framework AI, it is difficult to know whether or not the 6-coordinate AI atoms observed in the 27AI spectrum of the rehydrated calcined sample belong to the framework. We have therefore considered considerable research dealing with the selective reduction of nitrogen oxides.1 It is obvious that the amount of strongly chemisorbed water cannot be significant. If strong interactions were to occur between the OH groups and the water molecules, the resolution of the corresponding vibrations would be reduced and they would shift toward lower wavenumbers.13

The 31P MAS NMR spectrum of n-DPA-VPI-5 (not shown) contains three signals with chemical shifts of -23.3, -27.2, and -33.1 ppm in the intensity ratio 1:1:1. The 27Al MAS NMR spectrum (see Figure 6) shows the presence of 4-coordinated AlO4 and 6-coordinated AlO6 environments at 41.6 and ca. -15 ppm, respectively. The similarity of the 31P and 27Al MAS spectra of n-DPA-VPI-5 and TBA-VPI-5 suggests that the deficiency of phosphorus atoms on the three kinds of crystallographically inequivalent P sites in n-DPA-VPI-5 is random and that the distortion of Al environments due to this deficiency is not reflected in the 27Al MAS NMR spectrum.

After calcination of n-DPA-VPI-5 at 200 °C for 6 h and followed by rehydration of the calcined sample, both 31P and 27Al MAS NMR spectra of it are significantly changed (Figures 6 and 7) indicating the occurrence of a structural transformation. A deconvolution of the 31P spectrum reveals the presence of five peaks at -22.6, -25.7, -26.9, -29.1, and -31.1 ppm in the intensity ratio 1:1:1:4:4, while the 27Al spectrum of hydrated calcined n-DPA-VPI-5 shows the presence of 4- and 6-coordinate AI in the intensity ratio 2:1. Because VPI-5 contains 6-coordinate framework Al, it is difficult to know whether or not the 6-coordinate Al atoms observed in the 27Al spectrum of the rehydrated calcined sample belong to the framework. We have therefore investigated the effect of water upon the chemical environments of P and Al atoms in calcined n-DPA-VPI-5: the 31P spectrum of a sample carefully dehydrated at 200 °C under vacuum is poorly resolved, and the relative intensities of the signals are altered. The 27Al spectrum, particularly the relative intensities of the peaks, depends upon calcination conditions and the hydration state of the calcined sample. The 27Al spectrum of an anhydrous calcined sample shows a significant decrease in the intensity of the octahedral aluminum signal and a small amount of Al species at ca. 5.5 ppm.

Adsorption of N2 on calcined VPI-5 gives the surface area to be ca. 117 m2/g, corresponding to 3 N2 molecules/unit cell of VPI-5. This indicates that the pores are almost completely blocked by the extraframework species produced during calcination.

Several groups of researchers have suggested that the reason for the irreversible phase transformation in VPI-5 may be the presence of impurities.1,4 Derouane et al.1 claim that such impurities can be removed with hot ethanol. Following their procedures precisely, we washed our n-DPA-VPI-5 with hot absolute ethanol at 60 °C for 1 h and calcined the washed sample at 200 °C for 1.5 h. However, XRD showed that the washing does not prevent the onset of structural transformation.

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**Structural Determination of Supported V2O5-WO3/TiO2 Catalysts by In Situ Raman Spectroscopy and X-ray Photoelectron Spectroscopy**

Michael A. Vuurman, Israel E. Wachs,*

Zettlemoyer Center for Surface Studies, and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

and Andrew M. Hirt

Materials Research Laboratories, Inc., 720 King Georges Post Road, Fords, New Jersey 08863

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A series of supported V2O5/TiO2, WO3/TiO2 and V2O5-WO3/TiO2 samples have been characterized by means of Raman spectroscopy under ambient as well as in situ dehydrated conditions and by X-ray photoelectron spectroscopy. Under ambient conditions two different hydrated surface vanadia species and crystalline V2O5 have been identified in V2O5/TiO2 as a function of surface coverage. Under dehydrated conditions two types of surface vanadium oxide species are found in V2O5/TiO2 samples: a highly distorted vanadium oxide species and a moderately distorted vanadium oxide species, and their relative concentration is a function of the vanadia surface coverage. Under ambient conditions tetrahedrally coordinated surface tungsten oxide species, octahedrally coordinated surface polytungstate species, and crystalline WO3 are observed in WO3/TiO2 samples as a function of surface coverage. Dehydration converts all the two-dimensional tungsten oxide species into a highly distorted octahedrally coordinated structure. The molecular structures of the V2O5-WO3/TiO2 mixed samples are not influenced by the sequence of impregnation of the starting materials. Under ambient conditions and low vanadia coverage, the hydrated surface vanadium oxide species undergo a structural change due to the acidic nature of tungsten oxide species. Crystalline V2O5 and crystalline WO3 are not influenced by the presence of the other metal oxide. Under dehydrated conditions, both the highly distorted surface vanadium oxide species and the octahedrally coordinated surface tungsten oxide species do not appear to be influenced by each other at all loadings. The only influence observed in this study is that the moderately distorted vanadium oxide species becomes more abundant in the presence of tungsten oxide.

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**Introduction**

Interest in air quality and emission control has resulted in considerable research dealing with the selective reduction of nitrogen oxides.1 Commercial DeNOx catalysts contain V2O5-WO3/TiO2. These catalysts are less active than the V2O5/TiO2 catalyst for catalyzing the NOx + NH3 + O2 reaction but have an excellent thermal stability and a lower oxidation activity for the conversion of SO2 to SO3.2 At this moment, very little

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Structures of V₂O₅-WO₃/TiO₂ Catalysts

Information is available about the molecular structure of this supported mixed oxide system. Sutsuma et al. investigated the

vanadium oxide presence of molybdenum was found to increase the dispersion while information is available about the molecular structure of this

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provided direct structural information about the V₂O₅/TiO₂ system in the literature because of its superior catalytic activity in the reported for the V₂O₅-WO₃/TiO₂ system to date.

V₂O₅ in vanadiasilica catalysts by using low-temperature oxygen hydration, surface impurities, and calcination temperature. It has

nadium oxide species can be present. At low loading metavanadate coordination. One is highly distorted and is observed at all va-

V₂O₅ and is dependent upon the vanadium oxide loadings and the second species is moderately (d) Gasior, M.; Gasior, 21

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The 514.5-nm line of an Argon ion laser (Spectra Physics) was used in both the setups as the excitation source. The laser power at the sample was 40–60 mW for the ambient measurements and 60–100 mW for the in situ measurements.

XPS Surface Analysis. The XPS spectra were obtained on a Model DS800 XPS surface analysis system (Kratos Analytical Plc, Manchester UK). A hemispherical electron energy analyzer was used for electron detection. Mg Kα X-rays at a power of 360 W were employed in this study. Data were collected in 0.75-eV segments for each of the samples. The electron spectrometer was operated in the fixed analyzer transmission (FAT) mode. The samples were prepared by pressing the catalyst powders between stainless steel holders and a polished single-crystal silicon wafer. The powders adhered to the stainless steel holders without requiring additional adhesive materials and possessed relatively flat surfaces. Electrons with take-off angles of 90° from the sample holder plane were selected by the solid angle of acceptance of the focusing lens of the instrument. The XPS measurements were performed at 5 × 10⁻⁹ Torr. Elements detected using each spectrum were identified and concentration estimates within the 2–10-nm analyzed layer were made using typical normalization procedures. Sensitivity factors employed in the calculations were selected based on the peak envelope measured for each element of interest. The peaks included in this study were the Ti 2p (entire envelope), the W 4f (entire envelope), and the V 2p3/2 (only, to avoid O 1s peak interferences). Since the carbon concentrations were relatively low and the kinetic energy positions of the peaks of interest were similar for the elements of interest, the effect of carbon overlayer presence was ignored in this study. This was also unnecessary since only the changes of the surface rations W/Ti [atomic concentrations] against the total tungsten oxide loading were considered in this work.

Results

Raman Spectroscopy. Hydrated: \( V_2O_5/TiO_2 \) Hydrated. The Raman spectra for the supported vanadium oxide on TiO₂ samples recorded under ambient conditions are presented in Figure 1. All the spectra show the weak second-order feature of TiO₂ at \( \sim 795 \text{ cm}^{-1} \). The TiO₂ band becomes less pronounced as the vanadium oxide coverage is increased because of masking by the colored vanadium oxide overlayer. The 1% \( V_2O_5/TiO_2 \) sample reveals a broad Raman band at \( 943 \text{ cm}^{-1} \) which shifts upward to \( 988 \text{ cm}^{-1} \) for the 4.5% \( V_2O_5/TiO_2 \) sample. These broad bands do not belong to crystalline \( V_2O_5 \) and are assigned to the symmetrical \( V=O \) stretching modes of two-dimensional surface vanadate species. The Raman spectrum of the 6% \( V_2O_5/TiO_2 \) sample shows the sharp and intense band of crystalline \( V_2O_5 \) at \( 994 \text{ cm}^{-1} \). The 6% \( V_2O_5/TiO_2 \) sample only possesses a trace of \( V_2O_5 \) as indicated by the small 994-cm⁻¹ band. Thus, above 6% \( V_2O_5/TiO_2 \) the monolayer has been exceeded and crystalline \( V_2O_5 \) is present on the titania support. The presence of two-dimensional vanadium oxide species in addition to crystalline \( V_2O_5 \) at loadings of 6% and higher cannot be excluded because the strong 994-cm⁻¹ band of crystalline \( V_2O_5 \) may overshadow other bands.

\( WO_3/TiO_2 \) Hydrated. The Raman spectra of \( WO_3/TiO_2 \) under ambient conditions are presented in Figure 2. The Raman spectrum of the 1% \( WO_3/TiO_2 \) sample shows a weak and broad band at \( \sim 935 \text{ cm}^{-1} \) which is characteristic of two-dimensional tungsten oxide surface species. In addition to this 935-cm⁻¹ band, the second-order feature of TiO₂ at 783 cm⁻¹ is also present. As the loading is increased, the W=O stretching mode shifts upward to 965 cm⁻¹. At 10% \( WO_3/TiO_2 \), a second intense band at \( 800 \text{ cm}^{-1} \) is observed, showing the presence of crystalline \( WO_3 \) in addition to the two-dimensional tungsten oxide species (band at \( 965 \text{ cm}^{-1} \)). Thus, a monolayer of tungsten oxide on titania is formed at \( \sim 8\% \) \( WO_3/TiO_2 \).

\( V_2O_5-WO_3/TiO_2 \) Hydrated. Three series of \( V_2O_5-WO_3/TiO_2 \) samples have been studied to determine the influence of interaction between vanadium oxide and tungsten oxide on the titania surface. The Raman spectra of the first series, recorded under ambient conditions, are shown in Figure 3. The vanadium oxide loading is 1% and the tungsten oxide loading increases from 0 to 10%. The Raman spectrum exhibits a weak and broad band at \( 942 \text{ cm}^{-1} \). This band shifts upwards to \( 984 \text{ cm}^{-1} \) with increasing tungsten oxide loading. The Raman spectrum of the 1% \( V_2O_5-10\% \) \( WO_3/TiO_2 \) sample also reveals the presence of crystalline \( WO_3 \) because of the intense band at \( 800 \text{ cm}^{-1} \). The Raman spectra of the second set of \( V_2O_5-WO_3/TiO_2 \) mixed samples are presented in Figure 4. The vanadium oxide loading is 4.5% and the tungsten oxide loading increases from 0 to 10%. In the absence of tungsten oxide, the Raman spectrum


Structures of $V_2O_5$-$WO_3$/$TiO_2$ Catalysts


Figure 3. Raman spectra of 1% $V_2O_5$-$x\%$ $WO_3$/$TiO_2$ under ambient conditions. The tungsten oxide loading, $x$, increases from 0% to 10%.

Figure 4. Raman spectra of 4.5% $V_2O_5$-$x\%$ $WO_3$/$TiO_2$ under ambient conditions. The tungsten oxide loading, $x$, increases from 0% to 10%.

Figure 5. Raman spectra of 6% $V_2O_5$-$x\%$ $WO_3$/$TiO_2$ under ambient conditions. The tungsten oxide loading, $x$, increases from 0% to 10%.

Figure 6. Raman spectra of $V_2O_5$/$TiO_2$ under in situ dehydrated conditions. The vanadium oxide loading increases from 1% to 8%.

Dehydrated: $V_2O_5$/$TiO_2$ Dehydrated. Figure 6 shows the in situ Raman spectra of $V_2O_5$/$TiO_2$ recorded at 80 °C after heating at 450 °C in oxygen. All the spectra show a sharp band over 1000 cm$^{-1}$. This band shifts from 1027 cm$^{-1}$ for the 1% $V_2O_5$/$TiO_2$ sample to 1030 cm$^{-1}$ for the higher loading samples. In addition to this sharp band, a second broad band, indicating the presence of a second surface vanadium oxide species, appears at lower wavenumber with increasing vanadium oxide loading. This band shifts from ~920 to ~940 cm$^{-1}$ with increasing vanadium oxide loading. The spectrum of the 8% $V_2O_5$/$TiO_2$ sample shows the band of crystalline $V_2O_5$ at 994 cm$^{-1}$ in addition to the 1031 and ~940 cm$^{-1}$ bands. This indicates that crystalline $V_2O_5$ is not affected by the removal of water molecules and that above monolayer coverage crystalline $V_2O_5$ and two-dimensional dehydrated surface vanadium oxide species coexist on the titania surface.

$WO_3$/$TiO_2$ Dehydrated. Upon dehydration, the broad 935-cm$^{-1}$ band of the 1% $WO_3$/$TiO_2$ sample sharpens and shifts to 1010 cm$^{-1}$ as shown in Figure 7. The same results have been obtained...
at higher loadings: all the in situ Raman spectra reveal a sharp band at 1010 cm\(^{-1}\). In addition to this band, the Raman spectrum of the 10\% \(\text{WO}_3/\text{TiO}_2\) sample shows the strong 800-cm\(^{-1}\) band of crystalline \(\text{WO}_3\), which is not affected by the removal of the moisture. Thus dehydration converts the two-dimensional hydrated tungsten oxide species into a surface species which possesses a sharp band at 1010 cm\(^{-1}\). Above monolayer coverage crystalline \(\text{WO}_3\) as well as the surface tungsten oxide species exist on the surface as indicated by the presence of both the 1010- and 800-cm\(^{-1}\) bands in the Raman spectrum of 10\% \(\text{WO}_3/\text{TiO}_2\).

\(\text{V}_2\text{O}_5/\text{TiO}_2\) Dehydrated. The in situ Raman spectra of the three sets of \(\text{V}_2\text{O}_5/\text{TiO}_2\) mixed samples are presented in Figures 8–10. The Raman spectrum of the 1\% \(\text{V}_2\text{O}_5/\text{TiO}_2\) sample shows a sharp band at 1027 cm\(^{-1}\), which is similar to the 1\% \(\text{V}_2\text{O}_5/\text{TiO}_2\) sample. In addition to this 1027-cm\(^{-1}\) band, a shoulder is observed at 1010 cm\(^{-1}\), the intensity of which increases with increasing tungsten oxide loadings. This 1010-cm\(^{-1}\) band is identical to the band observed for the in situ Raman spectra of \(\text{WO}_3/\text{TiO}_2\). The spectrum of the 1\% \(\text{V}_2\text{O}_5/\text{TiO}_2\) sample shows that the cross-section of dehydrated

\(\text{V}_2\text{O}_5/\text{TiO}_2\) dehydrated

Raman Intensity (arbitrary units)

Raman Shift (cm\(^{-1}\))

1% \(\text{V}_2\text{O}_5\)-\(x\)% \(\text{WO}_3/\text{TiO}_2\) dehydrated

Raman Intensity (arbitrary units)

Raman Shift (cm\(^{-1}\))

4.5% \(\text{V}_2\text{O}_5\)-\(x\)% \(\text{WO}_3/\text{TiO}_2\) dehydrated

Raman Intensity (arbitrary units)

Raman Shift (cm\(^{-1}\))

6% \(\text{V}_2\text{O}_5\)-\(x\)% \(\text{WO}_3/\text{TiO}_2\) dehydrated

Raman Intensity (arbitrary units)

Raman Shift (cm\(^{-1}\))

Figure 7. Raman spectra of \(\text{WO}_3/\text{TiO}_2\) under in situ dehydrated conditions. The tungsten loading increases from 1\% to 10\%.

Figure 8. Raman spectra of 1\% \(\text{V}_2\text{O}_5\)-\(x\)% \(\text{WO}_3/\text{TiO}_2\) under in situ dehydrated conditions. The tungsten oxide loading, \(x\), increases from 0\% to 10\%.

Figure 9. Raman spectra of 4.5% \(\text{V}_2\text{O}_5\)-\(x\)% \(\text{WO}_3/\text{TiO}_2\) under in situ dehydrated conditions. The tungsten oxide loading, \(x\), increases from 0\% to 10\%.

Figure 10. Raman spectra of 6% \(\text{V}_2\text{O}_5\)-\(x\)% \(\text{WO}_3/\text{TiO}_2\) under in situ dehydrated conditions. The tungsten oxide loading, \(x\), increases from 0\% to 7\%.

surface vanadium oxide species is \(\sim 4\) times larger than the cross-section of the dehydrated tungsten oxide species. As the loading is increased to 10\% tungsten oxide, crystalline \(\text{WO}_3\) is observed on the titania surface by the presence of the 800-cm\(^{-1}\) band. Also, a weak band at \(\sim 930\) cm\(^{-1}\) shows up with increasing tungsten oxide loadings.

The Raman spectra of the second set of 4.5\% \(\text{V}_2\text{O}_5\)-(0–10)\% \(\text{WO}_3/\text{TiO}_2\) mixed samples basically reveal the same trend as the Raman spectra of the 1\% \(\text{V}_2\text{O}_5\)-(0–10)\% \(\text{WO}_3/\text{TiO}_2\) samples: two bands are present at 1030 and 1010 cm\(^{-1}\) with an intensity ratio that changes with increasing tungsten oxide loadings. All the spectra show also a broad band at \(\sim 930\) cm\(^{-1}\) which shifts to \(\sim 950\) cm\(^{-1}\) with increasing tungsten oxide loading. It is difficult to determine if the intensity of this broad band also increases with increasing tungsten oxide loading. The 4.5\% \(\text{V}_2\text{O}_5\)-10\% \(\text{WO}_3/\text{TiO}_2\) sample possesses crystalline \(\text{WO}_3\) on its surface since the 880-cm\(^{-1}\) band is present.

The Raman spectra of 6\% \(\text{V}_2\text{O}_5\)-(0–7)\% \(\text{WO}_3/\text{TiO}_2\) are shown in Figure 10. In addition to the 994-cm\(^{-1}\) band of crystalline \(\text{V}_2\text{O}_5\),
a band at 1030 cm\(^{-1}\) is observed for the 6\% V\(_{2}\)O\(_5\)-1\% W\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) and two bands at 1030 and \(\sim 1012\) cm\(^{-1}\) are observed for the 6\% V\(_{2}\)O\(_5\)-7\% W\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) sample. This indicates that under dehydrated conditions crystalline V\(_2\)O\(_5\) is not influenced by the tungsten oxide species and that above monolayer loading crystalline V\(_2\)O\(_5\) as well as two-dimensional vanadium oxide and tungsten oxide species exist on the titania surface. The influence of 1\% W\(_2\)O\(_5\) is less visible because of the low Raman cross-section of the dehydrated tungsten oxide species.

**XPS Surface Studies. Vanadium Oxide.** The surface V/Ti ratios [atomic concentrations], determined from the XPS measurements, versus the total vanadium oxide loading of the V\(_2\)O\(_5\)-(0-10)\% W\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) samples are presented in Figure 11. For the V\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) samples the surface V/Ti ratio increases almost linearly with the total vanadium oxide content until \(\sim 4.5\%\). For higher loadings the surface ratio V/Ti increases slowly with the total V\(_2\)O\(_5\) loading as indicated by the small slope of the curve above 4.5\%. These results are in agreement with our Raman data and previous reported XPS measurements.\(^{27,28}\) The change in slope has been explained by the fact that XPS can detect most of the surface metal oxide atoms up to monolayer coverage (so the XPS signal is directly proportional with the vanadium oxide surface content). Above monolayer loading the XPS signal increases very slowly because only those electrons which are emitted through the monolayer or from the top of the crystals are detected.\(^{29}\) This dependence has been previously used to study the dispersion of a metal oxide on a high surface area surface. If the metal oxide is poorly dispersed, the change in slope occurs at lower total metal oxide loading and vice versa.\(^{27-30}\)

Increasing the tungsten oxide loading from 0\% (Figure 11a) to 10\% (Figure 11e) does not significantly change the shape of the curve or the position at which the slope of the curve decreases. This indicates that the dispersion of the vanadium oxide is not influenced by the presence of tungsten oxide species on the titania surface.

**Tungsten Oxide.** Figure 12a reveals the dependence of the W/Ti surface ratio [atomic concentrations] on the total tungsten oxide loading for the W\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) samples. The surface ratio W/Ti increases linearly with the total tungsten oxide loading up to \(\sim 7\%\). Raman spectroscopy demonstrated that at higher loadings, crystalline W\(_2\)O\(_5\) is present on the surface and the surface ratio W/Ti does not increase, as demonstrated by the plateau observed in Figure 12a. In the presence of vanadium oxide the surface W/Ti ratios versus the total W\(_2\)O\(_5\) curves do not change (Figure 12, parts b–e). This shows that the presence of vanadium oxide does not influence the dispersion of the tungsten oxide phase on the Ti\(_2\)O\(_3\).

**Discussion**

**Hydrated: V\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) Hydrated.** In aqueous solution the molecular structure of vanadium oxide is a function of pH and vanadium oxide concentration.\(^{31}\) Decreasing the solution pH or increasing the vanadium oxide concentration results in a structural change from tetrahedral to more complex octahedrally coordinated structures. In a recent publication Deo and Wachs\(^{16}\) showed that under ambient conditions the structural dependence with loading for supported vanadium oxide is similar to what is observed in aqueous solution. Under supported conditions the vanadium oxide molecular structures were found to be a function of the net pH at the point of zero surface charge (pzc) which depends on the type of support and the vanadium oxide surface coverage. The pzc value of Ti\(_2\)O\(_3\) has been determined to be 5–6.\(^{32}\) Increasing the vanadium oxide loading decreases the net pH at pzc because of the acidic nature of vanadium oxide (pzc of 1.5).

The shift from 943 cm\(^{-1}\) for the 1\% V\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) sample to 987 cm\(^{-1}\) for the 4.5\% V\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) sample is in agreement with previously reported Raman spectra\(^{6,12,16}\) and suggests that under ambient conditions different two-dimensional vanadium oxide species may be present in the V\(_2\)O\(_5\)/Ti\(_2\)O\(_3\) samples. Based upon these band positions alone, however, it is impossible to determine the nature of these species since tetrahedral and octahedral, monomeric and polymeric vanadium oxide species give rise to bands in the 1200–800 cm\(^{-1}\) region.\(^{33}\) Additional vanadia modes, which are critical for a complete structural analysis, are obscured by titania, which itself exhibits very strong Raman bands below 700 cm\(^{-1}\).\(^{25}\) Recently the Raman spectra of V\(_2\)O\(_5\)/γ-Al\(_2\)O\(_3\) have been reported under ambient conditions.\(^{9,35}\) Since γ-Al\(_2\)O\(_3\) is Raman inactive, vanadium oxide Raman bands could be detected down to \(\sim 100\) cm\(^{-1}\). At low loadings, the Raman spectrum of V\(_2\)O\(_5\)/γ-Al\(_2\)O\(_3\) revealed bands at 940 cm\(^{-1}\) and weak bands at

crystalline V$_2$O$_5$ is also present. The Raman spectra of the WO$_3$/TiO$_2$ samples exhibit a strong TiO$_2$ Raman feature below 700 cm$^{-1}$ which is a function of the surface pH at the point of zero surface charge (pzc). The identification of the different two-dimensional tungsten oxide species is somewhat hampered by the presence of tungsten oxide under ambient conditions. However, the two-dimensional tungsten oxide species are expected to follow the same trend as the vanadium oxide species since the net pH at pzc depends on the surface tungsten oxide species. This is because the Raman bands of the surface tungsten oxide species are overshadowed by the stronger Raman bands of the surface vanadium oxide species. Adding tungsten oxide does not influence the decavanadate species because an acidic aqueous solution is being added to an acidic system, and only the decavanadate structure is stable in acidic aqueous solutions.

The second set contains 4.5% V$_2$O$_5$ and (0-10)% WO$_3$ and was chosen to determine the influence of the presence of tungsten oxide on the decavanadate structure and because 4.5% V$_2$O$_5$ on titania is slightly below monolayer coverage in the single V$_2$O$_5$/TiO$_2$ system. In the absence of tungsten oxide, the Raman spectrum reveals the presence of decavanadate species by the 985-cm$^{-1}$ band. Increasing the tungsten oxide loading does not change the position of this band, which shows that the decavanadate structure is not affected by the presence of tungsten oxide under ambient conditions. In the absence of tungsten oxide, the net pH at pzc is low since decavanadate species are present. Adding tungsten oxide does not influence the decavanadate species because an acidic aqueous solution is being added to an acidic system, and only the decavanadate structure is stable in acidic aqueous solutions.

The third set of samples contain 7% V$_2$O$_5$ and (0-7)% WO$_3$. Crystalline V$_2$O$_5$ is observed for all the samples. The 994-cm$^{-1}$ band becomes slightly more intense by the presence of tungsten oxide which may indicate that the dispersion of the vanadium oxide is decreased by the tungsten oxide species. This, however, is not supported by the XPS data which suggest that the spreading of vanadium oxide on the titania surface is not affected by the presence of tungsten oxide.

The Raman spectra, presented for the hydrated V$_2$O$_5$-WO$_3$/TiO$_2$ samples, yield little information about the influence of the presence of vanadium oxide on the two-dimensional structure of the tungsten oxide species. This is because the Raman bands of the surface tungsten oxide species are overshadowed by the stronger Raman bands of the surface vanadium oxide species. However, the two-dimensional tungsten oxide species are expected to follow the same trend as the vanadium oxide species since the net pH at pzc dependence is generally applicable.

The tetrahedrally coordinated tungsten oxide species at low loading and octahedrally coordinated tungsten oxide species at moderate loadings under ambient conditions is similar to the structural dependence of tungsten oxide in aqueous solutions.

V$_2$O$_5$-WO$_3$/TiO$_2$ Hydrated. The above Raman assignments for the single V$_2$O$_5$/TiO$_2$ and WO$_3$/TiO$_2$ systems are now used to interpret the Raman bands of the V$_2$O$_5$-WO$_3$/TiO$_2$ mixed samples. The first set of XPS measured samples contain 1% V$_2$O$_5$ and (0-10)% WO$_3$/TiO$_2$ and was chosen to study the influence of tungsten oxide on the molecular structure of metavanadate species. At first sight it is not clear if the broad band in the 942-984-cm$^{-1}$ region in Figure 3 belongs to vanadium oxide species, tungsten oxide species, or both. However, the broad band shifts to 988 cm$^{-1}$ while no tungsten oxide species has been observed on titania which exhibits a stretching band over 965 cm$^{-1}$ as shown in Figure 2. Furthermore, as shown above, the Raman cross-section of the dehydrated vanadium oxide species is ~4 times bigger than the Raman cross-section of the dehydrated tungsten oxide species. If one assumes that the cross-sections of the hydrated species are similar to those of the dehydrated species, then it is likely that the Raman bands of hydrated tungsten oxide species are overshadowed by the stronger vanadium oxide stretching mode. The 984-cm$^{-1}$ band matches the band of the decavanadate cluster, as shown above. Thus, the Raman spectra reveal that the hydrated metavanadate species are replaced by hydrated decavanadate species with increasing tungsten oxide loading. This effect occurs because under ambient conditions the vanadium oxide structure is dependent on the net surface pH at pzc. Increasing the tungsten oxide loading increases the aqueous acidity and the net pH at pzc decreases resulting in conversion of the metavanadate species to decavanadate species.

The second set contains 4.5% V$_2$O$_5$ and (0-10)% WO$_3$ and was chosen to determine the influence of the presence of tungsten oxide on the decavanadate structure and because 4.5% V$_2$O$_5$ on titania is slightly below monolayer coverage in the single V$_2$O$_5$/TiO$_2$ system. In the absence of tungsten oxide, the Raman spectrum reveals the presence of decavanadate species by the 985-cm$^{-1}$ band. Increasing the tungsten oxide loading does not change the position of this band, which shows that the decavanadate structure is not affected by the presence of tungsten oxide under ambient conditions. In the absence of tungsten oxide, the net pH at pzc is low since decavanadate species are present. Adding tungsten oxide does not influence the decavanadate species because an acidic aqueous solution is being added to an acidic system, and only the decavanadate structure is stable in acidic aqueous solutions.

The third set of samples contain 7% V$_2$O$_5$ and (0-7)% WO$_3$. Crystalline V$_2$O$_5$ is observed for all the samples. The 994-cm$^{-1}$ band becomes slightly more intense by the presence of tungsten oxide which may indicate that the dispersion of the vanadium oxide is decreased by the tungsten oxide species. This, however, is not supported by the XPS data which suggest that the spreading of vanadium oxide on the titania surface is not affected by the presence of tungsten oxide.

The Raman spectra, presented for the hydrated V$_2$O$_5$-WO$_3$/TiO$_2$ samples, yield little information about the influence of the presence of vanadium oxide on the two-dimensional structure of the tungsten oxide species. This is because the Raman bands of the surface tungsten oxide species are overshadowed by the stronger Raman bands of the surface vanadium oxide species. However, the two-dimensional tungsten oxide species are expected to follow the same trend as the vanadium oxide species since the net pH at pzc dependence is generally applicable. Thus, the tetrahedrally coordinated tungsten oxide species are expected to change into octahedrally coordinated tungsten oxide species with increasing vanadia content due to the acidic nature of vanadium oxide. All the mixed oxide samples containing 8% WO$_3$ show the presence of crystalline WO$_3$ by the 800-cm$^{-1}$ band. The 800-cm$^{-1}$ band, however, is less intense in the presence of vanadium oxide. This can be explained by the fact that the single WO$_3$/TiO$_2$ samples are white which would make them very good Raman scatterers, while mixed samples are dark yellow due to the vanadium(V) oxide and, therefore, poorer Raman scatterers. Thus,
Figure 13. Schematic representation of the highly distorted surface vanadium oxide species.

crystalline WO$_3$ is not influenced by the presence of vanadium oxide species. This is supported by the XPS measurements which show that in the presence or absence of vanadium oxide monolayer coverage of tungsten oxide is reached at ~7% WO$_3$. Raman spectroscopy demonstrates that under ambient conditions only the metavanadate structure is influenced by the presence of tungsten oxide. A similar effect has recently been reported for V$_2$O$_5$/TiO$_2$ and V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ catalysts contaminated with alkaline impurities [Na, K].

**Dehydrated: V$_2$O$_5$/TiO$_2$ Dehydrated.** In the in situ Raman spectra reveal that below monolayer coverage (<6% V$_2$O$_5$/TiO$_2$) two different vanadium oxide species are present on the dehydrated titania surface. One species is highly distorted and exhibits a sharp Raman band at 1030 cm$^{-1}$. This species is present at all loadings. Recent $^{51}$V NMR measurements have revealed that the highly distorted vanadium oxide species has distorted tetrahedral coordination and that the tetrahedron possesses cylindrical symmetry. The species only exhibits one Raman band at 1030 cm$^{-1}$ which indicates that this species is monooxo (one short V=O bond) since a dioxo (two V=O bonds) species would show two V=O stretching modes if the two V=O bonds were inequivalent and three bands if the two V=O bonds were equivalent (symmetrical stretch, asymmetrical stretch, and bending mode). Cristiani et al. reported an IR band at 1035 cm$^{-1}$ for a 10% V$_2$O$_5$/TiO$_2$ sample under dehydrated conditions. The coincidence of the Raman band at 1030 cm$^{-1}$ and the IR band at 1035 cm$^{-1}$ supports the monooxo model since a dioxo vanadate species would exhibit a more intense asymmetric stretching mode of the O-V-O metrical stretching mode. Thus, the combined $^{51}$V NMR, FTIR, and Raman data show that the highly distorted vanadium oxide species has a distorted tetrahedral structure with one short V=O bond (monooxo).

However, based upon these data alone it is not possible to present a more precise structure. Progress has been made in determining the molecular structure of V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ by applying the diatomic approximation method, presented by Hardcastle et al. They established an empirical stretching frequency/bond distances correlation by considering each V-O bond as a totally independent oscillator. The Raman spectrum of the V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ sample shows two Raman bands under dehydrated conditions, similar to the V$_2$O$_5$/TiO$_2$ system at 1026 cm$^{-1}$ (sharp) and 850 cm$^{-1}$ (broad). On the basis of the diatomic approximation method, Hardcastle et al. were able to determine the V-O bond distances of the highly distorted vanadate species and to propose a more precise structure. Since the Raman, FTIR, and $^{51}$V NMR data are similar for the V$_2$O$_5$/TiO$_2$ and V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ systems, and the same structure is proposed for the V$_2$O$_5$/TiO$_2$ system.

The second dehydrated vanadate species is moderately distorted and has a broad Raman band at ~920 cm$^{-1}$ which shifts to ~940 cm$^{-1}$ with increasing loading. The second species becomes more pronounced at higher loadings. This second vanadate species should also possess a tetrahedrally coordinated structure because in situ $^{51}$V NMR showed only the presence of tetrahedrons. Hardcastle et al. suggested that for the V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ system, two different, moderately distorted, tetrahedrally coordinated structures are possible. The first one is a monooxo structure, similar to the highly distorted structure but with different V=O and V-O bond distances. The V-O bonds were found to be consistent with possible V-OH bonds. The second possible structure is a dioxo which possesses two terminal V=O bonds and two bridging V-O bonds. It was argued that the V-O bonds were consistent with possible V-O-V linkages. Thus, the moderately distorted monooxo vanadate species is hydroxylated and isolated, whereas the dioxo is polymeric. A polymeric structure has also been proposed by other authors.

WO$_3$/TiO$_2$ Dehydrated. Upon dehydration, the broad bands in the 935–960 cm$^{-1}$ region disappear and are replaced by a single band at 1010 cm$^{-1}$ for all the tungsten oxide loadings. This shows that the dehydrating drastically changes the molecular structures and that the two-dimensional tetrahedrally coordinated WO$_3$ as well as the distorted octahedrally coordinated polytungstate species are converted into the same surface tungsten oxide species. This is in contrast with in situ Raman data of the WO$_3$/TiO$_2$ system which show two bands, a sharp band at 1016 cm$^{-1}$ and a weak, broad band at ~870 cm$^{-1}$, which indicates the presence of two different surface tungsten oxide species. The corresponding molecular structures in WO$_3$/$\gamma$-Al$_2$O$_3$ have recently been determined by Hardcastle et al. The 1016 cm$^{-1}$ Raman band matches the IR absorption at 1015 cm$^{-1}$. This indicated that the highly distorted tungsten oxide has a monooxo structure. Based upon the diatomic approximation method, a highly distorted octahedrally coordinated structure was proposed with one short W=O bond, one long opposing W=O bond and four bridging W-O bonds. The WO$_3$/TiO$_2$ system shows a similar 1010-cm$^{-1}$ Raman band and recent in situ XANES provided evidence for a highly distorted octahedrally coordinated structure of the tungsten oxide on the TiO$_2$ surface. Therefore the same highly distorted octahedrally coordinated structure is proposed for the WO$_3$/TiO$_2$ system (Figure 14).

The second broad band at ~870-cm$^{-1}$ in the spectra of the WO$_3$/TiO$_2$ system has not been observed in the Raman spectra of the WO$_3$/TiO$_2$ system. The inability to detect this weak, broad band may be caused by the increasing slope in the Raman spectrum due to the strong 639-cm$^{-1}$ band as well as the weaker 790-cm$^{-1}$ band of TiO$_2$. If, however, the second surface species is not present on the titania surface, then a possible explanation is that the formation of two types of surface tungsten oxide species on alumina is associated with the presence of specific surface hydroxyl groups. It is known that alumina possesses different surface hydroxyl groups than titania which may explain the presence of two types of surface tungsten oxide species on the alumina surface and one type of surface tungsten oxide species on the titania surface.

V$_2$O$_5$–WO$_3$/TiO$_2$ Dehydrated. Under ambient conditions it has been demonstrated that the two-dimensional metal oxide species are surrounded by water molecules and, therefore, more or less shielded from the support surface. Heating the catalyst removes the water and, consequently increases the interaction with the support. For supported metal oxide systems where more than one...
type of metal oxide is present a number of scenarios could occur upon dehydration: (a) The different types of surface metal oxides interact strongly and new hetero surface metal oxide species are formed. (b) The different types of surface metal oxides exist independently from each other on the support. (c) One of the surface metal oxide species interacts more strongly with the support than the second surface metal oxide species. The dispersion of the latter metal oxide is consequently decreased and the metal oxide is forced to change its two-dimensional structure, to form a three-dimensional crystalline phase or sit on top of the former metal oxide overlayer. (d) One of the surface metal oxide species is adsorbed on the support surface, and the second metal oxide species is absorbed into the support surface.

These various possibilities will be investigated below. The in situ Raman spectra of the mixed V$_2$O$_5$-WO$_3$/TiO$_2$ samples reveal that dehydration drastically changes the molecular structures of the surface species. This demonstrates that both the vanadium oxide and the tungsten oxide are present on the support and not in the support since metal oxides which are located in the support are not influenced by the presence of water molecules.

A vanadium oxide loading of 4.5% V$_2$O$_5$ is slightly below monolayer coverage in the single V$_2$O$_5$/TiO$_2$ system and an 8% tungsten oxide loading is approximately below monolayer coverage in the single WO$_3$/TiO$_2$ system. Therefore, it is expected that the greatest interaction between both metal oxides with regard to their two-dimensional structures would occur in the 4.5% V$_2$O$_5$-8% WO$_3$/TiO$_2$ sample. The in situ Raman spectrum of this sample, however, only shows the 1030-cm$^{-1}$ band of the highly distorted vanadium oxide species, the 930–950-cm$^{-1}$ band of moderately distorted vanadium oxide species and the 1010-cm$^{-1}$ band of the octahedrally coordinated tungsten oxide species. The band positions of two-dimensional metal oxides are sensitive to the support type under dehydrated conditions. The in situ Raman band of the highly distorted vanadium oxide species in V$_2$O$_5$/TiO$_2$ is found at 1030 cm$^{-1}$ while e.g. 1042 cm$^{-1}$ has been reported for V$_2$O$_5$/SIO$_2$. For WO$_3$/TiO$_2$, the Raman band position of the distorted octahedral is 1010 cm$^{-1}$ while e.g. 1016 cm$^{-1}$ has been found for WO$_3$/γ-Al$_2$O$_3$. Although the 1030- and 1010-cm$^{-1}$ bands in the Raman spectrum of the mixed 4.5% V$_2$O$_5$-8% WO$_3$/TiO$_2$ are not well resolved, the spectrum shows that these band positions are basically the same as the positions observed in the single component V$_2$O$_5$/TiO$_2$ and WO$_3$/TiO$_2$ systems, respectively. It can, therefore, be concluded that the highly distorted vanadium oxide and the octahedrally distorted tungsten oxide species are present on the TiO$_2$ support and not one on top of the other. Raman spectroscopy is a sensitive technique for the detection of metal oxide crystals, but the formation of crystalline V$_2$O$_5$ or crystalline WO$_3$ was not observed in the 4.5% V$_2$O$_5$-8% WO$_3$/TiO$_2$ sample. This is in agreement with the XPS data which also show that the dispersion of both metal oxides is not influenced by the presence of the other metal oxide.

Sutsumu et al. investigated the molecular structure of the bulk and the surface of V$_2$O$_5$-WO$_3$ catalysts. It was concluded that although V$_2$O$_5$ and WO$_3$ are not well mixed in the bulk of the catalyst, V and W ions are well-mixed in the surface of the catalyst. We have not observed any Raman features which would indicate the formation of V-O-W species. However, it is possible that very small amounts of V-O-W species are present on the surface. Thus, the Raman spectra show that the highly distorted surface vanadium oxide species and the highly distorted octahedrally coordinated surface tungsten oxide species essentially exist independently of each other on the titania surface. This is consistent with scenario b. However, there is an indication that the moderately distorted surface vanadium oxide is influenced by the presence of surface tungsten oxide. The 1% V$_2$O$_5$-(1-10)% WO$_3$/TiO$_2$ samples show a Raman band at ~930 cm$^{-1}$ and this band shifts from ~930 to ~950 cm$^{-1}$ in the spectra of 4.5% V$_2$O$_5$-(1-10)% WO$_3$/TiO$_2$ with increasing tungsten oxide loading. In the absence of tungsten oxide, the moderately distorted vanadium oxide species is not observed in the 1% V$_2$O$_5$/TiO$_2$ but is formed at higher vanadium oxide loadings where the band position shifts upwards with increasing vanadium loading. So,

in the presence of tungsten oxide, the moderately distorted surface vanadium oxide species becomes more abundant. This is in agreement with scenario c according to which one surface metal oxide is forced to change into a different two-dimensional structure due to the presence of the second surface metal oxide species. Thus for the mixed V$_2$O$_5$-WO$_3$/TiO$_2$ samples scenario b seems to operate at low coverage while at higher coverage both scenarios b and c are operating simultaneously.

A simple two-dimensional monolayer model does not explain how the titania surface can simultaneously accommodate a monolayer of vanadium oxide species and a monolayer of tungsten oxide species. A possible explanation is that the different surface species are interacting with different surface hydroxyl groups. The highly distorted surface vanadium oxide species and the surface tungsten oxide species may be interacting with two different types of surface OH groups and, therefore, do not "feel" each other. An FTIR study on the different hydroxyl groups could help clarify this matter.

Although the DeNO$_x$ reaction has been the subject of numerous investigations, the nature of the active species and reaction mechanism is still undetermined. It is generally agreed that the first step involves the adsorption of NH$_3$ on the catalyst surface. Inoue et al. proposed that NH$_3$ is adsorbed as NH$_4^+$, interacting with both a surface V=O group and a surface V--OH group. Wong et al. slightly modified this model while Jansen et al. proposed that NH$_3$ is chemisorbed on two surface V=O groups producing V--OH$_3$ and V--OH. Busca argued that the first step involves the breaking of the N--H bond of molecular coordinated ammonia on surface VO$_2^+$ cations. Gasior et al. proposed that only V--OH act as the active site which has recently been supported by Chen et al. who performed an extended Hückel molecular orbital calculation on a model V$_2$O$_5$/TiO$_2$ surface.

It has further been shown that the activity of the DeNO$_x$ reaction over V$_2$O$_5$/TiO$_2$ increases with increasing vanadia content up to ~7% V$_2$O$_5$. An IR study revealed that V$_2$O$_5$/TiO$_2$ possesses Brønsted acid sites which were associated with the surface vanadia species since titania does not possess Brønsted acidity. The Brønsted acidity follows the same trend as the activity for the DeNO$_x$ reaction and increases with increasing vanadia loading up to ~5% V$_2$O$_5$. Okazaki et al. demonstrated that Brønsted acidity is required for the DeNO$_x$ reaction. Our study shows that under dehydrated conditions the moderately distorted vanadium oxide species become more abundant with increasing vanadia coverage. Hardcastle et al. argued that the moderately distorted vanadium oxide species possibly possesses OH groups. It is therefore suggested that the moderately distorted vanadium oxide species is possibly the precursor of the active site in the DeNO$_x$ reaction. The role of the tungsten oxide species, which seem to enhance the formation of the moderately distorted vanadium oxide species, is yet not totally clear. On alumina, other metal oxide such as molybdenum oxide, tungsten oxide, iron oxide, cobalt oxide, and nickel oxide also seem to enhance the formation of the moderately distorted vanadium.

Conclusions

The molecular structures of V$_2$O$_5$/TiO$_2$, WO$_3$/TiO$_2$, and V$_2$O$_5$-WO$_3$/TiO$_2$ catalytic systems have been studied by Raman spectroscopy under hydrated and dehydrated conditions and by

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Colloid Particle Charge Determination via the Structure Factor $S(Q)$

H. Versmold,* U. Wittig, and W. Härtl

Institut für Physikalische Chemie, RWTH, D-5100 Aachen, F.R.G (Received: December 11, 1990)

The dependence of the structure factor $S(Q)$ of fluidlike ordered polymer colloid suspensions on ionic strength is investigated. It is found that a given amount of NaCl influences the structure much more than the same amount of NaOH. This behavior is explained in terms of an ion-exchange mechanism that takes place with NaOH but not with NaCl. By comparing the structure factor $S(Q)$ of samples titrated with NaOH with the $S(Q)$ of samples titrated with NaCl, one can determine the charge of the latex particles, if it is assumed that equal structure factors are due to equal ionic strength in corresponding suspensions.

Introduction

Considerable effort has been directed toward the understanding of self-organization of supermolecular systems to form fluid-, glass-, and crystallike states. Besides phenomenological and technological interest, the ultimate goal of such investigations is the understanding of the self-organization in terms of the interactions and properties of the constituents, from which the structure is formed.

In order to understand the structure of charge-stabilized systems from first principles, one should start with the determination of the particle charge. Next, statistical-mechanical methods would be necessary to determine the effective pair potential of mean force $V(r)$. Finally, statistical mechanics or computer simulation techniques could be used to predict the resulting structures. Despite the simplicity of this concept, each of the steps mentioned above is faced with severe difficulties.

In this paper we focus on the problem of how the charge of colloid particles can be determined experimentally. Various physicochemical methods are presently used to determine the charge of polymer latex particles like conductometric titration, conductivity measurements, and electrophoretic mobility. In the context of the present investigation, conductometric titration is of particular interest, since it shows an interesting behavior, which initiated this present investigation.

For conductometric titrations the particles are usually cleaned and transferred into the protonated form by means of ion-exchange resins. Thus, at the beginning of a titration experiment a high conductivity due to the $H^+$ counterions of the colloid particles is expected. By titration with NaOH, the conductivity should decrease until the equivalence point is reached since the highly mobile $H^+$ ions are replaced by $Na^+$ ions. Experiments show, however, that this simple concept does not work. Titration of a perfectly cleaned and protonated suspension with NaOH shows surprisingly little decrease of the conductivity. Similarly, on addition of $Ba(OH)_2$ the conductivity starts to decrease significantly only as the equivalence point is approached.


