

Insights into Oxygen Exchange Between Gaseous O₂ and Supported Vanadium Oxide Catalysts via ¹⁷O NMR

Christopher A. Klug,^{*,†,‡} Scott Kroeker,[§] Pedro M. Aguiar,^{§,⊥} Min Zhou,[†] Donald F. Stec,[†] and Israel E. Wachs[#]

[†]Department of Chemical Engineering, Stanford University, Stanford, California 94305, [§]Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada, and [#]Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015. [‡]Current address: Chemistry Division, Naval Research Laboratory, Washington, DC 20375. [⊥]Current address: Commissariat à l'Énergie Atomique, IRAMIS, Laboratoire de Structure et Dynamique par Résonance Magnétique, 91191 Gif-sur-Yvette, France.

Received October 2, 2008. Revised Manuscript Received July 10, 2009

Vanadium oxide reference compounds, KVO₃ and V₂O₅, and supported vanadium oxide catalysts (Al₂O₃, TiO₂, and SiO₂) were investigated using magic angle sample spinning ¹⁷O NMR. All samples were ¹⁷O-enriched using gas–solid exchange. Extraction of chemical shift and quadrupolar coupling information for the model compounds KVO₃ and V₂O₅ was performed via the simulation of MAS spectra obtained in one-pulse experiments and the observations were consistent with their known bulk structures. For the supported vanadia catalysts, it was found that the oxygen exchange process is dominated by ¹⁷O signal from the catalyst oxide supports. Spectra obtained via rotor-synchronized spin echoes revealed additional wide lines for Al₂O₃ and TiO₂ supported vanadia catalysts that arise from ¹⁷O in the surface vanadia species of the catalysts. Additional ¹⁷O–⁵¹V TRAPDOR (TRANSfer of Populations in DOuble Resonance) experiments support this assignment. The wide lines suggest that the local environments of the ¹⁷O nuclei associated with the dehydrated surface vanadia species are extremely heterogeneous and fall in the range of oxygen in singly (V=O) and/or doubly coordinated environments (V–O–V or V–O–Support). The relatively small total amount of ¹⁷O associated with the surface vanadia species contrasts with oxygen exchange models which commonly assume only the surface vanadium oxide layer is involved. These results demonstrate that the isotopic exchange of molecular O₂ with supported metal oxide catalysts, especially supported vanadia catalysts, is a much more complex process than originally perceived.

Introduction

Metal oxide materials are employed industrially as catalysts for a wide variety of oxidation processes, such as oxidation of hydrocarbons, ammoxidation of aromatic hydrocarbons, and reduction of nitrogen oxides.^{1–6} During catalytic oxidation reactions at elevated temperatures, the metal oxide materials relinquish their structurally incorporated oxygen and are subsequently reoxidized by gaseous molecular O₂. Such catalysts usually exhibit zero-order kinetics with respect to O₂ partial pressure because they operate via a Mars–van Krevelen reaction mechanism involving the participation of lattice oxygen.^{7,8}

There has been a significant amount of work by Boreškov, Winter, Novakova and others using isotopic ¹⁸O exchange of metal oxides to obtain insight into the extent of exchangeable oxygen, with the intent of correlating this parameter with the corresponding catalytic oxidation reaction rate.^{9–11} All of these global oxygen exchange measurements were conducted with bulk metal oxide catalytic materials and revealed no structural information about the location of oxygen incorporation.

In recent years, supported metal oxide catalysts containing a two-dimensional surface metal oxide phase have received much attention.¹² These materials consist of a dispersed metal oxide phase containing the catalytically active sites on a high surface area oxide support (e.g., Al₂O₃, SiO₂, TiO₂, etc.). Unlike bulk mixed metal oxides, supported metal oxide catalysts contain the catalytically active component exclusively at the surface, allowing for detailed molecular-level insights about the oxygen exchange process. However, the number of such studies has

*Corresponding author. E-mail: klug@nrl.navy.mil.

- (1) Hodnet, B. K. *Heterogeneous Catalytic Oxidation: Fundamental and Technological Aspects of the Selective and Total Oxidation of Organic Compounds*; Wiley: New York, 2000.
- (2) Bond, G. C.; Tahir, S. F. *Appl. Catal.* **1991**, *71*, 1.
- (3) Bosch, H.; Janssen, F. *Catal. Today* **1987**, *2*, 369.
- (4) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic Press: New York, 1974.
- (5) Kung, H. H. *Transition Metal Oxides: Surface Chemistry and Catalysis*; Elsevier: New York, 1989.
- (6) Wachs, I. E.; Weckhuysen, B. M. *Appl. Catal., A* **1997**, *157*, 67.
- (7) Mars, P.; van Krevelen, D. W. *Chem. Eng. Sci. Suppl.* **1954**, *3*, 41.
- (8) Chen, K.; Khodakov, A.; Yang, J.; Bell, A. T.; Iglesia, E. *J. Catal.* **1999**, *186*, 325.

- (9) Boreškov, G. K. *Adv. Catal.* **1964**, *15*, 285.
- (10) Winter, E. R. S. *J. Chem. Soc.* **1968**, 2889.
- (11) Novakova, J. *Catal. Rev.* **1970**, *4*, 77.
- (12) Wachs, I. E. *Catal. Today* **2005**, *100*, 79.

been rather limited. Isotopic oxygen exchange studies during propane oxidative dehydrogenation over supported vanadia catalysts confirm the Mars-van Krevelen mechanism.⁸ Koranne et al. measured the global oxygen exchange capacity of supported V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts, and found that both supported vanadia systems, as well as the vanadia-free Al_2O_3 (to a lesser extent the vanadia-free SiO_2 support) exhibited oxygen exchange at temperatures of 550–600 °C.¹³ Doornkamp et al. determined both the exchange rate and the isotopic distribution of supported vanadia catalysts and found that the exchange rate varied with the oxide support ($V_2O_5/TiO_2 \gg V_2O_5/Al_2O_3 \gg V_2O_5/SiO_2$).¹⁴ The oxygen exchange rates track the specific catalytic activity for oxidation reactions when normalized per surface vanadium site. Raman spectroscopy measurements determined that during such isotopic exchange ^{18}O was incorporated into the various oxygen functionalities (e.g., $V=O$, $V-O$ -Support, and $V-O-V$ bonds) associated with the surface vanadia species.¹⁵ It was not possible, however, to determine with Raman spectroscopy if any oxygen was also incorporated by the underlying oxide supports.

To determine the locations of the exchanged isotopic oxygen in the supported vanadia catalysts, we undertook solid-state ^{17}O NMR studies with $^{17}O_2$ exchanged model supported vanadia catalysts. Whereas solid-state ^{51}V and 1H NMR have proven to be excellent probes of the local structure in model supported vanadia catalysts,^{16–21} this study represents the first application of ^{17}O NMR to such materials. Comparisons of ^{17}O NMR spectra for oxygen-exchanged bulk supports with ^{17}O NMR spectra for the corresponding oxygen-exchanged vanadia catalysts reveal that only a relatively small fraction of ^{17}O nuclei is associated with the surface vanadia phase and the local environment for these nuclei is extremely heterogeneous. The oxygen exchange process is instead dominated by the underlying oxide supports. These new findings indicate that the support plays a significant role in the exchange of molecular O_2 with supported metal oxide catalysts, especially supported vanadia catalysts.

Experimental Section

Synthesis. Bulk V_2O_5 (Aldrich Chemical Co.) and KVO_3 (Alfa Aesar) were used as received. The supports used for this study were Al_2O_3 (Engelhard, $S_{BET} = 222 \text{ m}^2/\text{g}$), SiO_2 (Cabosil

EH-5, $S_{BET} = 332 \text{ m}^2/\text{g}$), and TiO_2 (Degussa P-25, $S_{BET} = 45 \text{ m}^2/\text{g}$). Supported vanadia catalysts were prepared by the incipient wetness impregnation of a 2-propanol solution of vanadium isopropoxide ($VO(O-Pr)_3$, Alfa-Aesar, 97% purity) onto the supports.²² The preparation was performed within a glovebox with continuously flowing N_2 because of the moisture sensitivity of the precursor. After impregnation, the samples were kept inside the glovebox to dry overnight. The samples were subsequently further dried in flowing N_2 at 120 °C for 1 h and 300 °C for 1 h, and were finally calcined in flowing air at 300 °C for 1 h and 450 °C for 2 h. The nominal catalyst compositions were 10% V_2O_5/SiO_2 (2.5 V/nm^2), 10% V_2O_5/Al_2O_3 (4 V/nm^2) and 5% V_2O_5/TiO_2 (8 V/nm^2), with $\sim 8 \text{ V}/\text{nm}^2$ representing one monolayer of surface vanadium oxide. The lower surface vanadia density of the supported V_2O_5/SiO_2 catalyst is a consequence of the weak interaction of the silica support with the supported vanadia phase. Raman spectra collected using in situ cells, to allow acquisition of spectra under controlled environmental conditions of the dehydrated supported vanadia catalysts, demonstrated the absence of nanocrystalline V_2O_5 and thus, the vanadia phase is fully dispersed on the surface.²³ Vanadium-51 MAS NMR showed that the dehydrated surface vanadia phase consists of surface VO_4 units.^{16,17} In situ UV-vis spectra of the dehydrated supported vanadia catalysts revealed that the surface vanadia species are present as $\sim 95\%$ monomeric VO_4 units for 10% V_2O_5/SiO_2 and $\sim 50\%$ monomeric VO_4 units for 10% V_2O_5/Al_2O_3 . The structural composition of the supported 5% V_2O_5/TiO_2 catalyst could not be quantified because of the strong UV-vis absorption by TiO_2 . However, it is expected to be dominated by polymeric surface VO_4 units.²³

^{17}O Exchange. All ^{17}O enrichments were conducted in a gas handling system of total volume of 1.7 L equipped with a turbomolecular vacuum pump. The reference compounds KVO_3 and V_2O_5 , 100 mg each, were heated under vacuum ($\sim 1 \times 10^{-6}$ Torr) to 400 and 500 °C, respectively, and exposed to 50 Torr of 46% ^{17}O -enriched O_2 gas (Isotec, Inc.) for 12 h. For the catalyst samples, a range of sample pretreatments and exchange temperatures were explored. The results presented in this paper were obtained for two series of samples where the exchange occurred at either 450 or 500 °C. These temperatures were chosen following previous work to avoid the expected instability of the surface vanadia monolayer at higher temperatures¹⁴ and to minimize effects due to oxygen diffusion within the supports which would appear at much higher temperatures, e.g., oxygen self-diffusion in Al_2O_3 has generally been measured for temperatures well above 1000 °C.²⁴ Each supported vanadia catalyst and its corresponding blank support, typically 50–100 mg, was simultaneously loaded in a quartz tube and the two samples were physically kept apart in different portions of the system. For the first series of samples, which were exchanged at 500 °C, the samples were dehydrated under a vacuum at 500 °C for a minimum of 1 h, reduced with H_2 , and oxidized with $^{16}O_2$ for 1–4 h each, and then, following the removal of $^{16}O_2$ by evacuation, the samples were exposed to 50 Torr of 46% ^{17}O -enriched O_2 gas for 10–14 h. For the second series of samples which were exchanged at 450 °C, the samples were dehydrated under vacuum at 450 °C for a minimum of 1 h and then exposed to 50 Torr of 46% ^{17}O -enriched O_2 gas for 4 h. The lower exchange temperature and modified pretreatment were chosen in an attempt to both reduce the total oxygen exchange

- (13) Koranne, M. M.; Goodwin, J. G. Jr.; Marcelin, G. *J. Catal.* **1994**, *148*, 378.
 (14) Doornkamp, C.; Clement, M.; Gao, X.; Wachs, I. E.; Ponc, V. *J. Catal.* **1999**, *185*, 415.
 (15) Weckhuysen, B. M.; Jehng, J.-M.; Wachs, I. E. *J. Phys. Chem. B* **2000**, *104*, 7382.
 (16) Eckert, H.; Wachs, I. E. *J. Phys. Chem.* **1989**, *93*, 6796.
 (17) Das, N.; Eckert, H.; Hu, H. C.; Wachs, I. E.; Walzer, J. F.; Feher, F. *J. Phys. Chem.* **1993**, *97*, 8240.
 (18) Fernandez, C.; Guelton, M. *Catal. Today* **1994**, *20*, 77.
 (19) Lapina, O. B.; Bal'zhiniaev, B. S.; Boghosian, S.; Eriksen, K. M.; Ferhmann, R. *Catal. Today* **1999**, *51*, 469.
 (20) Mastikhin, V. M.; Nosov, A. V.; Tersikh, V. V.; Zamaraev, K. I.; Wachs, I. E. *J. Phys. Chem.* **1994**, *98*, 13621.
 (21) Nielsen, U. G.; Topsøe, N.-Y.; Brorson, M.; Skibsted, J.; Jakobsen, H. *J. Am. Chem. Soc.* **2004**, *126*, 4926.

(22) Gao, X.; Wachs, I. E. *J. Phys. Chem. B* **2000**, *104*, 1261.

(23) Tian, H.; Ross, E. I.; Wachs, I. E. *J. Phys. Chem. B* **2006**, *110*, 9593.

(24) Heuer, A. H. *J. Eur. Ceram. Soc.* **2008**, *28*, 1495.

with the support and increase the oxygen exchange with the vanadia layer.

^{17}O MAS NMR of Crystalline Compounds. The solid-state ^{17}O NMR experiments were carried out using Varian Unity VXR 500 (11.7 T) and Inova 600 (14 T) spectrometers operating at Larmor frequencies of 67.9 and 81.3 MHz, respectively, for ^{17}O . A double-tuned Nicolet MAS probe with a 4 mm zirconia rotor was used with the Varian VXR 500. With the Varian Inova 600, ^{17}O spectra were obtained with a double-tuned 3.2 mm Varian MAS probe. Short excitation pulses (0.5 μs) at an RF nutation frequency of 55 kHz were employed in order to ensure even excitation over the observed spectral width of 400 kHz. The zirconia rotors were spun at speeds of 15–19.5 kHz with automatic spinning control. Recycle delays of 16 and 1 s were used for KVO_3 and V_2O_5 respectively. Five to six thousand transients were coadded. Oxygen-17 NMR spectra were referenced using deionized H_2^{17}O (0 ppm). Oxygen-17 NMR spectra were simulated to extract both quadrupolar and chemical shielding information using the STARS program, as implemented within the Varian Vnmr package.^{25,26} Simulations were performed manually to obtain best fits for the spectra at both fields, under the assumption of coincident principal axis systems of the quadrupolar and chemical shielding tensors. The principal components of the chemical shift tensor are assigned in the standard way, $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, and the isotropic chemical shift, δ_{iso} , is given by

$$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3 \quad (1)$$

the anisotropy of the shielding is given by the span

$$\Omega = \delta_{11} - \delta_{33} \quad (2)$$

and the skew is

$$\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega \quad (3)$$

The electric field gradient (EFG) tensor is symmetric and traceless, and may be described by C_Q and the associated asymmetry parameter, η

$$C_Q = \frac{eQV_{ZZ}}{h} \quad (4)$$

$$\eta = (V_{XX} - V_{YY})/V_{ZZ} \quad (5)$$

where e is the elementary charge, Q is the nuclear quadrupole moment, the principal components of the EFG tensor are defined such that $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, and h is Planck's constant.

^{17}O MAS NMR of Supports and Supported Catalysts. All spectra were acquired at 14.1 T, using a double-resonance 3.2 mm MAS probe (Varian). To avoid probe ringdown effects and, therefore, allow for better wide line identification, we used a rotor-synchronized spin–echo sequence. The echo sequence employed a 1.2 μs excitation pulse followed by a 2.4 μs refocusing pulse. These pulse lengths were calibrated using ^{17}O -enriched V_2O_5 . The total echo evolution time was two rotor periods: 111 μs for spinning speed of 18 kHz. Both single pulse and echo acquisitions as a function of recycle time showed only

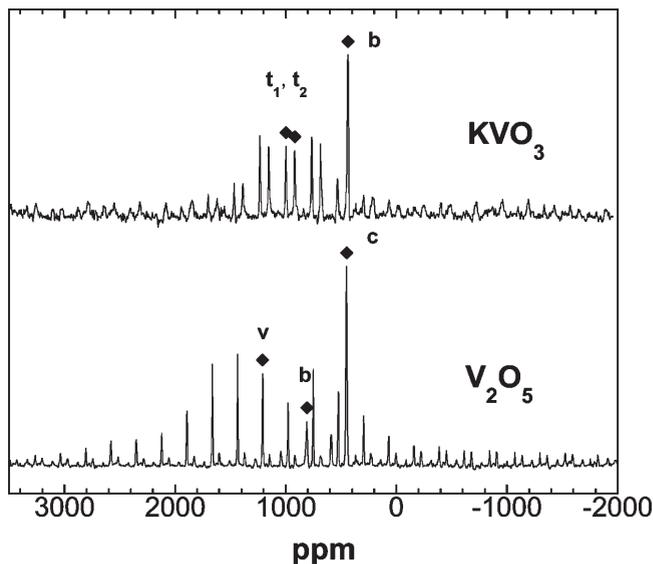


Figure 1. ^{17}O MAS NMR spectra for KVO_3 (41.5 mg, 19 kHz spinning, 5120 acquisitions) and V_2O_5 (31.8 mg, 18.5 kHz, 6144 acquisitions) at 14.1 T. The solid diamond symbols mark the positions of the center bands, whereas all other peaks are spinning side bands. For KVO_3 , the center bands are labeled t_1 , t_2 , and b , corresponding to the two types of terminal oxygen and the bridging oxygen. For V_2O_5 , the center bands are labeled v , b , and c corresponding to “vanadyl”, “bridge”, and “chain” oxygens.

minor signal intensity changes for relaxation times longer than 1 s and, therefore, all spectra were recorded with recycle delays of 1 s or longer. Spectra were referenced using deionized H_2^{17}O (0 ppm).

^{17}O – ^{51}V TRAPDOR. TRAPDOR (TRansfer of Populations in DOuble Resonance) experiments^{27,28} were carried out on a Varian Inova 600 (14.1 T) using a triple-tuned Varian MAS probe with 5.0 mm rotors spinning at 8 kHz with automatic spinning control. Evolution periods were set to multiples of the rotor period for rotor-synchronized acquisitions. The ^{17}O NMR echo sequence employed a 1.5 μs excitation pulse followed by a 3.0 μs refocusing pulse. TRAPDOR experiments were first performed for ^{17}O -enriched V_2O_5 , to allow optimization of the experimental parameters before application to the supported vanadia catalyst samples. Vanadium-51 RF field strengths, defined as the observed nutation rate for V_2O_5 , of 21 kHz, 32 kHz, and 42 kHz were tested for evolution times up to 4 ms. TRAPDOR experiments for the Al_2O_3 support alone were performed to ensure that dephasing was not a result of the ^{27}Al nuclei, due to the similar Larmor frequencies of ^{51}V and ^{27}Al (158.1 and 156.4 MHz, respectively, at 14.1 T).

Results and Discussion

Oxygen-17 MAS NMR of $^{17}\text{O}_2$ -exchanged reference compounds V_2O_5 and KVO_3 (Figure 1, Figures S5 and S6 in the Supporting Information) was used to identify the spectral signatures of the singly ($\text{V}=\text{O}$), doubly ($\text{V}-\text{O}-\text{V}$), and triply (OV_3) coordinated oxygen sites known to occur in crystalline vanadates. The structure of V_2O_5 consists of polymeric vanadia layers formed by oxygen-bridged chains of VO_5 polyhedra.²⁹ Three

(25) Skibsted, J.; Nielsen, N. C.; Bildsøe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1991**, *95*, 88.

(26) Skibsted, J.; Nielsen, N. C.; Bildsøe, H.; Jakobsen, H. J. *Chem. Phys. Lett.* **1992**, *188*, 405.

(27) Van Eck, E. R. H.; Janssen, R.; Maas, W. E. J. R.; Veeman, W. S. *Chem. Phys. Lett.* **1990**, *174*, 428.

(28) Grey, C. P.; Veeman, W. S. *Chem. Phys. Lett.* **1992**, *192*, 379.

(29) Enjalbert, R.; Galy, J. *Acta Crystallogr., Sect. C* **1986**, *C42*(11), 1467.

Table 1. Oxygen-17 NMR Parameters for Crystalline Model Compounds

| compound | site | CN ^a | δ_{iso} (ppm) ^b | Ω (ppm) ^c | κ^d | C_Q (MHz) | η^e |
|-------------------------------|----------------|-----------------|--|-----------------------------|------------|-------------|-----------|
| KVO ₃ | b | 3 | 449 ± 2 | n.d. | n.d. | 2.0 ± 0.5 | n.d. |
| | t ₁ | 1 | 1007 ± 2 | 1400 ± 100 | +0.2 ± 0.2 | 1.0 ± 0.3 | n.d. |
| | t ₂ | 1 | 929 ± 2 | 1400 ± 100 | +0.2 ± 0.2 | 1.0 ± 0.3 | n.d. |
| V ₂ O ₅ | c | 3 | 463 ± 2 | n.d. | n.d. | 2.0 ± 0.2 | 0.6 ± 0.1 |
| | b | 2 | 824 ± 1 | 950 ± 100 | +0.5 ± 0.4 | 2.5 ± 0.2 | >0.5 |
| | v | 1 | 1214 ± 1 | 2600 ± 200 | -0.4 ± 0.1 | 0.6 ± 0.1 | <0.4 |

^aOxygen coordination number. ^bIncludes a second-order quadrupole shift correction. ^c $\Omega = \delta_{11} - \delta_{33}$, where the chemical shift principal components are defined such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. ^d $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. ^e $\eta = (V_{XX} - V_{YY})/V_{ZZ}$, where V_{ii} are the principal components of the diagonalized EFG tensor, ordered such that $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$.

distinct oxygen sites are present: a “vanadyl” V=O ($r_{\text{VO}} = 1.58 \text{ \AA}$), a “bridging” V–O–V ($r_{\text{VO}} = 1.78$ and 1.78 \AA), and a “chain” OV₃ ($r_{\text{VO}} = 1.88, 1.88,$ and 2.02 \AA). Correspondingly, three distinct signals are observed in the ¹⁷O MAS NMR spectrum with isotropic chemical shifts of 1214, 824, and 463 ppm (Figure 1); these are assigned to V=O, V–O–V, and OV₃ in accord with previous results.³⁰ The relatively small quadrupole coupling constants ($C_Q \leq 2.5 \text{ MHz}$, Table 1) combined with the moderately high fields employed result in only slight second-order broadening of the central transition. In addition, many of the sites possess significant chemical shielding anisotropy (denoted by their spans, Ω in Table 1) which results in the large number of spinning sidebands of the central transition. Spans comparable to those of the V=O and V–O–V oxygens have been observed in the ¹⁷O NMR spectra of metal carbonyl compounds,^{31,32} and the Ti–O–Ti of titanite (CaTiSiO₅).³³ Potassium metavanadate, KVO₃, consists of polymerized VO₄ units, i.e., pseudotetrahedral chains, and possesses three equally abundant types of oxygen:³⁴ two terminal V–O oxygen with $r_{\text{VO}} = 1.66$ and 1.65 \AA , and a bridging V–O–V oxygen ($r_{\text{VO}} = 1.81$ and 1.81 \AA). The KVO₃ ¹⁷O MAS NMR peaks at 1007 and 929 ppm (Figure 1) possess very similar NMR parameters (Table 1) and are assigned to the terminal oxygens. On the basis of empirical correlations between oxide bond lengths and isotropic chemical shifts, the terminal oxygen with a longer bond length is assigned to the higher frequency resonance.³⁵ The remaining peak centered at 449 ppm (Figure 1), characterized by quite different NMR parameters, would then be assigned to the doubly coordinated oxygen. This is significantly more shielded than previous assignments for V–O–V oxygens. However, given the lack of ¹⁷O NMR data for structurally well-characterized vanadates, the actual chemical shift regions may be much larger than previously assumed (650–900 ppm).^{30,36} Further rationalization for an underestimation of the V–O–V chemical

shift range comes from the very large chemical shift tensor of the V–O–V site in V₂O₅, where the most and least shielded components are $\delta_{33} = 270 \pm 50 \text{ ppm}$ and $\delta_{11} = 1220 \pm 40 \text{ ppm}$, respectively. Given this large spatial dependence on the shielding, structural differences such as the presence of potassium and the difference in vanadium coordination number (five for V₂O₅, four in KVO₃) may well account for the pronounced shielding of this site. Thus, the solid state ¹⁷O NMR chemical shifts for different OV_{*n*} coordination correspond to ~900–1400 ppm for O=V, ~400–900 ppm for V–O–V, and 200–450 ppm for OV₃.

The ¹⁷O NMR signal intensities for the ¹⁷O₂ exchanged supported vanadia catalysts and vanadia-free supports are given in Table 2. The clean supports underwent appreciable isotopic oxygen exchange at both temperatures investigated. Normalized per unit surface area, the relative extent of exchange capacity of the supports is TiO₂ > Al₂O₃ > SiO₂ and there was a significant increase in total exchange at the higher temperature consistent with results from earlier ¹⁸O₂ exchange measurements.^{9–11} The addition of the surface vanadia phase resulted in a small increase in the total exchange at 450 °C. However, for the samples treated at 500 °C, there was enhanced oxygen exchange for V₂O₅/TiO₂ and V₂O₅/SiO₂ and decreased exchange for V₂O₅/Al₂O₃. Normalized per V atom, the relative exchange capacity of the catalysts is V₂O₅/TiO₂ > V₂O₅/SiO₂ ≈ V₂O₅/Al₂O₃ for both exchange temperatures, although this comparison does not necessarily reflect the amount of oxygen in the vanadia layer. Unexchanged samples yielded no ¹⁷O NMR signal because of the low natural abundance of ¹⁷O (0.037%).

Molecular-level insight into the locations of the exchanged ¹⁷O in the supported vanadia catalysts is obtained by closer examination of the ¹⁷O MAS NMR lineshapes. Representative spectra are shown in Figure 2, where it can be seen that spectral features in the supported vanadia catalysts are dominated by the signals from ¹⁷O in the oxide supports, homologous lineshapes are observed at both temperatures, and there are no additional distinct narrow peaks identifiable with the surface vanadia layer.

The ¹⁷O MAS NMR spectra of the 10% V₂O₅/Al₂O₃ catalyst (ca. 70% monolayer coverage since the actual vanadia content is found to be ~14% V₂O₅) and the vanadia-free Al₂O₃ support (panels a and b in Figure 2)

(30) Fontenot, C. J.; Wiench, J. W.; Schrader, G. L.; Pruski, M. J. *Am. Chem. Soc.* **2002**, *124*, 8435.

(31) McMahon, M. T.; deDios, A. C.; Godbout, N.; Salzmann, R.; Laws, D. D.; Le, H.; Havlin, R. H.; Oldfield, E. J. *Am. Chem. Soc.* **1998**, *120*, 4784.

(32) Salzmann, R.; Kaupp, M.; McMahon, M. T.; Oldfield, E. J. *Am. Chem. Soc.* **1998**, *120*, 4771.

(33) Kroeker, S.; Rice, D.; Stebbins, J. F. *Am. Mineral.* **2002**, *87*, 572.

(34) Evans, H. T., Jr. *Z. Kristallogr.* **1960**, *114*, 257.

(35) Klemperer, W. G. *Angew. Chem., Int. Ed.* **1978**, *17*, 246.

(36) Pozarnsky, G. A.; McCormick, A. V. *J. Mater. Chem.* **1994**, *4*, 1749.

Table 2. Normalized ^{17}O NMR Spin Echo Signal Intensities Following Exchange at 450 and 500 °C

| sample | wt % V_2O_5^a | normalized signal intensity (a.u.) ^b | | | | $\Delta S/S^d$ |
|--|-------------------------------|---|------------------|------------|-------------------------------|-----------------|
| | | per gram | per m^2 | per V atom | broad NMR signal ^c | |
| $T = 450\text{ °C}$ | | | | | | |
| TiO_2 (45 m^2/g) | | 20 | 4.5 | | | |
| 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ | 5.89 | 21 | | 5.3 | < 10% | |
| SiO_2 (332 m^2/g) | | 18 | 0.6 | | | |
| 10% $\text{V}_2\text{O}_5/\text{SiO}_2$ | 8.7 | 21 | | 3.7 | < 5% | |
| Al_2O_3 (222 m^2/g) | | 23 | 1.1 | | | |
| 10% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ | 14.05 | 28 | | 3.1 | 55% | |
| $T = 500\text{ °C}$ | | | | | | |
| TiO_2 (45 m^2/g) | | 83 | 18.5 | | | |
| 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ | 5.89 | 102 | | 26.2 | < 5% | 0.10 ± 0.05 |
| SiO_2 (332 m^2/g) | | 26 | 0.8 | | | |
| 10% $\text{V}_2\text{O}_5/\text{SiO}_2$ | 8.7 | 37 | | 6.5 | < 5% | 0.05 ± 0.05 |
| Al_2O_3 (222 m^2/g) | | 105 | 4.7 | | | |
| 10% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ | 14.05 | 53 | | 5.7 | ~35% | 0.30 ± 0.05 |

^aActual V_2O_5 concentration obtained by atomic absorption. ^bNormalization takes into account the number of acquisitions and the sample masses, but does not remove contributions due to natural abundance background signal from the zirconia rotor, resulting in a slight overestimation of the total amount of ^{17}O exchange. ^cEstimated from measurement of narrow component in spin echo time domain data and integration of spectral frequency domain data. ^dTRAPDOR fraction, see text.

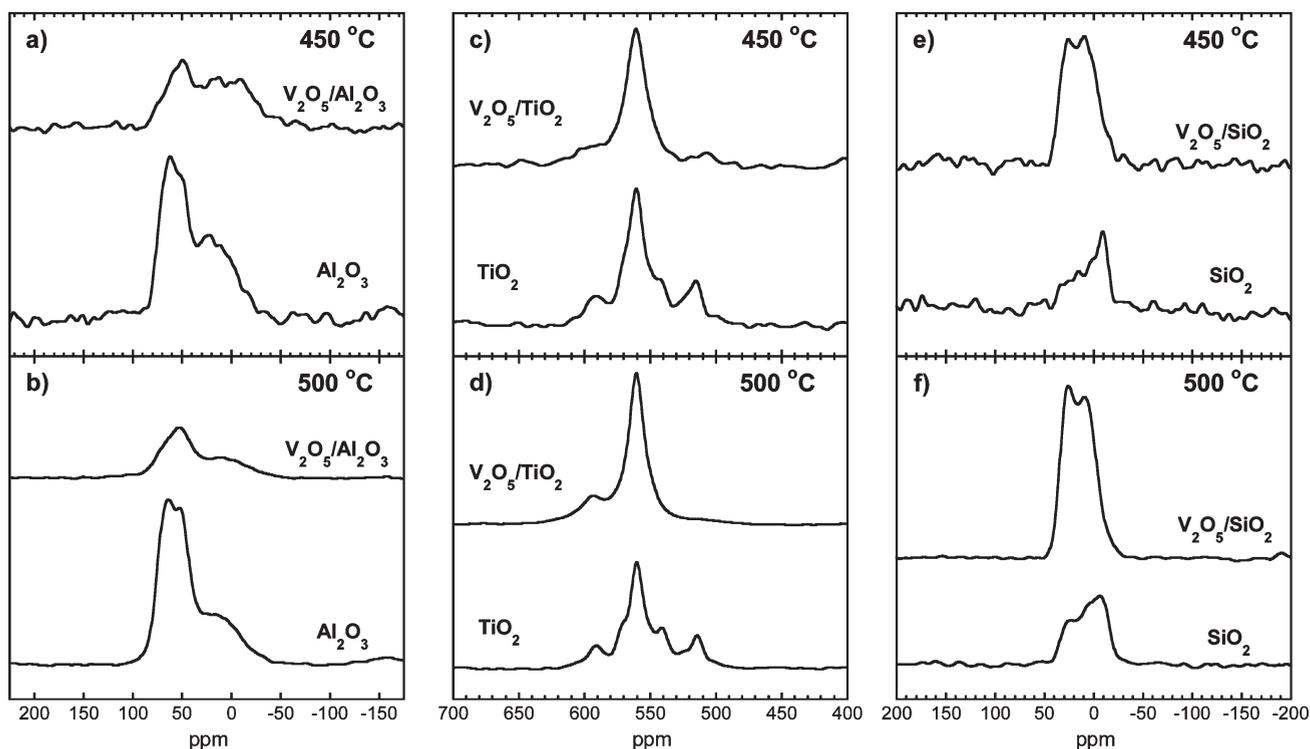


Figure 2. ^{17}O MAS NMR spectra for a series of supported vanadia catalysts and the corresponding supports exchanged at 450 and 500 °C: (a) $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst (14.2 mg) and Al_2O_3 support (15.8 mg); (b) $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst (17.7 mg) and Al_2O_3 support (16.1 mg); (c) $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst (30.1 mg) and TiO_2 support (28.1 mg); (d) $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst (33.2 mg) and TiO_2 support (31.2 mg); (e) $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst (13.4 mg) and SiO_2 support (10.5 mg); (f) $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst (17.1 mg) and SiO_2 support (10.9 mg). All spectra were obtained using a spinning speed of 18 kHz, a recycle delay of 1 s, and up to 90 000 total acquisitions. The pair of spectra within each panel are scaled by the weight of the samples.

have features consistent with oxygen within bulk Al_2O_3 and surface hydroxyl groups centered about 60 ppm and 0 ppm, respectively.³⁷ The most striking difference between the spectra, particularly for the samples treated at 500 °C, is the diminished signal intensity upon vanadia deposition on Al_2O_3 . This can be understood in part as due to the progressive titration of surface hydroxyls by vanadia species, as is known to occur.^{5,20} In Figure 2b,

there is ~3 times more peak intensity evident in the spectrum of the Al_2O_3 support than the supported $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst, confirming that the surface vanadia layer retards oxygen exchange with the bulk Al_2O_3 support. A better measure of the total ^{17}O NMR signal intensity is the amplitude of the time-domain spin echo. This measurement reveals that the ratio of total intensity of the ^{17}O NMR signal for the alumina support to the supported 10% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst is actually closer to 2 for the samples exchanged at 500 °C, suggesting

(37) Walter, T. H.; Oldfield, E. J. *Phys. Chem.* **1989**, *93*, 6744.

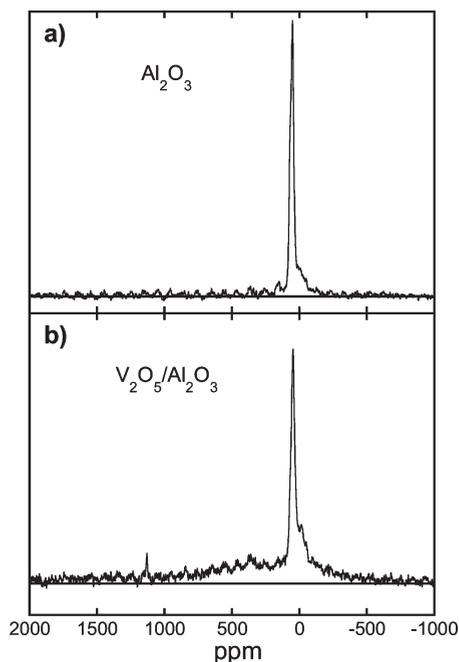


Figure 3. ^{17}O MAS NMR spectra for (a) Al_2O_3 (82.0 mg) and (b) supported $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ (88.8 mg) showing the broad component. The spectra were obtained using a spinning speed of 8 kHz, recycle delay 1 s, and 24 576 acquisitions each. The spurious signal at 1150 ppm was not observed in additional spectra of the same sample.

that the peaks in Figure 2b, which result from the Fourier transform of the spin echo, do not tell the whole story. Indeed, the full expansion of the ^{17}O NMR spectrum for the supported $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst exchanged at 500 °C exhibits a very broad feature ranging from roughly -300 ppm to 1200 ppm (Figure 3b), in contrast to the flat baseline in the ^{17}O NMR spectrum for Al_2O_3 (Figure 3a). This broad peak may be associated with ^{17}O in the surface vanadia species.

The ^{17}O - ^{51}V TRAPDOR (TRANSfer of Populations in DOuble Resonance) NMR experiments were undertaken to probe the oxygen nearest neighbors, and thereby assign the NMR signals. TRAPDOR recouples the through-space dipole-dipole interaction between nuclei, generally decoupled by MAS, via manipulation of the spins by RF pulses.^{27,28} Kim and Grey have previously used ^{17}O - ^{51}V TRAPDOR to establish the V-O connectivity for a series of anionic conductors.³⁸ The ^{17}O - ^{51}V TRAPDOR experiment yields two ^{17}O NMR data sets: a reference signal S_0 , recorded without recoupling, and a recoupled signal, S , where the intensity is reduced ($\Delta S = S_0 - S$) for those ^{17}O nuclei with significant dipolar coupling to ^{51}V . TRAPDOR experiments were first performed for ^{17}O -enriched V_2O_5 , chosen as a reference to allow optimization of the experimental parameters before application to the supported vanadia catalyst samples. Figure 4 shows typical ^{17}O NMR spectra corresponding to S_0 , without ^{51}V RF irradiation, and S , with ^{51}V RF irradiation. The significant reduction in ^{17}O signal size with ^{51}V RF irradiation confirms the strong internuclear ^{17}O - ^{51}V dipolar coupling for all oxygen sites in bulk V_2O_5 . Figure 5 is a plot of the amount of dephasing, $\Delta S/S_0$,

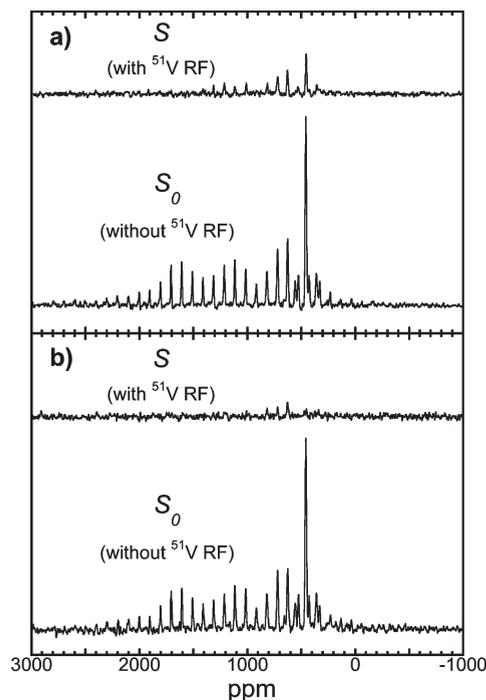


Figure 4. ^{17}O MAS NMR spectra obtained via ^{17}O - ^{51}V TRAPDOR for ^{17}O -exchanged V_2O_5 . The spectra were obtained using a spinning speed of 8 kHz with a ^{51}V RF field strength of 42 kHz and a dipolar evolution period of 1 ms (a) and 2 ms (b).

for the 463 ppm peak of V_2O_5 corresponding to the triply coordinated oxygen as a function of total evolution time for ^{51}V RF field strengths of 21 kHz, 32 kHz, and 42 kHz. As expected, there is significant variation in the total amount of dephasing as a function of ^{51}V RF field strength, with a $\Delta S/S_0$ ratio for the triply coordinated oxygen of 96% for an evolution time of 2 ms and ^{51}V RF field strength of 42 kHz, reflecting the connectivity of ^{17}O and ^{51}V . Furthermore, the early portion of the dephasing curves for the three oxygen sites are qualitatively consistent with the relative magnitudes of the nearest-neighbor vanadium-oxygen dipole-dipole couplings (Figure S1 in the Supporting Information). In all subsequent catalyst experiments, ^{51}V RF field strengths of 42 kHz were employed.

The time-domain TRAPDOR data of the supported $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst clearly reveal a narrow echo in the difference data (Figure 6), corresponding to a broad peak after Fourier transformation and confirming that the broad component arises solely from oxygen bound to vanadium in the surface vanadia phase. Similar results were obtained for the supported $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, although the signal reduction was smaller than for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. For the same experimental conditions, the $\Delta S/S_0$ values are $30 \pm 5\%$ for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, $10 \pm 5\%$ for $\text{V}_2\text{O}_5/\text{TiO}_2$ and almost negligible ($\Delta S/S_0 = 5 \pm 5\%$) for $\text{V}_2\text{O}_5/\text{SiO}_2$ (Table 2). Quantification of the broad components in the ^{17}O MAS NMR spectra via analysis of the narrow component in spin echo time domain data and spectral integration confirm these values (Table 2). No reduction in the total signal was observed in TRAPDOR measurements for any of the pure supports alone, further supporting the assignment of the broad component to ^{17}O nuclei associated with surface vanadia species.

(38) Kim, N.; Grey, C. P. *Science* **2002**, 297, 1317.

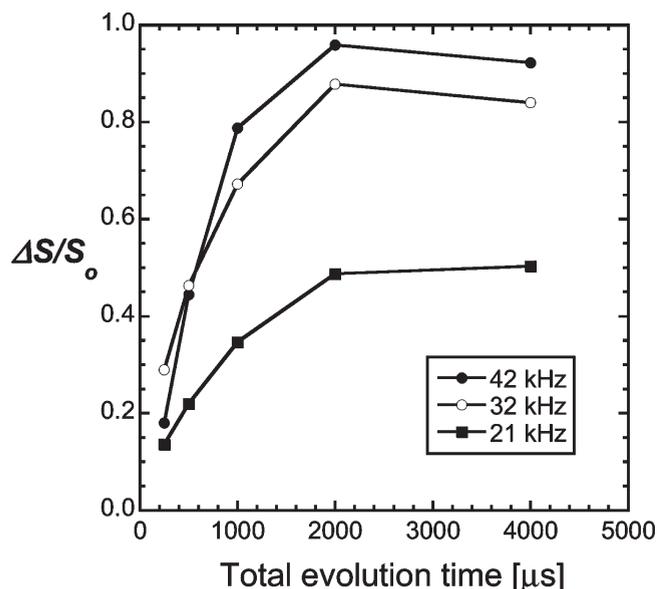


Figure 5. Results from a ^{17}O - ^{51}V TRAPDOR experiment for ^{17}O -exchanged V_2O_5 spinning at 8 kHz: the dependence of the measured ratio $\Delta S/S$ for the 463 ppm peak in the ^{17}O MAS NMR spectra on the dipolar evolution time at three different ^{51}V RF field strengths: 21 kHz (solid squares), 32 kHz (open circles), and 42 kHz (solid circles).

The ^{17}O NMR spectra of the supported 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, corresponding to monolayer surface vanadia coverage, and the vanadia-free TiO_2 support following exchange at 450 and 500 °C are shown in Figure 2c and d. As was observed for the alumina-supported samples, the lineshapes of the corresponding spectra at both temperatures are very similar, with the spectra for the samples exchanged at 500 °C possessing better signal-to-noise because of the enhanced total exchange at that temperature (see Table 2). On the basis of previous ^{17}O NMR studies of TiO_2 ,^{39–41} the 591 ppm peak may be assigned to oxygen in the bulk lattice of rutile, the 560 ppm peak corresponds to planar $\mu_3\text{-O}$ sites in the bulk lattice of anatase, while the 542 ppm and 516 ppm sites are from distorted $\mu_3\text{-O}$ and/or tetrahedral sites near the anatase surface (the predominant phase of Degussa P-25 TiO_2).⁶ Peaks for Ti-OH , expected at ~ 200 ppm,⁴² are not observed for either the catalyst or the vanadia-free TiO_2 support (see Figure S2 in the Supporting Information), consistent with titration of the surface Ti-OH sites by the surface vanadium oxide monolayer⁴³ and the low surface area of the support. Although the total integrated ^{17}O NMR intensities are similar for the supported 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst and the TiO_2 support, there is a significant reduction of the 542 and 516 ppm peaks in the spectra for the supported $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst. This suggests that the surface vanadia monolayer blocks the oxygen exchange of

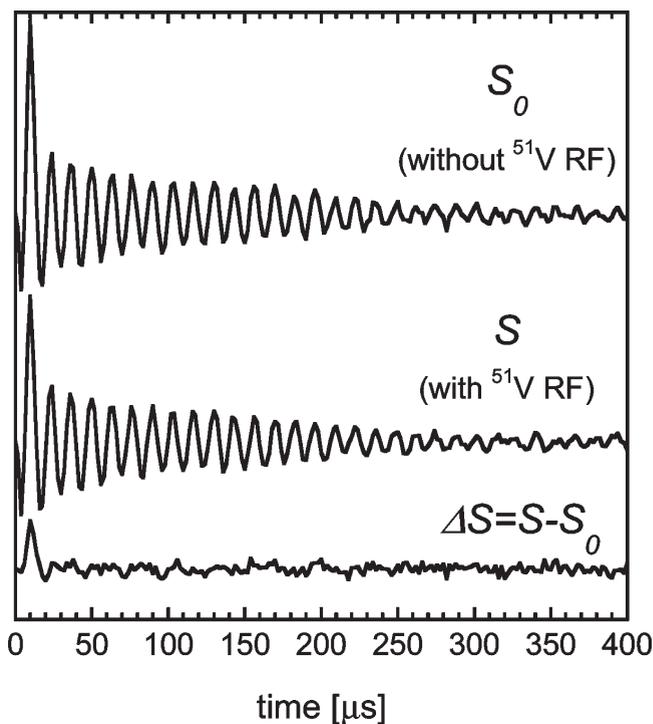


Figure 6. ^{17}O MAS NMR spin echoes, S_0 , S , and ΔS , obtained via ^{17}O - ^{51}V TRAPDOR of 88.8 mg $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ exchanged at 450 °C at a spinning speed of 8 kHz and with dipolar evolution period of 1 ms, recycle delay 1 s, and 40 960 acquisitions. The narrow ΔS spin echo corresponds to a broad signal in frequency space.

these titania sites. Although less clear than in the alumina-supported catalyst, an extremely broad ^{17}O NMR peak (-300 to 2000 ppm) can be identified in the expanded spectrum, and represents $< 10\%$ of the total ^{17}O signal intensity for the sample exchanged at 450 °C and $< 5\%$ of the total ^{17}O signal intensity for the sample exchanged at 500 °C (Table 2).

The ^{17}O NMR spectra of the 10% $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst ($\sim 75\%$ of the maximum vanadia dispersion on silica) and the pure SiO_2 support are shown in panels e and f in Figure 2. The peak at -7 ppm and asymmetric shoulder extending to ~ 30 ppm may be assigned to oxygen sites in surface hydroxyls (Si-OH) and surface/bulk Si-O-Si , respectively.⁴⁴ Simulation of the spectra (see Figures S3 and S4 in the Supporting Information), reveals NMR parameters consistent with previously reported values ($\delta_{\text{iso}} = 41 \pm 3$, $C_Q = 5.25 \pm 0.1$, $\eta = 0.25 \pm 0.15$). The C_Q -dependence of the intensities, and the inability to estimate the C_Q of the -7 ppm signal hampers accurate quantification. However, a simple measure of relative intensities provides an upper bound of about 30% Si-OH . In contrast to the supported $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, the presence of the surface vanadia overlayer significantly increases the total oxygen exchange reflected by a 2.5-fold increase in the peak intensity, although the absolute amount of ^{17}O incorporated in the SiO_2 samples remains small compared to the other materials studied. The increase in oxygen exchange may reflect the rupture of surface Si-O-Si bonds caused by anchoring of the surface vanadia species

(39) Bastow, T. J.; Moodie, A. F.; Smith, M. E.; Whitfield, H. J. *J. Mater. Chem.* **1993**, *3*, 697.

(40) Scolan, E.; Magnenet, C.; Massiot, D.; Sanchez, C. *J. Mater. Chem.* **1999**, *9*, 2467.

(41) Oldfield, E.; Coretsopoulos, C.; Yang, S.; Reven, L.; Lee, H. C.; Shore, J.; Han, O. H.; Ramli, E.; Hinks, D. *Phys. Rev. B* **1989**, *40*, 6832.

(42) Blanchard, J.; Bonhomme, C.; Maquet, J.; Sanchez, C. *J. Mater. Chem.* **1998**, *8*, 985.

(43) Burcham, L. J.; Deo, G.; Gao, X.; Wachs, I. E. *Top. Catal.* **2000**, *11/12*, 85.

(44) Walter, T. H.; Turner, G. L.; Oldfield, E. *J. Magn. Reson.* **1988**, *76*, 106.

onto the SiO₂ support.⁴⁵ Unlike the spectra for Al₂O₃- and TiO₂-supported catalysts, there is only a hint of a broad signal in the full spectrum for the silica-supported catalyst, extending from 100 to 500 ppm.

The breadth of the surface vanadia peaks in the spectra provides additional information about the structural nature of the surface vanadia layers. The broadest signal is observed for V₂O₅/TiO₂ (−300 to 2000 ppm), whereas the V₂O₅/SiO₂ signal is the narrowest (100 to 500 ppm). The V₂O₅/Al₂O₃ broad signal is comparable to that in TiO₂, except that it does not extend to such high frequency (−300 to 1200 ppm). The general width and location of these signals for supported 10% V₂O₅/Al₂O₃ and 5% V₂O₅/TiO₂ are consistent with the overall peak manifolds for oxygen in singly and/or doubly coordinated environments. Moreover, the width of these signals is consistent with what is known about the molecular structures of these supported vanadia catalysts from other spectroscopic characterization studies.^{6,12} The dehydrated surface vanadia species on all oxide supports possess one terminal V=O bond and three bridging V–O–M bonds, where M can be either a support cation (e.g., Al, Ti, Si) or an adjacent fully oxidized V atom. For the dehydrated V₂O₅/SiO₂ sample, all the surface VO₄ units are isolated and possess the O=V(O–Si)₃ coordination structure.^{17,22,23,46} Because all the surface vanadia species are structurally

identical but anchored to a heterogeneous surface, it is not surprising that the supported 10% V₂O₅/SiO₂ catalyst has the narrowest line. For the dehydrated V₂O₅/Al₂O₃ and V₂O₅/TiO₂ catalysts containing ~75–100% monolayer coverage, the surface VO₄ units are both isolated and polymerized,^{22,23} accounting for the broader ¹⁷O NMR lines of these samples relative to the dehydrated V₂O₅/SiO₂ sample.

Conclusion

The current ¹⁷O NMR results reveal that in addition to oxygen exchange with the surface vanadia species, significant exchange also occurs between gas-phase molecular O₂ and the oxygen atoms associated with the oxide supports. Since the rate-determining step during heterogeneous catalytic oxidation reactions generally does not involve activation of gas-phase molecular O₂,^{7,8} this finding suggests that the accepted relationship of isotopic oxygen exchange during oxidation reactions over supported vanadia catalysts must be examined more closely.

Acknowledgment. This work supported by NSERC of Canada (S.K.), an NSF CAREER award (C.A.K.), and NSF Nanoscale Interdisciplinary Research Team (NIRT) under Grant 0609018 (I.E.W.).

Supporting Information Available: Additional information (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(45) Gao, X.; Bare, S. R.; Weckhuysen, B. M.; Wachs, I. E. *J. Phys. Chem. B* **1998**, *102*, 10842.

(46) Lee, E. L.; Wachs, I. E. *J. Phys. Chem. B* **2007**, *111*, 1410.