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

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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 Ti–OCH$_3$/Ti–OH pairs, and (3) across V–O–Tl bonds to form V–OCH$_3$/Ti–OH pairs. Upon heating, two desorption peaks for CH$_2$OH and H$_2$O were observed on all samples below 500 K. Although TiO$_2$ produced small amounts of CH$_2$O, 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$_2$O. The apparent activation energy of V/TiO$_2$ for the formation of CH$_2$O is 16 kcal/mol.

Introduction

Isolated vanadate groups supported on metal oxides such as SiO$_2$, Al$_2$O$_3$, 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.$^3$ 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 Ti–OCH$_3$/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 Ti–OCH$_3$/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 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 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 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 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.
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)₂] (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⁻¹. 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.

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 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.

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. 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. 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. 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. Upon addition of vanadium, a new broad band centered at 1025 cm⁻¹ appears. This band is attributed to V=O symmetric stretching vibrations.
in isolated VO$_4$ units on anatase. Also shown in Figure 1 is Raman (A) and infrared (B) spectra of V/TiO$_2$ (black) and the infrared spectrum of V/TiO$_2$ taken after dehydration. The peak at 2051 cm$^{-1}$, which is not observed for TiO$_2$, is assigned to the overtone of the symmetric stretch of V=O in isolated VO$_4$ units of the support. 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 V$_2$O$_5$.

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/TiO$_2$ taken after dehydration. XANES spectra for NaVO$_3$ and V$_2$O$_5$ are also shown for reference. For calcined V/TiO$_2$, the edge energy is 5484.3 eV. This value lies between the edge energies for V$^{5+}$ in NaVO$_3$ at 5483.5 eV and V$_2$O$_5$ at 5484.8 eV, strongly suggesting that after calcination the oxidation state of the V/TiO$_2$ is +5.

Vanadium in NaVO$_3$ has tetrahedral symmetry, whereas the V in V$_2$O$_5$ 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, 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 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/TiO$_2$ has a distorted tetrahedral geometry similar to that of NaVO$_3$.

Interactions of Methanol with TiO$_2$.

The infrared spectrum of TiO$_2$ 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. The methoxide species are formed by the reaction of methanol with Ti–O–Ti linkages to form Ti–OCH$_3$/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.

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 TiO$_2$ are presented in Figure 4, and assignments of the observed bands are given in Table 1. The intensities of the Ti–OCH$_3$ 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 CH$_3$OH and H$_2$O. The release of CH$_3$OH is attributed to desorption of the small amount of molecularly adsorbed CH$_3$OH and to recombination of Ti–OCH$_3$/Ti–OH pairs. The formation of H$_2$O is ascribed to the condensation of pairs of Ti–OH groups and leads to an increase in the ratio of Ti–OCH$_3$ 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...
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. 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 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
formation of CH₃ OH as a result of hydrolysis of some isolated 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 CH₄. 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. However, the total amount of DME is only about 30% of that observed during TPD, indicating that all of the C in the 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.

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 673 K, is attributed to the formation of formate species on the surface of TiO₂. 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 CH₂OH.

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 CO₂, CO, 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 CH₂OH across V–O–Ti bonds. 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-workers 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 in the red region of the spectrum, is assigned to Ti–OCH₃ groups.

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* 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.
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\(_3\)OH, as Ti\(=\)OCH\(_2\)/Ti\(=\)OH pairs, and as V\(=\)OCH\(_3\)/Ti\(=\)OH pairs. While the formation of V\(=\)OH/Ti\(=\)OCH\(_3\) pairs might also be considered, theoretical calculations suggest that the formation of V\(=\)OCH\(_3\)/Ti\(=\)OH 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\(_3\)OH.

Table 2 shows that the total amount of methanol adsorbed on V/TiO\(_2\) is less than that adsorbed on TiO\(_2\) alone, \(\sim\)1.9 molecules of CH\(_3\)OH/nm\(^2\) as compared to 2.6 molecules of CH\(_3\)OH/nm\(^2\). The lower surface concentration of adsorbed methanol on V/TiO\(_2\) in comparison to TiO\(_2\) can be explained...
as follows. TiO$_2$ contains 10.8 Ti sites/nm$^2$, and, hence, it can be shown that there are also 10.8 O atoms/nm$^2$ in Ti–O–Ti bonds on the surface of anatase. The introduction of 2.0 V atoms/nm$^2$ as isolated VO$_4$ 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/nm$^2$. 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–OCH$_3$ and V–OCH$_3$) is predicted to decrease from 2.6 methoxide species/nm$^2$ for TiO$_2$ to 2.1 methoxide species/nm$^2$ for V/TiO$_2$, in reasonable agreement with what is seen in Table 2. Using the same assumptions leads to the expectation of approximately equivalent concentrations of Ti–OCH$_3$ and V–OCH$_3$, 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/TiO$_2$ are presented in Figure 11. With increasing temperature, the bands for Ti–OCH$_3$ groups diminish more rapidly than those for V–OCH$_3$ 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 TPD on TiO$_2$. The weak bands in the 1340–1400 cm$^{-1}$ region are only observed on V/TiO$_2$ due to the large concentration of formate 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/TiO$_2$, shown in Figure 12, with that for TiO$_2$, shown in Figure 5, reveals several significant differences. While CH$_3$OH and H$_2$O 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$_2$O appears at about 410 K. This low-temperature peak is attributed to the reaction of V–OCH$_3$ species, because it was not observed during TPD of methanol adsorbed on TiO$_2$. Theoretical studies have shown that CH$_2$O is formed by transfer of an H atom from the methyl group of V–OCH$_3$ to the V=O bond associated with the same V atom. 26–28 The decrease in production of CH$_2$O above 425 K coincides with a rapid increase in the appearance of CO and H$_2$O, suggesting that the latter products are formed by the decomposition and partial combustion of CH$_2$O. 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$_2$O 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 Ti–OCH$_3$ groups. The reason for the observed decrease in DME formation is due to both a decrease in the amount of Ti–OCH$_3$ species present on the surface and a rapid decomposition and combustion of Ti–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 Ti–OCH$_3$ groups with H atoms released during the decomposition of DME. It is also notable that the total amount of H$_2$O 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 O/nm$^2$ are taken from the supported vanadate species, of which there are 2.0 V/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 Ti–OCH$_3$ and V–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$_2$O, because this is the temperature where the H$_2$O desorption is maximized during TPO. The TPO spectrum of CH$_3$OH 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$_3$OH begins at 350 K. This process is accompanied by the immediate onset of CH$_2$O and H$_2$O formation at virtually equivalent rates. Above 425 K the rate of CH$_2$O formation reaches a maximum as CO now forms, and the rate of H$_2$O formation accelerates. Table 2 shows that the total amount of H$_2$O formed, 2.32 H$_2$O/nm$^2$, agrees perfectly with that expected from the production of CH$_2$O and CO, assuming that the later product comes from the decomposition of CH$_3$O to CO and H$_2$ followed by the immediate combustion of H$_2$ to H$_2$O. The infrared spectra taken during TPO presented in Figure 13 show that the methoxide species present as Ti–OCH$_3$ react much more rapidly than those present as V–OCH$_3$. This suggests that most of the CH$_3$OH desorbed in the initial part of the TPO spectrum is due to the reaction of Ti–OCH$_3$/Ti–OH pairs to form CH$_3$OH and Ti–O–Ti bonds.
A possible mechanism for the formation of CH$_2$O during the TPO of CH$_3$OH adsorbed on V/TiO$_2$ is shown in Figure 15. V$-$OCH$_3$ groups are shown as the source of CH$_2$O and H$_2$O. CO, CO$_2$, and additional H$_2$O are then formed in secondary processes involving the decomposition and oxidation of CH$_2$O. The infrared spectra presented in Figure 13 are consistent with the idea that CO and CO$_2$ result from the secondary reaction of CH$_2$O. 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 423–573 K. This is the same temperature range over which the peaks for CO, CO$_2$, and H$_2$O 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$_3$OH adsorbed on V/TiO$_2$, no product peaks are observed above 550 K during TPO of adsorbed CH$_3$OH. 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 V$-$OCH$_3$ groups to CH$_2$O, as well as increasing the rate of subsequent decomposition of CH$_2$O to CO and H$_2$O. The scheme shown in Figure 15 assumes that all of the CH$_2$O, CO, and CO$_2$ observed during the TPO of methanol adsorbed on V/TiO$_2$ originate from V$-$OCH$_3$ groups. This would suggest that 1.50 C atoms/nm$^2$ are present as V$-$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$_3$OH as V$-$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 Ti$-$OCH$_3$ species disappear from the infrared spectrum at lower temperatures for V/TiO$_2$ than for TiO$_2$ during TPO of adsorbed CH$_3$OH.

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$_2$O with V$^{5+}$ centers produced during the formation of CH$_2$O, followed by the transfer of a hydrogen atom; however, in the presence of gas-phase oxygen, the vanadium is rapidly reoxidized, and the CH$_2$O 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 to 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$_2$O.

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 Ti$-$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$_2$O. The formation of CH$_2$O and H$_2$O 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$_2$O formation increase rapidly, as the rate of CH$_2$O 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 Ti$-$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 CH$_3$OH/O$_2$ over TiO$_2$ and V/TiO$_2$. During TPRx on TiO$_2$, some Ti$-$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 CH$_3$OH/O$_2$ over 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 to form the species CH$_2$O. This would lead to a reverse spillover of the methoxide groups from Ti to V, similar to the results proposed by S Arabian and Oyama$^{39}$ for Mo/SiO$_2$ and Chen and Falconer$^{31}$ for Ni/Al$_2$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$_2$O. When vanadate species are present on the surface of TiO$_2$, these species can undergo reduction to form V(−O$=$Ti$=$O$=$) species. A recent theoretical study has shown that the latter species can readily adsorb O$_2$. Migration of one of the O atoms of the newly formed peroxy 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 Ti$-$OCH$_3$ groups on the surface of the support so that they could desorb as methanol by condensation with Ti$-$OH groups. This interpretation would require, though, for defects to have a long-range effect, since work by Henderson and coworkers has shown that 8% of the surfaces 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 Ti$-$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
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 $5.3 \times 10^6$ atm$^{-1}$ 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 energy is 23 kcal/mol and the apparent preexponential factor is $2.3 \times 10^7$ atm$^{-1}$ s$^{-1}$. Based on these values, the specific activity of V/TiO$_2$ is 6.5 times higher than that of V/SiO$_2$ at 450 K. This ratio of activities is on the same order of magnitude as that reported by Wachs and co-workers. What remains to be established, though, is whether the significantly higher activity of V/TiO$_2$ 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, CH3, 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. CH3O 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, CH3O adsorbs to form formate species, which then undergo decomposition to form CO and H2, and in the presence of O2 to form CO2 and H2O. The activity of V/TiO2 for the formation of CH3O 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).

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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

(23) 10.8 Ti/nm2 calculated on the basis of the Ti–Ti nearest neighbor distance on anatase.