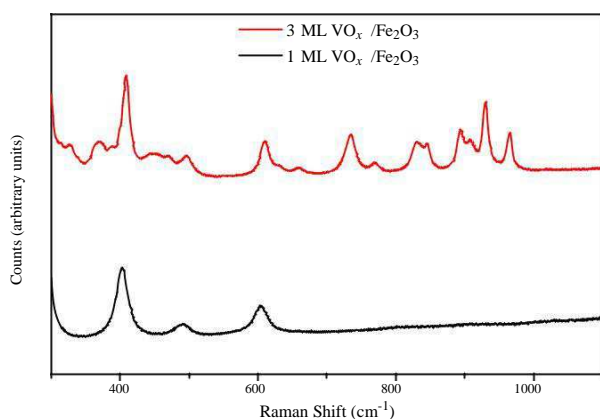


Fig. 6. Raman spectra of 1 and 3 ML  $\text{VO}_x/\text{Fe}_2\text{O}_3$ . The limited dimensionality of 1 ML  $\text{VO}_x$  makes it difficult to see whereas, in contrast, 3 ML displays iron vanadate peaks clearly.

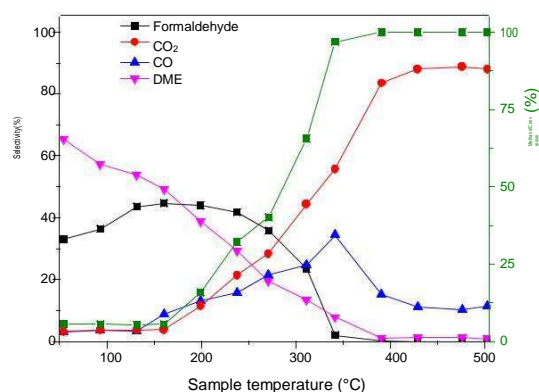


Fig. 7. Selectivity/conversion data for 1 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$ .

$T_{50}$  of  $\sim 300\text{ }^\circ\text{C}$ .

In methanol TPD measurements, 1 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$  does not produce formaldehyde in any significant quantity (Figure 8). Instead, DME is observed between  $200\text{--}300\text{ }^\circ\text{C}$ , and at higher temperatures mainly  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}$  are seen. Smaller peaks are seen for  $\text{CO}_2$ , mainly coincident with the  $\text{CO}$ . In comparison to the  $\text{CO}_2$  generated by methanol TPD from  $\text{Fe}_2\text{O}_3$ , they are markedly reduced. This indicates that direct combustion of methanol by the haematite core is partially inhibited, suggesting that the core is not as fully isolated as for Mo and V.

Even for 3 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$ , the Raman spectrum does not reveal any significant peaks, in contrast to the Mo and V counterparts above (Figure 9). XPS of the samples shows that Nb exists in its highest oxidation state,  $\text{Nb}^{5+}$ , b.e.  $207.3\text{ eV}$  (Figure S3), but cannot assist in understanding the apparent differences in catalytic behaviour [16].

### 3.4. Discussion

TPD is in some ways the most effective technique for verifying that the shell of a second oxide has been obtained on the core material. Due to the inherent differences in catalytic properties between the shell metal oxide and the haematite core, reliable inferences about the state of the surface can be made. It has been reported previously that shell integrity is a key requirement for a selective catalyst [9]. For an iron molybdate

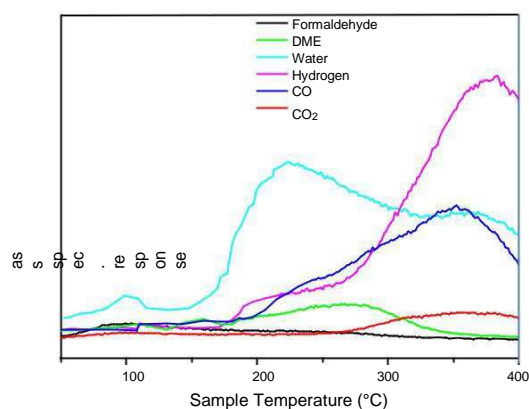
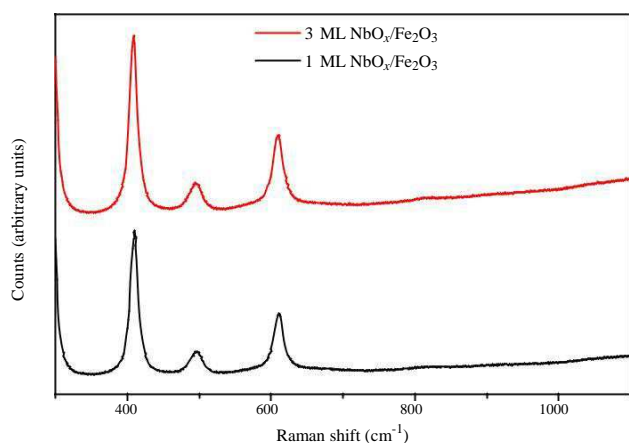


Fig. 8. TPD data for 1 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$  under a helium atmosphere.



**Fig. 9.** Raman spectrum of 1 and 3 ML NbO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>.

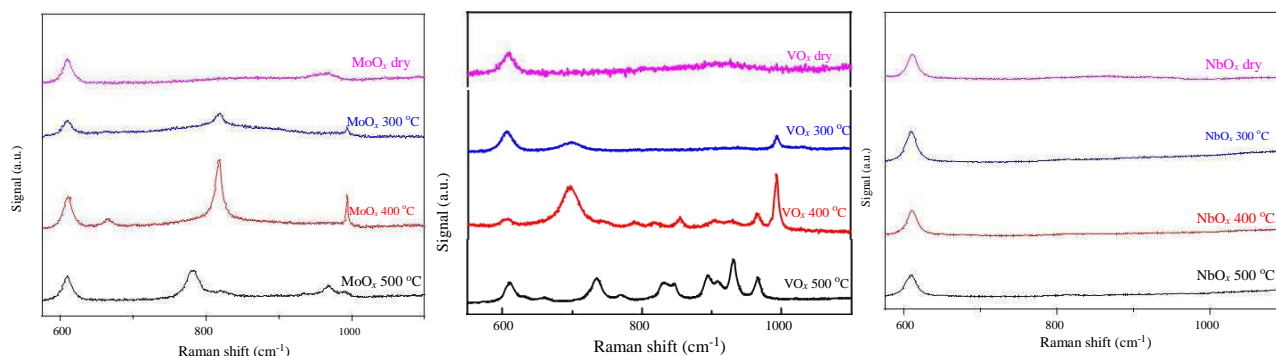
catalyst with very low Mo content, the surface is not exclusively Mo: instead, there are plentiful neighbouring Fe sites at the surface. In cases where multiple Fe sites can interact directly at the surface, CO<sub>2</sub> is the majority product; the high selectivity of Mo is outcompeted by the higher activity (and worse selectivity) of Fe at the surface [9]. When higher Mo loadings are used, formaldehyde and CO are observed by TPD, but no longer any CO<sub>2</sub>. This is a result of the surface becoming increasingly covered with Mo, leaving only occasional isolated Fe sites at the surface amongst the Mo. During reaction, isolated Fe sites produce CO [9]: since neighbouring Fe within range to interact is required for CO<sub>2</sub> production, and due to the high surface oxygen requirement for combustion, no CO<sub>2</sub> is produced [9]. For high Mo loadings, iron molybdate demonstrates selectivity to formaldehyde only, with no other products in TPD under inert gas. An analogous process exists for MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalysts and VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalysts, but for these catalysts small quantities of CO are always observed, indicating that single Fe sites continue to reach the surface [7–9]. We have also shown that Mo remains at the surface in such catalysts by line scans using EELS in an aberration corrected STEM [17], and by EDAX [8].

MoO<sub>x</sub> and VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalysts are both selective to formaldehyde and demonstrate this in their respective TPD results; however, Mo is noticeably superior in this regard to V. This is not unexpected, since Mo is known as the catalyst of choice for formaldehyde production. For 1 ML MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>, formaldehyde production is greater than that of CO; however, for 1 ML VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>, formaldehyde and CO are produced in approximately equivalent quantities. 1 ML NbO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>, however, does not display the same behaviour. It is known that Nb<sub>2</sub>O<sub>5</sub> when used as a catalyst generates Brønsted acidic sites, which affect selectivity in the reaction with methanol [18,19]. Catalysts incorporating Nb<sub>2</sub>O<sub>5</sub> or similar Nb oxides have been investigated for their ability to produce DME by dehydration, typically using alumina supports [19,20]. While the systems investigated here are designed to be shell-core catalysts on haematite, and not alumina, it is likely that NbO<sub>x</sub> would be similarly selective to DME (given that Nb<sub>2</sub>O<sub>5</sub> is present, Figure S4). Indeed this is observed in TPD of 1 ML NbO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>, with DME produced at moderate temperatures; however, CO<sub>2</sub> is a significant product

in 1 ML NbO<sub>x</sub> TPD. Since CO<sub>2</sub> can only be formed from multiple exposed Fe core sites at the surface, it is clear that 1 ML NbO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> does not achieve the same degree of core segregation. Nb is visible by XPS, suggesting that Nb is indeed present in the surface layers but does not seem to exist as a layer of NbO<sub>x</sub> alone.

Raman spectroscopy is a useful means of determining shell metal oxide speciation, and has greatly benefited studies of other MoO<sub>x</sub> and VO<sub>x</sub> systems [7,9]. Observation of 1 ML catalysts by Raman can be difficult due to the limited dimensionality of the surface layer at low loadings: instead, Raman spectroscopy is performed on multi-ML systems, whose shells are deep enough for the shell constituents to appear in Raman. We have previously suggested a schematic model for the processes occurring during the calcination of shell-core metal oxide catalysts; we suggest that selective catalysts are generated when their formation proceeds *via* this model [7,9]. This model suggests that certain intermediate surface phases are formed during calcination at particular temperatures: amorphous oxide units on the haematite surface convert into metal oxide crystallites which then spread evenly to form the MoO<sub>x</sub>/VO<sub>x</sub> surfaces. At 400 °C for MoO<sub>x</sub> and VO<sub>x</sub> catalysts, clear signals for MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> respectively are seen by Raman at 3 ML coverage (the metal oxide crystallites); however, for NbO<sub>x</sub> no such band is observed at any ML coverage (Figure 10). We suggest that the presence of the metal oxide band close to 1000 cm<sup>-1</sup>, indicative of the terminal M=O species in Raman spectra is a key marker of selectivity to formaldehyde: where it is not seen, neither is selectivity.

Considering the poorer performance of NbO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> in TPD and pulsed flow reaction, we suggest that Nb cannot be fashioned into a shell-core catalyst in a manner similar to MoO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> or VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalysts. The TPD results for NbO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> are crucial, due to the inherent surface sensitivity of TPD as a technique. CO<sub>2</sub> is not observed for MoO<sub>x</sub> and VO<sub>x</sub> catalysts, but it is in small quantities for NbO<sub>x</sub>. This indicates that the catalyst surface is not as well-formed for Nb in comparison to Mo and V. It is possible that the Nb cannot be as efficiently segregated to the surface layers, leaving portions of the haematite core exposed, or that an alternative iron niobate structure (e.g. Fe<sub>x</sub>Nb<sub>y</sub>O<sub>z</sub>) is formed in at the surface with inferior catalytic properties. XRD analysis, however, does not show any differences from haematite, with no iron niobate structures visible. Raman corroborates structural differences during formation through the absence of a visible Nb=O peak at any point during calcination: this suggests that the haematite and Nb form a mixed structure, rather than segregating into separate oxide components as seen for Mo and V. The Tamman temperature, the temperature at which the mobility of species in a solid become significant, could provide the explanation for this behaviour. We have suggested that the formation process for MoO<sub>x</sub> and VO<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub> catalysts during calcination proceeds stepwise, during which Mo and V diffuse on the surface and aggregate before spreading across the surface to form the desired catalyst structure. The Tamman temperatures for MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> (the closest analogues to the systems described here) are 261 and 209 °C respectively [21]: therefore, the calcination



**Fig. 10.** Comparison of Raman spectra at different points during calcination for 3 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$ , 3 ML  $\text{MoO}_x/\text{Fe}_2\text{O}_3$  and 3 ML  $\text{VO}_x/\text{Fe}_2\text{O}_3$ . In comparison to Mo and V, Nb does not display peaks of interest in Raman: crucially, the Nb=O peak at approx.  $1000\text{ cm}^{-1}$  is absent in the  $400\text{ }^\circ\text{C}$   $\text{NbO}_x/\text{Fe}_2\text{O}_3$  sample, where it is expected to appear. Both  $\text{MoO}_x$  and  $\text{VO}_x$  display this crucial M=O signal at  $400\text{ }^\circ\text{C}$  (M = Mo/V).

temperatures in use will exceed these values, and permit effective diffusion of the Mo and V around the surface. For  $\text{Nb}_2\text{O}_5$ , however, the Tamman temperature is  $620\text{ }^\circ\text{C}$ , beyond the maximum  $500\text{ }^\circ\text{C}$  used for catalyst calcination [22]. Consequently, the Nb-haematite mixture does not exceed the temperature at which  $\text{NbO}_x$  will become fully mobile, which may prevent it from forming  $\text{Nb}_2\text{O}_5$  aggregates necessary at the surface to then spread to form the intended catalyst. In essence, calcination of  $\text{MoO}_x$  and  $\text{VO}_x$  finishes the development of the catalyst, resulting in properly formed shell-core catalysts; however, we suggest that  $\text{NbO}_x$  is unable to complete its formation process at  $500\text{ }^\circ\text{C}$ , instead remaining improperly formed.

#### 4. Conclusions

Catalysts based on Mo remain the superior catalysts for methanol oxidation to formaldehyde. We have found that V-based catalysts also function as formaldehyde-producing catalysts, but not to the same efficiency as Mo. The shell-core architecture explored initially for Mo catalysts was a means to replicate the surface of the bulk iron molybdate catalyst, but with a greater quantity of surface and less bulk material. Greater surface areas are achieved, alongside significant advantages during analysis (since the analyte of interest, Mo, is present only in the surface layers, non-surface-sensitive, but element-specific techniques become quasi-surface sensitive).

We have subsequently seen that this model system can be extended to V systems, with similar trends in formation, reactivity and characterisation observed. It was expected that Nb, being close to V and Mo in the periodic table, might respond similarly to attempts to fashion it into a shell-core catalyst. In terms of reactivity,  $\text{Nb}_2\text{O}_5$  is catalytically active, although not selective to formaldehyde (instead displaying acidic behaviour by producing significant amounts of DME). With the current synthetic methodology, Nb seems unable to form a fully selective  $\text{NbO}_x/\text{Fe}_2\text{O}_3$  catalyst; instead, the  $\text{NbO}_x/\text{Fe}_2\text{O}_3$  catalyst produces  $\text{CO}_2$  by TPD alongside selective product DME. We suggest this is due to its vastly greater Tamman temperature, and the consequent inability of  $\text{NbO}_x$  to diffuse as easily as Mo

and V across the surface of the haematite during calcination.

#### Acknowledgments

The authors thank HarwellXPS, the EPSRC National Facility for X-Ray Photoelectron Spectroscopy, for their assistance in performing XPS measurements, and EPSRC for support via the UK Catalysis Hub (EP/K014854/1, EP/K014714/1), and EPSRC and Diamond Light Source for funding the studentship to PH.

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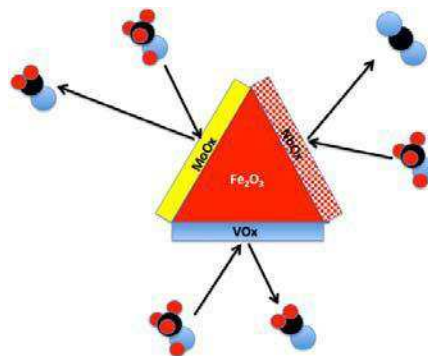
## Graphical Abstract

### Methanol oxidation over shell-core $\text{MO}_x/\text{Fe}_2\text{O}_3$ ( $\text{M} = \text{Mo}, \text{V}, \text{Nb}$ ) catalysts

Pip Hellier, Peter P. Wells, Michael Bowker \*

UK Catalysis Hub, UK; Cardiff University, UK; University of Southampton, UK; Diamond Light Source Ltd, UK

Methanol oxidation on three surface oxides on  $\text{Fe}_2\text{O}_3$  showing the main carbon products. Mo and V monolayers are selective to formaldehyde, while Nb does not make complete monolayers and mainly combusts to  $\text{CO}_2$ .



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## 核壳结构 $\text{MO}_x/\text{Fe}_2\text{O}_3$ ( $\text{M} = \text{Mo}, \text{V}, \text{Nb}$ )催化剂上甲醇氧化反应

Pip Hellier <sup>a,b</sup>, Peter P. Wells <sup>c,d</sup>, Michael Bowker <sup>a,b,\*</sup>

<sup>a</sup>卢瑟福-阿普尔顿实验室, 哈韦尔研究综合体, 英国催化中心, 哈韦尔, 英国

<sup>b</sup>卡迪夫大学化学学院, 卡迪夫, 英国

<sup>c</sup>南安普顿大学化学学院, 南安普顿, 英国

<sup>d</sup>哈韦尔科学与创新园区, 钻石光源有限公司, 迪德科特, 英国

**摘要:** 本文比较了赤铁矿为核, Mo, V和Nb氧化物为壳层的材料在选择性甲醇氧化反应中的性能。

Mo和V对甲醛都有很高的选择性, 而Nb则没有. Nb的反应模式非常不同, 主要表现为脱氢(生成CO)和脱水(生成三甲醚), 表明缺乏完整的壳层, 同时Raman光谱发现,  $\text{NbO}_x$ 的形成过程与Mo和V的并不相同。

我们推测这是由于固体材料在形成过程中的流动性差异很大,  $\text{NbO}_x$ 需要明显较高(和有害)的焙烧温度, 以便为壳层的形成提供足够的流动性。**关键词:** 甲醇; 氧化; 甲醛; 钼酸铁; 核壳结构催化剂

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\*通讯联系人. 电子信箱: bowkerm@cardiff.ac.uk

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For Author Index:

HELLIER Pip, WELLS Peter P., BOWKER Michael



# Methanol oxidation over shell-core $\text{MO}_x/\text{Fe}_2\text{O}_3$ (M = Mo, V, Nb) catalysts

Pip Hellier <sup>a,b</sup>, Peter P. Wells <sup>c,d</sup>, Michael Bowker <sup>a,b,\*</sup>

<sup>a</sup> UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell,

UK <sup>b</sup> School of Chemistry, Cardiff University, Cardiff, UK

<sup>c</sup> School of Chemistry, University of Southampton, Southampton, UK

<sup>d</sup> Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, UK

\* Corresponding author. E-mail: bowkerm@cardiff.ac.uk

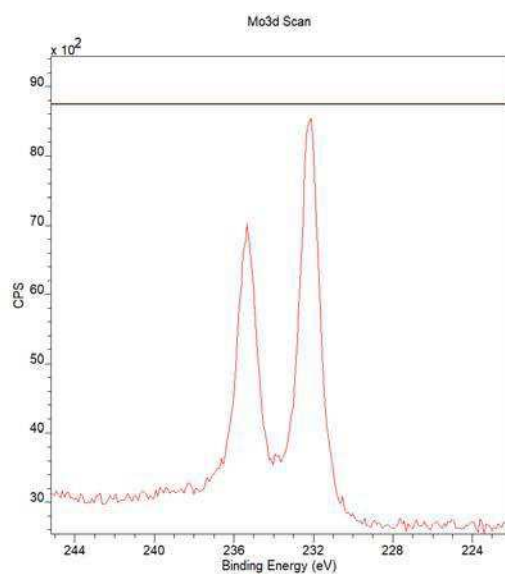


Fig. S1. Mo region of XPS data from 1 ML  $\text{MoO}_x/\text{Fe}_2\text{O}_3$ .

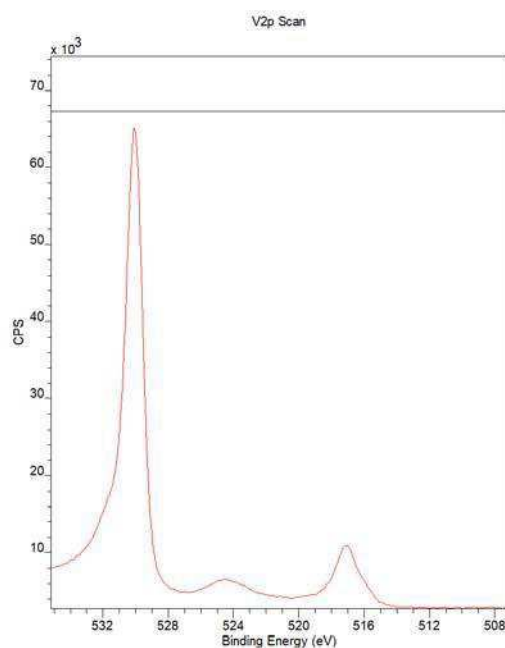
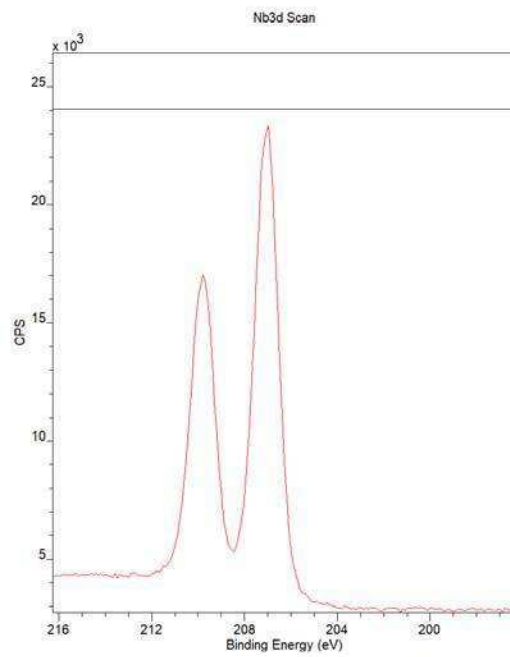
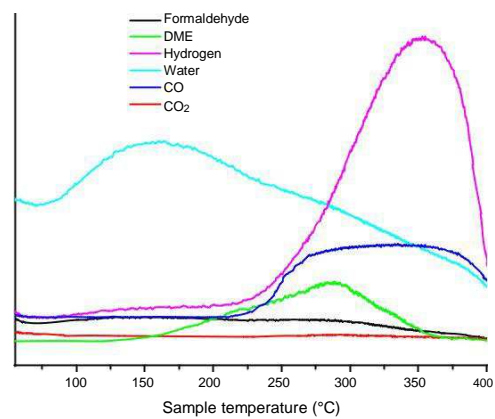


Fig. S2. V region of XPS data from 1 ML  $\text{VO}_x/\text{Fe}_2\text{O}_3$ .



CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

**Fig. S3.** Nb region of XPS data from 1 ML  $\text{NbO}_x/\text{Fe}_2\text{O}_3$ .



**Fig. S4.** TPD data for  $\text{Nb}_2\text{O}_5$  calcined to 500°C. Major products are DME and CO – no significant  $\text{CO}_2$  is produced.