Site-specific oxygen-18 labelling of silica-supported vanadium(V) complexes: Implications for oxidation catalysis

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Abstract

The incorporation of ^{18}O isotope labels into specific positions of oxide-supported vanadium complexes has been achieved by grafting $VOCl_3$ onto silica. The gas phase reaction of $VOCl_3$ with the hydroxyl groups of the silica surface yields exclusively $\equiv SiOV(O)Cl_2$. When the hydroxyl groups are first exchanged with $H_2{}^{18}O$, the subsequent reaction with $V^{16}OCl_3$ gives uniquely $\equiv Si^{18}OV^{16}OCl_2$. Reaction of $V^{18}OCl_3$ with unlabelled silica gives only $\equiv Si^{16}OV^{18}OCl_2$. Exchange of the chloride ligands with alcohols gives $\equiv SiOV(O)Cl(OR)$ and $\equiv SiOV(O)(OR)_2$ sequentially, without displacing or diluting the isotope labels. The thermal and photochemical reactions of $\equiv SiOV(O)Cl_2$ with the substrates ArNCO and CO, respectively, proceed by oxygen transfer uniquely from the terminal oxo position, as shown by the isotope distribution of the CO_2 product formed in each reaction. When the reactions are run under catalytic conditions, below 70°C, no incorporation of the lattice oxygen of silica into CO_2 was observed. © 1997 Elsevier Science B.V.

1. Introduction

Vanadium oxide dispersed on high surface area oxide supports is widely used for the selective catalytic oxidation of hydrocarbons [1] and for the selective catalytic reduction of NO_x [2,3]. Three types of V species have been identified by Raman spectroscopy on oxide surfaces: monomeric pseudo-tetrahedral complexes, 2D oxo-bridged chains and bulk crystallites of V_2O_5 [4]. The reactivity of these mixed oxide catalysts containing V is highly dependent on the strength of the metal–support interaction, and seems to be enhanced when vanadium is present as a monolayer on the oxide support.

V/oxide-catalyzed oxidations of CO [5,6] and olefins [7], 2-butene isomerization [8] and dehydrogenation [8] and hydroxylation of benzene to phenol [9] have all been proposed to take place at active sites containing the terminal V=O group. With a formal bond order of 3, the oxo ligand is very strongly π-bonded, compared to the mostly ionic interaction of vanadium with 'basal' oxygen atoms from the support [10]. Some studies have inferred the participation of this lattice oxygen in catalytic oxidation reactions. [5,7].

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Oxygen labelling studies have been used in the study of heterogeneous mechanisms of oxidation over mixed metal oxides. For example, by rehydration of Mo/SiO_2 with $H_2^{18}O$, both basal and terminal oxygen atoms were exchanged and vibrational assignments were based on the magnitude of the observed isotope shifts [11]. Labelling of bulk MoO_3 by reduction followed by reoxidation in the presence of $^{18}O_2$ was used to identify the active sites for reoxidation. [12]. Similarly, V–P–O catalysts for the conversion of n-butane to maleic anhydride were enriched using $^{18}O_2$ to determine the location of active oxygen for combustion and selective oxidation [13]. However, in all of these systems, it was not possible to incorporate the isotope label exclusively in specific coordination sites on the catalyst surface. Our approach, using molecular precursors to graft vanadium to oxide surfaces [14], allows specific oxygen atoms of the surface species to be labelled. In this paper, we report ^{18}O labelling of the surface complex $\equiv SiOVOCl_2$, which allows us to trace the fate of oxygen in subsequent surface reactions.

2. Experimental

2.1. Preparation and characterization of silica-supported vanadium complexes

Surface complexes were prepared from $VOCl_3$ (Aldrich) and $V^{18}OCl_3$, according to a previously established procedure [14]. Both vanadium reagents were stored in grease-free glass bulbs equipped with high vacuum teflon (Young) stopcocks, and were transferred into reaction vessels using standard breakseal and high vacuum techniques. $V^{18}OCl_3$ was synthesized by the reaction of VCl_3 (Aldrich) with $^{18}O_2$ (95% ^{18}O, Cambridge Isotopes) in a closed grease-free reactor at 400°C. 50 mg of purple VCl_3 was transferred under N_2 into the reactor, which was then evacuated and filled with 25 Torr $^{18}O_2$. As the VCl_3 was heated in a tube furnace, yellow $VOCl_3$ condensed on the inner

walls of the reactor outside the furnace region. When the reaction was complete, the $V^{18}OCl_3$ was frozen with liquid N_2 while the remaining $^{18}O_2$ was evacuated, then $V^{18}OCl_3$ was transferred under vacuum to a glass bulb by trap-to-trap distillation with liquid N_2. The isotope enrichment of the $V^{18}OCl_3$ was judged to be ca. 95% from the relative intensities of the $\nu(V=O)$ modes at 1042 ($V=^{16}O$) and 996 ($V=^{18}O$) cm^{-1} in the gas phase IR spectrum.

Pyrogenic silica (Degussa Aerosil-200, 200 m^2/g) was used in all experiments. A standard pretreatment procedure was followed in order to ensure reproducibility. For transmission infrared experiments, silica was pressed (125 kg/cm^2) into a self-supporting disk of diameter 1.6 cm (2–4 mg silica/cm^2) or smeared in a thin film (0.1–0.5 mg silica/cm^2) onto a 25 × 2 mm ZnSe disk. For all other experiments, silica was compacted into pellets (20–30 mg/cm^2) which were then finely ground in a mortar. In all reactions, silica-500 was prepared by calcination in 200 Torr O_2 (Air Products, ultrapure carrier grade) at 500°C for 2 h, followed by dehydroxylation for 2 h at 500°C in dynamic vacuum (10^{-4} Torr). ^{18}O-labelled silica was prepared by four cycles of exposing the silica to $H_2^{18}O$ vapor at 400°C, followed by evacuation at 450°C. The isotope enrichment of surface hydroxyl groups was estimated to be > 80% from the intensity ratio $\nu(^{16}O-H)/\nu(^{18}O-H)$ at 3747 and 3736 cm^{-1}, respectively, in the IR transmission spectra of self-supporting disks.

Infrared experiments were performed in a high vacuum in situ IR cell equipped with KCl windows. Transmission spectra were recorded on a dry-air purged Mattson Research Series FTIR spectrometer equipped with a DTGS detector. 32 scans were recorded at a resolution of 2 cm^{-1}.

Diffuse reflectance UV-vis spectra were recorded on a Varian Cary 1E spectrometer equipped with an integrating sphere diffuse reflectance attachment, and referenced to Spectralon. Samples were transferred in vacuum to cells of 2 × 5 mm rectangular quartz tubing.

2.2. Reactions of silica-supported vanadium complexes

Tert-butanol (Aldrich) was dried over $MgSO_4$, vacuum-distilled and stored under nitrogen in a glass bulb. Arylisocyanates (phenyl, *p*-tolyl) were distilled and stored under nitrogen in grease-free glass bulbs. Before use, each liquid reagent was subjected to three freeze-pump-thaw cycles, then introduced into the reactor via vapor phase transfer through a high vacuum line equipped with a Hg diffusion pump. CO (Air Products) and N_2O (Matheson) were stored in glass bulbs, and a known pressure was transferred into the reactors via a vacuum line equipped with a Baratron capacitance manometer. $C^{18}O$ (97% ^{18}O, MSD Isotopes) was purchased in a glass bulb and used without further purification.

3. Results and discussion

The reaction of $VOCl_3$ with the surface hydroxyl groups of silica partially dehydroxylated at 500°C (silica-500) gives uniquely the surface
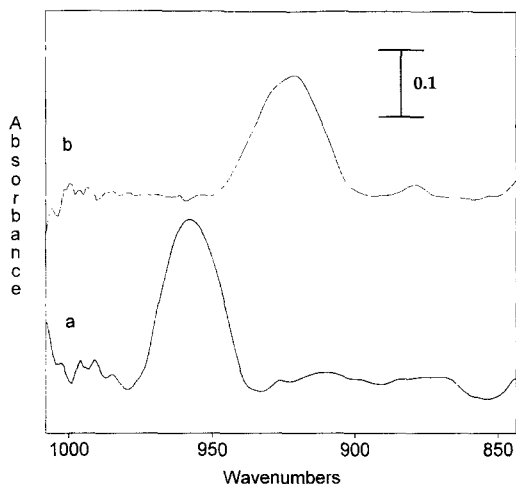

Fig. 1. Transmission IR spectra in the spectral 'window' region, between zones of strong absorbance by silica. (a) $\equiv SiOVOCl_2$, (b) $\equiv Si^{18}OVOCl_2$. The spectrum of silica was subtracted to give a flat baseline.
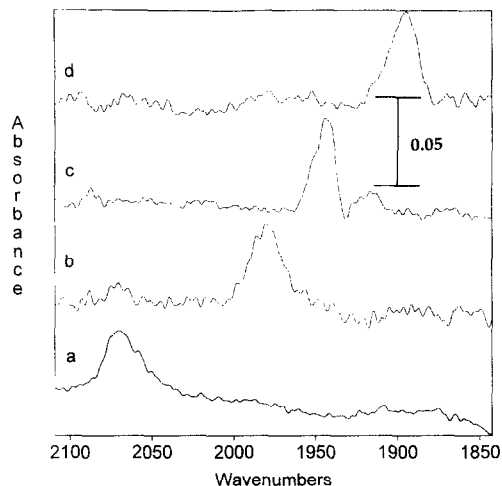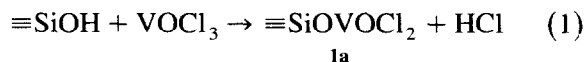

Fig. 2. Transmission IR spectra in the overtone region, $2\nu(V=O)$, for silica-supported complexes (a) $\equiv SiOVOCl_2$, (b) $\equiv SiOV^{18}OCl_2$, (c) $\equiv SiOV^{18}OCl(O^tBu)$, (d) $\equiv SiOV^{18}O(O^tBu)_2$. The spectrum of silica was subtracted to give a flat baseline.

complex $\equiv SiOVOCl_2$, **1a**, according to Eq. (1) [14].

$$\equiv SiOH + VOCl_3 \rightarrow \equiv SiOVOCl_2 + HCl \qquad (1)$$
$$\textbf{1a}$$

The mid-IR spectrum of a self-supporting silica disk containing **1a** consists of a band at 959 cm^{-1}, assigned to the $\nu(V-O-Si)$ fundamental, Fig. 1a, and a weak band at 2068 cm^{-1} attributed to the overtone $2\nu(V=O)$, Fig. 2a. The $\nu(V=O)$ fundamental is obscured by the very high absorbance of silica between 1300 and 1000 cm^{-1}, but can be observed at 1043 cm^{-1} in spectra of extremely thin silica films [14].

The reaction of $V^{18}OCl_3$ with silica-500 causes the $2\nu(V=O)$ overtone to appear at 1970 cm^{-1}, Fig. 2b, while the position of the $\nu(V-O-Si)$ mode at 959 cm^{-1} remains unchanged. These observations are consistent with the formation of **1b**, where only the terminal oxygen of the surface complex is labelled, as in Eq. (2).

$$\equiv SiOH + V^{18}OCl_3 \rightarrow \equiv SiOV^{18}OCl_2 + HCl$$
$$\textbf{1b}$$
$$(2)$$
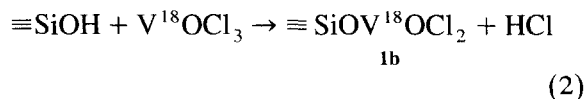
The isotope shift of the overtone frequency, 98 cm^{-1}, is approx. double the shift expected

for the fundamental mode. By comparison, the $^{16}O - ^{18}O$ isotope shift for $VOCl_{3(g)}$ is 46 cm^{-1} [1]. The predicted isotope shift for a V=O harmonic oscillator, based on reduced masses, is 45 cm^{-1}.

When the hydroxyl groups of the silica surface are labelled with ^{18}O, the IR spectrum of the surface product of the reaction with $V^{16}OCl_3$ contains bands at 2068 and 929 cm^{-1}, Fig. 1b. The latter is assigned to $\nu(V-^{18}O-Si)$, due to the formation of **1c**, Eq. (3).

$$\equiv Si^{18}OH + VOCl_3 \rightarrow \equiv \underset{\textbf{1c}}{Si^{18}OVOCl_2} + HCl$$

$$(3)$$
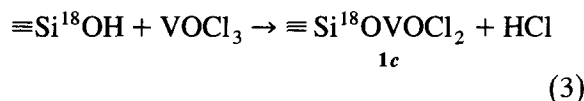
The isotope shift due to ^{18}O substitution in the basal position is therefore 30 cm^{-1}, which is significantly less than the shift observed for the terminal oxo ligand. A similar analysis of the magnitudes of isotope shifts was used to assign stretching modes of terminal and bridging oxygens in oxide-supported molybdenum catalysts prepared by a traditional impregnation route [11]. The absence of a shifted overtone mode for **1c** demonstrates that ^{18}O is not exchanged between the basal and terminal positions in the surface complex.^{18}O

The doubly-labelled surface complex $\equiv Si^{18}OV^{18}OCl_2$, **1d**, was prepared by the reaction of $V^{18}OCl_3$ with a $H_2^{18}O$-exchanged silica thin film. Consistent with the observations on self-supporting disks, the $\nu(V=O)$ fundamental shifts by 43 cm^{-1} from 1043 to 1000 cm^{-1}, as expected for the stretching mode of a terminal oxo ligand, while the $\nu(V-O-Si)$ mode shifts only 30 cm^{-1}, from 959 to 929 cm^{-1}. The IR frequencies of the selectively labelled complexes are summarized in Table 1.

We have previously reported ligand exchange reactions of **1a** with alcohols and *tert*-butyl-hydroperoxide [14]. For example, the reaction of
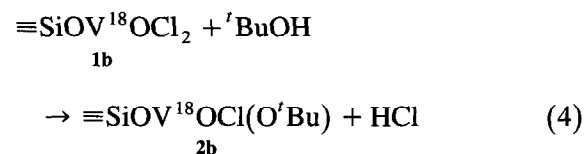
Table 1
Infrared frequencies (cm^{-1}) of silica-supported vanadium complexes

Surface complex	$\nu(V=O)$ [a,b]	$2\nu(V=O)$ [b]	$\nu(V-O-Si)$
$\equiv SiOVOCl_2$, **1a**	1043[14]	2068	959
$\equiv SiOV^{18}OCl_2$, **1b**	994 (998)	1970 (1978)	959
$\equiv Si^{18}OVOCl_2$, **1c**		2068	929
$\equiv Si^{18}OV^{18}OCl_2$, **1d**	1000 (998)	1970 (1978)	929
$\equiv SiOVOCl(O'Bu)$, **2a**		2038	961
$\equiv SiOV^{18}OCl(O'Bu)$, **2b**		1941 (1948)	958
$\equiv SiOVO(O'Bu)_2$, **3a**		2022	961
$\equiv SiOV^{18}O(O'Bu)_2$, **3b**		1920 (1932)	959

[a] Observed only by the thin film technique, due to the strong absorbance of silica in this region.
[b] Values in parentheses are calculated isotope shifts based on reduced masses.

tert-butanol with **1a** at room temperature gives the monosubstituted complex $\equiv SiOVOCl(O'Bu)$, **2a**, with an overtone $2\nu(V=O)$ at 2038 cm^{-1}. Reaction of *tert*-butanol with **1b**, Eq. (4), causes the overtone to shift to 1941 cm^{-1}, Fig. 2c.

$$\equiv \underset{\textbf{1b}}{SiOV^{18}OCl_2} + {}'BuOH$$

$$\rightarrow \equiv \underset{\textbf{2b}}{SiOV^{18}OCl(O'Bu)} + HCl \qquad (4)$$

Scrambling of terminal and basal oxygens was not observed, since there is no shift of the $\nu(V-O-Si)$ mode and only one $2\nu(V=O)$ overtone was detected. The second chloride substitution can be effected by heating **2** to 60°C in the presence of excess *tert*-butanol, Eq. (5). The product **3a** has $2\nu(V={}^{16}O)$ at 2022 cm^{-1}.

$$\equiv \underset{\textbf{2}}{SiOVOCl(O'Bu)} + {}'BuOH$$

$$\rightarrow \equiv \underset{\textbf{3}}{SiOVO(O'Bu)_2} + HCl \qquad (5)$$
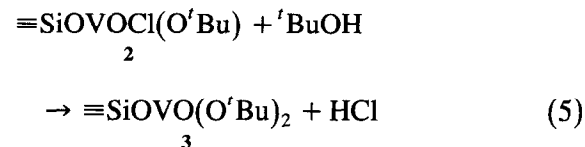
The observed isotope shift, $\Delta 2\nu(V=O)$, for $\equiv SiOV^{18}O(O'Bu)_2$ is 102 cm^{-1} to 1920 cm^{-1}, Fig. 2d.

Grafting and basal ligand exchange reactions are depicted in Scheme 1.

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[1] The $\nu(V=O)$ fundamental and overtone at 1042 and 2077 cm^{-1} ($V^{16}OCl_3$) shift to 996 and 1984 cm^{-1} ($V^{18}OCl_3$).

2v(V=¹⁶O) 2068   2038   2022
2v(V=¹⁸O) 1970   1941   1920

Scheme 1.

$C^{16}O_2$ is the exclusive product, with a single sharp band at 667 cm⁻¹. Reaction with **1b** leads to the formation of $C^{16}O^{18}O$, for which the deformation mode is shifted to 662 cm⁻¹. A small band at 667 cm⁻¹ is attributed to $C^{16}O_2$ is derived from ca. 5% of **1a**, due to incomplete labelling of the molecular precursor $V^{18}OCl_3$. There is no evidence for $C^{18}O_2$ (658 cm⁻¹, see below). The reaction of ArNCO with **1c** gives only $C^{16}O_2$. We conclude that CO_2 is formed in a concerted reaction without exchange of oxy-

3.1. Oxygen-transfer reactions of labelled surface complexes

3.1.1. Thermal reaction with arylisocyanates

The reaction of **1** with a stoichiometric amount of ArNCO (Ar is phenyl or *p*-tolyl) at room temperature causes an immediate color change from colorless to purple and is accompanied by the liberation of CO_2, detected in the gas phase by its characteristic IR deformation mode at 667 cm⁻¹. These observations are consistent with the formation of a surface vanadium imido complex, **4**, Eq. (6), which has precedent in the chemistry of molecular transition metal complexes [16] and silica-supported metal oxo species [17,18].

$$\equiv SiOVOCl_2 + ArNCO$$
$$\mathbf{1}$$
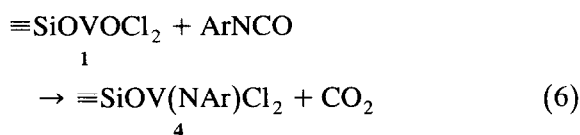
$$\rightarrow \equiv SiOV(NAr)Cl_2 + CO_2 \qquad (6)$$
$$\mathbf{4}$$

The diffuse reflectance UV-vis spectrum of **4** (where Ar is *p*-tolyl) consists of a broad band at 570 nm, Fig. 3, compared to the spectrum of a molecular analogue $V(NC_6H_4CH_3)Cl_3$ with λ_{max} at 516 nm [19]. In the infrared, the overtone $2\nu(V=O)$ of **1a** at 2068 cm⁻¹ disappears, Fig. 4, and new vibrations appear in the regions 3100–2800 and 1600–1300 cm⁻¹ due to the *p*-tolyl group.

The isotopic composition of the CO_2 product is readily determined from its gas phase IR spectrum. In the reaction of ArNCO with **1a**,
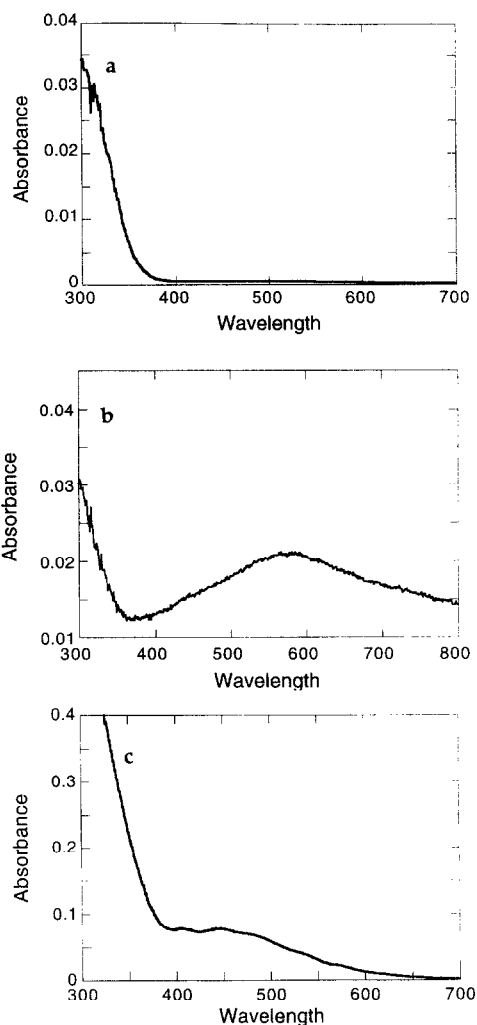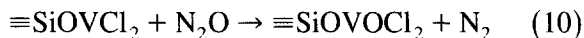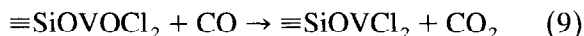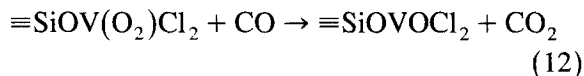

Fig. 3. Diffuse reflectance UV-visible spectra of ≡SiOVOCl₂ (a) in vacuum, (b) after reaction with 1 equiv. *p*-tolylisocyanate, followed by evacuation, (c) different sample of ≡SiOVOCl₂, after 120 min broad band UV irradiation in the presence of 5 Torr CO.

Fig. 4. Transmission IR spectra of reactions on a self-supporting silica disk (a) after reaction with $VOCl_3$ to give $\equiv SiOVOCl_2$, (b) after reaction of $\equiv SiOVOCl_2$ with 1 equiv. p-tolylNCO to give $\equiv SiOV(NC_6H_4Me)Cl_2$, (c) after reaction with 2 equiv. p-tolylNCO, regenerating $\equiv SiOVOCl_2$.

gen between terminal and basal positions at vanadium, or between isocyanates. A probable transition state for the reaction is shown in Eq. (7).

The addition of a second equivalent of ArNCO causes the $\nu(VO)$ overtone to reappear at 2068 cm^{-1}, Fig. 4c, as **1a** is reformed, Eq. (8).

$$\equiv SiOV(NAr)Cl_2 + ArNCO$$
$$\mathbf{4}$$
$$\rightarrow \ \equiv SiOVOCl_2 + [ArNCNAr] \qquad (8)$$
$$\mathbf{1a}$$

The formation of CO_2 is thus catalytic at room temperature in the presence of excess ArNCO, Eqs. (7) and (8). These reactions are analogous to the catalytic condensation of isocyanates to carbodiimides by similar molecular vanadium(V) complexes, although $V(NC_6H_4Me)Cl_3$ itself was reported to be inactive [20].

3.2. Photochemical reaction with CO

There is no reaction between **1** and CO at room temperature in the absence of UV light. UV irradiation of **1** leads to a color change from white to purple, and CO_2 is produced. The diffuse reflectance UV-visible spectrum after reaction shows a broad band at ca. 450 nm, Fig. 3c, assigned to one or more d–d transitions of a reduced vanadium surface species. The $2\nu(V=O)$ overtone in the infrared spectrum disappears. The CO_2 product is singly labelled as $C^{16}O^{18}O$ (ca. 95%) when **1b** (95% ^{18}O-enriched) is the reactant; with **1c** (85% ^{18}O-enriched), only $C^{16}O_2$ is produced. When **1b** oxidizes $C^{18}O$, $C^{18}O_2$ is formed, (deformation mode at 658 cm^{-1}) with a small amount of $C^{16}O^{18}O$ from incomplete labelling of the catalyst and the substrate. These results imply that one oxygen atom of the CO_2 product is derived from CO, while the other originates in the terminal oxo ligand of the vanadium surface complex. There is no evidence for exchange between surface oxygen atoms.

The mechanism of oxidation of CO over silica-supported vanadia catalysts has been proposed to be atom transfer from a photo-activated surface species, $[(\equiv SiO)_3V^{IV}(O^-)]^*$ [21]. Charge transfer from oxygen to vanadium was suggested to render the oxo ligand more nucleophilic. Recently, it was suggested that photon absorption occurs at the HOMO located on the basal Si–O–V group. [10]. Regardless of the nature of the excited state, it is clear that oxygen transfer in these system occurs exclusively from the terminal oxo position.

The photooxidation of CO by **1** becomes catalytic in the presence of either O_2 or N_2O. When **1a** was reduced by CO, then reoxidized by $^{18}O_2$ in the presence of $C^{18}O$, $C^{18}O_2$ was formed as the major product (85% doubly labelled, with 15% $C^{16}O^{18}O$ from incomplete labelling of both reactants). When **1c** (i.e., ^{18}O label in the lattice oxygen of the silica surface) was used to catalyze the oxidation of CO by N_2O, $C^{16}O_2$ was the only isotopomer detected.

We propose that reoxidation of reduced vanadium replaces oxygen exclusively in the terminal position. Possible mechanisms are shown in Eqs. (9)–(12).

$$\equiv SiOVOCl_2 + CO \rightarrow \equiv SiOVCl_2 + CO_2 \qquad (9)$$

$$\equiv SiOVCl_2 + N_2O \rightarrow \equiv SiOVOCl_2 + N_2 \qquad (10)$$

or

$$\equiv SiOVCl_2 + O_2 \rightarrow \equiv SiOV(O_2)Cl_2 \qquad (11)$$

$$\equiv SiOV(O_2)Cl_2 + CO \rightarrow \equiv SiOVOCl_2 + CO_2 \qquad (12)$$

4. Conclusion

Using molecular precursors and gas–solid reactions, we have demonstrated the preparation of oxide-supported vanadium complexes with ^{18}O isotope labels in nonequivalent ligand sites. There is no exchange or dilution of labels during grafting or subsequent reactions. This property can be exploited to study mechanisms of surface reactions, for example, oxygen transfer, since we can follow the path of individual ligands in stoichiometric and catalytic reaction cycles. On oxides other than silica, lattice oxygen may be significantly more mobile. Investigations of other supports for vanadium catalysts are in progress.

Acknowledgements

References

[1] S.T. Oyama, Res. Chem. Intermed. 15 (1991) 165–182.
[2] M.J. Groeneveld, G. Boxhoorn, H.P.C.E. Kuipers, P.F. A. van Grinsven, R. Gierman, P.L. Zuideveld, in: M.J. Phillips, M. Ternan (Eds.), 9th Int. Congr. Catal., CIC, Calgary, 1988, pp. 1743–1749.
[3] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[4] G. Went, T. Oyama, A. Bell, J. Phys. Chem. 94 (1990) 4240–4246.
[5] Y. Yoshida, Y. Matsumura, S. Noda, T. Funabiki, J. Chem. Soc., Farad. Trans. 1 77 (1981) 2237–2245.
[6] M. Anpo, I. Tanahashi, Y. Kubokawa, J. Phys. Chem. 84 (1980) 3440–3443.
[7] Y. Yoshida, Y. Magatani, S. Noda, T. Funabiki, J. Chem. Soc. Chem. Commun. (1981) 601–602.
[8] M. Anpo, T. Suzuki, Y. Yamada, M. Che, in: M.J. Phillips, M. Ternan (Eds.), 9th Int. Congr. Catal.. CIC, Calgary, 1988, pp. 1513–1520.
[9] M. Iwamoto, J. Hirata, K. Matsukami, S. Kagawa, J. Phys. Chem. 1983 (1983) 903–905.
[10] K. Tran, M. Hanning-Lee, A. Biswas, A.E. Steigman, G. Scott, J. Am. Chem. Soc. 117 (1995) 2618–2626.
[11] M. Cornac, A. Janin, J.C. Lavalley, Polyhedron 5 (1986) 183–186.
[12] T. Ono, H. Numata, N. Ogata, J. Mol. Catal. A: Chem. 105 (1996) 31–37.
[13] G.L. Schrader, T.P. Moser, M.E. Lashier, in: M.J. Phillips, M. Ternan (Eds.), 9th Int. Congr. Catal., C.I.C., Calgary, 1988, pp. 1624–1631.
[14] G.L. Rice, S.L. Scott, Langmuir 13 (1997) 1545–1551.
[16] W.A. Nugent, J.M. Mayer, Metal Ligand Multiple Bonds, Wiley, New York, 1988.
[17] S.L. Scott, J.M. Basset, J. Am. Chem. Soc. 116 (1994) 12069–12070.
[18] V. Vidal, A. Théolier, J. Thivolle-Cazat, J.M. Basset, J. Corker, J. Am. Chem. Soc. 118 (1996) 4595–4602.
[19] D. Devore, J. Lichtenhan, F. Takusagawa, E. Maatta, J. Am. Chem. Soc. 109 (1987) 7408–7416.
[20] K.R. Birdwhistell, T. Boucher, M. Ensminger, S. Harris, M. Johnson, S. Toporek, Organomet. 12 (1993) 1023–1025.
[21] M. Iwamoto, H. Furukawa, K. Matsukami, T. Takenaka, S. Kagawa, J. Am. Chem. Soc. 105 (1983) 3719–3720.