Mechanistic Studies of Methanol Oxidation to Formaldehyde on Isolated Vanadate Sites Supported on High Surface Area Anatase

Jason L. Bronkema, Dewi C. Leo, and Alexis T. Bell*

Chemical Sciences Division, Lawrence Berkeley National Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720-1462

Received: May 17, 2007; In Final Form: July 17, 2007

The mechanism for methanol oxidation on both TiO_2 and V/TiO_2 was investigated using temperature-programmed experiments with in-situ infrared spectroscopy. Infrared and Raman spectroscopy, along with XANES, show that the V/TiO_2 sample consists predominantly of isolated VO_4 units after calcination. Methanol was found to adsorb on the catalyst in three ways at 323 K: (1) molecularly, (2) across Ti-O-Ti bonds to form $\text{Ti-OCH}_3/\text{Ti-OH}$ pairs, and (3) across V-O-Ti bonds to form $\text{V-OCH}_3/\text{Ti-OH}$ pairs. Upon heating, two desorption peaks for CH_3OH and H_2O were observed on all samples below 500 K. Although TiO_2 produced small amounts of CH_2O , the addition of vanadium greatly enhanced the rate of formaldehyde formation. Also, on the V/TiO_2 samples, it was noticed that the Ti-OCH_3 groups disappear much more rapidly than on TiO_2 alone. This is likely due to the reverse spillover of methoxide species from Ti to V, with the reaction occurring at lower temperatures at the vanadium center. Formate species were also detected during the experiments, and they are assumed to be intermediates in the decomposition of formaldehyde to CO , CO_2 , and H_2O . The apparent activation energy of V/TiO_2 for the formation of CH_2O is 16 kcal/mol.

Introduction

Isolated vanadate groups supported on metal oxides such as SiO_2 , Al_2O_3 , ZrO_2 , and TiO_2 have been shown to be active for the selective oxidation of methanol to formaldehyde.^{1–3} Characterization of the vanadate centers by multiple techniques has demonstrated that at low vanadium coverages the supported VO_4 species have a distorted tetrahedral geometry containing a single V=O bond and three V-O-M bonds (M = support metal), irrespective of support composition.^{4–7} The composition of the support, however, has a large effect on catalyst activity. For example, it has been reported that the activity of VO_x/TiO_2 is 3 orders of magnitude higher than that of VO_x/SiO_2 under comparable reaction conditions.¹ The cause for this remarkable sensitivity to support composition is not well understood and, in particular, why TiO_2 should increase the activity for formaldehyde formation by such a large degree. In this connection, it has been reported that the activation energies for the oxidation of methanol to formaldehyde occurring on titania- and silica-supported vanadia are similar, suggesting that support composition affects the preexponential factor in some manner.¹

Attempts to understand the interactions of methanol with TiO_2 and VO_x/TiO_2 have been reported by several investigators. For example, studies of methanol adsorption on both anatase powder and titania single crystals by Barteau and co-workers have shown that methanol can adsorb both molecularly and dissociatively.^{8,9} In the latter case, methanol reacts with Ti-O-Ti bonds to form $\text{Ti-OCH}_3/\text{Ti-OH}$ pairs. During temperature-programmed desorption (TPD), methanol and water desorb from the catalyst at temperatures below 600 K due to the recombination of $\text{Ti-OCH}_3/\text{Ti-OH}$ and Ti-OH/Ti-OH pairs, respectively. At temperatures above 600 K, small amounts of formaldehyde, dimethylether, methane, carbon monoxide, and carbon dioxide are produced via a variety of reactions involving

Ti-OCH_3 species. Henderson and co-workers and Vohs and co-workers have conducted similar studies on single-crystal $\text{TiO}_2(110)$ surfaces.^{10,11} Both groups found that only methanol desorbed into the gas phase during temperature-programmed desorption (TPD); however, Henderson and co-workers did observe the formation of small amounts of formaldehyde when the $\text{TiO}_2(110)$ surface was first dosed with O_2 . Vohs and co-workers also examined the interactions of methanol with vanadia dispersed on a $\text{TiO}_2(110)$ surface. In this case, a small amount of formaldehyde was observed in addition to desorption of methanol. Similar studies have been conducted more recently by Wang and Madix.¹² These authors observed the desorption of methanol at 410 K and the formation of a very small amount of formaldehyde at 650 K following methanol absorption onto a $\text{TiO}_2(110)$ surface. Predosing the surface with oxygen prior to the adsorption of methanol resulted in the formation of a second methanol peak at 650 K and a significant enhancement in the production of formaldehyde. The addition of submonolayer quantities of vanadia onto the titania surface led to a decrease in the amount of methanol adsorbed and to a shift in the peak temperature for formaldehyde formation to lower values.

The objective of this study was to investigate the mechanism of methanol oxidation to formaldehyde catalyzed by isolated vanadate species supported on titania. Raman spectroscopy, infrared spectroscopy, and XANES were used to characterize the catalyst, and in-situ infrared spectra acquired during temperature-programmed desorption (TPD), temperature-programmed oxidation (TPO), and temperature-programmed reaction (TPRx) were used to determine reaction intermediates leading to the formation of formaldehyde as well as other products observed in the gas phase. These studies show that while titania will adsorb methanol and promote its oxidation to formaldehyde, the introduction of isolated vanadate species onto the support greatly enhances the rate of formaldehyde formation.

* Corresponding author. E-mail: alexbell@berkeley.edu.

It is also found that the presence of vanadate groups on the surface of titania enhances the reactivity of Ti–OCH₃ groups relative to what is observed in the absence of vanadia.

Experimental Methods

Vanadium oxide was deposited onto anatase (Aldrich, 99.7%) by chemical vapor deposition. Vanadium acetylacetonate [VO(acac)₃] (Aldrich, 98%) and TiO₂ were mixed in a mortar and pestle and then placed inside a quartz reactor. The mixture was heated to 513 K at 5 K min^{−1} in N₂ flowing at 30 cm³ min^{−1} and then held at this temperature for 3 h to ensure complete reaction. The gas flow was changed to zero-grade air flowing at 100 cm³ min^{−1}, and the material was calcined at 773 K for 17 h. The loading of V was determined to be 1.6 wt % by ICP.

The BET surface area of the sample was measured using an Autosorb-1 instrument. Prior to carrying out N₂ adsorption/desorption measurements, each sample (50 mg) was outgassed for 16 h at 393 K. Using the five-point BET method, the surface area was calculated to be 97 m²/g. Based on this surface area, the surface density of vanadium is 2.0 V/nm², which is well below the level of 7 V/nm² at which isolated vanadate groups begin to form polyvanadate species and V₂O₅ crystallites.¹³

Raman spectra were recorded using a Kaiser Optical HoloLab series 5000 Raman spectrometer equipped with a Nd:YAG laser that is frequency-doubled to 532 nm. The laser was operated at a power level of 20 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 5000 psi and placed within a rotary quartz Raman cell. The samples were rotated at 100 rpm during the measurements to reduce the effects of sample heating by the laser.

Infrared spectra were recorded using a Thermo-Nicolet NEXUS 670 FT-IR equipped with an MCT-A detector. Spectra were recorded with a resolution of 2 cm^{−1}, with 32 scans averaged for each spectrum. Samples (40 mg) were pressed into 20 cm diameter pellets at 10 000 psi and placed within a low dead volume in-situ infrared cell, containing CaF₂ windows, capable of reaching temperatures up to 773 K.

Pulsed-adsorption of methanol was performed to determine the amount of methanol adsorbed on TiO₂ and V/TiO₂. For these experiments, ~40 mg of catalyst was placed into a quartz microreactor. The reactor was flushed with UHP He and then heated to 323 K. Methanol was introduced by flowing UHP He through a methanol-filled bubbler maintained at 293 K. The methanol/He mixture was passed through a six-way valve to which was attached a 0.49 cm³ dosing volume held at 338 K. Under these conditions, the amount of methanol in each pulse was 2.28 μmol. The exit stream from the microreactor was monitored by a mass spectrometer to quantify the methanol leaving the reactor during each pulse. Pulses of methanol were supplied to the reactor until three successive pulses of equal size were observed. The total amount of methanol adsorbed, N_{MeOH} , was calculated by the equation:

$$N_{\text{MeOH}} = N_{\text{MeOH}}^0 (nA_{\text{max}} - \sum_{i=1}^n A_i) / nA_{\text{max}} \quad (1)$$

where N_{MeOH}^0 is the amount of methanol in each pulse, n is the total number of pulses, A_{max} is the average area of the three successive pulses measured at the point of adsorbent saturation, and A_i is the area of the i th pulse of methanol observed by the mass spectrum.

Temperature-programmed desorption, oxidation, and reaction experiments (TPD, TPO, and TPRx, respectively) were carried out in both the infrared cell and a quartz microreactor. Methanol was adsorbed from a mixture of 4% methanol in helium flowing at 30 cm³ min^{−1}. A catalyst sample weighing ~40 mg was exposed to the methanol-containing gas at 323 K for 3 min. A short exposure time was used to minimize the loss of vanadium from the catalyst.⁷ Following adsorption, the reactor was purged with a flow of 100 cm³ min^{−1} of He for at least 45 min to remove any residual gas-phase methanol. For TPD experiments, the samples were then heated in He flowing at 30 cm³ min^{−1}, whereas for TPO experiments, the samples were heated in a 5% O₂/He mixture flowing at 30 cm³ min^{−1}. For TPRx experiments, the samples were exposed to a mixture of 6% MeOH/12% O₂/He flowing at 30 cm³ min^{−1}. For all three types of experiment, the temperature was ramped from 323 to 773 K at 4 K/min. Infrared spectra were collected every 75 s to obtain a scan every 5 K. The effluent from both the infrared cell and the microreactor was analyzed by an MKS Mini-Lab quadrupole mass spectrometer. Data were collected for 27 masses every 7.5 s. Response factors and fragmentation patterns were determined for H₂, H₂O, O₂, CO, CO₂, CH₃OH, CH₂O, CH₃OCH₃, and CH₄ relative to the He signal, which was used as an internal standard, and the values were adjusted to account for the isotopic abundance of both carbon and oxygen. Because the fragmentation pattern of methanol, formaldehyde, oxygen, and carbon monoxide produces overlapping peaks in the range of $m/e = 28$ –33, a matrix deconvolution procedure was used to quantify the gas-phase contributions of each species. After analysis, the data were smoothed using adjacent-averaging of 15 points.

X-ray absorption (XAS) measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 2-3. These 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 5465 eV. The optimal sample amount was calculated on the basis of the weight fraction of all atomic species to obtain an absorbance of ~2.5, with boron nitride added if necessary to make a stable pellet. Samples were placed in a controlled-atmosphere cell that allowed for heating to 823 K in the presence of flowing gas.¹⁴ The V/TiO₂ sample was pretreated for 2 h at 773 K in 10% O₂/He flowing at 30 cm³ min^{−1}. 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.

The software program IFEFFIT, along with its complementary GUIs Athena and Artemis, were used for the data analysis.^{15,16} First, a linear pre-edge was subtracted from the data, fit to the range of −150 to −75 eV relative to the edge energy. Next, a quadratic polynomial fit to the range of 100–300 eV, relative to the edge energy, was used to determine the postedge line. The difference between the two lines at the edge energy was set to 1 to normalize the data.

Results and Discussion

Catalyst Characterization. Figure 1 shows the Raman spectra for both TiO₂ and V/TiO₂ after dehydration in synthetic air at 773 K for 2 h. The sharp peaks at 146, 197, 397, 516, and 640 cm^{−1}, as well as the small peak at 800 cm^{−1}, are present in both the pure TiO₂ and the V/TiO₂ samples and are attributed to vibrations of the anatase crystal lattice.¹⁷ Upon addition of vanadium, a new broad band centered at 1025 cm^{−1} appears. This band is attributed to V=O symmetric stretching vibrations

Figure 1. Raman (A) and infrared (B) spectra of V/TiO₂ (black) and TiO₂ (red) after dehydration in dry air at 773 K for 2 h. Inset in Raman plot shows the difference between V/TiO₂ and TiO₂ in the region between 900 and 1075 cm⁻¹.

in isolated VO₄ units on anatase.^{6,18} Also shown in Figure 1 is the infrared spectrum of V/TiO₂ taken after dehydration. The peak at 2051 cm⁻¹, which is not observed for TiO₂, is assigned to the overtone of the symmetric stretch of V=O in isolated VO₄ units of the support.^{5,19} The absence of Raman peaks at 995, 704, 529, 288, and 147 cm⁻¹ and infrared bands at 1970 and 2012 cm⁻¹ indicates that the sample does not contain any nanocrystals of V₂O₅.

X-ray absorption experiments were performed to identify the oxidation state and local structure of the vanadium centers dispersed on the anatase. Figure 2 shows the normalized XANES spectrum of V/TiO₂ after calcination. XANES spectra for NaVO₃ and V₂O₅ are also shown for reference. For calcined V/TiO₂, the edge energy is 5484.3 eV. This value lies between the edge energies for V⁵⁺ in NaVO₃ at 5483.5 eV and V₂O₅ at 5484.8 eV, strongly suggesting that after calcination the oxidation state of the V/TiO₂ is +5.

Vanadium in NaVO₃ has tetrahedral symmetry, whereas the V in V₂O₅ has square planar or distorted octahedral symmetry. The height of the pre-edge peak at 5470 eV can be used to determine the coordination of the vanadium atom if the standards and samples have the same formal oxidation state and the same ligands in the first coordination shell. This peak is attributed to electron transitions from the vanadium 1s to 3d level,²⁰ which are spin forbidden and therefore should be weak. However, when the geometry around the vanadium atom becomes noncentrosymmetric, mixing between the oxygen 2p and the vanadium 3d levels can occur, leading to an increase in the observed

Figure 2. Normalized XANES spectra of (a) NaVO₃, (b) V₂O₅, and (c) V/TiO₂.

intensity. This means that a purely octahedral geometry will have almost no pre-edge feature, whereas tetrahedrally coordinated V will have a large pre-edge feature. Based on a comparison to the geometry of the standards, the calcined V/TiO₂ has a distorted tetrahedral geometry similar to that of NaVO₃.

Interactions of Methanol with TiO₂. The infrared spectrum of TiO₂ taken during methanol adsorption is shown in Figure 3. Upon methanol exposure, new features appear at 1440, 1460, 1640, 2822, 2833, 2922, and 2946 cm⁻¹. After purging in He to remove gas-phase methanol, the intensities of the features at 1460, 2833, and 2946 cm⁻¹ diminish continually, suggesting that these features are due to molecularly adsorbed methanol. These species are likely formed by the reaction of methanol with Lewis acid centers on the surface of anatase. The peaks at 1440, 2822, and 2922 cm⁻¹ do not change in intensity during the He purge and are therefore assigned to surface methoxide groups on the titania surface.²¹ The methoxide species are formed by the reaction of methanol with Ti–O–Ti linkages to form Ti–OCH₃/Ti–OH pairs. It was also observed that the isolated hydroxyl groups, characterized by a sharp peak at 3660 cm⁻¹, disappeared upon methanol adsorption and that a broad feature between 3100 and 3400 cm⁻¹ appeared. This feature has been attributed to hydrogen-bonding surface hydroxyl groups.²² The peak observed at 1640 cm⁻¹ is attributed to a small amount of water in the gas phase that was removed from the sample during the addition of methanol.

Infrared spectra recorded during the TPD of methanol adsorbed on TiO₂ are presented in Figure 4, and assignments of the observed bands are given in Table 1. The intensities of the Ti–OCH₃ bands are seen to decrease monotonically as the temperature increases and the positions of the bands shift to higher wavenumbers, due likely to the decrease in hydrogen bonding as the surface coverage is decreased. There are no residual methoxide species present on the surface at 773 K, indicating that all of the adsorbed methoxide species have been removed by this temperature.

As seen in Figure 5, the primary products observed below 500 K during the TPD of methanol adsorbed on anatase are CH₃OH and H₂O. The release of CH₃OH is attributed to desorption of the small amount of molecularly adsorbed CH₃OH and to recombination of Ti–OCH₃/Ti–OH pairs. The formation of H₂O is ascribed to the condensation of pairs of Ti–OH groups and leads to an increase in the ratio of Ti–OCH₃ to Ti–OH groups remaining on the surface of anatase above 500 K. A very broad formaldehyde peak is also observed in the TPD spectrum below 500 K, which may be formed by

Figure 3. Low and high wavenumber infrared spectra of TiO₂ taken during methanol adsorption at 323 K and subsequent He purge. (a) After 1 min in methanol, (b) after 3 min in methanol, (c) after He purge for 2 min, and (d) after He purge for 45 min.

transfer of a proton from a Ti–OCH₃ group to form CH₂O and a Ti–H group. The reaction of this surface hydride with a Ti–OH group could also contribute to the formation of H₂O, creating an oxygen vacancy at the surface of anatase. CH₃OH and H₂O continue to desorb above 500 K but are now accompanied by additional products. DME appears above 500 K, CH₄ and CO appear above 575 K, and H₂ appears above 600 K. The formation of DME is attributable to the condensation of two Ti–OCH₃ groups, whereas the formation of CH₄ is ascribed to the reaction of Ti–OCH₃ groups with Ti–H groups. The Ti–H groups required for the formation of CH₄ most likely come from the decomposition of isolated Ti–OCH₃ groups, a process which would also release CO. Finally, the formation of H₂ is likely due to the reaction of pairs of Ti–H groups. The products formed in the present study and the temperatures of their appearance are very similar to those reported by Kim et al.⁸ for methanol adsorbed on low-surface area anatase.

Assuming that the infrared absorption coefficients for C–H stretching vibrations associated with molecularly adsorbed CH₃OH and Ti–OCH₃ groups are the same, it is estimated that following a He purge at 323 K for 45 min, 90% of the methanol

Figure 4. Low and high wavenumber infrared spectra of TiO₂ taken during TPD of adsorbed methanol. Flow rate of He: 30 cm³ min⁻¹. (a) 323 K, (b) 373 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, (g) 623 K, (h) 673 K, (i) 723 K, (j) 773 K.

Figure 5. Gas-phase concentrations observed during TPD of methanol adsorbed on TiO₂. Flow rate of He: 30 cm³ min⁻¹. Methanol-black, formaldehyde-green, water-pink, carbon monoxide-blue, hydrogen-gold, methane-navy, dimethylether-purple.

adsorbed on anatase is in the form of Ti–OCH₃ and 10% is in the form of molecularly adsorbed CH₃OH. The total amount of methanol adsorbed at 323 K can be determined from the amount of carbon removed from the catalyst during TPD or TPO. Table 2 shows that this amount corresponds to ~2.6 molecules of CH₃OH/nm², in very close agreement with the amount of adsorbed CH₃OH determined from pulsed adsorption measurements. The surface concentration of methanol observed in the

TABLE 1: Assignment of Infrared Bands Detected on the Surface of Anatase and V/TiO₂^a

	Ti—OCH ₃	V—OCH ₃	ads. CH ₃ OH
δ C—H	1440–1443	1435–1436	1460–1463
ν_{asym} O—C—O	1570	1575 (TPD) 1555 (TPO)	
ν_{sym} C—H	2819–2833	~2832	2833–2850
ν_{asym} C—H	2921–2932	2929–2939	2945–2956

^a A range is given for each assignment due to the shift in the peak positions at different temperatures or surface coverages.

present study is only slightly less than the value of 3.14 molecules of CH₃OH/nm² reported by Kim et al.⁸ for anatase having a surface area of 10.3 m²/g. From these measurements, it is calculated that ~48% of the surface Ti atoms are involved with the dissociative adsorption of methanol to form Ti—OCH₃/Ti—OH pairs.²³ The total amount of H present in all desorbing species is approximately 4 times that of the total amount of C present in all of the desorbing species, indicating that all of the C and H in the desorbing products originate from adsorbed CH₃OH. However, the total amount of O present in all desorbing species, 2.79 O/nm², is somewhat greater than the amount of O associated with the adsorbed CH₃OH, 2.62 O/nm², indicating that during TPD 0.17 O/nm² are abstracted from the surface of anatase.

Infrared spectra recorded during the TPO of methanol adsorbed on TiO₂ are shown in Figure 6, and the composition of gas-phase species produced during this process is presented in Figure 7. Comparison of Figures 5 and 7 reveals that below 500 K the TPO spectrum of CH₃OH adsorbed on anatase is very similar to the corresponding TPD spectrum. Here too CH₃OH and H₂O are observed as the principal desorption products, together with a small amount of CH₂O. The principal differences between the TPO and TPD spectra occur above 500 K. The formation of DME during TPO begins above 500 K, and reaches a maximum at 580 K similar to DME formation during TPD, but the total amount of DME is only about 30% of that observed during TPD. However, over this temperature range large amounts of CO and H₂O are observed, which very likely are formed by combustion of nascent DME. The higher concentration of H₂O in the temperature interval of 500–600 K observed during TPO than TPD appears to contribute to a burst in the formation of CH₃OH as a result of hydrolysis of some isolated Ti—OCH₃ groups. Above 600 K the remaining Ti—OCH₃ groups undergo combustion to form CO and H₂O. Some H₂ is also observed, but there is no evidence for methane formation during TPO.

The infrared spectrum taken during TPO (Figure 6) shows a broad feature at 1575 cm⁻¹. This band, which first appears at 523 K and then disappears above 673K, is attributed to the formation of formate species on the surface of TiO₂.²⁴ Because these formate species were not observed during TPD, it is likely that they are formed by the oxidation of surface methoxide

species in the presence of gas-phase oxygen and are likely intermediates in the formation of CO and H₂O above 600 K. As in the case of TPD, the ratio of H/C in the product formed during TPO is again close to 4, indicating that all of the C and H appearing in the products arises from adsorbed CH₃OH. However, during TPO the O/C ratio of the desorbing products is 1.8, indicating that 0.8 O/C is obtained from O₂. It is also noted that during TPD and TPO approximately 40% of the adsorbed methanol desorbs as CH₃OH.

Infrared spectra recorded during the TPRx of methanol adsorbed on TiO₂ are shown in Figure 8, and the composition of gas-phase species produced during this process is shown in Figure 9. A mixture of 6% MeOH/12% O₂/balance He was flowed over the catalyst as the temperature was ramped from 373 to 773 K. A comparison of Figures 6 and 8 shows that the infrared features are nearly the same as those observed during TPO, indicating that surface formate species are present during TPRx at temperatures between 473 and 673 K. This suggests that the same surface processes occur during both TPO and TPRx. Under TPRx conditions, products are not produced at a significant rate below 475 K. Between 475 and 580 K, the main products are DME and CH₂O, with mainly CH₂O formed initially and DME being formed in preference to CH₂O above 565 K. Above 580 K CO is formed at an increasingly rapid rate. The formation of DME reaches a maximum at about 685 K and CH₂O at about 720 K. The formation of H₂O begins at 475 K and accelerates once the formation of DME reaches a maximum. The trends seen in Figure 9 are very similar to those observed during TPO seen in Figure 7. Both sets of data and the TPD spectrum shown in Figure 5 indicate that anatase is a poor catalyst for the formation of CH₂O from Ti—OCH₃ groups but a better catalyst for the condensation of these groups to DME. However, at temperatures above 700 K, both unreacted Ti—OCH₃ groups and DME undergo complete combustion to form CO, CO₂, and H₂O.

Interactions of Methanol with V/TiO₂. Figure 10 shows infrared spectra taken during the adsorption of methanol on V/TiO₂. The peaks at 2841 and 2950 cm⁻¹ disappear rapidly during the He purge and are, therefore, assigned to gas-phase methanol or very weakly physisorbed methanol. The bands that remain after the He purge are at 1434, 1449, 2827, 2850, 2922, 2932, and 2956 cm⁻¹. The peak at 2922 cm⁻¹ was previously observed on pure TiO₂ and has been assigned to Ti—OCH₃ groups. Consequently, the feature at 2932 cm⁻¹ is assigned to asymmetric C—H vibrations of V—OCH₃ groups formed by the addition of CH₃OH across V—O—Ti bonds.²⁵ The band observed at 2827 cm⁻¹ is likely due to symmetric C—H vibrations associated with both Ti—OCH₃ and V—OCH₃ groups. Vibrations were observed for Ti—OCH₃ groups at 2822 cm⁻¹, whereas Wachs and co-workers⁵ have observed a band for V—OCH₃ groups at 2832 cm⁻¹ on a monolayer V/TiO₂. The loss of the peak at 3660 cm⁻¹ for isolated Ti—OH species during methanol addition, along with the formation of a broad feature

TABLE 2: Total Amounts of Each Product Released into the Gas Phase during TPD and TPO of Methanol Adsorbed on TiO₂ and V/TiO₂^a

		CH ₃ OH	CH ₂ O	CO	CO ₂	H ₂ O	H ₂	CH ₄	DME	total C	total H	total O	MeOH adsorbed
TiO ₂	TPD	1.02	0.22	0.37	0	0.92	0.18	0.49	0.26	2.62	10.27	2.79	2.60
TiO ₂	TPO	1.07	0.31	0.88	0.19	2.13	0.16	0	0.11	2.66	10.14	4.87	2.62
V—TiO ₂	TPD	0.46	0.26	0.83	0.10	1.78	0.30	0.21	0.06	1.97	7.70	3.59	1.73
V—TiO ₂	TPO	0.59	0.32	1.00	0.18	2.32	0	0	0	2.09	7.63	4.59	1.93

^a Also shown are the total amounts of carbon, hydrogen, and oxygen removed from the surface based on the species observed in the gas phase. The right-hand-most column is the amount of methanol adsorbed on the surface based on the methanol pulsing experiments. All quantities are in atoms/nm².

Figure 6. Low and high wavenumber infrared spectra of TiO_2 taken during TPO of adsorbed methanol. Flow rate of $5\% \text{O}_2/\text{He}$: $30 \text{ cm}^3 \text{ min}^{-1}$. (a) 323 K, (b) 373 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, (g) 623 K, (h) 673 K, (i) 723 K, (j) 773 K.

Figure 7. Gas-phase concentrations observed during TPO of methanol adsorbed on TiO_2 . Flow rate of $5\% \text{O}_2/\text{He}$: $30 \text{ cm}^3 \text{ min}^{-1}$. Left axis: methanol-black, formaldehyde-green, water-pink, carbon monoxide-blue, carbon dioxide-light blue, hydrogen-gold, dimethylether-purple. Right axis: oxygen-red.

from 3100 to 3400 cm^{-1} , is attributed to the formation of hydrogen-bonding hydroxyl groups on the surface, as was observed for TiO_2 (see above).

The infrared spectra presented in Figure 10 show that methanol adsorption on anatase containing 2 V atom/nm^2 occurs in three modes: as adsorbed CH_3OH , as $\text{Ti}-\text{OCH}_3/\text{Ti}-\text{OH}$ pairs, and as $\text{V}-\text{OCH}_3/\text{Ti}-\text{OH}$ pairs. While the formation of $\text{V}-\text{OH}/\text{Ti}-\text{OCH}_3$ pairs might also be considered, theoretical calculations suggest that the formation of $\text{V}-\text{OCH}_3/\text{Ti}-\text{OH}$

Figure 8. Low and high wavenumber infrared spectra of TiO_2 taken during TPRx in $6\% \text{MeOH}/12\% \text{O}_2/\text{He}$ flowing at $30 \text{ cm}^3 \text{ min}^{-1}$. (a) 373 K, (b) 423 K, (c) 473 K, (d) 523 K, (e) 573 K, (f) 623 K, (g) 673 K, (h) 723 K, (i) 773 K.

Figure 9. Gas-phase concentrations observed during TPRx of TiO_2 in $6\% \text{MeOH}/12\% \text{O}_2/\text{He}$ flowing at $30 \text{ cm}^3 \text{ min}^{-1}$. Methanol-black, oxygen-red, formaldehyde-green, water-pink, carbon monoxide-blue, carbon dioxide-light blue, hydrogen-gold, dimethylether-purple.

pairs is strongly preferred thermodynamically.²⁶ As in the case of anatase alone, about 90% of the adsorbed methanol is present as methoxide groups and only 10% as molecularly adsorbed CH_3OH . Table 2 shows that the total amount of methanol adsorbed on V/TiO_2 is less than that adsorbed on TiO_2 alone, ~ 1.9 molecules of $\text{CH}_3\text{OH}/\text{nm}^2$ as compared to 2.6 molecules of $\text{CH}_3\text{OH}/\text{nm}^2$. The lower surface concentration of adsorbed methanol on V/TiO_2 in comparison to TiO_2 can be explained

Figure 10. Low and high wavenumber infrared spectra of V/TiO₂ taken during methanol adsorption at 323 K and subsequent He purge. (a) After 1 min in methanol, (b) after 3 min in methanol, (c) after He purge for 2 min, and (d) after He purge for 45 min.

as follows. TiO₂ contains 10.8 Ti sites/nm², and hence, it can be shown that there are also 10.8 O atoms/nm² in Ti–O–Ti bonds on the surface of anatase. The introduction of 2.0 V atoms/nm² as isolated VO₄ species, each of which grafts to 3 O atoms on the surface, reduces the surface concentration of O atoms in Ti–O–Ti bonds to 4.8 O atom/nm². If it is assumed that only one V–O–Ti bond per V center is able to react with methanol and that only 48% of the Ti–O–Ti and V–O–Ti bonds undergo methanolysis, the same percentage observed on anatase, then the predicted surface coverage of all methoxide species (both Ti–OCH₃ and V–OCH₃) is predicted to decrease from 2.6 methoxide species/nm² for TiO₂ to 2.1 methoxide species/nm² for V/TiO₂, in reasonable agreement with what is seen in Table 2. Using the same assumptions leads to the expectation of approximately equivalent concentrations of Ti–OCH₃ and V–OCH₃, which also matches what is seen by infrared spectroscopy at 323 K after He purge (see Figure 10).

Infrared spectra recorded during TPD of methanol adsorbed on V/TiO₂ are presented in Figure 11. With increasing temperature, the bands for Ti–OCH₃ groups diminish more rapidly than those for V–OCH₃ groups. At temperatures between 423 and 673 K, a sharp peak appears at 1575 cm^{−1} along with four overlapping bands in the region between 1340 and 1400 cm^{−1} and two weak bands at 2880 and 2898 cm^{−1}. These peaks are assigned to surface formate species. The band at 1575 cm^{−1} is similar to that observed at 1570 cm^{−1} during TPO on TiO₂. The weak bands in the 1340–1400 cm^{−1} region are only observed on V/TiO₂ due to the large concentration of formate

Figure 11. Low and high wavenumber infrared spectra of V/TiO₂ taken during TPD of adsorbed methanol. Flow rate of He: 30 cm³ min^{−1}. (a) 323 K, (b) 373 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, (g) 623 K, (h) 673 K, (i) 723 K, (j) 773 K.

Figure 12. Gas-phase concentrations observed during TPD of methanol adsorbed on V/TiO₂. Flow rate of He: 30 cm³ min^{−1}. Methanol-black, formaldehyde-green, water-pink, carbon monoxide-blue, carbon dioxide-light blue, hydrogen-gold, methane-navy, dimethylether-purple.

species present under these conditions, and decrease in intensity at the same rate as the large band at 1575 cm^{−1}.

Comparison of the TPD spectrum for methanol adsorbed on V/TiO₂, shown in Figure 12, with that for TiO₂, shown in Figure 5, reveals several significant differences. While CH₃OH and H₂O both appear in the gas phase at temperatures above 350 K, the rates at which these products are formed are lower when isolated vanadate species are present on the surface of the

support. It is also evident that in this case a well-defined peak of CH_2O appears at about 410 K. This low-temperature peak is attributed to the reaction of $\text{V}-\text{OCH}_3$ species, because it was not observed during TPD of methanol adsorbed on TiO_2 . Theoretical studies have shown that CH_2O is formed by transfer of an H atom from the methyl group of $\text{V}-\text{OCH}_3$ to the $\text{V}=\text{O}$ bond associated with the same V atom.^{26–28} The decrease in production of CH_2O above 425 K coincides with a rapid increase in the appearance of CO and H_2O , suggesting that the latter products are formed by the decomposition and partial combustion of CH_2O . The mechanisms for these processes were not studied as a part of the present investigation; however, Raskó et al.²⁹ have shown that formaldehyde will decompose under similar conditions. The coincidence of CO formation with the appearance of an intense formate band at 1575 cm^{-1} (see Figure 11) supports the hypothesis that formate species formed by the adsorption of CH_2O are intermediates along the path to CO and H_2 .

With further increase in temperature, a small DME peak appears along with large peaks for CO, CH_4 , and H_2 . The DME peak appears at the same temperature on V/TiO_2 during TPD as on TiO_2 , suggesting that this product is formed exclusively by the condensation of two $\text{Ti}-\text{OCH}_3$ groups. The reason for the observed decrease in DME formation is due to both a decrease in the amount of $\text{Ti}-\text{OCH}_3$ species present on the surface and a rapid decomposition and combustion of $\text{Ti}-\text{OCH}_3$ species in the presence of supported vanadate groups. The temperature at which CH_4 is formed on V/TiO_2 is significantly lower than that seen for TiO_2 alone, 575 K versus 650 K. While the exact origin of CH_4 in this case is not clear, a possible source is the decomposition of DME or the reaction of $\text{Ti}-\text{OCH}_3$ groups with H atoms released during the decomposition of DME. It is also notable that the total amount of H_2O produced during the TPD of adsorbed methanol on V/TiO_2 is nearly twice that observed in the TPD spectrum for methanol adsorbed on TiO_2 . Consistent with this, Table 2 shows that the total amount of O atoms present in the products of TPO from V/TiO_2 is 1.8 times that contained in the methanol initially adsorbed. Because, as noted above, TiO_2 is a poor source of O, this observation suggests that $1.6\text{ O}/\text{nm}^2$ are taken from the supported vanadate species, of which there are $2.0\text{ V}/\text{nm}^2$. Therefore, during the TPD of methanol adsorbed on V/TiO_2 , 80% of the V^{5+} in isolated vanadate species is reduced to V^{3+} .

Infrared spectra recorded during the TPO of methanol adsorbed on V/TiO_2 are presented in Figure 13, and the composition of the gas phase is presented in Figure 14. Figure 13 shows that the loss of both $\text{Ti}-\text{OCH}_3$ and $\text{V}-\text{OCH}_3$ surface species occurs at much lower temperatures than is seen during TPD (compare with Figure 11) and that nearly all of the surface methoxide species are removed by 523 K. There are also two new features at 1350 and 1555 cm^{-1} formed at temperatures between 423 and 573 K, which are attributed to surface formate species. The feature at 1640 cm^{-1} , which is only observed at 473 K, is attributed to gas-phase H_2O , because this is the temperature where the H_2O desorption is maximized during TPO. The TPO spectrum of CH_3OH adsorbed on V/TiO_2 , shown in Figure 14, is much simpler than the corresponding TPD spectrum (Figure 12). As in the TPD spectrum, desorption of CH_3OH begins at 350 K. This process is accompanied by the immediate onset of CH_2O and H_2O formation at virtually equivalent rates. Above 425 K the rate of CH_2O formation reaches a maximum as CO now forms, and the rate of H_2O formation accelerates. Table 2 shows that the total amount of H_2O formed, $2.32\text{ H}_2\text{O}/\text{nm}^2$, agrees perfectly with that expected

Figure 13. Low and high wavenumber infrared spectra of V/TiO_2 taken during TPO of adsorbed methanol. Flow rate of $5\%\text{ O}_2/\text{He}$: $30\text{ cm}^3\text{ min}^{-1}$. (a) 323 K, (b) 373 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, (g) 623 K, (h) 673 K, (i) 723 K, (j) 773 K.

Figure 14. Gas-phase concentrations observed during TPO of methanol adsorbed on V/TiO_2 . Flow rate of $5\%\text{ O}_2/\text{He}$: $30\text{ cm}^3\text{ min}^{-1}$. Left axis: methanol-black, formaldehyde-green, water-pink, carbon monoxide-blue, carbon dioxide-light blue. Right axis: oxygen-red.

from the production of CH_2O and CO, assuming that the later product comes from the decomposition of CH_2O to CO and H_2 followed by the immediate combustion of H_2 to H_2O . The infrared spectra taken during TPO presented in Figure 13 show that the methoxide species present as $\text{Ti}-\text{OCH}_3$ react much more rapidly than those present as $\text{V}-\text{OCH}_3$. This suggests that most of the CH_3OH desorbed in the initial part of the TPO spectrum is due to the reaction of $\text{Ti}-\text{OCH}_3/\text{Ti}-\text{OH}$ pairs to form CH_3OH and $\text{Ti}-\text{O}-\text{Ti}$ bonds.

Figure 15. Scheme of catalytic cycle at isolated VO_4 species on TiO_2 showing the conversion of methanol to formaldehyde and water. Reoxidation of the catalyst does not occur during TPD.

A possible mechanism for the formation of CH_2O during the TPO of CH_3OH adsorbed on V/TiO_2 is shown in Figure 15. $\text{V}-\text{OCH}_3$ groups are shown as the source of CH_2O and H_2O . CO , CO_2 , and additional H_2O are then formed in secondary processes involving the decomposition and oxidation of CH_2O . The infrared spectra presented in Figure 13 are consistent with the idea that CO and CO_2 result from the secondary reaction of CH_2O . As seen in this figure, a strong formate band appears at 1555 cm^{-1} , reaches a maximum, and then disappears over the temperature range of $423\text{--}573\text{ K}$. This is the same temperature range over which the peaks for CO , CO_2 , and H_2O are observed in the TPO spectrum (Figure 14). A further point of interest is that in contrast to what is seen during the TPD of CH_3OH adsorbed on V/TiO_2 , no product peaks are observed above 550 K during TPO of adsorbed CH_3OH . This is very likely a consequence of the rapid reoxidation of V^{3+} to V^{5+} occurring at lower temperatures in the presence of gas-phase oxygen, enabling the complete conversion of $\text{V}-\text{OCH}_3$ groups to CH_2O , as well as increasing the rate of subsequent decomposition of CH_2O to CO and H_2O . The scheme shown in Figure 15 assumes that all of the CH_2O , CO , and CO_2 observed during the TPO of methanol adsorbed on V/TiO_2 originate from $\text{V}-\text{OCH}_3$ groups. This would suggest that 1.50 C atoms/nm^2 are present as $\text{V}-\text{OCH}_3$ groups at the start of TPO. However, this figure is larger than the value of 1.0 C/nm^2 determined on the basis of the total uptake of CH_3OH as $\text{V}-\text{OCH}_3$ groups (see above), which leads to the suggestion that during TPO methoxide groups attached to Ti atoms migrate across the support and are transferred to the vanadate groups via reverse spillover. This interpretation would also explain why the bands for $\text{Ti}-\text{OCH}_3$ species disappear from the infrared spectrum at lower temperatures for V/TiO_2 than for TiO_2 during TPO of adsorbed CH_3OH .

The positions of the formate band on V/TiO_2 observed during the TPD and TPO experiments are different. During TPD, the band is at 1575 cm^{-1} , but during TPO the band shifts to 1555 cm^{-1} . A possible reason for these differences is shown in Figure 16. During TPD, the formates are created by the reaction of CH_2O with V^{3+} centers produced during the formation of CH_2O , followed by the transfer of a hydrogen atom; however, in the presence of gas-phase oxygen, the vanadium is rapidly reoxidized, and the CH_2O would, therefore, be more likely to interact with V^{5+} centers. The formate species at the reoxidized vanadium centers are expected to be more active toward further oxidation, which would also explain both the large increase in the amount of CO and CO_2 formed during the TPO

experiment and the shift of all oxidation products to lower temperatures. Formates on reduced vanadium centers during the TPD experiment on V/TiO_2 are not as active toward decomposition to form CO and H_2O .

The results of TPRx on V/TiO_2 are illustrated in Figures 17 and 18. The infrared spectra recorded at reaction temperatures between 373 and 773 K , shown in Figure 17, are very similar to those shown in Figure 13 for the TPO of adsorbed methanol taken over the same temperature range. Here again, the $\text{Ti}-\text{OCH}_3$ species are observed to disappear first. It is also noted that the formation of formate species coincides with the onset of CO formation. However, a new feature is observed at 1612 cm^{-1} between 623 and 723 K , which is due to adsorbed H_2O . The formation of CH_2O and H_2O at equivalent rates was also observed during the TPRx of methanol over anatase. Below 475 K these are the only products formed, but above 475 K , the rates of CO and H_2O formation increase rapidly, as the rate of CH_2O formation passes through a maximum. These observations are consistent with the reaction sequence presented in Figure 15. Also notable is the absence of any evidence for the oxidation of methanol over TiO_2 , as can be concluded by comparison of the data presented in Figures 9 and 18.

A point of considerable interest is that $\text{Ti}-\text{OCH}_3$ species appear to be much more reactive on V/TiO_2 than on TiO_2 . This is clearly evident, for example, from a comparison of the infrared spectra observed during TPRx of $\text{CH}_3\text{OH}/\text{O}_2$ over TiO_2 and V/TiO_2 . During TPRx on TiO_2 , some $\text{Ti}-\text{OCH}_3$ species remain on the surface of the solid at 723 K . By contrast, the same species are removed completely by 523 K during the TPRx of $\text{CH}_3\text{OH}/\text{O}_2$ on V/TiO_2 . A definitive explanation for this phenomenon cannot be developed on the basis of the data obtained in this study. One possibility is that the methoxide groups associated with Ti cations diffuse along the catalyst surface until they come into proximity with supported vanadate groups leading to the formation of CH_2O . This would lead to a reverse spillover of the methoxide groups from Ti to V, similar to the results proposed by Seman and Oyama³⁰ for Mo/SiO_2 and Chen and Falconer³¹ for $\text{Ni}/\text{Al}_2\text{O}_3$. Another possibility is that, in the absence of vanadate species, the formation of anionic vacancies in TiO_2 leads to a stabilization of the remaining methoxide groups in the form of structures in which the O atom of the methoxide bridges between two Ti cations. Such bridging methoxide groups would then be stable until they began to condense and form DME or undergo other reactions leading to CH_4 and H_2 . In the presence of O_2 such bridging methoxide groups would oxidize to form CO and H_2O . When vanadate species are present on the surface of TiO_2 , these species can undergo reduction to form $\text{V}(-\text{OTi})_3$ species. A recent theoretical study has shown that the latter species can readily adsorb O_2 .²⁷ Migration of one of the O atoms of the newly formed peroxo group into TiO_2 could then result in the removal of an oxygen anion defect in the support. Under this hypothesis, the removal of anionic defects in TiO_2 would restore the reactivity of $\text{Ti}-\text{OCH}_3$ groups on the surface of the support so that they could desorb as methanol by condensation with $\text{Ti}-\text{OH}$ groups. This interpretation would require, though, for defects to have a long-range effect, since work by Henderson and co-workers has shown that 8% of the surface of TiO_2 had defects in the absence of O_2 and 2% in the presence of O_2 .¹⁰ Attempts to develop a clearer understanding of the role of vanadate species on the reactivity of $\text{Ti}-\text{OCH}_3$ species are currently in progress.

The TPRx data presented in Figure 18 were analyzed to determine the apparent first-order rate coefficient for formaldehyde formation. To this end, the natural logarithm of the rate

Figure 16. Possible reaction pathways to explain the presence of formates on the surface. The first pathway is for TPD on V/TiO₂, and the second pathway is for TPO on V/TiO₂.

Figure 17. Low and high wavenumber infrared spectra of V/TiO₂ taken during TPRx in 5%MeOH/12%O₂/He flowing at 30 cm³ min⁻¹. (a) 373 K, (b) 423 K, (c) 473 K, (d) 523 K, (e) 573 K, (f) 623 K, (g) 673 K, (h) 723 K, (i) 773 K.

of formaldehyde formation was plotted versus inverse temperature. The apparent activation energy calculated from the slope of the line is 16 kcal/mol, and the apparent preexponential factor is $5.3 \times 10^6 \text{ atm}^{-1} \text{ s}^{-1}$. The values of these parameters can be compared with those obtained by similar means for methanol oxidation to formaldehyde occurring on isolated vanadate species supported on silica. In that case, the apparent activation

Figure 18. (A) Gas-phase concentrations observed during TPRx of V/TiO₂ in 5%MeOH/12%O₂/He flowing at 30 cm³ min⁻¹. Methanol-black, oxygen-red, formaldehyde-green, water-pink, carbon monoxide-blue, carbon dioxide-light blue. (B) An Arrhenius plot for the formaldehyde formation.

energy is 23 kcal/mol and the apparent preexponential factor is $2.3 \times 10^7 \text{ atm}^{-1} \text{ s}^{-1}$.⁷ Based on these values, the specific activity of V/TiO₂ is 6.5×10^2 times higher than that of V/SiO₂ at 450 K. This ratio of activities is on the same order of magnitude as that reported by Wachs and co-workers.¹ What remains to be established, though, is whether the significantly higher activity of V/TiO₂ is due solely to the intrinsic effect of the support on

the activity of the isolated vanadate units or, alternatively, to oxygen vacancies on the anatase surface or reverse spillover of methoxide species from the support. A theoretical effort is currently being undertaken to identify the role of each factor. It should be noted that an earlier theoretical study of methanol oxidation catalyzed by vanadate species supported on silica and titania showed the apparent activation energy to be 3 kcal/mol higher for isolated vanadates species supported on titania than on silica.²⁶ This suggests that another mechanism, such as reverse spillover to the vanadate species, may be responsible for the increased activity of titania-supported vanadia.

Conclusions

The interactions of methanol with TiO₂ (anatase) and V/TiO₂ (2 V/nm²) were investigated by a number of techniques. Methanol adsorbs on TiO₂ both molecularly and by addition across Ti–O–Ti bonds to form Ti–OCH₃/Ti–OH pairs. Upon heating in the absence of O₂, a portion of the Ti–OCH₃/Ti–OH pairs recombine to form CH₃OH, and H₂O is formed by the recombination of pairs of Ti–OH groups. At higher temperatures, Ti–OCH₃ groups react to form DME, CH₄, CO, and H₂. The decomposition and oxidation of Ti–OCH₃ groups to form CO, CO₂, and H₂O occur when heating is carried out in the presence of O₂. Evidence for V–OCH₃/Ti–OH pairs as well as Ti–OCH₃/Ti–OH pairs is seen when methanol is adsorbed on V/TiO₂. CH₂O is produced at low temperatures during heating of methanol adsorbed onto V/TiO₂ both in the presence and in the absence of O₂. This product appears to originate from V–OCH₃ groups formed either upon the adsorption of CH₃OH or by reverse spillover from methoxide groups present on the titania support. At higher temperatures, CH₂O adsorbs to form formate species, which then undergo decomposition to form CO and H₂, and in the presence of O₂ to form CO, CO₂, and H₂O. The activity of V/TiO₂ for the formation of CH₂O at 450 K is nearly 3 orders of magnitude higher than that of V/SiO₂. Most of the higher activity of V/TiO₂ is associated with the lower apparent activation energy for this catalyst (16 kcal/mol) relative to that for V/SiO₂ (23 kcal/mol).

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Portions of this research were carried out at the Stanford Synchrotron Radiation

Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

Supporting Information Available: Plots of the –OH stretching region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Deo, G.; Wachs, I. E. *J. Catal.* **1994**, *146*, 323.
- (2) Baltes, M.; Cassiers, K.; Van Der Voort, P.; Weckhuysen, B. M.; Schoonheydt, R. A.; Vansant, E. F. *J. Catal.* **2001**, *197*, 160.
- (3) Lim, S.; Haller, G. L. *Appl. Catal., A* **1999**, *188*, 277.
- (4) Olthof, B.; Khodakov, J.; Bell, A. T.; Iglesia, E. *J. Phys. Chem. B* **2000**, *104*, 1516.
- (5) Burcham, L. J.; Deo, G.; Gao, X.; Wachs, I. E. *Top. Catal.* **2000**, *11/12*, 85.
- (6) Deo, G.; Turek, A. M.; Wachs, I. E. *Appl. Catal., A* **1992**, *91*, 27.
- (7) Bronkema, J.; Bell, A. T. *J. Phys. Chem. C* **2007**, *111*, 420.
- (8) Kim, K. S.; Barteau, M. A.; Farneth, W. E. *Langmuir* **1988**, *4*, 533.
- (9) Kim, K. S.; Barteau, M. A. *Surf. Sci.* **1989**, *223*, 13.
- (10) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. *Faraday Discuss.* **1999**, *114*, 313.
- (11) Feng, T.; Vohs, J. M. *J. Catal.* **2002**, *208*, 301.
- (12) Wang, Q.; Madix, R. J. *Surf. Sci.* **2001**, *474*, 213.
- (13) Wachs, I. E.; Weckhuysen, B. M. *Appl. Catal., A* **1997**, *157*, 67.
- (14) Jentoft, R. E.; Deutsch, S. E.; Gates, B. C. *Rev. Sci. Instrum.* **1996**, *67*, 2111.
- (15) Newville, M. J. *Synchrotron Radiat.* **2001**, *8*, 322.
- (16) Ravel, B.; Newville, M. J. *Synchrotron Radiat.* **2005**, *12*, 537.
- (17) Ohsake, T.; Izumi, F.; Fujiki, Y. *J. Raman Spectrosc.* **1978**, *7*, 321.
- (18) Xie, S.; Iglesia, E.; Bell, A. T. *Langmuir* **2000**, *16*, 7162.
- (19) Chiker, F.; Nogier, J. Ph.; Bonardet, J. L. *Catal. Today* **2003**, *78*, 139.
- (20) Wong, J.; Lytle, F. W.; Messmer, R. P.; Maylotte, D. H. *Phys. Rev. B* **1984**, *30*, 5596.
- (21) Rossi, P. F.; Busca, G. *Colloids Surf.* **1985**, *16*, 95.
- (22) Araña, J.; Garriga i Cabo, C.; Doña-Rodríguez, J. M.; González-Díaz, O.; Herrera-Melián, J. A.; Pérez-Peña, J. *Appl. Surf. Sci.* **2004**, *239*, 60.
- (23) 10.8 Ti/nm² calculated on the basis of the Ti–Ti nearest neighbor distance on anatase.
- (24) Hayden, B. E.; King, A.; Newton, M. A. *J. Phys. Chem. B* **1999**, *103*, 203.
- (25) Burcham, L. J.; Wachs, I. E. *Catal. Today* **1999**, *49*, 467.
- (26) Khaliullin, R.; Bell, A. T. *J. Phys. Chem. B* **2002**, *106*, 7832.
- (27) Goodrow, A.; Bell, A. T. *J. Phys. Chem. C*, in press.
- (28) Döbler, J.; Pritzsche, M.; Sauer, J. *J. Am. Chem. Soc.* **2005**, *127*, 10861.
- (29) Raskó, J.; Kecskés, T.; Kiss, J. *J. Catal.* **2004**, *226*, 183.
- (30) Seman, M.; Kondo, N.; Domen, K.; Oyama, S. T. *Chem. Lett.* **2002**, *11*, 1082.
- (31) Chen, B.; Falconer, J. L. *J. Catal.* **1993**, *144*, 214.