The generality of surface vanadium oxide phases in mixed oxide catalysts

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The nature of VO\(_x\) sites in mixed oxides of supported VO\(_x\) (on both pure oxide and mixed oxide supports), molecular sieves, zeolites, clays, hydrotalcites, stochiometric bulk oxides and bulk solid solutions were investigated. For supported metal oxides, zeolites and molecular sieves, the VO\(_x\) species are exclusively present as surface VO\(_x\) phases below monolayer coverage or the maximum dispersion limits. For layered clays and hydrotalcites, the VO\(_x\) is present in the hydroxide layers at modest temperatures and react with the clays and hydrotalcites at higher temperatures (>350°C) when their layered structures decompose. Surface VO\(_x\) species are always also present for bulk oxides and bulk solid solutions. The rapid diffusion kinetics of VO\(_x\), due to its low Tammann temperature, coupled with the lower surface free-energy of vanadium oxide are responsible for the universal presence of surface VO\(_x\) sites on all mixed oxide materials. Furthermore, surface reactivity studies demonstrate that the surface VO\(_x\) sites are the catalytic active sites for all V-containing mixed oxide catalytic materials.

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1. Introduction

The class of mixed metal oxide catalytic materials consists of many different metal oxide arrangements as depicted in Fig. 1. Supported metal oxides possess two-dimensional surface metal oxide phases on a high surface area supports such as pure oxides, mixed oxides, zeolites or molecular sieves\([1–11]\). Layered clays and hydrotalcites allow for intercalation of metal oxides between the hydroxide layers\([12,13]\). Polyoxometalate (POM) clusters are nanometer sized mixed oxide clusters such as XM\(_{12−}\)\(_x\)\(_{VxO40}\) or X\(_2M_{18−}\)\(_x\)\(_{VxO62}\) where the central XO\(_4\) unit can be PO\(_4\), SiO\(_4\), etc. and coordinated to exposed mono-oxo MO\(_6\) (M = Mo, W, Cr, Nb, Ta or Re) or VO\(_x\) units via its oxygen linkages\([14,15]\). Bulk mixed oxides can be present as stochiometric compounds (e.g., FeVO\(_4\))\([5,16]\) or solid solutions (e.g., V\(_2\)Ti\(_{1−}\)O\(_2\))\([17]\). Such mixed metal oxides can occur in both isotropic (e.g., POMs and FeVO\(_4\)) as well as anisotropic platelet morphologies (i.e., V\(_2\)O\(_5\) and (VO\(_2\))\(_2\)P\(_2\)O\(_7\)).

This paper will only focus on the presence of surface VO\(_x\) phases in V-containing mixed oxide materials and the catalytic consequences of the presence of surface vanadium oxide sites in different mixed oxide catalytic materials. The V-containing mixed oxide materials are selected because of their extensive employment for catalytic as well as non-catalytic applications. The surface chemistry of the V-containing mixed oxides will be chemically probed with oxidation reactions because of the known redox nature of vanadium oxide. Model supported vanadium oxide catalysts will serve as references since they are known to possess 100% dispersed VO\(_x\) species below monolayer coverage or maximum dispersion limit. The V-containing mixed oxides will be characterized with IR and Raman vibrational spectroscopy, CH\(_3\)OH-temperature programmed surface reaction (TPSR) spectroscopy and steady-state oxidation reactions. The collective experimental information will show that surface VO\(_x\) phases are a general phenomenon in V-containing mixed oxide catalytic materials employing numerous examples from the author’s research.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Supported metal oxides

The supported vanadium oxide catalysts were synthesized by incipient wetness impregnation of V-isopropoxide dissolved in an isopropanol solution into high surface area oxide supports (e.g., Al\(_2\)O\(_3\), ZrO\(_2\), TiO\(_2\), Nb\(_2\)O\(_5\), SiO\(_2\), supported TiO\(_2\)/SiO\(_2\), silicalite molecular sieves and ZSM-5 zeolite) under a N\(_2\) atmosphere in a
duced onto the surface of TPA, and this catalyst is denoted as VOTPA. TPAV2 and TPAV3, respectively. In addition, vanadia was also intro-
duced into the support lattice[16,17]. The bulk V–Nb–O mixed oxides were prepared by mixing the corresponding aqueous solutions of the starting precurs-
sors. The aqueous mixture was subsequently evaporated to dryness by stirring and heating at 150 °C. The dry precursor was sub-
sequently calcined in air for 2 h at 600 °C to form the bulk V–Nb–O mixed oxide catalysts.

2.2. Raman spectroscopy

The in situ Raman spectra of the mixed metal oxides were collected with a Horiba-Jobin Yvon LabRam-HR spectrometer equipped with a confocal microscope, 2400/900 grooves/mm gratings, and a notch filter. The visible laser excitation at 532 nm (visible/green) was supplied by a Yag doubled diode pumped laser (20 mW). The scattered photons were directed and focused onto a single-stage monochromator and measured with a UV-sensitive LN2-cooled CCD detector (Horiba-Jobin Yvon CCD-3000 V). The powdered samples, ~5–10 mg, were loosely spread onto a small ceramic boat inside the environmental cell (Linkam T-1500) and maintained below the confocal microscope. Dehydration of the catalyst samples was carried out by heating the environmental cell to different temperatures under O2/He or CH3OH/O2/He flow (30 ml/min). After the desired treatment temperature was reached, the samples were dehydrated for 30 min before the Raman spectrum was recorded [18].

2.3. IR spectroscopy

The in situ IR vibrational measurements were performed with a Fourier transform infrared spectrometer (IlluminaIR II, Smith Detection) attachment that was mounted on the Horiba-Jobin Yvon LabRam-HR spectrometer equipped with mercury telluride (HgTe) and cadmium telluride (CdTe) photoconductive detectors (MCT) and cooled using liquid nitrogen. The reflectance FT-IR spectra were collected in the total reflection mode employing 0.3 s/scan with a resolution of ~4 cm⁻¹ and 1000 scans for the steady-state mode and 200 scans for temperature programmed mode.

2.4. CH3OH-TPSR spectroscopy

The CH3OH-TPSR spectroscopy measurements were performed on an Altamira (AMI-200) system equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). About 200 mg of sample was typically loaded into a U-shaped quartz tube and initially treated at 250 °C (ultra zero grade O2/He, 30 ml/min) for ~1 h to remove any combustible impurities that may be present. To ensure that the catalysts remain in a fully oxidized state, the pretreated samples were first cooled in flowing air to 110 °C and then the gas stream was switched to an ultra-
high-purity He flow with further cooling to 100 °C. After flushing with continuously flowing He for another 3 h at 100 °C to remove any physically adsorbed oxygen or potential background gases, a CH3OH/He gas mixture (2000 ppm methanol) feed was introduced at 30 ml/min for CH3OH chemisorption and maintained for ~40 min. Previous work demonstrated that the adsorption tempera-
ture of 100 °C almost completely minimizes the presence of physically adsorbed methanol on the catalyst samples since the physically adsorbed CH3OH desorbs below this temperature [18]. After methanol adsorption, the mixed metal oxide catalysts were again purged at 100 °C with an ultra-high-purity (UHP) He flow for an additional 1 h to remove any residual physically adsorbed methanol. The CH3OH-TPSR spectroscopy experiment was then performed with a heating rate of 10 °C/min in the flowing UHP He, and desorption products were monitored with the online mass
3. Results and discussion

3.1. Supported metal oxides

3.1.1. Pure oxide supports

Supported vanadium oxide phases on conventional high surface area oxide supports (e.g., SiO2, Al2O3, TiO2, ZrO2, CeO2, Nb2O5, and Ta2O5) have been extensively investigated over the past three decades and are formed when vanadium oxide precursors or even bulk V2O5, due to its low Tammann temperature of ~200 °C, are deposited on high surface area oxide materials [1–4]. Only isolated, mono-oxo surface VO4 species are present for supported V2O5/SiO2 catalysts under dehydrated conditions and below the maximum dispersion limit [5–8]. Isolated, mono-oxo surface VO4 species are also almost exclusively present at low surface coverage (<2 <m>/m2) on oxide supports [9]. At higher surface coverage, and especially as monolayer coverage is approached, polymeric surface VOx clusters species become predominant species on oxide supports [9,10]. Supported vanadium oxide phases have also been successfully synthesized on some less traditional oxide supports such as Fe2O3, Cr2O3, NiO, MnO, Co3O4, and Ta2O5 [4,21].

The specific catalytic reaction rates (TOF: turnover frequency is defined as the number of molecules reacting per surface VO4 site per second determined at low reactant conversions of ~10%) have been found to be essentially independent or only weakly dependent of the surface VO4 coverage on oxide supports for two e− reactions:

\[
\text{CH}_3\text{OH} \rightarrow \text{HCHO}[1,18]
\]

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO}[22]
\]

\[
\text{SO}_2 \rightarrow \text{SO}_3[23]
\]

Alkanes → olefins[9, 24–26], etc.

For catalytic reaction involving more than 2e−, which involve the participation of more than one O atom, the TOF increases with surface coverage VO4 coverage because multiple surface VO4 sites need to be involved:

\[
n\cdot\text{C}_4\text{H}_{10} \rightarrow \text{maleic anhydride}[27]
\]

\[
\text{CH}_2=\text{CHCH}_3 \rightarrow \text{CH}_2=\text{CHCHO}[20]
\]

\[
\text{NO} + \text{NH}_3 \rightarrow \text{N}_2[28], \text{etc.}
\]

For all oxidation reactions over supported vanadium oxide catalysts, however, the TOF values vary dramatically as a function of the specific oxide support by as much as a factor of 103 for many oxidation reactions [1,9,23–28] depending on the properties of the underlying oxide support. This general trend of the effect of the underlying support on the TOF values for oxidation reactions is shown below for methanol oxidation over supported vanadium oxide catalysts in Table 1. The origin of this pronounced support effect is not completely understood and is still being extensively discussed in the literature [18,29,30].

3.1.2. Model mixed oxide supports

Mixed oxide supports consist of two or more oxides intimately mixed in the bulk and the surface. Model mixed oxide supports were prepared by depositing a metal oxide on a high surface}

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF_{redox} (s(^{-1}))</th>
<th>Selectivity_{redox} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V2O5/CoO2</td>
<td>1.0 × 10^8</td>
<td>100</td>
</tr>
<tr>
<td>V2O5/ZnO2</td>
<td>1.7 × 10^4</td>
<td>99</td>
</tr>
<tr>
<td>V2O5/ThO2</td>
<td>1.1 × 10^4</td>
<td>100</td>
</tr>
<tr>
<td>V2O5/Nb2O5</td>
<td>8.5 × 10^2</td>
<td>98</td>
</tr>
<tr>
<td>V2O5/Ta2O5</td>
<td>7.6 × 10^2</td>
<td>100</td>
</tr>
<tr>
<td>V2O5/Al2O3</td>
<td>6.8 × 10^2</td>
<td>50</td>
</tr>
<tr>
<td>V2O5/SiO2</td>
<td>2.0 × 10^3</td>
<td>97</td>
</tr>
</tbody>
</table>

Methanol oxidation over supported vanadia at monolayer surface coverage catalysts at 230 °C (6% CH3OH, 13% O2, 81% He; ~100 mL/min).
area oxide support (e.g., TiO$_2$/SiO$_2$, ZrO$_2$/SiO$_2$, Al$_2$O$_3$/SiO$_2$, etc.) followed by calcination to form the supported metal oxide phase (e.g., TiO$_2$, ZrO$_2$, Al$_2$O$_3$, etc.). The synthesized model mixed oxide supports allow for control of the composition and structure of the mixed oxide surface. At low surface coverage, the impregnated oxide is typically present as a surface oxide overlayer and can form oxide nanoparticles at high surface coverage [31–35]. Such model mixed oxide supports can then be employed as oxide supports to for supported vanadium oxide catalysts [31–35]. For the multilayered supported V$_2$O$_5$/TiO$_2$/SiO$_2$ catalyst system [34–36], characterization studies demonstrated that the surface VO$_4$ species preferentially anchor to the surface TiO$_2$ sites because of the higher surface free-energy of the exposed TiO$_2$ sites than the SiO$_2$ support [37]. The formation of bridging V–O–Ti bonds has a dramatic effect on the TOF value of the isolated supported VO$_4$ species as tabulated in Table 2.

This enhancement is related to the greater reactivity of surface VO$_4$ sites coordinated to TiO$_2$ sites than SiO$_2$ sites [34–36]. The deposited TiO$_2$ phase is 100% dispersed as surface TiO$_2$ species up to 12% TiO$_2$/SiO$_2$ and is present as 3–9 nm crystalline TiO$_2$ (anatase) rafts at higher surface coverage [32,34–36]. The Si-free supported 1% V$_2$O$_5$/TiO$_2$ catalyst contains ~25 nm TiO$_2$ crystalline particles (mainly the anatase phase). These catalytic results demonstrate that for redox surface VO$_4$ sites the TOF values increase with the domain size of the TiO$_2$ substrate in the ~0.4–25 nm range. The increased redox activity of the surface VO$_4$ sites with increasing TiO$_2$ loading also improves the HCHO selectivity by suppressing the competitive MF formation on the supported TiO$_2$ sites [32]. These model studies with mixed oxide supports further demonstrate the sensitivity of redox surface VO$_4$ sites to the nature of the underlying oxide support ligands and that surface vanadia phases also readily form on mixed oxide supports.

### 3.1.3. Molecular sieve and zeolite supports

The molecular sieve V–silicate exclusively possesses isolated VO$_4$ sites [38]. To examine the influence of the oxide long-range environment, the reactivity and selectivity of crystalline, nanoporous V–silicate were compared with that of amorphous mesoporous supported V$_2$O$_5$/SiO$_2$ which also contains isolated VO$_4$ sites. Raman and solid-state $^{51}$V NMR analyses confirmed that both catalyst systems indeed contained isolated VO$_4$ units under dehydrated conditions and exhibit V=O vibrations at ~1038 cm$^{-1}$ [38]. The reactivity and product selectivity of the two types of SiO$_2$-containing vanadia catalysts are listed in Table 3 and are essentially indistinguishable. The identical TOF and product selectivity for the amorphous supported V$_2$O$_5$/SiO$_2$ and crystalline V–silicate catalysts reveal that the long-range order and nano- or mesoporosity of the underlying oxide support do not affect the TOF and selectivity when the same support ligands are present (in this case V–O–Si bonds).

### Table 2

Activity and product selectivity for methanol oxidation at 270 °C for supported vanadium oxide catalysts for methanol oxidation at 270 °C (6% CH$_3$OH, 13% O$_2$, 81% He; ~100 mL/min).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (10$^{-3}$/s)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCHO</td>
<td>HCOOCH$_3$</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/SiO$_2$</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/TiO$_2$/SiO$_2$</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/5% TiO$_2$/SiO$_2$</td>
<td>52</td>
<td>82</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/10% TiO$_2$/SiO$_2$</td>
<td>57</td>
<td>85</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/12% TiO$_2$/SiO$_2$</td>
<td>72</td>
<td>85</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/30% TiO$_2$/SiO$_2$</td>
<td>140</td>
<td>89</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/50% TiO$_2$</td>
<td>420</td>
<td>87</td>
</tr>
<tr>
<td>1% V$_2$O$_5$/TiO$_2$</td>
<td>750</td>
<td>93</td>
</tr>
</tbody>
</table>

*a* Methanol conversion is too low to accurately determine selectivity.

### Table 3

Activity and product selectivity for methanol oxidation at 380 °C over supported 1% V$_2$O$_5$/SiO$_2$ (amorphous and mesoporous) and V–silicate molecular sieve with ~1% V$_2$O$_5$ (crystalline and nanoporous) at 380 °C (6% CH$_3$OH, 13% O$_2$, 81% He; ~100 mL/min).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (10$^{-3}$/s)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCHO</td>
<td>HCOOCH$_3$</td>
</tr>
<tr>
<td>Supported 1% V$_2$O$_5$/SiO$_2$</td>
<td>43</td>
<td>84.6</td>
</tr>
<tr>
<td>V–Silicate</td>
<td>53</td>
<td>87.0</td>
</tr>
</tbody>
</table>

Impregnation of vanadium oxide precursors into ZSM-5 zeolites, that are subsequently calcined, also results in isolated surface VO$_4$ species that exhibit the characteristic mono-oxo V=O Raman vibration at 1038 cm$^{-1}$ [39]. The same Raman band is also found for the supported V$_2$O$_5$/Al$_2$O$_3$/SiO$_2$ catalyst system under dehydrated conditions as well as supported V$_2$O$_5$/SiO$_2$ preventing discrimination of the coordination site of the surface VO$_4$ species [34]. However, titration of all the AlO$_4$ sites in ZSM-5 leads to crystalline V$_2$O$_5$ formation since the additional vanadium precursor has no sites to bind suggesting preferential coordination of the VO$_4$ units to the AlO$_4$ sites in ZSM-5. The preferential anchoring of the surface VO$_4$ sites to AlO$_4$ sites in ZSM-5 is confirmed by the enhanced specific rate of methanol oxidation for V$_2$O$_5$/ZSM-5 compared to V$_2$O$_5$/SiO$_2$ [39,40] as suggested by the reactivity findings for the supported V$_2$O$_5$/SiO$_2$ and V$_2$O$_5$/Al$_2$O$_3$ catalysts contained in Table 2.

### 3.2. Layered clays and hydrotalcites

Metal oxides, and especially vanadium oxide, have been successfully intercalated into layered metal hydroxides found in clays and hydrotalcites such as Zn$_2$Al(OH)$_6$$^{2+}$ [33], Zn$_2$Cr(OH)$_6$$^{2+}$ [41], Ni$_2$Al(OH)$_6$$^{2+}$ [41], Mg$_2$Al(OH)$_6$$^{2+}$ [41,42], and Li$_2$Al(OH)$_6$$^{2+}$ [12]. Vanadium was ion exchanged into Li$_2$Al(OH)$_6$$^{2+}$ layered hydroxide over the pH range of 3–11 [13]. Characterization studies showed that the vanadia in the interlayer was present as hydrated V$_2$O$_7$$^{4–}$ and V$_4$O$_{12}$$^{4–}$ species at room temperature. Heating to ~100 °C induced demerization of V$_2$O$_4$$^{4–}$ to V$_2$O$_7$$^{4–}$ species in the interlayer, with further extent of polymerization upon heating to ~350 °C. At higher temperatures the degradation of the layered framework took place with concomitant formation of crystalline Li$_3$VO$_4$ and LiVO$_3$. Intercalation of decavanadate (V$_{10}$O$_{28}$$^{6–}$) into Mg$_2$Al(OH)$_6$$^{2+}$ was also examined as a function of temperature [13]. At room temperature the intercalated decavanadate V$_{10}$O$_{28}$$^{6–}$ ion is present and begins to transform to simpler vanadate species (cyclic (VO)$_n$$^{2n–}$ with n equal to 3 or 4, HVO$_4$$^{2–}$) polymeric metavanadates (~O–VO$_2$–O–VO$_2$–O–)n upon heating in the ~160–450 °C temperature range. The layered hydroxide structure is only stable until ~450 °C. At ~650 °C, the metavanadate species react with the decomposed hydrotalcite to form the crystalline Mg$_2$V$_2$O$_7$ and Mg(VO$_4$)$_3$ bulk mixed oxides. The hydrated vanadate species observed in these layered hydroxides are similar to those found on hydrated oxide surfaces of simple oxides and their structures only depend on the net pH at point of zero charge (pzc) of the hydrated interlayer [43]. Although no catalytic data have been reported for the intercalated vanadium oxides in clays and hydrotalcites, it is important to point out that the interfacial vanadia species in clays and hydrotalcites are no different than the surface vanadia species observed for supported vanadium oxide catalysts. Thus, the catalytic properties of V–intercalated clays and hydrotalcites should be related to those reported for supported V$_2$O$_5$/Al$_2$O$_3$ and V$_2$O$_5$/MgO catalysts [1]. The major difference between the vanadate species intercalated into the hydroxide layers and more traditional supported metal oxides is that the former tend to thermally decompose at rather mild temperatures (~350 °C) in the presence of vanadium oxide.
3.3. Polyoxometalates (POMs)

V-containing POMs are usually prepared by substituting VO$_x$ units for WO$_x$ or MoO$_x$ units in the PW$_{12}$O$_{40}$ and PMo$_{12}$O$_{40}$ sub-nanometer Keggin structures, respectively [14]. The substituted VO$_x$ units take on distorted mono-oxo O=VO$_x$ coordination with four of the oxygen atoms bonded to adjacent W or Mo cations and the fifth oxygen atom weakly bonded to the central P heteroatom. Typically, only 1–3 VO$_x$ units are introduced into the Keggin structures since additional units will destabilize the POM [15]. It is generally assumed that all the VO$_x$ units have been substituted into the Keggin structure. The surface chemistry of a series of PW$_{12-x}$V$_x$O$_{40}$ Keggins was probed with CH$_3$OH-temperature programmed surface reaction (TPSR) spectroscopy and the findings are presented in Fig. 2. Without vanadia, the tungstophosphoric acid Keggin does not produce any HCHO because of the absence of surface redox sites in H$_3$PW$_{12}$O$_{40}$.

Substitution of one vanadia for a WO$_x$ site of tungstophosphoric acid, TPAV1, introduces redox sites that are reflected in the formation of the sharp HCHO peak at 205 $^\circ$C. Substitution of two and three vanadia for WO$_x$ units of tungstophosphoric acid, TPAV2 and TPAV3, respectively, leads to broadening of the sharp HCHO/CH$_3$OH-TPSR band and introduction of a second redox site that forms HCHO at higher temperatures. The origin of the high temperature redox site was determined by impregnating a vanadium oxide precursor onto the tungstophosphoric acid Keggin, VOTPA, which results in formation of surface VO$_x$ species on the Keggin and the appearance of a broad HCHO/CH$_3$OH-TPSR peak at 245 $^\circ$C. The VOTPA TPSR experiment reveals that the broad HCHO/CH$_3$OH-TPSR features observed above 205 $^\circ$C for TPAV2 and TPAV3 are a consequence of the presence of surface VO$_x$ species in addition to the vanadial sites substituted for WO$_x$ in TPA. Consequently, when more than one vanadia unit is substituted for a WO$_x$ site some of the vanadia is not incorporated into the Keggin structure.

The presence of the surface VO$_x$ species has significant catalytic consequences for the PW$_{12-x}$V$_x$O$_{40}$ Keggins. The more vanadia units incorporated into the Keggin structure, the more VO$_x$ species are present on the surface, resulting in a broad HCHO/CH$_3$OH-TPSR peak and a decrease in the TOF values. Table 4 summarizes the TOF values and selectivity for the various catalysts. The high HCHO selectivity is a consequence of the redox nature of bulk V$_2$O$_5$, which is known to have a high TOF for HCHO production [29,44].

Table 4

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Activity (mol/g cat s)</th>
<th>Selectivity</th>
<th>TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DME</td>
<td>HCHO</td>
</tr>
<tr>
<td>TPA</td>
<td>225</td>
<td>9.6</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>TPAV1</td>
<td>225</td>
<td>14.7</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>TPAV2</td>
<td>225</td>
<td>7.4</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>TPAV3</td>
<td>225</td>
<td>3.0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>VOTPA</td>
<td>250</td>
<td>12.5</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>225(extrapolated)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4. Bulk mixed metal oxides

3.4.1. Bulk V$_2$O$_5$

Bulk V$_2$O$_5$ possesses an anisotropic morphology as depicted in Fig. 1 with the edge planes accounting for a minor fraction of the exposed surface area and the basal planes accounting for the majority of the exposed surface area. The basal planes terminate with V=O bonds and the edge planes possess V=OH and bridging V–O–V bonds. The surface chemistry of bulk V$_2$O$_5$ was chemical probed with CH$_3$OH chemisorption and methanol was found to selectively chemisorb on the edge planes. Consequently, the number of reactive exposed VO$_x$ species on bulk V$_2$O$_5$ only corresponds to ~0.4 V/nm$^2$ [29,44], whereas supported vanadium oxide catalysts with monolayer surface VO$_x$ coverage (see Section 3.1 above on supported metal oxide catalysts).

The surface chemistry of bulk V$_2$O$_5$ was further chemically probed with CH$_3$OH-TPSR spectroscopy and found to exclusively produce HCHO as a reaction product reflecting the redox nature of the reactive surface VO$_x$ sites in bulk V$_2$O$_5$. The surface reactivity of bulk V$_2$O$_5$ was also examined with steady-state methanol oxidation at 230 $^\circ$C and found to exhibit 90% HCHO selectivity and a TOF of ~4 x 10$^{-1}$/s. The high HCHO selectivity is a consequence of the redox nature of bulk V$_2$O$_5$ with the minor amount of acid sites responsible for 10% DME formation. Comparison of the TOF$_{\text{redox}}$ for bulk V$_2$O$_5$ with those for the supported vanadium oxide catalysts indicates that bulk V$_2$O$_5$ is rather reactive and is only surpassed by the supported V$_2$O$_5$/CeO$_2$ catalyst system.

The low reactivity of bulk V$_2$O$_5$ usually reported in the literature is then related to the low number of reactive surface VO$_x$ sites (~0.4 V/nm$^2$) because the basal planes are not active, and not to the true activity of the reactive surface VO$_x$ sites (~4 x 10$^{-1}$/s).
Furthermore, this fact also reveals that the enhanced activity of supported V₂O₅ catalysts is mostly related to the high number of reactive surface VOₓ sites (~8 V/nm²) at monolayer coverage.

3.4.2. Bulk metal vanadates

Bulk FeVO₄ consists of three distinct, isolated VO₄ units that are distorted and are each coordinated to four Fe₂O₃ units [46]. The Raman spectrum of bulk FeVO₄ exhibits three bands at 971, 936 and 910 cm⁻¹ representing the shortest V=O bonds of the each of the three distinct VO₄ sites, respectively [5]. Chemisorption of CH₃OH in bulk FeVO₄ only exhibits IR vibrations of surface CH₃O⁻ intermediates, ~2820–2830 and 2920–2930 cm⁻¹, and intact chemisorbed surface CH₃OH⁻ species, ~2850–2860 and ~2950–2960 cm⁻¹, on surface Lewis acid sites as shown in Fig. 3. For comparison, the M–OCH₃ vibrations for Fe–OCH₃ on bulk Fe₂O₃ occur at 2820 and 2924 cm⁻¹ and are shifted to 2828 and 2930 cm⁻¹ for V–OCH₃ on bulk V₂O₅. The M–OCH₃ vibrations on bulk FeVO₄ line up with the vibrations of V–OCH₃ and there is no evidence of significant Fe–OCH₃ IR bands. The absence of surface Fe–OCH₃ vibrations reveals that the surface CH₃O⁻ intermediate preferentially bonds to surface VOₓ sites and suggests that surface of bulk FeVO₄ is significantly enriched with surface VOₓ sites. The surface chemistry of bulk Fe₂O₃, V₂O₅ and FeVO₄ was chemically probed with CH₃OH-TPSR spectroscopy as shown in Fig. 4. The bulk Fe₂O₃ catalyst primarily yields dimethyl ether (DME:CH₃OCH₃) from surface acid sites and a minor amount of HCHO from surface redox sites [44,47]. In contrast, bulk V₂O₅ almost exclusively produces HCHO because of the dominance of surface redox sites in this material [5,48]. Bulk FeVO₄ also gives rise to HCHO reflecting the predominance of surface redox sites on its surface and only gives rise to a minor amount of DMM without the formation of any DME. The bulk FeVO₄ catalyst, however, behaves very similar to the bulk V₂O₅ catalyst with its surface redox sites and exhibits almost the same product selectivity and TOF value. Consequently, the catalytic properties of bulk FeVO₄ do not reflect the characteristics of acidic FeOₓ sites and are completely overwhelmed by the redox properties of the surface redox VOₓ sites.

The conclusion that a surface enriched VOₓ outer layer is present for the bulk FeVO₄ phase is further supported by steady-state methanol oxidation over a supported 4% V₂O₅/Fe₂O₃ catalyst that contains about monolayer coverage of surface VOₓ species on the Fe₂O₃ support [5]. Methanol oxidation over the supported V₂O₅/Fe₂O₃ catalyst leads to a very high HCHO selectivity reflecting the dominance of redox surface VOₓ sites, whereas, bulk Fe₂O₃ yields significant amounts of DME from its surface acid sites.

3.4.3. Bulk mixed oxide solid solutions

Bulk mixed oxide solid solutions of vanadium oxide with other oxides are well known (e.g., VₓTi₁₋ₓO₂ (rutile) and VₓNb₂₋ₓO₅ [17]). Such catalytic materials are inherently inactive since the redox VOₓ sites are incorporated inside the mixed metal oxide structure and, consequently, are not accessible to the reactant molecules at its surface. For example, the bulk mixed oxide VₓTi₁₋ₓO₂ (rutile) solid solution phase is essentially inactive and unselective for o-xylene oxidation to phthalic anhydride, but its catalytic performance is significantly improved once additional vanadium oxide is impregnated onto its surface [17]. In the case of VₓNb₂₋ₓO₅ solid solutions, Raman spectroscopy reveals that dehydrated surface VOₓ species are present on the surface of VₓNb₂₋ₓO₅ [49]. By comparing the two surface CH₃O⁺ intermediates [48]. The predominance of DME on Fe₂O₃ is a consequence of the dominance of acid sites on its surface. In contrast, bulk V₂O₅ primarily gives rise to HCHO reflecting the dominance of redox sites on its surface and only gives rise to a minor amount of DMM without the formation of any DME. The bulk FeVO₄ catalyst, however, behaves very similar to the bulk V₂O₅ catalyst with its surface redox sites and exhibits almost the same product selectivity and TOF value. Consequently, the catalytic properties of bulk FeVO₄ do not reflect the characteristics of acidic FeOₓ sites and are completely overwhelmed by the redox properties of the surface redox VOₓ sites.

Table 5

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (s⁻¹)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCHO</td>
<td>DME</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.4</td>
<td>87</td>
</tr>
<tr>
<td>FeVO₄</td>
<td>0.16</td>
<td>83</td>
</tr>
</tbody>
</table>
catalytic activity of the mixed $V_2\mathrm{O}_5\cdot\mathrm{Nb}_2\mathrm{O}_5$ solid solution with that of supported $V_2\mathrm{O}_5/\mathrm{Nb}_2\mathrm{O}_5$ containing a monolayer of surface VO$_x$ species for oxidative dehydrogenation (ODH) of propane to propylene, which requires only one surface VO$_x$ site to proceed, it was possible to estimate the fraction of VO$_x$ that is present on the surface and bulk of the mixed $V_2\mathrm{O}_5\cdot\mathrm{Nb}_2\mathrm{O}_5$ solid solution since NbO$_x$ sites are essentially inactive for this ODH reaction. The distribution of VO$_x$ between the bulk and surface of $V_2\mathrm{O}_5\cdot\mathrm{Nb}_2\mathrm{O}_5$ as well as the corresponding catalytic data are listed in Table 6.

The propane ODH studies over the bulk $V_2\mathrm{O}_5\cdot\mathrm{Nb}_2\mathrm{O}_5$ mixed oxide solution reveal that the activity of this catalytic reaction is significantly enhanced when surface VO$_x$ sites are present on $V_2\mathrm{O}_5\cdot\mathrm{Nb}_2\mathrm{O}_5$ solid solution, which are the catalytic active sites. Furthermore, the data show that a significant fraction of the VO$_x$ that has been introduced into the mixed $V_2\mathrm{O}_5\cdot\mathrm{Nb}_2\mathrm{O}_5$ solid solution is always on the surface of this mixed oxide solid solution. Thus, surface VO$_x$ species are always present on the surfaces of mixed oxide solid solutions and are the active sites that control their catalytic properties.

4. Conclusions

V-containing mixed oxides (supported metal oxides, zeolites and molecular sieves, layered clays and hydroxalicates, polyoxometalates (POMs), bulk mixed oxides and mixed oxide solid solutions) were investigated for the presence of surface VO$_x$ phases and their influence on catalytic reactions. Supported VO$_x$ catalysts on traditional oxide supports were used as model systems to better understand the structure and property of surface VO$_x$ species since they are 100% dispersed on the high surface area oxide supports below monolayer coverage. Surface VO$_x$ species were found to be present on all types of V-containing mixed oxides (zeolites and molecular sieves, layered clays and hydroxalicates, polyoxometalates (POMs), bulk mixed oxides and mixed oxide solid solutions). Furthermore, the surface VO$_x$ species were found to be the catalytic active sites for all types of the V-containing mixed oxides. These findings reveal the generality of vanadium oxide phases in V-containing mixed oxide catalytic materials. Furthermore, surface MO$_x$ phases are generally also present for other mixed oxide system containing low Tammann temperature oxides (e.g., MoO$_x$, CrO$_x$, WO$_3$ and Re$_2$$O_7$).