

A new model for the molecular structure of supported vanadium oxide catalysts

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Received 19 May 2004; in final form 31 August 2004

Available online 15 September 2004

Abstract

Raman spectroscopy experiments found the V=O stretching frequency for the supported VO₄ species to decrease with increasing catalyst temperature. Calculations on the vibrational frequencies of several models using density functional theory show that a consistent description of the experimental data can be obtained if we assume that the VO₄ species are anchored to the oxidic surface by one V–O bond only, in contrast to the traditional pyramidal model, which assumes three V–O_{support} bonds and one V=O. The proposed VO₃ structure points away from the surface and consists of one V=O unit and an active oxygen ‘molecule’ loosely bound to the vanadium atom, a peroxide species.

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1. Introduction

Supported vanadium oxide catalysts are widely used in chemical industries in various selective oxidation reactions as well as for the selective reduction of NO_x with ammonia [1–5]. They consist of a vanadium oxide phase deposited on the surface of a high-surface oxide support, such as SiO₂, Al₂O₃, TiO₂ and ZrO₂. During the last two decades many research groups have studied the molecular structure of supported vanadium oxides under hydrated, dehydrated and reduced catalyst conditions with e.g., Raman, infra-red, UV–Vis and extended X-ray absorption fine structure (EXAFS) spectroscopies. A review of the literature to date has been published recently [6]. There is a consensus that supported vanadium oxides at low vanadium oxide loadings are present as isolated vanadium centres surrounded by four oxygen atoms.

The model currently accepted in the literature [7–9] is depicted in Fig. 1, where vanadium is bound to three support oxygens with equal bond lengths. The fourth oxygen atom points upwards away from the surface and is doubly bonded to the vanadium. This model, which might be called the pyramidal model, predicts the existence of one vibrational mode which is predominantly the V=O stretch, that should be close to that found in simple V=O structures like VOX₃, with X = F, Cl, Br or I. This mode is indeed reported at around 1030 cm⁻¹ by many authors [10–16]. The structure of the pyramidal model also complies with EXAFS studies [17]. These indicate that a V atom is surrounded by four oxygen atoms, three of these are found at a distance of 1.70–1.77 Å, the exact value depending on the nature of the support (alumina, niobia, zirconia) and one at a much shorter distance of 1.58–1.59 Å.

At higher vanadium oxide loadings the presence of polymeric vanadium oxide species on various amorphous supports has been proposed. A second vibrational mode is seen at around 920 cm⁻¹. As it is most

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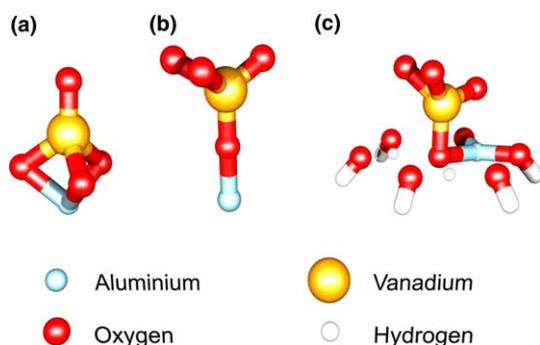


Fig. 1. The molecular structure of the three cluster models for a supported vanadium oxide (VO_4) catalyst considered in this Letter. The cluster (a) can be described as a pyramid, with three oxygen atoms forming part of the support lattice. Only one free $\text{V}=\text{O}$ bond is present, perpendicular to the support surface. The clusters (b) and (c) can be described as an umbrella, where only one oxygen atom is part of the support. Two equivalent $\text{V}-\text{O}$ bonds and one shorter $\text{V}=\text{O}$ bond are now formed.

clearly seen at higher loadings it is commonly attributed to a polymeric species, either a $\text{V}-\text{O}-\text{V}$ or an $\text{O}-\text{V}-\text{O}$ bending vibration [16]. However, it has also been reported for a 1 wt% vanadium catalyst on CeO_2 [15]. Alternatively, the band around 920 cm^{-1} has been assigned to a VOAl vibration [14] in studies on a flat Al_2O_3 model catalyst. Thus, two bands are clearly documented in the literature, but only the 1030 cm^{-1} is unambiguously assigned. For now we will call the band at 1030 cm^{-1} the $\text{V}=\text{O}$ stretching mode and the band at 920 cm^{-1} the polymeric band.

A conventional way to ascertain the assignment of a vibration to a stretching mode is the use of isotopic labelling. For the present case available data are relatively scarce, as it requires the use of ^{18}O . It was found for low loadings of vanadium [15,16] that upon substituting ^{18}O the $\text{V}=\text{O}$ stretching mode decreased 45 cm^{-1} in frequency. This is entirely consistent with the change in frequency for a one-dimensional $\text{V}=\text{O}$ oscillator. However, the polymeric band also decreases in frequency by about the same amount upon substituting labelled oxygen [15,16]. This is somewhat surprising since as a rule bending modes are less susceptible to isotopic substitution.

The $\text{V}=\text{O}$ stretching mode observed at 1030 cm^{-1} has also been reported to shift to lower wavenumbers with increasing temperature [15,18], although no explanation for this effect has been proposed. One would intuitively expect the frequency to increase due to a weakening of the bond between the adsorbate and the surface. For example, the $\text{C}-\text{O}$ stretch frequency of the adsorbed molecule is much lower than the gas phase frequency. The effect of temperature on the Raman frequencies of bulk compounds and large crystallites has been noted before [18].

The controversies and unexplained features of the supported vanadium oxide system led us to reinvestigate

this system both experimentally and theoretically. In the present Letter, we wish to propose a completely different molecular structure for the VO_4 moiety also shown in Fig. 1 as the umbrella model. Here, a VO_3 entity is bound to the surface by one $\text{V}-\text{O}$ bond only. We will show that this model is capable of describing all observed data correctly and consistently.

2. Experimental

Raman spectra of supported vanadium catalysts were obtained with the aid of a Kaiser RXN spectrometer equipped with a 532 nm diode laser. A 5.5" non-contact objective was used for beam focusing and collection of scattered radiation. A total of 25 data accumulations was done in an exposure time of 2 s for each datapoint.

Quantum chemical calculations were done with the GAMESS-UK program [19]. DFT calculations were performed using the B3LYP density functional [20]. All calculations were performed with a triple zeta basis set augmented with polarisation functions (TZVP) [21]. Harmonic frequencies were obtained from analytical hessian calculations. As is well known the frequencies resulting from B3LYP DFT calculations are slightly too high, compared with experiments [22]. Commonly a scaling factor around 0.95 is used to correct for this deficiency [23,24]. This factor has been incorporated in all data.

Several cluster models were investigated, the pyramidal cluster model shown in Fig. 1 where the support was modelled by three oxygen atoms and one aluminium atom. The umbrella model is also shown in Fig. 1. The support material now consists of one oxygen atom and one aluminium atom only. As this might be a rather simplified representation of an adsorbed molecule, also a larger cluster was considered as shown in Fig. 1. The support is now represented by a layer of seven close packed co-planar oxygen atoms, the six boundary atoms being terminated with hydrogen atoms. A second layer of atoms, consisting of one aluminium atom and two hydrogen atoms was added.

As quantum mechanics deals with energies only and we wish to investigate the effect of temperature on observed vibrational frequencies, we must devise a way to do so. Generally the effect of temperature on a solid is to increase its volume. The interatomic distances are increased due to the anharmonicity of the lattice vibrations [25,26]. The linear thermal expansion coefficient ($\Delta\ell/\ell$) is a quantitative measure of this effect. They are generally of the order of $1-5 \times 10^{-5}\text{ K}^{-1}$ [25,26]. Thus an increase in the lattice constant of the cluster corresponds with a lattice at higher temperature. This first order approximation defines the cluster structure at each temperature. When adsorption takes place on this solid cluster the adsorbed entities will be allowed to find their

optimum geometry, consistent with the underlying solid lattice structure. In order to simulate a truly rigid lattice the solid atoms are kept at a fixed position. Thus, referring to Fig. 1, in the pyramidal cluster model we increase (simultaneously) all O–O and Al–O distances. The adsorbed V=O entity is then allowed to find its equilibrium geometry. For the umbrella models in Fig. 1 we likewise restrain the position of all atoms except for those of the adsorbed $-\text{VO}_3$ moiety.

3. Results and discussion

Supported vanadium oxide catalysts show under dehydrated conditions and room temperature Raman transitions at around 920 and 1030 cm^{-1} . The former is displayed as a broad band and is commonly assigned to either a V–O–V or an O–V–O bending vibration, a polymeric species [16]. The latter is displayed as a narrow band and assigned to a V=O stretching vibration. Both modes have the same integrated intensity. The frequency of the V=O stretching mode decreases with increasing temperature. This is illustrated in Fig. 2, for a run where the temperature was decreased stepwise from 600 to 100 $^{\circ}\text{C}$, followed by two runs with increasing temperature and decreasing temperature. As can be seen the data are very reproducible and show a clear trend. The peak frequency decreases with increasing temperatures by about 10 cm^{-1} . Data below 100 $^{\circ}\text{C}$ are influenced by heating of the sample through the exciting laser beam. This temperature effect has been seen before [15,18], albeit in a smaller temperature range.

From the calculations on the pyramidal cluster model shown in Fig. 1 only a transition at 1030 cm^{-1} can be found, which corresponds to the V=O stretch vibration. If the temperature is increased in this cluster model the frequency of this mode increases as shown in Fig. 3. Thus, the pyramidal model contradicts the experimentally observed Raman frequency decrease shown in Fig. 2. The computed V–O distances, 1.59 Å for the V=O separation and 1.85 Å for the three V–O_{support} distances are close to those found in the EXAFS analysis [17].

The umbrella model is essentially one support oxygen atom to which a $-\text{VO}_3$ entity is bound by a O–V bond, as shown in Fig. 1. The support can, in a very simplified form, be described by the addition of one aluminium atom below the catalyst surface, which is now composed of one oxygen atom only. This molecular structure has an equilibrium geometry with two equivalent V–O bonds with length 1.80 Å and one shorter bond of 1.59 Å, all pointing away from the surface. The bond between the vanadium atom and the surface oxygen is 1.77 Å, very close to the distance of the vanadium and the two equivalent oxygens. The umbrella model is consist-

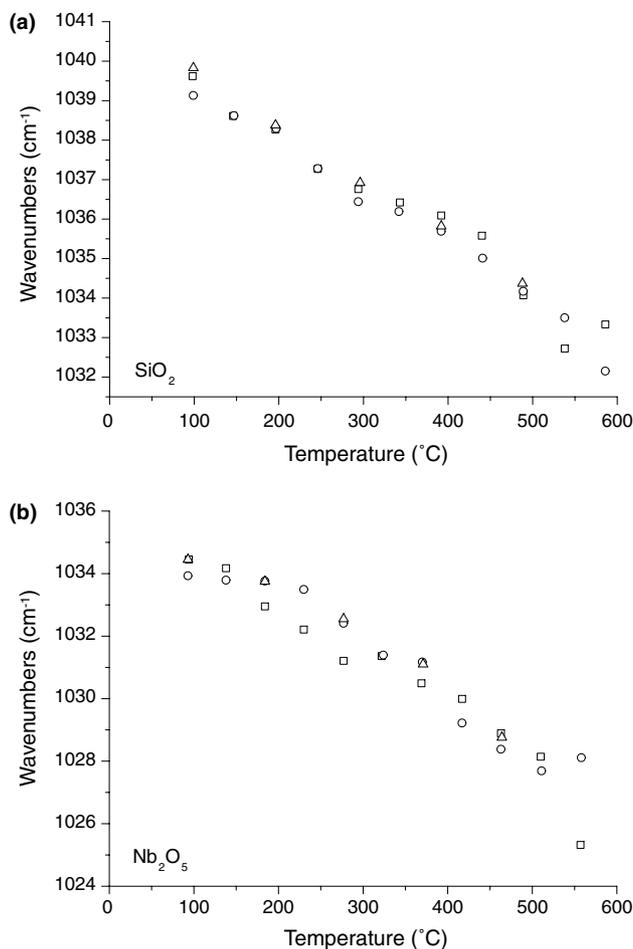


Fig. 2. The temperature dependence of peak maximum of the V=O stretching mode as observed on a silica (a) and niobia (b) supported vanadium oxide catalyst. Three consecutive runs are shown in which the temperature was decreased stepwise from 600 to 100 $^{\circ}\text{C}$ (\square), increased again (\circ) followed by a last cooling down cycle (\triangle).

ent with the reported EXAFS data [17] on the experimental V–O internuclear distances showing only two different distances. Similar results were found when adsorbing the $-\text{VO}_3$ entity on the central atom of a plane consisting of seven oxygen atoms in a twodimensional close-packed structure, with one Al and two H atoms located below this oxygen surface, as also shown in Fig. 1. Structural data are given in Table 1 for the clusters considered. It is noteworthy that the structure of the VO_3 contains one V=O bond and two equivalent VO bonds. The separation between the two equivalent oxygen atoms is only some 1.44–1.46 Å, barely larger than that in an oxygen molecule. The structure $-\text{VO}_3$ might thus be described as $\text{VO}(\text{O}_2)$, roughly speaking an oxygen molecule adsorbed on a supported V=O species, or a peroxy species.

Above 800 cm^{-1} two high frequency modes are now found for the small cluster, one at 1027 cm^{-1} , which is predominantly the V=O stretch vibration of the short

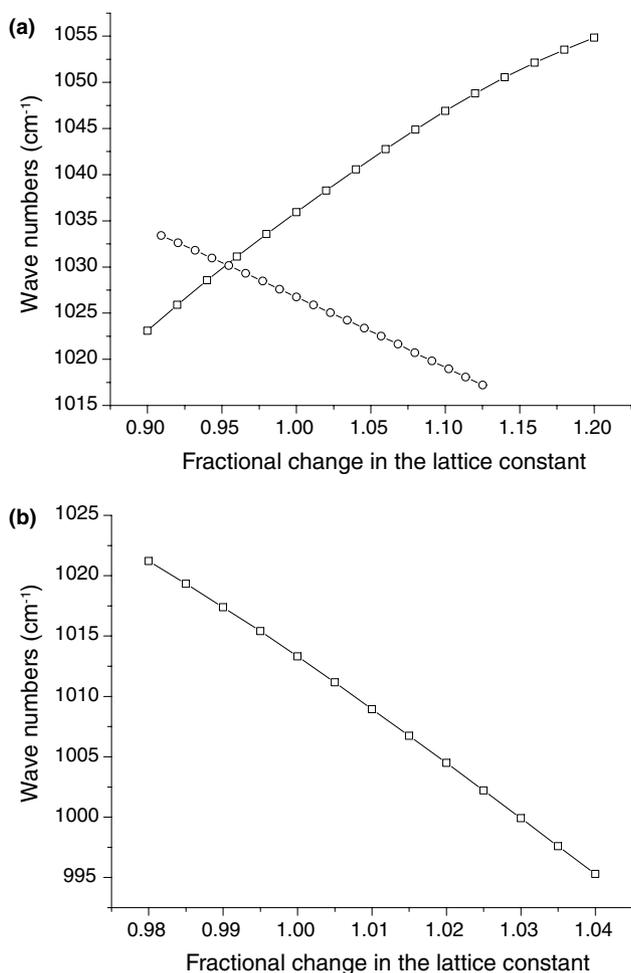


Fig. 3. The dependence of the frequency of the V=O stretching mode on the fractional change in the lattice constant of the support lattice for the three models are shown in Fig. 1. (a) shows the computed data for the adsorbed -VO_3 species on a small support cluster. An increase in the fractional lattice constant corresponds to a higher temperature due to thermal expansion of the lattice. The pyramidal cluster, with only one oxygen atom pointing away from the surface (\square) shows a temperature dependence, opposite to that found experimentally, whereas the smaller umbrella cluster (\circ) reproduces to experimental trend nicely. (b) shows the same data for the large cluster.

V–O bond and one at 892 cm^{-1} , which is predominantly the stretching vibration of the two equivalent oxygen atoms. It can be considered as the vibration of a free oxygen molecule (1580 cm^{-1}) weakened by the interaction of this molecule with the V=O entity. The numbers change slightly for the larger cluster, but the conclusion holds for both umbrella cluster models as shown by the data in Table 1. Also the calculated intensities of the 892 and 1027 cm^{-1} show a 1:1 ratio, which is in agreement with our measurements.

It is found that for both clusters the two vibrational frequencies decrease with increasing temperature, which is in agreement with the experimental results. A plot of the data is shown in Fig. 3. Here the x -axis is given as

Table 1

Computed data for the two umbrella structures considered in this work. The oxygen atom denoted as O_s refers to the oxygen atom of the support

Cluster	AlO-VO_3	$\text{AlH}_2\text{O}_7\text{-VO}_3$
$R(\text{V-O}_s)$	1.766	1.827
$R(\text{V-O})$	1.802	1.788
$R(\text{V-O})$	1.802	1.788
$R(\text{V=O})$	1.586	1.597
$R(\text{O-O})$	1.456	1.440
$h\nu(\text{O-O})$	892	918
$h\nu(\text{V=O})$	1027	1008

Experimentally three oxygen atoms are found at a distance of 1.70 – 1.77 \AA from the vanadium and one 1.58 – 1.59 \AA , while the vibrational modes are found at 1030 and 920 cm^{-1} .

the fractional change in the ‘lattice constant’ of the cluster. For the larger cluster it can be seen from Fig. 3 that a decrease in the vibrational frequency of around 10 cm^{-1} (as observed experimentally) is caused by a fractional bond length change of 0.014 . This implies a linear thermal expansion ($\Delta \ell/\ell$) of 0.014 . Using an experimental thermal expansion coefficient for bulk solids 1 – $5 \times 10^{-5}\text{ K}^{-1}$ [25,26] a thermal expansion of 0.005 – 0.025 over a temperature range of 500 K is obtained. This range brackets the computed value nicely.

The isotopic substitution experiments reported in [15,16] can also be included simply by replacing one, two or three oxygen atoms pointing away from the surface by ^{18}O atoms. As can be expected both bands shift to lower wavenumbers if the oxygen atom involved is replaced by its heavier isotope. As the three oxygens pointing upwards from the surface are not equivalent, one (or two) of them can be exchanged in two distinct ways. All possible cases have been considered and the calculated and observed vibrational frequencies are given in Table 2 for both clusters considered. The agree-

Table 2

Observed and calculated frequencies (cm^{-1}) for partially ^{18}O exchanged OVO_3

Observed ^{16}O		920		1030
Observed $^{18}\text{O}/^{16}\text{O}$	≈ 880	920	985	1030
$\text{Al-O-V-}^{16}\text{O}_3$		892		1027
$\text{Al-O-V-}^{16}\text{O}_2^{18}\text{O}$	870			1027
$\text{Al-O-V-}^{16}\text{O}^{18}\text{O}_2$		891	985	
$\text{Al-O-V-}^{16}\text{O}^{18}\text{O}_2$	869		985	
$\text{Al-O-V-}^{16}\text{O}^{18}\text{O}_2$	847			1026
$\text{Al-O-V-}^{18}\text{O}_3$	846		985	
$\text{AlH}_2\text{O}_7\text{-V-}^{16}\text{O}_3$		918		1008
$\text{AlH}_2\text{O}_7\text{-V-}^{16}\text{O}_2^{18}\text{O}$	897			1008
$\text{AlH}_2\text{O}_7\text{-V-}^{16}\text{O}^{18}\text{O}_2$		914	971	
$\text{AlH}_2\text{O}_7\text{-V-}^{16}\text{O}^{18}\text{O}_2$	894		969	
$\text{AlH}_2\text{O}_7\text{-V-}^{16}\text{O}^{18}\text{O}_2$	873			1008
$\text{AlH}_2\text{O}_7\text{-V-}^{18}\text{O}_3$	870		968	

All possible cases for the exchange of 1, 2 or 3 oxygen atoms have been included.

ment is excellent. Thus, the umbrella model is able to explain these observations as well without invoking the presence of polymeric species. This assignment of the so-called polymeric band to the stretching mode of the two oxygen atoms is further substantiated by the fact that, generally, stretching modes are influenced by isotopic substitution, whereas bending modes are much less influenced. E.g. the CO₂ bending mode is calculated to shift only some 9 cm⁻¹ upon substituting two ¹⁸O atoms, whereas the totally symmetric stretch shift 75 cm⁻¹. This argues against the assignment of the V–O 939 cm⁻¹ band as a (polymeric) bending mode.

4. Conclusions

The molecular structure of supported vanadium oxide catalysts can be described as a chemisorbed – V=O(O₂) species. All three oxygen atoms point away from the support surface. Two equal V–O distances are found at 1.79–1.80 Å and one shorter V=O bond at 1.59 Å. The equivalent oxygens are separated by only 1.44–1.46 Å. This proposal challenges the classical pyramidal cluster model present in the literature.

The observed vibrational frequencies in the range 900–1130 cm⁻¹ can all be assigned to either V=O (1030 cm), O–O (939 cm⁻¹), without invoking the presence of polymeric species.

Since the ‘so called polymeric’ band is in fact an O–O stretching vibration, it can better be termed the peroxo–O–O stretching band.

Acknowledgements

We acknowledge partial financial support from NWO/NCF for the use of supercomputer time on TERAS, SARA, The Netherlands, Project number, SGO32. B.M.W. thanks NRS CC and NWO/CW-VICI for financial support.

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