Methanol oxidation over shell-core MO*x*/Fe2O3 (M = Mo, V, Nb) catalysts

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ABSTRACT

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 NbO_x. We suggest this is due to the large differences in mobility within the solid materials during formation, NbO_x requiring significantly higher (and deleterious) calcination temperatures to allow sufficient mobility for shell completion.

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 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, ($Fe_2(MoO_4)_3$) [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 calcina-tion) 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 deter-mine why Mo is the cation of choice for such catalysts by find-ing 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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2. Experimental

2.1. Catalyst synthesis

1 ML MO_x/Fe_2O_3 catalysts (where M = Mo, Nb) were pre-pared by incipient wetness impregnation, in which the relevant amount of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, or am-monium niobate oxalate hydrate, $C_{10}H_5NbO_{20}{\cdot}xH_2O$ (both Sig-ma-Aldrich, >99%), to achieve 1 ML coverage was dissolved in water and added dropwise to Fe_2O_3 (Sigma-Aldrich, nano-powder, 99%). MoO_3 and Nb_2O_5 references were ob-tained commercially. 1 ML VO_x/Fe_2O_3 catalysts were prepared by an analogous incipient wetness impregnation method, but with ethanolamine as the solvent and ammonium meta-vanadate, NH_4VO_3, as the precursor. V_2O_5 was obtained com-mercially as a reference material. All reference compounds were calcined at 500 °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 spectro-metric 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 °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 mL min^{-1} flow of 10% O_2/He during a 10 °C min^{-1} ramp to 500 °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 ± 5% on conversion and on selectivity at any one temper-ature. The products shown in the figures are the only ones seen and the mass balance was 100 (± 2%).

2.3. Characterisation

Vibrational spectroscopy was primarily used to identify component speciation at different calcination stages and after full calcination at 500 °C. Raman measurements were under-taken using a Renishaw Raman microscope with an 830 nm laser under ambient conditions, with typical measurements ranging between 300 and 1200 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 load-ing. For this study, Al $K\alpha$ (1486.6 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 $m_2\ g^{-1}$.

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 H_2O, CO_2 and H_2 as products, the latter two appearing co-incidently, indicating the presence of a surface intermediate formate species which was confirmed by DRIFTS [9,10]. Simi-larly in reactivity it is only moderately active (T_{50} at 230 °C, where T_{50} is defined as the temperature required for 50% con-version). 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 tem-perature (~140 °C), has a T_{50} of ~170 °C and reaches close to full conversion by ~250 °C. Selectivity to formaldehyde is high; at low temperatures the other product is dimethyl ether (DME), selectivity to formaldehyde reaches a maximum at ~220 °C, and declines after that due mainly to CO production, but CO_2 is also made at higher temperatures. By 390 °C nearly equal amounts of each are produced and the formaldehyde selectivity has dropped to ~15%.

Figure 2 shows TPD data after dosing methanol at 40 °C. Here it can be seen that formaldehyde is produced with a peak at ~160 °C, but significant amounts of CO are also produced, peaking at 205 °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-

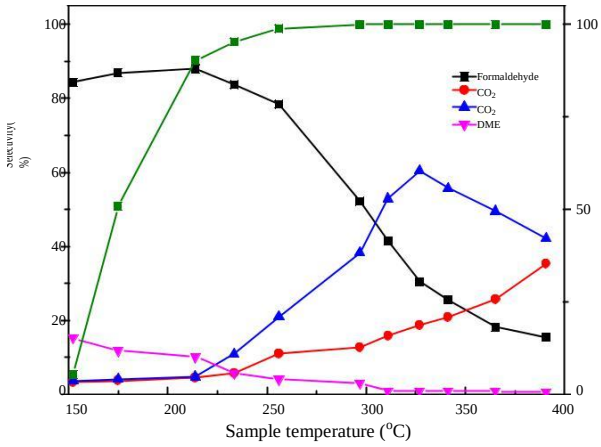

Fig. 1. Selectivity/conversion data for 1 ML MoO_x/Fe_2O_3: 50% conver-sion at 180 °C.

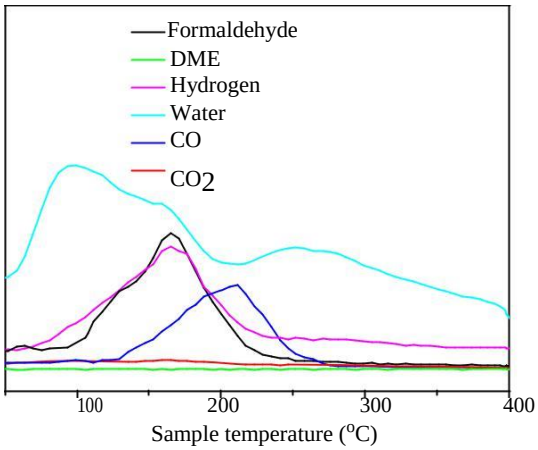

Fig. 2. TPD data for 1 ML MoO_x/Fe_2O_3.

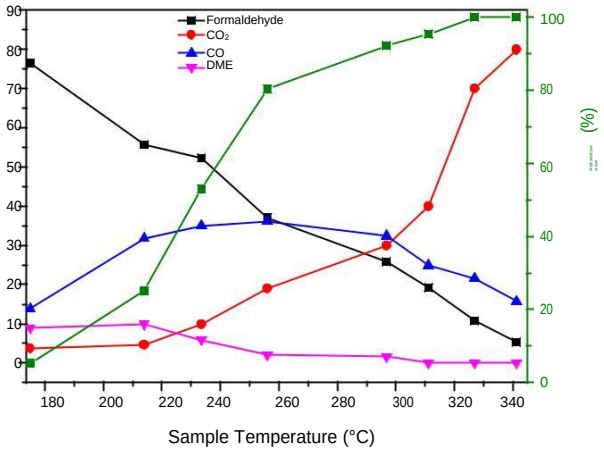

Fig. 4. Selectivity/conversion data for 1 ML VO_x/Fe_2O_3: 50% conversion occurs at 230 °C.

mation from Raman which is sensitive enough to see changes. The limited dimensionality of a 1 ML MoO_x catalyst does not afford any observable peaks by Raman. A 3 ML MoO_x catalyst, however, displays Raman peaks resembling iron molybdate which are partially visible (Figure 3). There are additional bands in the region 780–1000 cm^{-1} from the Mo layer com-pared with Fe_2O_3 alone, but due to the low dimensionality they are very broad. However, they seem to be related to bands seen for $Fe_2(MoO_4)_3$ (780 and 960 cm^{-1}), and there may possibly be bands for MoO_3 (820 and 980 cm^{-1}) too [8,11]. Note that for 3 ML equivalent, only 1 ML remains at the surface as a MoO_x lay-er, while the other two make $Fe_2(MoO_4)_3$ 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^{6+}) with Mo $3d_{5/2}$ 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 resultant VO_x/Fe_2O_3 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_{50} at 230 °C; however, clear differences in product selectivities from Mo are observed. At temperatures up to T_{50}, formaldehyde is the major product, with small amounts of DME and CO observed. Above T_{50}, however, formaldehyde selectivity decreases rapidly, ini-tially due to increased CO production but then to greater pro-duction of CO_2 (rising to 90% CO_2 by 340 °C).

In TPD, 1 ML VO_x/Fe_2O_3 demonstrates strong selectivity to formaldehyde (Figure 5). Formaldehyde and CO are the signif-icant products observed, and little CO_2 is produced, demon-strating that the haematite core is sufficiently shielded to pre-vent 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_x/Fe_2O_3 catalyst, indicating lower selectivity to for-maldehyde for VO_x catalysts: this is to be expected, since Mo is the metal of choice for methanol oxidation catalysts.

Similarly to 1 ML MoO_x/Fe_2O_3, the low dimensionality of the 1 ML VO_x/Fe_2O_3 catalyst renders invisible the peaks which

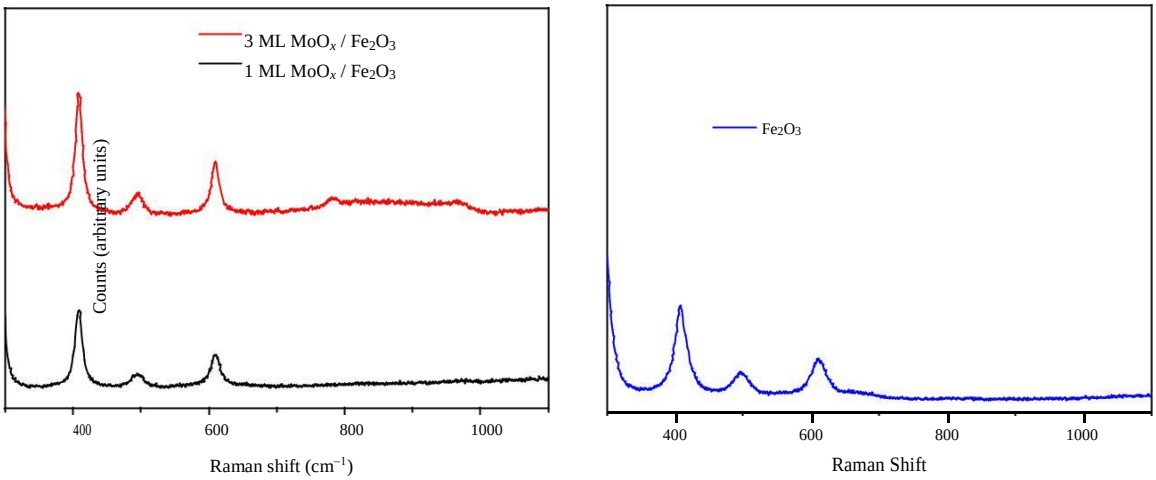

Fig. 3. Left: Raman spectra of 1 and 3 ML MoO_x/Fe_2O_3 – limited dimensionality reduces the Mo contribution to the 1 ML sample spectrum, which shows the core haematite spectrum, but iron molybdate is visible in 3 ML at approximately 780 and 960 cm^{-1}. Right: Raman spectrum of α-Fe_2O_3 for comparison.

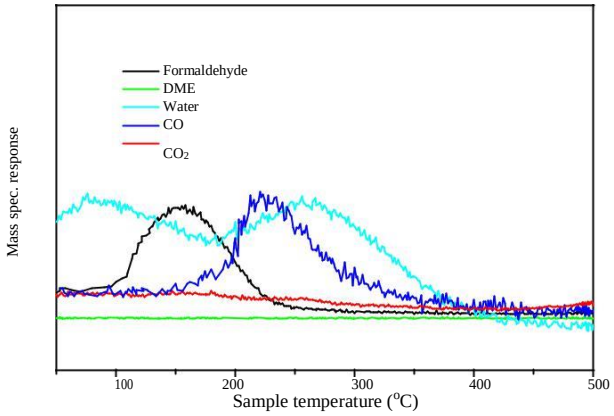

Fig. 5. TPD data for 1 ML VO_x/Fe_2O_3.

could be expected in its Raman spectrum, namely those of V_2O_5 (~700 and 990 cm^{-1}) and $FeVO_4$ (930–970 cm^{-1}). However, the Raman peaks of $FeVO_4$ 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 VO_x/Fe_2O_3 confirms that each ele-ment is present in its highest oxidation state, namely V^{5+} and Fe^{3+} (Figure S2): the $2p_{3/2}$ peak at ~517 eV confirms this for V [15].

3.3. Niobium

The analogous 1 ML NbO_x/Fe_2O_3 catalyst displays very sig-nificant differences from the other two transition metal cations in both pulsed flow reaction and TPD. Pulsed flow reaction of 1 ML NbO_x/Fe_2O_3 gives high selectivity to DME at lower temper-atures and conversions, which is superseded by CO_2 production at higher temperatures; however, CO_2 production becomes significant at lower temperatures than equivalent Mo and V catalysts (commencing <200 °C). Some formaldehyde selectiv-ity is seen at low conversions, but it decreases rapidly above 250 °C and is completely absent above 350 °C when conversion is near 100%. The material has much lower reactivity, having a

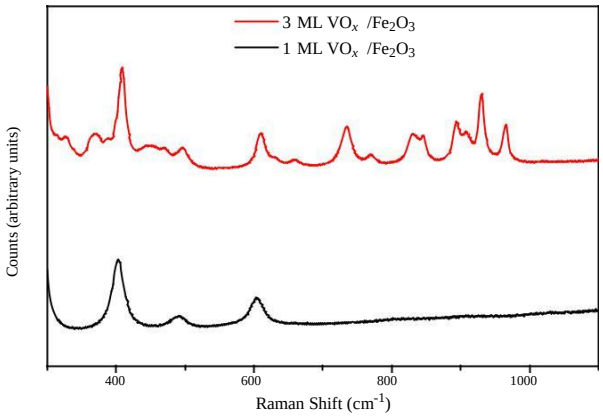

Fig. 6. Raman spectra of 1 and 3 ML VO_x/Fe_2O_3. The limited dimension-ality of 1 ML VO_x makes it difficult to see whereas, in contrast, 3 ML displays iron vanadate peaks clearly.

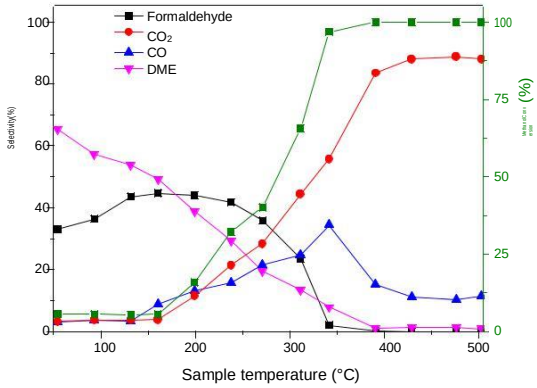

Fig. 7. Selectivity/conversion data for 1 ML NbO_x/Fe_2O_3.

T_{50} of ~300 °C.

In methanol TPD measurements, 1 ML NbO_x/Fe_2O_3 does not produce formaldehyde in any significant quantity (Figure 8). Instead, DME is observed between 200–300 °C, and at higher temperatures mainly H_2, H_2O and CO are seen. Smaller peaks are seen for CO_2, mainly coincident with the CO. In comparison to the CO_2 generated by methanol TPD from Fe_2O_3, they are markedly reduced. This indicates that direct combustion of methanol by the haematite core is partially inhibited, suggest-ing that the core is not as fully isolated as for Mo and V.

Even for 3 ML NbO_x/Fe_2O_3, the Raman spectrum does not reveal any significant peaks, in contrast to the Mo and V coun-terparts above (Figure 9). XPS of the samples shows that Nb exists in its highest oxidation state, Nb^{5+}, b.e. 207.3 eV (Figure S3), but cannot assist in understanding the apparent differ-ences in catalytic behaviour [16].

3.4. Discussion

TPD is in some ways the most effective technique for veri-fying that the shell of a second oxide has been obtained on the core material. Due to the inherent differences in catalytic prop-erties 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 re-quirement for a selective catalyst [9]. For an iron molybdate

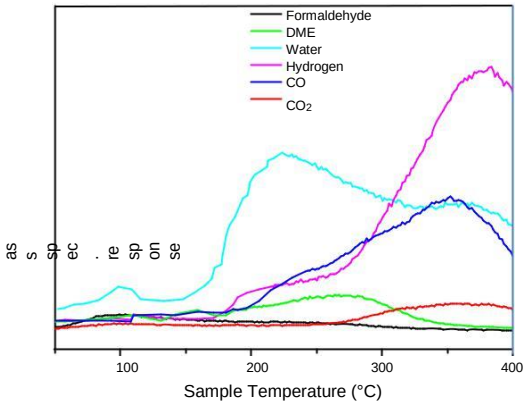

Fig. 8. TPD data for 1 ML NbO_x/Fe_2O_3 under a helium atmosphere.

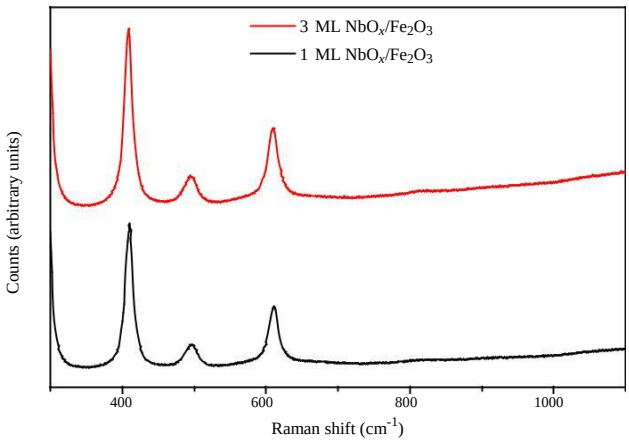

Fig. 9. Raman spectrum of 1 and 3 ML NbO_x/Fe_2O_3.

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_2 is the majority product; the high selectivity of Mo is outcompeted by the higher activity (and worse selectivi-ty) of Fe at the surface [9]. When higher Mo loadings are used, formaldehyde and CO are observed by TPD, but no longer any CO_2. This is a result of the surface becoming increasingly cov-ered with Mo, leaving only occasional isolated Fe sites at the surface amongst the Mo. During reaction, isolated Fe sites pro-duce CO [9]: since neighbouring Fe within range to interact is required for CO_2 production, and due to the high surface oxy-gen requirement for combustion, no CO_2 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_x/Fe_2O_3 catalysts and VO_x/Fe_2O_3 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 re-mains at the surface in such catalysts by line scans using EELS in an aberration corrected STEM [17], and by EDAX [8].

MoO_x and VO_x/Fe_2O_3 catalysts are both selective to formal-dehyde 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_x/Fe_2O_3, formaldehyde production is greater than that of CO; however, for 1 ML VO_x/Fe_2O_3, formaldehyde and CO are produced in approxi-mately equivalent quantities. 1 ML NbO_x/Fe_2O_3, however, does not display the same behaviour. It is known that Nb_2O_5 when used as a catalyst generates Brønsted acidic sites, which affect selectivity in the reaction with methanol [18,19]. Catalysts in-corporating Nb_2O_5 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_x would be similarly selective to DME (given that Nb_2O_5 is present, Figure S4). Indeed this is observed in TPD of 1 ML NbO_x/Fe_2O_3, with DME produced at moderate temperatures; however, CO_2 is a significant product in 1 ML NbO_x TPD. Since CO_2 can only be formed from multiple exposed Fe core sites at the surface, it is clear that 1 ML NbO_x/Fe_2O_3 does not achieve the same degree of core segrega-tion. 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_x alone.

Raman spectroscopy is a useful means of determining shell metal oxide speciation, and has greatly benefited studies of other MoO_x and VO_x systems [7,9]. Observation of 1 ML cata-lysts by Raman can be difficult due to the limited dimensionali-ty of the surface layer at low loadings: instead, Raman spec-troscopy 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 cata-lysts; we suggest that selective catalysts are generated when their formation proceeds *via* this model [7,9]. This model sug-gests that certain intermediate surface phases are formed dur-ing calcination at particular temperatures: amorphous oxide units on the haematite surface convert into metal oxide crystal-lites which then spread evenly to form the MoO_x/VO_x surfaces. At 400 °C for MoO_x and VO_x catalysts, clear signals for MoO_3 and V_2O_5 respectively are seen by Raman at 3 ML coverage (the metal oxide crystallites); however, for NbO_x 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^{-1}, 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_x/Fe_2O_3 in TPD and pulsed flow reaction, we suggest that Nb cannot be fash-ioned into a shell-core catalyst in a manner similar to MoO_x/Fe_2O_3 or VO_x/Fe_2O_3 catalysts. The TPD results for NbO_x/Fe_2O_3 are crucial, due to the inherent surface sensitivity of TPD as a technique. CO_2 is not observed for MoO_x and VO_x catalysts, but it is in small quantities for NbO_x. This indicates that the catalyst surface is not as well-formed for Nb in com-parison to Mo and V. It is possible that the Nb cannot be as effi-ciently segregated to the surface layers, leaving portions of the haematite core exposed, or that an alternative iron niobate structure (e.g. $Fe_xNb_yO_z$) is formed in at the surface with inferi-or catalytic properties. XRD analysis, however, does not show any differences from haematite, with no iron niobate structures visible. Raman corroborates structural differences during for-mation 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 temper-ature, 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_x and VO_x/Fe_2O_3 catalysts during calcination proceeds step-wise, during which Mo and V diffuse on the surface and aggregate before spreading across the surface to form the de-sired catalyst structure. The Tamman temperatures for MoO_3 and V_2O_5 (the closest analogues to the systems described here) are 261 and 209 °C respectively [21]: therefore, the calcination

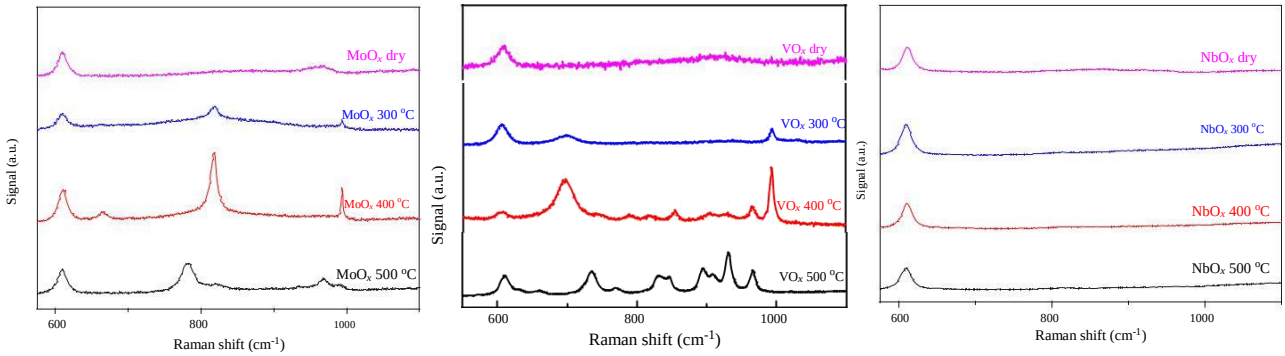

Fig. 10. Comparison of Raman spectra at different points during calcination for 3 ML NbO_x/Fe_2O_3, 3 ML MoO_x/Fe_2O_3 and 3 ML VO_x/Fe_2O. In compari-son to Mo and V, Nb does not display peaks of interest in Raman: crucially, the Nb=O peak at approx. 1000 cm^{-1} is absent in the 400 °C NbO_x/Fe_2O_3 sample, where it is expected to appear. Both MoO_x and VO_x display this crucial M=O signal at 400 °C (M = Mo/V).

temperatures in use will exceed these values, and permit effec-tive diffusion of the Mo and V around the surface. For Nb_2O_5, however, the Tamman temperature is 620 °C, beyond the maximum 500 °C used for catalyst calcination [22]. Conse-quently, the Nb-haematite mixture does not exceed the tem-perature at which NbO_x will become fully mobile, which may prevent it from forming Nb_2O_5 aggregates necessary at the sur-face to then spread to form the intended catalyst. In essence, calcination of MoO_x and VO_x finishes the development of the catalyst, resulting in properly formed shell-core catalysts; however, we suggest that NbO_x is unable to complete its for-mation process at 500 °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 ad-vantages 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, reac-tivity 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, Nb_2O_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 selec-tive NbO_x/Fe_2O_3 catalyst; instead, the NbO_x/Fe_2O_3 catalyst produces CO_2 by TPD alongside selective product DME. We suggest this is due to its vastly greater Tamman temperature, and the consequent inability of NbO_x to diffuse as easily as Mo and V across the surface of the haematite during calcination.

Acknowledgments

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Graphical Abstract

Methanol oxidation over shell-core MO_x/Fe_2O_3 (M = Mo, V, Nb) cata-lysts

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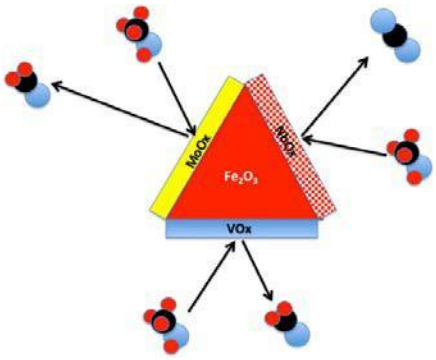

Methanol oxidation on three surface oxides on Fe_2O_3 showing the main carbon products. Mo and V monolayers are selective to formaldehyde, while Nb does not make complete monolayers and mainly combusts to CO_2.

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核壳结构MO_x/Fe_2O_3 (M = Mo, V, Nb)催化剂上甲醇氧化反应

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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, 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, 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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Supporting Information for

Methanol oxidation over shell-core MO_x/Fe_2O_3 (M = Mo, V, Nb) catalysts

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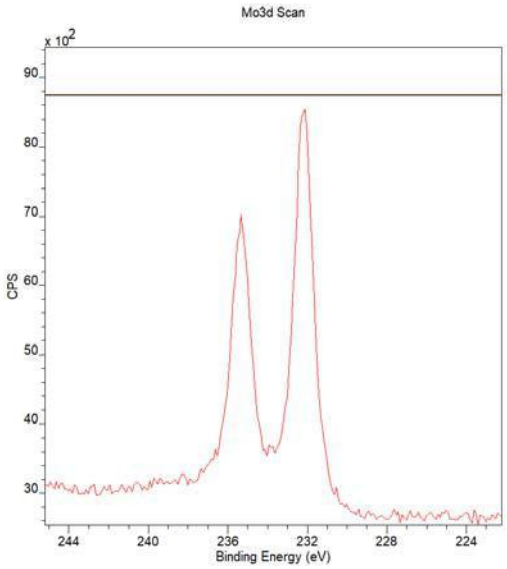

Fig. S1. Mo region of XPS data from 1 ML MoO_x/Fe_2O_3.

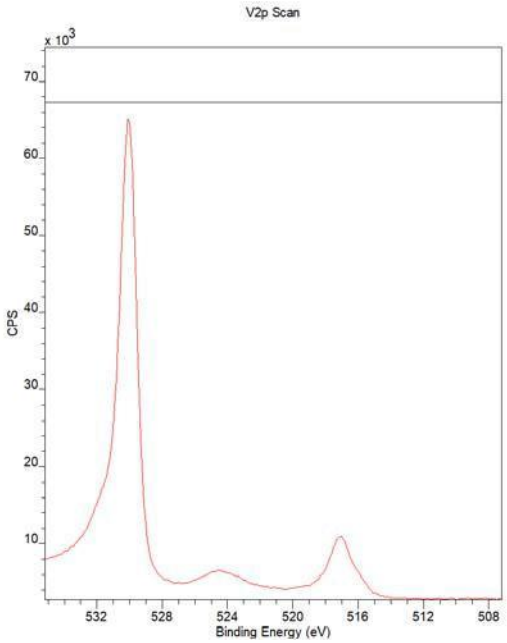

Fig. S2. V region of XPS data from 1 ML VO_x/Fe_2O_3.

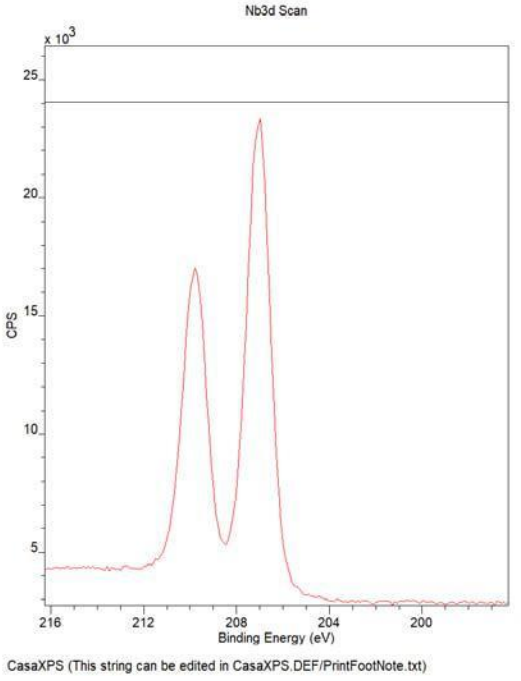

Fig. S3. Nb region of XPS data from 1 ML NbO_x/Fe_2O_3.

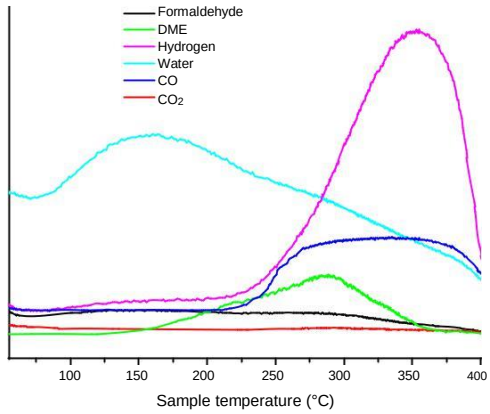

Fig. S4. TPD data for Nb_2O_5 calcined to 500°C. Major products are DME and CO – no significant CO_2 is produced.