The effects of hydration and dehydration of silica-supported vanadia have been investigated with the aim of understanding how these processes alter the structure of the dispersed vanadia. Samples containing either 9 or 12 wt % V2O5/SiO2 were examined by in situ Raman spectroscopy during hydration at 300°C and dehydration at temperatures between 298 and 773 K. The vanadia in freshly dehydrated 9 wt % V2O5/SiO2 is present exclusively in the form of monovanadate species. Monovanadate species are predominant in the 12 wt % V2O5/SiO2, but a small amount of V2O5 is present as well. Room-temperature hydration causes a progressive loss of the Raman band at 1043 cm\(^{-1}\), characteristic of a hydrated vanadia gel. Dehydration at elevated temperatures decomposes the gel and partially restores the presence of isolated monovanadate species. V2O5 particles are also formed during dehydration. Repeated low-temperature hydration and high-temperature dehydration leads to an irreversible conversion of isolated monovanadate species into V2O5 particles. A mechanism by which this process occurs is proposed.

Introduction

Supported vanadia catalysts exhibit high activity and selectivity for a number of oxidation reactions. These include the partial oxidation of methane and methanol to formaldehyde and ethanol to ethene and propane to propene. Since the relationship of the structure of dispersed vanadia to its catalytic properties is illustrated by the following two examples. Investigations of methanol oxidation to formaldehyde and the oxidative dehydrogenation of ethane to ethene and propane to propene have been devoted to the characterization of dispersed vanadia and their relationship to catalytic performance. Raman spectroscopy has confirmed that, in the absence of water vapor, vanadia is present as three types of structures: isolated monovanadate (VO\(_x\)) species; polyvanadate species (chains and ribbons of VO\(_x\) units); and V2O5 crystallites. The distribution of vanadium among these structural types depends on the identity of the support, the composition of the vanadia precursor, the surface vanadia concentration, and the thermal history of the sample. At low vanadia surface densities vanadia (\(\sim 2.3 \text{ VO}_x/\text{nm}^2\)), monovanadate species are predominant on all supports. With increasing VO\(_x\) content, polyvanadate species are formed; on some supports, V2O5 crystallites also form. In general, TiO\(_2\), ZrO\(_2\), and Al2O3 support vanadia crystallites on all supports. With increasing VO\(_x\) content, these structural types depend on the identity of the support. Investigations of methanol oxidation to formaldehyde and the oxidative dehydrogenation of ethane to ethene and propane to propene have been devoted to the characterization of dispersed vanadia and their relationship to catalytic performance.
isolated monovanadate species and proceeds with cleavage of the bond between the monovanadate species and the support (e.g., V–O–Si, V–O–Ti bond). By contrast, studies of the oxidative dehydrogenation of propane have shown that propene formation turnover rates per total V-atom increase with increasing VO$_2$ surface density up to the point at which V$_2$O$_5$ crystallites form. This appears to reflect the higher reducibility and intrinsic activity of polyvanadates relative to monovanadate species. The ultimate decrease in turnover rate as VO$_2$ surface density increases further reflects the loss of VO$_2$ surface species as bulk V$_2$O$_5$ crystallites form.

Water is a common product of alkane and alcohol oxidation reactions. Because water can hydrate VO$_2$–M (M = Si, Ti, Zr, etc.) bonds, the presence of water can influence the structure of dispersed vanadia species. A number of studies of this issue have been reported in the literature, the most detailed of which have been for the effects of H$_2$O on the dispersion of silica-supported vanadia. Raman and UV-visible spectra have shown that prolonged exposure to water vapor in ambient air causes the hydration of V–O–Si bonds in isolated monovanadate species (SiO)$_3$V=O) to form species resembling V$_2$O$_5$–H$_2$O gels. It remains unclear, however, whether the subsequent dehydration of such gels can fully redisperse VO$_2$ as isolated monovanadates or leads to the formation of V$_2$O$_5$ crystallites. The present study was undertaken in order to determine the dynamics and temperature dependence of the interaction of H$_2$O with VO$_2$/SiO$_2$, the species contributing to the formation of the hydrated V$_2$O$_5$–H$_2$O gel, and the role of hydration/dehydration processes on the nucleation and growth of V$_2$O$_5$ crystallites.

**Experimental Section**

Two VO$_2$/SiO$_2$ samples were used in this study. A 9 wt % V$_2$O$_5$/SiO$_2$ sample was prepared by incipient-wetness impregnation of Cabosil EH-5 SiO$_2$ (dried at 393 K) with a solution of vanadium triisopropoxide (Alfa-Aesar; 97% purity) in 2-propanol. After impregnation, the sample was treated in flowing N$_2$ at 393 K for 1 h and then at 573 K for 1 h. A 12 wt % V$_2$O$_5$/SiO$_2$ catalyst was prepared by incipient wetness impregnation methods using a NH$_4$VO$_3$ aqueous solution. Ammonium metavanadate (Aldrich, 99%) was dissolved in a solution of oxalic acid (NH$_4$VO$_3$/oxalic acid molar ratio = 1:2) at a pH of 1.8. The sample was treated in 20% O$_2$/He (Bay Air; 40 cm$^3$/min) in a quartz in-situ Raman cell. The intensity of the Raman band for crystalline V$_2$O$_5$ depends on temperature (see discussion below); as a result, it was necessary to rotate the sample stage at 20 Hz in order to reduce laser heating of the samples. Hydration experiments were carried out using a 20% O$_2$/He mixture containing 3.0 kPa H$_2$O vapor, introduced by saturating the stream with liquid water at 298 K. After treatment with this mixture for a given time, the saturator was bypassed; the sample was then flushed with dry 20% O$_2$/He and heated to 773 K at 10 K/min.

**Results**

Figure 1 shows the room-temperature spectrum for the 9 wt % V$_2$O$_5$/SiO$_2$ sample after treatment in 20% O$_2$/He at 773 K for 2 h (spectrum a). The sharp band at 1043 cm$^{-1}$ is characteristic of isolated monovanadate (VO$_x$)$_{4}$, which correspond to Si–O$^-$ functionalities in silica produced by the formation of V–O–Si bonds. Exposure of the calcined sample to 3.0 kPa of H$_2$O at 298 K leads to an evolution in the structure of the supported vanadia as shown in Figure 1. The band at 1043 cm$^{-1}$ becomes weaker, and a weak broad band appears at ~1021 cm$^{-1}$ after about 10 min. At longer times, additional bands appear at 986, 895, 773, 706, 666, 512, 415, 325, 267, and 168 cm$^{-1}$. These new bands and the band at 1021 cm$^{-1}$ are consistent with the gradual formation of a V$_2$O$_5$–H$_2$O gel. The Raman spectrum of V$_2$O$_5$–H$_2$O gel formed by exposing V$_2$O$_5$ to H$_2$O vapor at room temperature exhibits bands at 1020 (w), 895 (s), 707 (s), 667 (m), 510 (m), 485 (sh), 400 (vw), 350 (m), 325 (m), 278 (w), 265 (m), 155 (s), and 135 (s).

Heating this hydrated 9 wt % V$_2$O$_5$/SiO$_2$ at 773 K for 1 h in 20% O$_2$/He restores the band at 1043 cm$^{-1}$, and new bands, corresponding to V$_2$O$_5$ crystallites, appear at 998, 704, 529, 483, 408, 305, 288, 199, and 147 cm$^{-1}$ (Figure 2). Subsequent hydration/dehydration cycles lead to the continuous growth of the V$_2$O$_5$ bands, without significant weakening of the band at 1043 cm$^{-1}$, corresponding to isolated monovanadates. To determine the amount of V$_2$O$_5$ formed after each hydration/dehydration cycle, it is necessary to know the relative Raman cross sections for V=O stretches in isolated monovanadate species and V$_2$O$_5$. These Raman cross sections were estimated by comparing

---


---

the intensity of the band at 1043 cm$^{-1}$ for the 9 wt % V$_2$O$_5$/SiO$_2$ sample (see Figure 1), which contains only monovanadate species, with the intensity of the band at 997 cm$^{-1}$ for a physical mixture of bulk V$_2$O$_5$ and pure SiO$_2$ containing 9 wt % V$_2$O$_5$. The V$_2$O$_5$ crystallites in this physical mixture have an average diameter of $\sim$0.5 $\mu$m. Assuming that the efficiency of sampling V=O vibrations in the 9 wt % V$_2$O$_5$/SiO$_2$ sample and the sample containing 9 wt % bulk V$_2$O$_5$ mixed with SiO$_2$ are identical, their relative Raman cross sections for bulk V$_2$O$_5$ ($\sigma_{997\ cm^{-1}}$) is estimated to be 10 times larger than that for isolated monovanadate species ($\sigma_{1043\ cm^{-1}}$). Using this ratio of Raman scattering cross sections, an upper limit can be estimated for the fraction of the well-dispersed monovanadate species that are converted to V$_2$O$_5$ after one hydration/dehydration cycle. For the 9 wt % sample, less than 1% of the monovanadate species are converted to V$_2$O$_5$ after one hydration–dehydration cycle; this value approaches 10% after two cycles.

Spectrum a in Figure 3 was obtained after dehydration at 773 K for 1 h in 20% O$_2$/He of a fresh 12 wt % V$_2$O$_5$/SiO$_2$ sample that had been exposed to ambient air. Raman bands for both monovanadate species and V$_2$O$_5$ are clearly evident. The relative intensities of all bands are very similar to those for the 9 wt % V$_2$O$_5$/SiO$_2$ after two hydration/dehydration cycles (compare spectrum c in Figure 2 with spectrum a in Figure 3). Exposing the 12 wt % V$_2$O$_5$/SiO$_2$ sample to 3.0 kPa of water vapor at 298 K leads to a gradual change in the appearance of the spectrum (Figure 3). The band at 1043 cm$^{-1}$ for the monovanadate species decreases in intensity, and it disappears completely after 10 min. The bands for bulk V$_2$O$_5$ at 998, 702, 528, 483, 406, 306, 285, 199, and 146 cm$^{-1}$ also decrease in intensity with time. After 0.3 h, the spectrum changes gradually until spectrum k in Figure 3 is obtained after 1 h. This spectrum is again similar to that for 9 wt % V$_2$O$_5$/SiO$_2$ after the same treatment. These observations suggest that upon extended exposure to water vapor, both isolated monovanadate and supported V$_2$O$_5$ particles are converted to a hydrated vanadia gel.

The Raman spectra obtained during dehydration of the hydrated 12 wt % V$_2$O$_5$/SiO$_2$ samples are shown in Figure 4. Spectrum b was obtained after exposing the sample to 3 kPa of H$_2$O for 12 h. Spectra c–g show the changes that occur as the hydrated sample was heated to higher temperatures in 20% O$_2$/He. Each spectrum was recorded at the indicated temperature of treatment, which was maintained constant for 1 h before recording the spectrum.
During dehydration, the bands characteristic of a hydrated vanadia gel gradually disappear and bands for isolated vanadate species (1043 cm\(^{-1}\)) and for dispersed V\(_2\)O\(_5\) (998, 702, 400, and 146 cm\(^{-1}\)) reappear. Spectrum h was recorded after treatment at 773 K for 1 h and subsequent cooling to 298 K. The general appearance of the spectrum changes appreciably upon cooling the sample from 773 to 298 K, and the bands shift to slightly higher frequencies as the sample is cooled. All bands for V\(_2\)O\(_5\) become more intense upon cooling, but the band for monovanadate species is unchanged. These effects of temperature on the intensity of Raman bands for V\(_2\)O\(_5\) have been reported previously and are attributable to the formation of anionic defects in V\(_2\)O\(_5\) crystallites at higher temperatures.\(^{35}\)

Absorption of both the incident and scattered light by defects within V\(_2\)O\(_5\) crystallites causes a reduction in the sampling depth and, hence, a reduction in the intensity of the Raman signal observed for a given amount of V\(_2\)O\(_5\) in the sample. The small increase in the Raman frequency with decreasing temperature reflects a small decrease in the V=O bond length due to thermal contraction. The intensity of the peak at 1043 cm\(^{-1}\) is unaffected by temperature because the monovanadate species do not lose oxygen over the temperature range of the present experiments. There is a slight blue shift in the position of this band with decreasing temperature, due to V=O bond contraction.

Figure 5A shows a plot of the intensities of the bands at 1043 and 998 cm\(^{-1}\) as a function of the number of hydration/dehydration cycles for the 12 wt % V\(_2\)O\(_5\)/SiO\(_2\) sample. The V\(_2\)O\(_5\) band at 998 cm\(^{-1}\) grows significantly after two hydration/dehydration cycles, but the band at 1043 cm\(^{-1}\) remains unchanged. As the number of hydration/dehydration cycles increases, the band at 998 cm\(^{-1}\) becomes more intense and the band at 1043 cm\(^{-1}\) becomes weaker. The relative amounts of the two species can be calculated using the estimates of the relative cross sections for the two species, and they are shown in Figure 5B. For the fresh sample, about 3% of the vanadia in the sample is present as V\(_2\)O\(_5\), but after seven cycles, this value increases to 34%. The sigmoidal shape of the curve in Figure 5B indicates that the rate of the monovanadate conversion to V\(_2\)O\(_5\) increases with number of cycles. This behavior may reflect an acceleration of the reaction rate once V\(_2\)O\(_5\) nuclei of a critical size are formed. In contrast to what is observed upon low-temperature hydration and subsequent dehydration at elevated temperature, prolonged heating at 773 K in 20% O\(_2\)/He does not affect the distribution of isolated monovanadate species and V\(_2\)O\(_5\).

The effect of the temperature of exposure to H\(_2\)O was also examined. At 393–573 K, H\(_2\)O had no effect on the Raman spectrum of 12 wt % V\(_2\)O\(_5\)/SiO\(_2\) in agreement with previous observation.\(^{36}\) Detectable structural changes occurred only upon water exposure at 353 K or lower temperatures. The slower kinetics observed for the monovanadate to V\(_2\)O\(_5\) transformation at high temperatures may reflect a compromise between the adsorption of H\(_2\)O required for hydrolysis of V=O–Si bonds, which is favored at low temperatures, and the rates of the hydrolysis and migration processes, which become faster as the temperature increases.

**Discussion**

The results of this study show that hydration (298 K)–dehydration (773 K) cycles cause the irreversible and gradual transformation of isolated monovanadate species into V\(_2\)O\(_5\) crystallites on SiO\(_2\) supports. A V\(_2\)O\(_5\)/SiO\(_2\) sample with 9 wt % V\(_2\)O\(_5\) and a surface density of 1.9 VO\(_x\)/nm\(^2\) contains predominantly isolated monovanadate (Figure 1), in agreement with previous observations.\(^{19}\) The geometric “footprint” of a monovanadate species suggests that the saturation monovanadate coverage is about 2.3 VO\(_x\)/nm\(^2\),\(^{10,11,19}\) thus, the exclusive presence of monovanadate in this sample is not unexpected.

The surface density in the V\(_2\)O\(_5\)/SiO\(_2\) sample with 12 wt % V\(_2\)O\(_5\) is 2.6 VO\(_x\)/nm\(^2\), and V\(_2\)O\(_5\) bands are detected along with those for isolated vanadate species in the Raman spectrum. On the basis of estimates of the relative scattering cross sections for isolated monovanadate and crystalline V\(_2\)O\(_5\) reported above, less than 3% of the V atoms in the sample are present as V\(_2\)O\(_5\) (Figure 5B). It appears that V\(_2\)O\(_5\) crystallites first form on SiO\(_2\) as the theoretical monovanadate capacity of the SiO\(_2\) surface is exceeded.

\(^{(35)}\) Xie, S.; Iglesia, E.; Bell, A. T. To be submitted for publication.

The reaction of H$_2$O with monovanadate species is slow at room temperature (Figure 1), and it does not occur above 393 K when the partial pressure of H$_2$O is 3 kPa. Thus, it appears that the concentration of adsorbed water critically influences the restructuring process. In fact, if the enthalpy for water adsorption is greater than the activation energy for the hydrolysis or migration of monovanadate species, the rate of restructuring can actually decrease with increasing temperature.

The Raman spectra in Figure 1 show that, over ~0.5 h of hydration, the isolated vanadate species initially present on 9 wt % V$_2$O$_5$/SiO$_2$ are transformed into structures with Raman features similar to those in V$_2$O$_5$ gels formed by hydration of V$_2$O$_5$ crystallites. Similar effects were observed for the 12 wt % V$_2$O$_5$/SiO$_2$ sample (see Figure 3). In the latter sample, the small amounts of V$_2$O$_5$ present initially also form a hydrated V$_2$O$_5$ gel. The extent of V$_2$O$_5$ hydration appears to depend on the size of the V$_2$O$_5$ crystallites. As V$_2$O$_5$ crystallites become more abundant with repeated hydration/dehydration cycles, they do not undergo complete hydration at 298 K in 3 kPa of H$_2$O (see Figure 3). This may be due to the formation of progressively larger V$_2$O$_5$ crystallites that intercalate water with increasing difficulty. Indeed, the Raman spectrum of a large unsupported crystallite that forms bulk V$_2$O$_5$ (~500 nm diameter) is unchanged by exposure to H$_2$O vapor at 298 K.

The reversibility of the structural effects of hydration depends also on the length of the hydration at 298 K. When either one of the V$_2$O$_5$/SiO$_2$ samples was exposed to 3 kPa of H$_2$O at 298 K for less than 10 min, subsequent dehydration in 20% O$_2$/He at 773 K completely restored the initial Raman spectrum and the isolated monovanadate species initially present in these samples. Dehydration after longer hydration times (~10 min), however, led to the irreversible formation of V$_2$O$_5$ crystallites after repeated hydration/dehydration cycles (see Figures 2, 4, and 5).

Figure 6 depicts schematically the processes occurring during hydration/dehydration processes for VO$_x$ species supported on SiO$_2$. At 298 K, water is assumed to adsorb by interaction between the O-atom of H$_2$O and a V$^{IV}$ center in isolated monovanadate species and by concurrent interactions of the H-atoms with neighboring O-atoms in V–O–Si structures. These interactions are relatively weak and consequently H$_2$O desorbs slightly above room temperature. Near room temperature, the hydrolysis of V–O–Si bonds occurs slowly, as evidenced by the slow changes in the Raman spectrum of dispersed vanadania upon exposure of V$_2$O$_5$/SiO$_2$ samples to H$_2$O water vapor at 298 K (Figures 1 and 3). After all three V–O–Si bonds in isolated monovanadate species have undergone hydrolysis, the resulting detached vanadyl trihydroxide species should be able to migrate on the silica surface and react with similar species via olation and oxolation processes to form V–O(–H)–V and V–O–V bonds, respectively. These oligomerization processes lead to the formation of two-dimensional polyvanadate domains. As the degree of oxolation increases, these structures begin to resemble that of fully hydrated V$_2$O$_5$, as suggested by Raman spectroscopy. Small crystallites of V$_2$O$_5$ (e.g., in 12 wt % V$_2$O$_5$/SiO$_2$), can also interact with water to form hydrated vanadania gels. While the hydrolysis of V–O–Si bonds was not observed at 393 K in the presence of 3 kPa of H$_2$O, this does not exclude the possibility that, in the presence of higher H$_2$O partial pressures, hydrolysis could occur at elevated temperatures.

Dehydration of the two-dimensional polyvanadate species initially formed during the early stages of water exposure involves the dehydration of V–O(–H)–V bonds and the partial hydrolysis of V–O–V bonds. The latter process would require the participation of adsorbed water, because water vapor is no longer available in the gas phase. Both processes can contribute to the re-formation of the vanadyl trihydroxide species required to redisperse the vanadia. Some of the two-dimensional structures continue to react with migrating trihydroxide species using on-top V–OH groups away from the periphery of these domains; this leads to the formation of small three-dimensional structures, which continue to grow isotropically to form larger V$_2$O$_5$ crystallites. These small crystallites of V$_2$O$_5$ serve as nuclei for the additional formation of V$_2$O$_5$ during subsequent hydration–dehydration cycles. The nucleation and growth of V$_2$O$_5$ crystals causes the plot of V$_2$O$_5$ fraction as a function of the number of hydration–dehydration cycles (Figure 5B) to have a sigmoidal shape.

The interpretation of the effects of hydration and dehydration on silica-supported vanadia presented here differs from that developed by Gao et al. They have proposed that the formation of a hydrated vanadia gel can occur only when sufficiently large quantities of water are present to ensure that VO$_x$ species are completely detached from the surface of silica. They have also suggested that once the gel is formed its dehydration does not lead to the redispersion of vanadia as isolated monovanadate species. The results reported here indicate that during dehydration a competition occurs between disaggregation of the vanadia gel to form isolated monovanadate species and crystallites of V$_2$O$_5$. This suggests that the initially formed gel has regions in which the vanadium atoms are not fully linked to each other by V–O–V bonds. It is hypothesized that such regions undergo hydrolytic cleavage of the V–O–V bonds to form V–OH groups and ultimately OV(OH)$_x$ species that can migrate along the silica surface. The regions of the gel that are more fully connected may serve as the nuclei for the formation of small V$_2$O$_5$ crystallites.

Conclusions

At surface densities below one monolayer (2.3 VO$_x$/nm$^2$) vanadia can be dispersed on the surface of silica exclusively as isolated monovanadate species. Above monolayer coverage small particles of V$_2$O$_5$ are observed. Low-temperature hydration of samples containing only isolated monovanadate species or a mixture of monovanadate
species and a small amount of V₂O₅ results in structural changes that are only partially reversible upon dehydration. Water vapor slowly hydrolyzes the V=O-Si bonds by which monovanadate species are bonded to the SiO₂ surface near room temperature. The resulting O=V(OH)₃ species then migrate to form two-dimensional structures via the processes of olation and oxolation. The Raman spectrum of this structure closely resembles that for fully hydrated V₂O₅. If particles of V₂O₅ are present, they also undergo hydration to form a vanadia gel. Upon dehydration at elevated temperatures, the two-dimensional vanadia structure is destroyed. The V-O(H)-V bonds formed via olation are broken to form separate V-OH units, and the V-O-V bonds formed via oxolation undergo partial hydrolysis by reaction with bound water. These processes contribute to the generation of mobile O=V(OH)₃ species that can react with Si-OH groups on the silica surface to re-form the monovanadate groups. Oxolation can also occur during dehydration leading to the formation of two-dimensional and ultimately three-dimensional V₂O₅ structures. Repeated low-temperature hydration/high-temperature dehydration of silica-supported vanadia results in the irreversible conversion of isolated monovanadate species to V₂O₅ particles. Hydrolysis of V-O-Si bonds is not observed upon water vapor exposure at elevated temperatures because of the low H₂O coverage on isolated monovanadate species.

Acknowledgment. The authors express their appreciation to Professor Israel E. Wachs of Lehigh University for supplying the 9 wt % V₂O₅/SiO₂ sample. This work was supported by the Director, Office of Basic Science, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098. LA0003342