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An Investigation of the Reduction and Reoxidation of Isolated Vanadate Sites Supported on MCM-48

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Abstract The reduction and subsequent reoxidation of isolated vanadate species supported on silica was investigated using temperature-programmed reduction and oxidation, along with in-situ XANES and Raman spectroscopy. Approximately 70–80% of the vanadium was reduced to V^{3+} after reduction in H_2 at temperatures up to 923 K. Upon reduction, the vanadyl oxygen was removed and the three remaining V–O bonds are lengthened by 0.2 Å. The vanadate species are rapidly reoxidized when exposed to O_2, with the amount of oxygen uptake matching well with the amount removed during reduction. In-situ Raman spectroscopy during reoxidation in $^{18}O_2$ showed that significant scrambling occurs between gas phase oxygen and surface oxygen species during the reoxidation of the vanadate species.

Keywords Vanadate · Silica · Reduction · Oxidation

1 Introduction

Supported vanadium oxide catalysts have been shown to be active for the partial oxidation of methane and methanol to formaldehyde, the oxidative dehydrogenation of light alkanes, and the selective reduction of NO_x. Interest in understanding the mechanism and kinetics of these reactions has motivated studies of the structure of the vanadate species and of the dynamics of reduction and oxidation of the supported vanadia. The structure of vanadia on the surface of metal oxide supports such as silica, alumina, titania, and zirconia has been studied using infrared and Raman spectroscopy [1–3], UV-Visible spectroscopy [3, 4], 51V NMR [5], XANES, and EXAFS [6]. Application of these techniques has shown that depending on the surface density of vanadium, vanadia can be present as isolated monovanadate species, two-dimensional polyvanadate species, and bulk V_2O_5. At very low surface densities (less than about 0.2 V/nm^2), vanadium is present exclusively as isolated vanadate species. As the surface density of vanadium increases polyvanadate species are formed. Finally, as monolayer coverage by polyvanadate species is approached, nanoparticles of V_2O_5 are observed.

Several investigators have examined the reduction of supported vanadate species. Kanervo et al. [7]. have reported that samples containing mainly isolated monovanadate species could be reduced by 50% from V^{5+} to V^{3+}; however, at higher vanadium loadings, they obtained reductions of 62%. A broad TPR peak was observed in the range of 600–800 K, with the maximum for samples containing exclusively monovanadate species occurring at 750 K. Work by Koranne et al. on V/SiO$_2$ and V/Al$_2$O$_3$ showed that 70–90% of the V^{5+} could be reduced to V^{3+} in 5% H_2 in Ar by raising the temperature up to 1,173 K [8]. Similar levels of reduction have also been reported by Nag and Massoth [9]. Finally, Argyle et al. have shown using transient-response UV-visible spectroscopy that under conditions of propane oxidative dehydrogenation the rate of vanadia reduction for alumina-supported vanadia is 10^4 slower than the rate at which the partially reduced vanadia is reoxidized [10]. It is noted, though, that in none of these studies was the structure and oxidation state characterized before and after reduction and after reoxidation.

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Consequently, understanding the dynamics of the reduction and oxidation of well-defined vanadate species remains a subject of interest.

The objective of this investigation was to obtain a fundamental understanding of the dynamics of reduction and reoxidation of isolated monovanadate species supported on silica. Silica was chosen as the support because it is relatively inert. The loading of vanadium was kept low so that all of the vanadium would be present as isolated monovanadate species. XANES and EXAFS were used to determine the oxidation state of vanadium and the local geometry of the vanadate species before and after reduction, and following reoxidation. The dynamics of vanadia reduction and oxidation were investigated using temperature-programmed reduction and oxidation (TPR and TPO). Additional information about the structure of vanadia during reduction and reoxidation was obtained by in-situ Raman spectroscopy.

2 Experimental Methods

A high-surface area mesoporous silica, MCM-48, was prepared following procedures reported in the literature [11, 12]. Vanadium oxide was deposited onto MCM-48 by chemical vapor deposition of vanadium acetylacetonate. The weight loading, as determined by elemental analysis, was 3.43 wt.% vanadium and the surface area of the catalyst was 1,370 m^2/g as determined by analysis of the BET isotherm. The apparent surface density of vanadium was 0.3 V/nm^2.

Raman spectra were recorded using a Kaiser Optical HoloLab series 5,000 Raman spectrometer equipped with a Nd:YAG laser that is frequency-doubled to 532 nm. The laser was operated at a power level of 25 mW measured at the sample with a power meter. A Princeton Instruments TEA/CCD detector was operated at −40 °C. Spectra were recorded with a resolution of 2 cm^{-1}. Samples (approximately 25 mg each) were pressed into pellets at 5,000 psi and placed within on a rotating sample holder in a quartz Raman cell. The samples were rotated at 100 rpm during the measurements to reduce the effects of sample heating by the laser. During reoxidation, the samples were heated in 30 cm^3 min^{-1} flow of 5% O_2/He. The temperature was increased from 323 to 773 K at 4 K/min. Raman spectra were collected every 75 s in order to obtain a scan every 5 K.

X-ray absorption (XAS) measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam lines 2–3. The measurements were performed at the vanadium K-edge. The edge energy for each sample was determined as the first inflection point of the main peak in the spectrum, and the edge energy of the vanadium foil was set to 5,465 eV. The optimal sample amount was calculated based upon the weight fraction of all atomic species to obtain an absorbance of ~2.5, which corresponds to 14 mg of catalyst, with 30–40 mg of boron nitride added to make a stable pellet. Samples were placed in a controlled-atmosphere cell that allowed for heating up to 823 K in the presence of flowing gas [13]. UHP He and 10% O_2 in He were used in these experiments to pretreat the catalyst samples before the XAS measurement. After the pretreatment was completed, the cell was evacuated to 6×10^{-4} Pa and cooled to 77 K before the XAS data were collected. For in-situ XANES measurements, scans were made approximately every 7 min at reaction temperature and under gas flow.

The EXAFS portion of the XAS data was analyzed to determine the local coordination around each vanadium atom. The software program IFEFFIT, along with its complementary GUIs Athena and Artemis, were used for the data analysis [14, 15]. First, a linear pre-edge was subtracted from the data, fit to the range of −150 to −75 eV relative to the edge energy. Then a quadratic polynomial fit to the range of 150–850 eV for EXAFS and 100–300 eV for in-situ XANES, both relative to the edge energy, was used to normalize the data. A cubic spline was fit to the normalized data from 2 to 16 Å^{-1} to remove the background absorption and minimize the signal in R space below 1 Å. These data were then Fourier transformed over the k range of 2.7–9.5 using the Kaiser-Bessel window functions with a dk of 1 and a k weight of 3. The EXAFS fits were performed in R space, with data fit from 1.0 to 3.0 Å. The value for S_o^2, determined by performing a fit on vanadium foil, used in the EXAFS analysis was 0.7.

Temperature-programmed reduction and oxidation were carried out using 50 mg of catalyst placed in a quartz microreactor heated by a small furnace. TPR was carried out by flowing 2% H_2 in He at 60 cm^3/min while heating the reactor from 298 to 923 K at 10 K/min and monitoring the effluent by mass spectrometry. TPO was carried out in a similar manner using 0.5% O_2 in He flowing at 60 cm^3/min. The effluent from the reactor was analyzed using a MKS Cirrus quadrupole mass spectrometer.

3 Results and Discussion

A detailed analysis of the local structure of the V/MCM-48 catalyst in the oxidized state has been published previously [6]. The catalyst consists of isolated vanadate species in a pseudotetrahedral geometry and all of the vanadium is in the 5+ oxidation state. EXAFS analysis shows that the sample contains one V=O bond with a length of 1.59 Å and three V–O bonds with a length of 1.80 Å.

Figure 1a shows the TPR of the V/MCM-48 sample upon heating in 2% H_2/He to 923 K at 10 K/min. No H_2 is

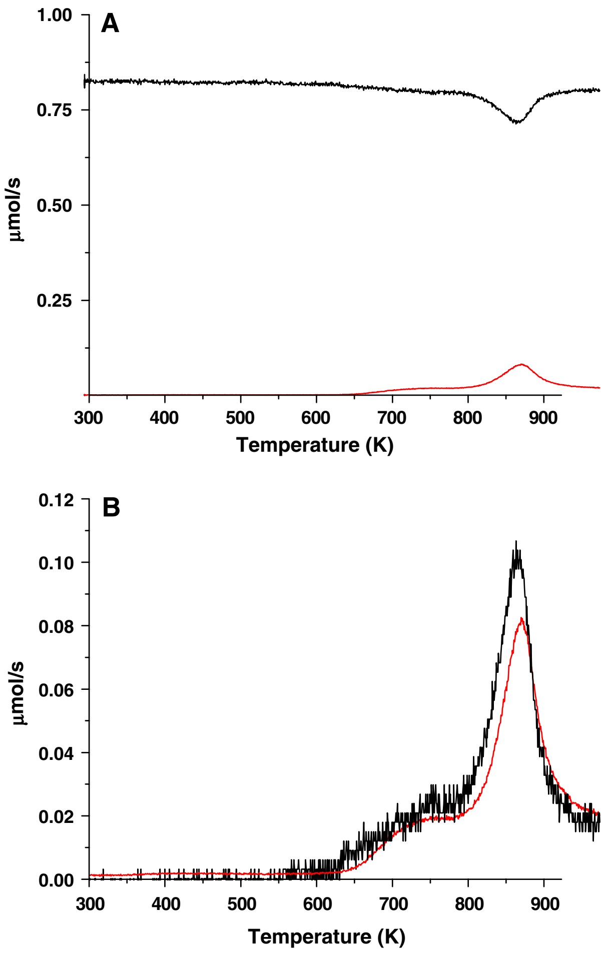

Fig. 1 (**a**) TPR of V/MCM-48 catalyst in 2% H_2/He at 10 K/min. (**b**) Comparison of hydrogen uptake and water desorption during TPR. Black-hydrogen, red-water

consumed when a similar experiment was performed with MCM-48 alone. Reduction starts at 600 K and reaches a maximum rate of reduction at 860 K. Integrating the amount of hydrogen consumed and normalizing it to the amount of vanadium in the sample gives a ratio of H_2 consumed per V of 0.85. This suggests that most but not all of the vanadium centers are reduced from V^{5+} to V^{3+}. It is also observed in Fig. 1b that the hydrogen consumption and water desorption peaks are roughly equivalent, suggesting that each H_2 removes one oxygen atom from the vanadium to produce one H_2O.

The TPR spectrum presented in Fig. 1 consists of two distinct peaks. Deconvolution of these features was performed to determine their positions and relative intensities. The first peak is broad, is centered at 810 K, and comprises 74.5% of the total area. The second peak is much sharper, is centered at 850 K, and comprises 25.5% of the total area. The positions of these peaks are similar to those reported by Koranne et al., who suggested they are due to the reduction of oligomeric vanadia [8]. This interpretation is inconsistent, though, with the results of Raman spectroscopy, which shows no traces of V_2O_5, and EXAFS analysis of the oxidized catalyst, which detects no evidence for V-V backscattering as would be expected if significant surface concentrations of oligomers were present. Hence, a more likely interpretation is that the two peaks seen in Fig. 1 are attributable to the reduction of distorted and undistorted pseudo-tetrahedrally coordinated monovanadate species.

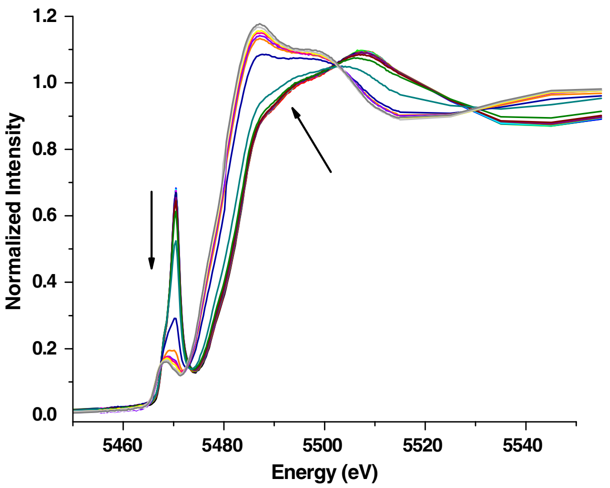

Fig. 2 In-situ XANES scans during TPR of V/MCM-48. Sample was heated at 10 K/min to 823 K and held for 1 h under a 10% H_2/He flow. The arrows show the direction of changes in the spectrum as the reduction temperature increases

Figure 2 shows XANES spectra of V-MCM-48 while it is heated at 10 K/min to 823 K in 10% H_2/He and then held at this temperature for 1 h. The position of the edge energy, which is defined as the maximum of the first derivative of the main edge, contains information about the oxidation state of the sample. Prior to the onset of reduction, the edge energy of the V/MCM-48 is 5,484.0 eV, indicating that all of the vanadium is in the 5+ state. As reduction proceeds, the edge energy shifts to lower energies, with the largest changes in the edge energy occurring over the temperature range of 650–823 K.

The XANES data presented in Fig. 2 were analyzed with a linear combination fitting algorithm in the Athena software in order to determine the extent of reduction during each scan [15]. The standard for the V^{5+} species was the first scan in the experiment, since the catalyst is fully oxidized under these conditions, and bulk V_2O_3 was used as the standard for V^{3+}. The results of the fitting are plotted in Fig. 3a. It is observed that the sample consists of almost entirely V^{5+} species up to 680 K. Above this temperature, the sample reduces rapidly. The results of this experiment show that after the sample has been reduced in H_2 at 823 K for 1 h, 85% of the V^{5+} cations have been converted to V^{3+} cations. This value is higher than 0.71 H_2/V that was calculated from a TPR experiment carried out with a heating

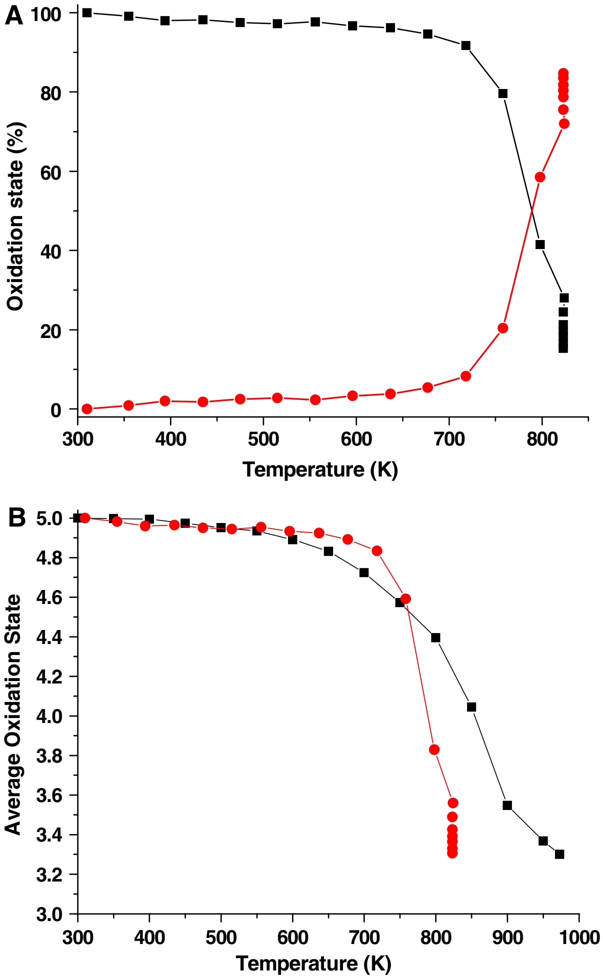

Fig. 3 (**a**) Linear combination fitting results of XANES during TPR in 10% H_2/He at 60 cm^3/min. (**b**) Oxidation State versus Temperature during TPR experiments. Black-TPR data in Fig. 1, red-XANES TPR data in Fig. 2

protocol identical to that used for the acquisition of XANES data. The reason for the slight increase in the calculated amount of reduction calculated by the linear combination fit is likely due to small differences in the XANES of reduced V/MCM-48 compared to V_2O_3. Small changes in the edge or pre-edge features of reduced V/MCM-48 would lead to relative changes in the extent of reduction. However, since the sample was never fully reduced, the best standard available for use is bulk V_2O_3.

Plots of the average oxidation state of V/MCM-48 as a function of reduction temperature determined from the TPR spectrum presented in Fig. 1 and the analysis of the XANES data presented in Fig. 2 are shown in Fig. 3b. While the two methods for determining the average oxidation state are similar, the curve based on the XANES data exhibits a shaper decrease in oxidation state with temperature than the curve based on the TPR data. This could be due to differences in the hydrogen concentration between experiments, 2% H_2 during TPR and 10% H_2 during XANES. However, the more likely cause is that while the heating rates in both experiments are the same, the temperature measurement in the TPR reactor is more accurate than that in the cell used for XAS measurements. As a result, the latter data are believed to provide a more accurate representation of the change in the average oxidation state of vanadium with reduction temperature.

EXAFS data, obtained for V/MCM-48 after it had been reduced under the conditions used to acquire the XANES data, are shown in Fig. 4. The Fourier transform of $k^3\chi(k)$ was fitted using the Artemis software. In carrying out this analysis it was assumed that the reduced vanadate species is bonded to silica by three equivalent V–O–si bonds [16]. The best fit to the data shows that the sample contains three V–O bonds of length 2.02 Å. This suggests that upon reduction, the V=O oxygen is removed and that the V–O bonds lengthen from 1.79 Å to 2.02 Å. The increase in length of the V–O bond is consistent with what is seen upon comparison of the V–O bond lengths in V_2O_5 and V_2O_3. V_2O_5 consists of one V=O bond of length 1.58 Å and four V–O bonds with lengths between 1.78 and 2.02 Å. By contrast, V_2O_3 has three V–O bonds that are 2.02 Å in length and three V–O bonds that are 2.12 Å in length. The Debye-Waller factor (σ^2) increases to 0.0085 upon reduction, suggesting that the reduced sites are more disordered than the fully oxidized sites, for which σ^2 was only 0.0014. The peak centered at 2.6 Å in the plot corresponds well to a V-Si backscattering path of length 3.40 Å. No evidence was seen for V-V backscattering in the reduced sample, indicating that the vanadium centers remain isolated upon reduction. The R-factor for the fit of the reduced sample is 0.08. The lack of a better fit is very likely due to the

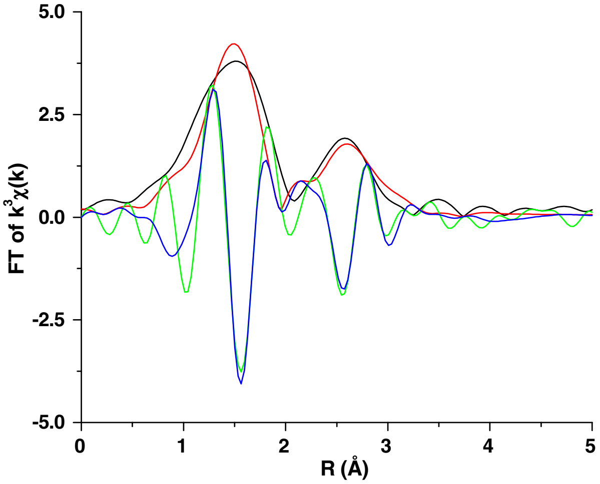

Fig. 4 Experimental and fitted EXAFS data for reduced V/MCM-48. Black—magnitude of experimental data, red—magnitude of fit, green—imaginary part of experimental data, blue—imaginary part of fit

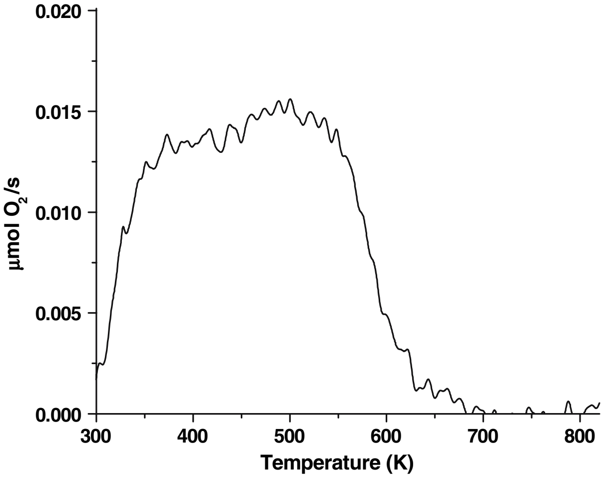

Fig. 5 TPO of V/MCM-48 in 0.5% O_2/He at 10 K/min. Sample was initially reduced in H_2 at 823 K for 1 h

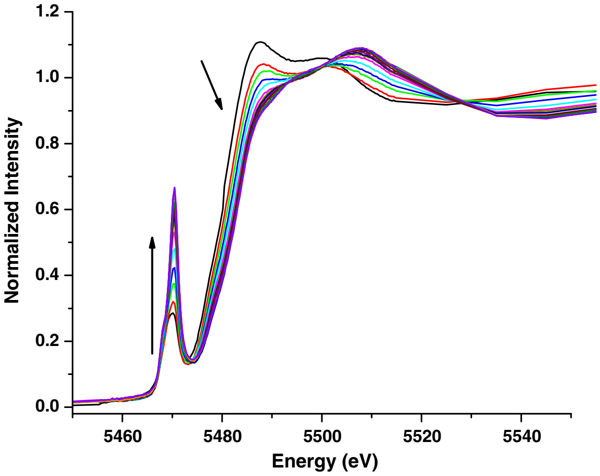

Fig. 6 In-situ XANES during TPO of V/MCM-48 in a flow of 10% O_2/He at 60 cc/min. The arrows show the direction of the changes in the spectrum as the oxidation temperature increases

assumption that the reduced sample contains only V^{3+} species, whereas the actual extent of reduction for the sample is 0.71–0.85. Thus, the experimentally observed EXAFS pattern contains some oxidized centers as well as reduced centers.

Figure 5 shows the TPO spectrum of the V/MCM-48 after it had been reduced using the protocol described above for the XANES experiments. The oxidation of the reduced sample begins at 300 K and reaches completion near 650 K. The total amount of oxygen consumed was 0.7 O/V, which suggests that the sample was about 70% reduced to V^{3+} at the beginning of the experiment. This value agrees very well with the calculated hydrogen consumption (0.71 H_2/V) during conditions identical to the initial reduction of the sample.

The total amount of oxygen needed to reoxidize the catalyst was also determined by pulsed oxygen chemisorption. For these experiments, the sample was reduced under conditions identical to the XANES TPR experiments. After purging in helium, pulses of oxygen were sent to the sample to determine the amount of oxygen necessary to completely reoxidize the catalyst. The results show that between 0.72 and 0.76 O/V are necessary to fully reoxidize the catalyst. This number is in excellent agreement with the amount of oxygen uptake determined by TPO (see above).

XANES data were acquired during reoxidation of the catalyst. Figure 6 shows the normalized XANES data during reoxidation, while Fig. 7a shows the results of the linear combination fitting of these spectra. The standards for V^{3+} and V^{5+} were the same as those used to represent the XANES data obtained during reduction. It is noted that a small amount of reoxidation is likely to have occurred in the 10 min during which the EXAFS cell was flushed with O_2 at 293 K. Therefore, at the start of the temperature ramp, the sample is only 60% reduced. Reoxidation occurs

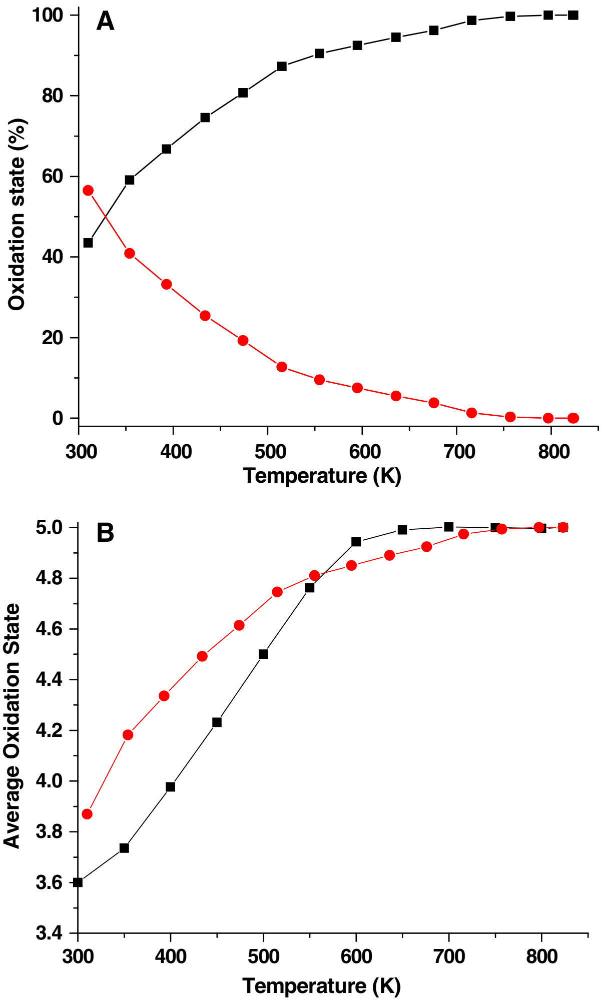

Fig. 7 (**a**) Linear combination fitting results of XANES spectra during TPO. (**b**) Oxidation State versus Temperature during TPO experiments. Black-TPO data in Fig. 5, red-XANES data in Fig. 6

rapidly and is completed between 650 and 700 K, in very good agreement with the results of the TPO described above. It was also observed that the XANES spectrum of the sample at the end of the experiment matches that for the fully oxidized sample recorded prior to reduction. This observation demonstrates that the sample was fully reoxidized.

Figure 7b shows the average oxidation as a function of the reoxidation temperature determined from the TPO data of Fig. 5 and from the XANES data of Fig. 6. While qualitatively similar, the average oxidation state determined from the XANES data is higher than that determined from the TPO data. As in the case of Fig. 3b, the differences are likely to differences in the accuracy of the temperature measurements and in the flow rates of O_2 relative to the weight of the catalyst used in the two types of experiment.

In-situ Raman observations were made in order to observe the changes occurring in the supported vanadate species during the reduction and the subsequent reoxidation of the catalyst. Shown in Fig. 8a are background-subtracted Raman spectra taken during the reoxidation of V/MCM-48 previously reduced in the Raman cell for 1 h at 773 K in flowing H_2. Due to changes in the sample color, and therefore the sampling depth of the laser, the intensity of all bands decreased during reduction. Since silica does not reduce under the conditions used to reduce the supported VO_x species, the silica feature at 500 cm^{-1} was used to normalize the data at each temperature, as shown in Fig. 8b. It is observed in this figure that the intensity of the V=O band at 1,033 cm^{-1} is lower after the reduction, suggesting that O atoms in V=O bonds are consumed upon reduction. During reoxidation, this feature is restored to its original height prior to reduction. Above 670 K, a small band is observed at 996 cm^{-1}, which is likely due to the formation of a small amount of V_2O_5 upon reoxidation. The formation of small nanoparticles of V_2O_5 can be ascribed to the hydration of VO_x species in the presence of water produced during reduction and oligomerization of these species during reoxidation. This interpretation is suggested by hydration/dehydration experiments reported by Xie et al. [17]. To determine the amount of V_2O_5 formed, the two peaks in the spectrum were deconvoluted assuming Lorenzian peak shapes, and the V_2O_5 area was corrected for the ten-fold higher Raman scattering cross-section compared to that of isolated VO_4 species [17]. By this means it is estimated that only 0.5% of the vanadium formed V_2O_5.

The same experiment was performed using 18-labeled oxygen in an attempt to gain further insights into the process by which gas-phase oxygen reoxidizes the isolated vanadium centers. Figures 9a and 9b show that in the presence of $^{18}O_2$, the principal feature reappearing in the Raman spectrum is the band at 1,033 cm^{-1} for V=^{16}O and only a small band is seen at 987 cm^{-1} for V=^{18}O. These spectra were deconvoluted in order to determine the relative fraction of V=^{18}O/V=^{16}O, assuming that the Raman scattering cross-sections for both species were identical, and the results are presented in Table 1. The fraction ^{18}O-labeled V=O groups is initially 2.5% and increases by the end of the experiment to 14.8%. The total area of the V=O band returns to the original area, indicating that the sample is completely reoxidized. These observations suggest that ^{16}O in the silica support can replace the O atoms removed from V=O species in the isolated vanadate structures. A similar observation has been reported earlier by Ohler and Bell, when isolated molybdate species are first reduced in H_2 and then reoxidized in $^{18}O_2$ [18].

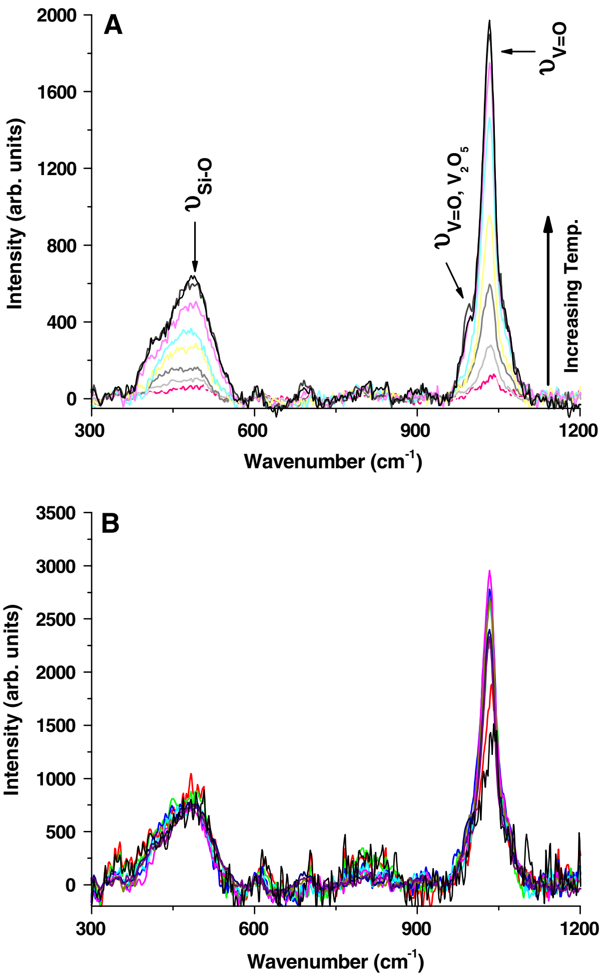

Fig. 8 Raman spectra during reoxidation in $^{16}O_2$ after reduction in H_2 for 1 h at 773 K. (**a**) Background subtracted spectra. (**b**) Spectra normalized by SiO_2 band at 500 cm^{-1}. Scans in increasing temperature: black-310 K; red-370 K; green-430 K; blue-490 K; light blue-550 K; pink-610 K; gold-670 K; dark blue-730 K; purple-773 K

A mechanism by which reduced vanadate centers could be oxidized by O_2 has been proposed recently by Goodrow and Bell as a part of their theoretical study of methanol

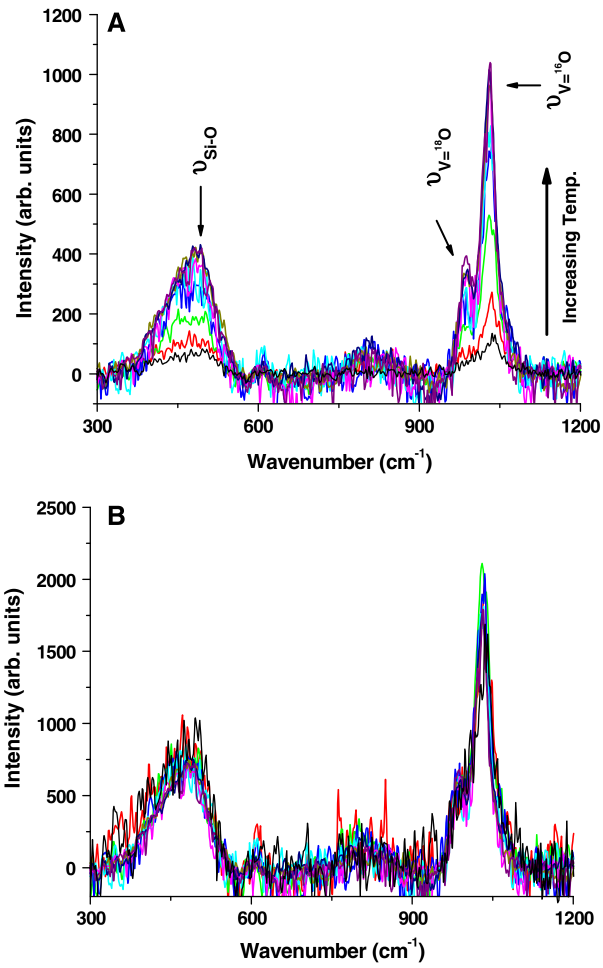

Fig. 9 Raman spectra during reoxidation in $^{18}O_2$ after reduction in H_2 for 1 h at 773 K (**a**) Background subtracted spectra (**b**) Spectra normalized by SiO_2 band at 500 cm^{-1}. Scans in increasing temperature:/time black-473 K; red-573 K; green-673 K; blue-773 K; light blue-2.5 min; pink-5 min; gold-7.5 min; dark blue-10 min; purple-12.5 min

oxidation to formaldehyde over isolated vanadate species supported on silica [16]. The reoxidation scheme that they propose begins with the rapid adsorption of O_2 by the reduced center, resulting in the formation of a vanadium peroxo species. This species then undergoes rearrangement so that one of the two O atoms forms a V=O bond, whereas the second O atom forms a V–OO–si structure. In the next step the peroxo group moves to form a Si–OO–si species, similar to that observed to form during the migration of oxygen in silica [19, 20]. Migration of the peroxo group continues until it encounters a second reduced vanadate species, at which point the peroxo species is used to oxidize the vanadium in this group back to V^{5+} and form a second V=O bond. If $^{18}O_2$ is used for reoxidation, it is easy to understand how the small amount of $^{18}O_2$ required to reoxidize the sample can scramble with the significantly larger pool of ^{16}O present on the surface of silica. Assuming that ^{18}O and ^{16}O scramble completely, it is estimated that 4.1% of the V=O bonds upon reoxidation should contain an ^{18}O label. This figure is in reasonable agreement with what is observed experimentally.

Table 1 Relative percentage of ^{18}O in V=O bonds determined by deconvolution of Raman spectra shown in Fig. 9

Temp/Time	Percent ^{18}O (%)
473	0.0
573	2.5
673	4.6
773	9.2
2.5 min	9.3
5 min	10.7
7.5 min	12.8
10 min	12.1
12.5 min	14.7

4 Conclusions

The results of this study indicate that V^{5+} in isolated vanadate species supported on silica can be reduced by approximately 70–80% to V^{3+} in flowing H_2 at temperatures up to 923 K. XANES data confirm that the oxidation state of vanadium in changes from V^{5+} to V^{3+} upon reduction, and Raman spectroscopy indicates that the oxygen in the V=O bond of the original vanadate group is removed during reduction. Analysis of EXAFS data show that the three V–O bonds that connecting the vanadate species to the support lengthen by 0.2 Å after reduction. Complete reoxidation of the reduced vanadate species can be achieved with O_2, and occurs at significantly lower temperatures than does reduction. Raman spectroscopy reveals that upon reoxidation of reduced vanadate species using $^{18}O_2$, considerable scrambling occurs between ^{16}O atoms in the support and those in the oxidizing gas.

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References

1. Deo G, Wachs IE (1994) J Catal 146:323
2. Wachs IE, Jehng JM, Deo G, Wechkuysen BM, Guliants VV, Benzinger JB, Sundaresan SJ (1997) J Catal 170:75
3. Olthof B, Khodakov J, Bell AT, Iglesia E (2000) J Phys Chem B 104:1516
4. Burcham LJ, Deo G, Gao X, Wachs IE (2000) Top Catal 11/12:85

5. Wang C-B, Deo G, Wachs IE (1998) J Catal 178:640
6. Bronkema JL, Bell AT (2007) J Phys Chem C 111:420
7. Kanervo JM, Harlin ME, Krause AOI, Bañares MA (2003) Catal Today 78:171
8. Koranne MM, Goodwin JG, Marcelin G (1994) J Catal 148:369
9. Nag NK, Massoth FE (1990) J Catal 124:127
10. Argyle MD, Chen K, Resini C, Krebs C, Bell AT, Iglesia E (2004) J Phys Chem B 108:2345
11. Morey MS, Davison A, Stucky GD (1998) J Por Mat 5:195
12. Huo Q, Margolese DE, Stucky GD (1996) Chem Mater 8:1147
13. Jentoft RE, Deutsch SE, Gates BC (1996) Rev Sci Instrum 67:2111
14. Newville M (2001) J Synchrotron Radiat 8:322
15. Ravel B, Newville M (2005) J Synchrotron Radiat 12:537
16. Goodrow A, Bell AT (2007) J Phys Chem C 111:14753
17. Xie S, Iglesia E, Bell AT (2000) Langmuir 16:7162
18. Ohler N, Bell AT (2005) J Phys Chem B 109:23419
19. Skuja L, Güttler B (1996) Phys Rev Lett 77:2093; Orellana W, da Silva AJR, Fazzio A (2001) Phys Rev Lett 87:155901; Bongiorno A, Pasquarello A (2002) Phys Rev Lett 88:125901; Hoshino T, Hata M, Neya S, Nishioka Y, Watanabe T, Tatsumura K, Ohdomari I (2003) Jpn J Appl Phys Part 1 42:6535; Tatsumura K, Shimura T, Mishima E, Kawamura K, Yamasaki D, Yamamoto H, Watanabe T, Umeno M, Ohdomari I (2005) Phys Rev B 72:045205
20. Hamann DR (1998) Phys Rev Lett 81:3447; Ng KO, Vanderbilt D (1999) Phys Rev B 59:10132; Hoshino T, Hata M, Nishioka Y, Watanabe T, Tatsumura K, Ohdamari I (2003) Jpn J Appl Phys Part 1 42:3560