

In Situ Laser Raman Spectroscopy of Supported Metal Oxides

S. S. Chan,[†] I. E. Wachs,* L. L. Murrell,

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

L. Wang, and W. Keith Hall

Department of Chemistry, Laboratory for Surface Studies, The University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201 (Received: March 14, 1984)

The in situ laser Raman spectra of crystalline and amorphous supported oxide phases were obtained for a series of oxides (WO_3 , MoO_3 , and V_2O_5) supported on TiO_2 and Al_2O_3 . The changes in the Raman features of crystalline phases at elevated temperatures are due to thermal broadening and are reversed by cooling the sample to ambient temperatures. The Raman bands of the amorphous, supported surface oxide species sharpen and simultaneously shift in frequency at elevated temperatures due to the desorption of water from the surface. The removal of the weakly coordinated water molecules from the supported surface oxide species decreases the degree of disorder and affects the symmetric $\text{M}=\text{O}$ stretch. Readsorption of water on the oxide surface reverses the process. The shift in the Raman band with coverage of the supported surface oxide species appears to be related to the extent of hydration of the surface oxide species with coverage. The changes in the Raman spectra of the supported metal oxide phases with extent of hydration confirm earlier conclusions that the metal oxides are present on the support as highly dispersed surface oxide species bound to the support surface.

Introduction

Laser Raman spectroscopy (LRS) has been used extensively in the past 5 years to characterize heterogeneous oxide catalysts. A recent review of Raman spectroscopy as applied to heterogeneous catalysis points out why Raman spectroscopy is a powerful tool for oxide systems while infrared spectroscopy is not.¹ Oxides as catalysts or as supports in the mid- and low-frequency infrared region are strong absorbers while they are poor Raman scatterers. Thus, bands from the support are suppressed, making the detection of quite low levels of a transition-metal oxide on an oxide such as alumina or silica by LRS possible. Considerable success in detecting different structures of the supported oxide phase as a function of surface coverage has made LRS a standard research tool in the study of such systems.

Laser Raman spectroscopy has been widely employed to characterize alumina and silica supported molybdenum oxide,²⁻¹³ tungsten oxide,¹⁴⁻¹⁸ vanadium oxide,¹⁹ and rhenium oxide.^{20,21} The bonding of transition-metal oxides to inorganic supports can be viewed as a subclass of functional groups on solid surfaces.²² Two excellent reviews of this subject have recently been published, one by Boehm and Knözinger²² and the other by Yermakov et al.²³ Three primary models of the supported surface phase oxide structure of these metal oxides on alumina have been proposed: a surface compound consisting of one layer on the oxide surface of isolated transition-metal oxide units, a surface compound consisting of one layer on the oxide surface of polymeric, octahedrally coordinated units, and a surface structure consisting of bi- and trilayer structures of the transition-metal oxide. Despite considerable work to distinguish between the above surface structures, the problem has not been entirely settled for all cases. Nevertheless, LRS is a very powerful technique in detecting the presence of the different crystalline and amorphous oxide phases on the alumina surface.²⁻²¹ Studies of the catalytic activity of supported oxides as a function of surface coverage have shown considerable variation in activity with surface coverage.²⁴⁻²⁷ Since LRS can detect the different oxide structures as a function of surface coverage, the presence of these oxide phases can be compared to changes in catalytic activity.²⁴⁻²⁷

Schrader and Cheng have recently reported in situ LRS studies of sulfided molybdena on γ -alumina.²⁸ As they point out, LRS is ideally suited to in situ studies because there is no inherent limitation on the temperatures, pressures, or the presence of re-

action gases during the investigation. Hall and Wang have also reported in situ Raman data for rhenia on alumina catalysts.²¹

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[†] Present address: Technical Center, The BOC Group, 100 Mountain Ave, Murray Hill, NJ 07974.

In the present paper in situ LRS studies of tungsta on TiO_2 at different temperatures are reported. The changes of the symmetric $\text{W}=\text{O}$ stretching mode have been found to be sensitive to dehydration of the sample and to surface concentration of the supported oxide. Other surface phase oxide samples such as vanadia, molybdena, and tungsta on alumina show related behavior. The present study demonstrates that assignment of the coordination structures of surface phase oxide samples based on LRS studies of the hydrated materials is clearly inappropriate without comparison with the results for the dehydrated samples.

In this paper we will not resolve the controversy of the structure of surface phase oxides on oxide supports; rather, we will present unambiguous evidence using in situ LRS that water coordination to the surface phase oxides dramatically affects the Raman bands of the surface phase oxides. These results support earlier conclusions that these surface phase oxide structures are indeed highly dispersed and have coordinatively unsaturated sites (CUS) associated with the transition-metal center.^{29,30} The CUS of supported transition-metal oxides may be associated with isolated transition-metal centers, polymeric oxide phases, or multilayer phases. For example, in the case of tungsta on silica, at loading levels of <5 wt %, small clusters having an average diameter of 1.2 nm are observed by transmission electron microscopy.³¹ These small tungsta clusters, when dehydrated at 500 °C, show coordinative unsaturation as measured by butylamine titration. Peri,²⁹ Hall and co-workers,³² and Topsoe and Topsoe³³ have recently reported NO to be a sensitive probe of CUS sites of supported molybdenum oxide and molybdenum sulfide systems. Dumesic and co-workers³⁴ have similarly shown by NO chemisorption that FeO raft structures on SiO_2 are coordinatively unsaturated.

Experimental Section

The vanadia on alumina, tungsta on alumina, and molybdena on alumina samples were prepared on a high-purity γ -alumina (Ketjen CK-300; 192 m^2/g). ACS grade $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was obtained from Fischer Scientific Co., and tungstic acid and ammonium metavanadate were Alfa-Ventron products. The samples were made by the liquid phase equilibrium adsorption method.³⁵ Molybdenum, tungsten, and vanadium oxy anion solutions were made by dissolving the salts in water. The solution pH was adjusted to the desired value by either HNO_3 or NH_4OH . These mixtures were agitated for up to 100 h on an automatic shaker. Initial and final pH values were recorded before the supernatant liquid was filtered away. The wet catalysts were dried in air at 150 °C for 6 h and calcined at 500 °C for 10 h. A more detailed description of the preparation method is given elsewhere.^{35,36}

The vanadia on titania sample was prepared on a low surface area TiO_2 (100% anatase, 8–9 m^2/g) obtained from Mobay. This sample was prepared by dissolving V_2O_5 (Alfa) in an aqueous solution of oxalic acid and impregnating the support. The tungsta on titania samples were prepared on a higher surface area TiO_2 support (66% anatase, 34% rutile; 55 m^2/g) obtained from Degussa (P-25). They were prepared by dissolving ammonium tungstate (Aldrich Chemical Co.) in water and impregnating the support. The vanadia on titania and tungsta on titania samples were dried

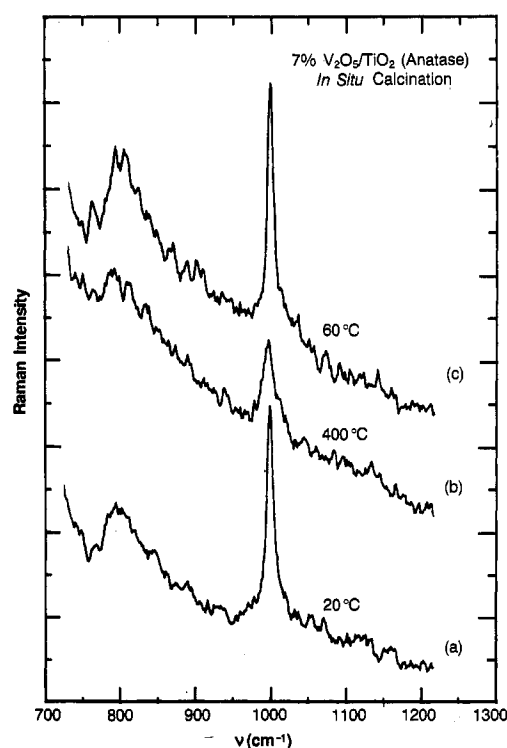


Figure 1. In situ Raman spectra of 7 wt % V_2O_5 (anatase): (a) initial conditions at room temperature, (b) calcination at 400 °C in dry air for 5 min, (c) postcalcination at 60 °C in dry air.

at 110 °C and calcined at 450 °C for 2 h.

Two Raman spectrometers located at different laboratories were used in the present study. The Raman spectrometer located at the Laboratory for Surface Studies at the University of Wisconsin—Milwaukee is a Spex-Ramalog Model 1401. The 488-nm line of the argon ion laser (Spectra Physics, Model 164) was used as the exciting source and was adjusted to 50 mW (measured at the sample position). An in situ cell was designed which allow pretreatments with O_2 at 500 °C and then subjected the sample to other treatments. In this configuration the sample could not be rotated. The sample wafer was attached underneath a cold finger filled with liquid N_2 during the recording of the spectrum. This arrangement was used to reduce the heat from the continuous laser radiation. Where cross-comparison was possible this procedure gave identical results to those obtained by spinning in air. The Raman spectrometer at the Corporate Research Science Laboratories of Exxon Research and Engineering Co. is a triple monochromator (Instruments S.A., Model DL 203) coupled to an optical multichannel analyzer (Princeton Applied Research, Model OMA2) equipped with an intensified photodiode array detector cooled to -15 °C. An argon ion laser (Spectra Physics, Model 165) was tuned to the 514.5-nm line for excitation. The laser power at the sample location was set in the range 0.4–40 mW by adding or removing neutral density filters. A sample chamber was designed which was capable of sample spinning and in situ treatments. The sample was heated by a cylindrical heater coil surrounding the chamber, and the temperature was determined with an internal thermocouple. The chamber was capable of operating up to 600 °C. More detailed descriptions of the Raman equipment are presented elsewhere.^{21,36,37}

Results

The in situ laser Raman spectra for the low surface area 7 wt % vanadia on titania (anatase) sample is shown in Figure 1 for the range 750–1250 cm^{-1} . In this range two Raman features are present: the symmetrical stretching mode of the terminal oxygen atom ($\text{V}=\text{O}$) of crystalline V_2O_5 at 997 cm^{-1} and the weak

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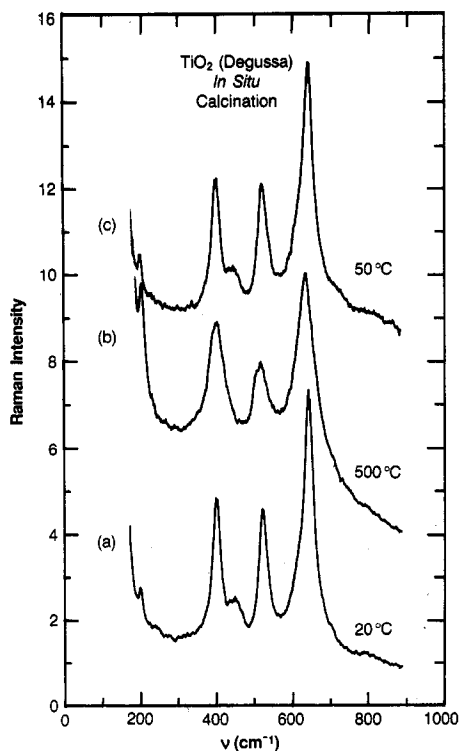


Figure 2. In situ Raman spectra of TiO_2 (Degussa): (a) Initial conditions at room temperature, (b) calcination at 500°C in dry air for 5 min, (c) postcalcination at 50°C in dry air.

second-order feature of TiO_2 (anatase) at 794 cm^{-1} .³⁸ The low surface area of the TiO_2 support ($8\text{--}9\text{ m}^2/\text{g}$) assures that all but a small fraction of the vanadia is present as crystalline V_2O_5 .³⁹ The V_2O_5 X-ray diffraction lines of this sample are barely detectable, and their relative intensities deviate from that of bulk V_2O_5 . This observation suggests that the V_2O_5 crystallites are small, $\sim 10\text{ nm}$, and somewhat distorted on the TiO_2 (anatase) support. Upon heating the 7% vanadia on titania (anatase) sample in dry air to 400°C , the Raman features measured in situ at 400°C of the small V_2O_5 crystallites and the TiO_2 support broaden. The full width at half-maximum (fwhm) of the peak at 997 cm^{-1} increases from 11 to 19 cm^{-1} . The peak positions of both the V_2O_5 and TiO_2 crystalline phases, however, are not affected by the thermal treatment. Cooling the sample back to room temperature restored the sharper Raman features present in the 7% vanadia on titania (anatase) sample prior to the thermal treatment. The completely reversible nature of the Raman line broadening shows that there are no significant structural changes in the crystalline V_2O_5 and TiO_2 phases due to the thermal treatment and that the changes with temperature are due to thermal broadening.

Similar thermally induced broadening in the Raman bands were observed for a high surface area TiO_2 ($55\text{ m}^2/\text{g}$; 66% anatase, 34% rutile) support, as shown in Figure 2. The major anatase Raman bands occur at 144, 199, 399, 520, and 643 cm^{-1} , and the major rutile Raman bands occur at 144, 448, and 611 cm^{-1} .³⁸ The Raman spectra of the intermediate surface area TiO_2 sample are dominated by the anatase features with the exception of the small rutile feature at 448 cm^{-1} . Heating the crystalline TiO_2 to 500°C in dry air caused a broadening of the Raman bands, and the rutile band at 448 cm^{-1} cannot be discerned. The Raman peak positions are essentially unchanged by the thermal treatment. Cooling the TiO_2 sample back to room temperature (Figure 2c) restored the sharper Raman features present prior to the thermal treatment (Figure 2a). This example further demonstrates that the changes in the Raman features of crystalline phases at elevated

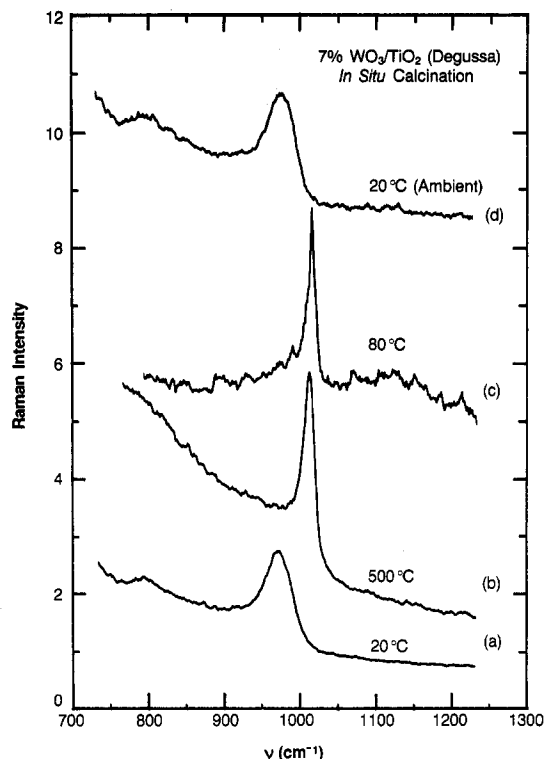


Figure 3. Raman spectra of 7 wt % tungsta on titania (Degussa): (a) in situ initial conditions at room temperature, (b) in situ calcination at 500°C in dry air, (c) in situ postcalcination at 80°C in dry air, (d) postcalcination with exposure to ambient air for 12 h at room temperature.

temperatures are due to thermal broadening and are reversed by cooling the sample to ambient temperatures.

The in situ Raman spectra for 7 wt % tungsta on titania ($55\text{ m}^2/\text{g}$, 66% anatase) sample is presented for the range $750\text{--}1250\text{ cm}^{-1}$ in Figure 3. The concentration of tungsten oxide was less than that required to achieve a complete monolayer of the surface tungsten oxide complex on the TiO_2 support.⁴⁰ The absence of crystalline WO_3 in this sample is suggested by the lack of the WO_3 Raman transition at 808 cm^{-1} . The major Raman feature at 966 cm^{-1} is due to the symmetrical stretching mode ($\text{W}=\text{O}$) of the tungsten oxide complex coordinated to the TiO_2 surface. The smaller Raman band at 794 cm^{-1} is due to the weak TiO_2 (anatase) transition. Heating the 7% WO_3/TiO_2 sample in dry air to 500°C produces very dramatic changes in the Raman spectra. The TiO_2 (anatase) Raman transition is not discernible from the background, and the Raman feature associated with the surface tungsten oxide complex becomes sharper (full width at half-maximum (fwhm) decreases from 37 to 19 cm^{-1}) and shifts from 966 to 1011 cm^{-1} . Cooling the 7% tungsta and titania sample to 80°C in the in situ cell causes a small sharpening of the 1011 cm^{-1} feature in the Raman spectrum (fwhm decreases from 19 to 16 cm^{-1}). This change in line width is due to thermal effects. However, opening the cell to ambient air restores the original Raman spectra of the WO_3/TiO_2 sample prior to the thermal treatment. The absence of major changes in the Raman band for the tungsten oxide surface complex upon cooling the sample back to room temperature (Figure 3b,c) implies that the band shifts and line-width changes in the Raman spectra are not due to thermal effects (Figure 3a,b). The original Raman features could only be restored after exposure of the sample to ambient air or equivalent vapor pressure of water. This implies that the adsorption of water vapor on the tungsta on titania sample is responsible for these changes in the Raman spectra. The initial heating cycle (Figure 3a,b) desorbed the chemically and physically adsorbed water, and subsequent exposure of the sample to ambient air (Figure 3d) resulted in re-adsorption of water. The broadening

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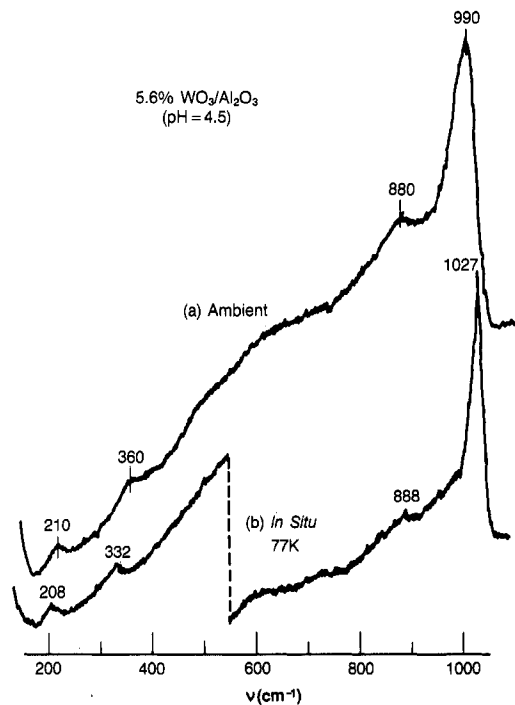


Figure 4. Raman spectra of 5.6 wt % tungsta on alumina prepared at pH 4.5: (a) under ambient conditions, (b) in situ postcalcination at 77 K under vacuum.

of the Raman band due to the coordination of water to the tungsten oxide surface complex on the TiO_2 support implies that adsorbed water is bonding directly to the tungsten oxide species of the monolayer surface phase or partially hydrolyzing it from the support. The response of the TiO_2 supported tungsten oxide surface species to thermal treatment is in sharp contrast to the response of the crystalline phases, V_2O_5 and TiO_2 , to thermal treatment.

This phenomenon of Raman band sensitivity to thermal treatment is not unique to tungsten oxide supported on TiO_2 and can be observed with other supported oxide surface species by removing H_2O by evacuation (usually) at elevated temperatures. Several examples are shown here for supported oxide systems containing much less than a monolayer of the supported oxide phase. Figure 4 depicts such changes in the Raman spectra for tungsten oxide supported on alumina (5.6% $\text{WO}_3/\text{Al}_2\text{O}_3$). The spectrum for the tungsta on alumina sample determined in air had the major Raman transition at 990 cm^{-1} . When dehydrated, it exhibited a much sharper Raman peak shifted to 1027 cm^{-1} . The lower frequency Raman features also shifted somewhat with extent of dehydration.

The effect of hydration on the Raman spectra for 2.0% vanadia on alumina is shown in Figure 5. The hydrated vanadia on alumina sample showed two main Raman features at 795 and 930 cm^{-1} , while after dehydration only the sharper major peak at 1034 cm^{-1} was resolved. Similar behavior is observed for the molybdena on alumina system. The Raman spectra of 4.6% molybdena on alumina is presented in Figure 6. The hydrated molybdena on alumina sample exhibited a major Raman peak at 975 cm^{-1} , and this peak sharpened and shifted to 1012 cm^{-1} upon dehydration. The lower frequency Raman transitions were also somewhat affected by the dehydration process. This behavior has been demonstrated for many different supported oxide systems (molybdena on silica, molybdena on titania, and chromia and rhenia on alumina).^{21,35,36} Thus, the effect of hydration on the state of the supported oxide surface species and the associated Raman spectra is a general phenomenon.

Discussion

The in situ Raman studies of supported V_2O_5 and TiO_2 demonstrate that the Raman peaks of crystalline oxides broaden at elevated temperature due to thermal effects. The Raman bands

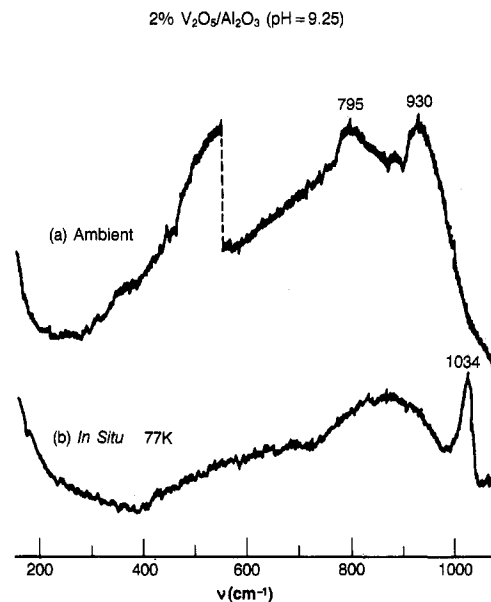


Figure 5. Raman spectra of 2 wt % vanadia on alumina prepared at pH 9.25: (a) under ambient conditions, (b) in situ postcalcination at 77 K under vacuum.

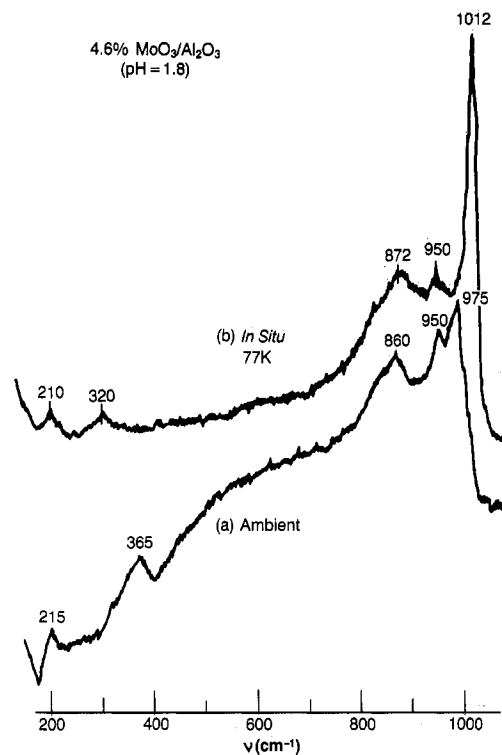


Figure 6. Raman spectra of 4.6 wt % molybdena on alumina prepared at pH 1.8: (a) under ambient conditions, (b) in situ postcalcination at 77 K under vacuum.

of the supported surface oxide species respond very differently to thermal treatments than those from crystalline materials. The Raman bands of the surface oxide species assigned to the symmetric $\text{M}=\text{O}$ stretch sharpen and shift $\sim 30\text{--}40\text{ cm}^{-1}$ to higher frequency. This rather unexpected observation of the Raman bands becoming sharper and simultaneously shifting in frequency is related to the desorption of water. Apparently, the interaction of water molecules with the supported surface oxide species increases the degree of disorder or changes the symmetry of surface bonding and thus affects the symmetric $\text{M}=\text{O}$ stretch. The increased disorder may well be a consequence of nonuniform coordination of water to the surface metal oxide complex (i.e., $\text{MO}_x \cdot (\text{H}_2\text{O})_n$ where $n = 0, 1, 2, \dots$). The broadened band cor-

TABLE I: Change in Raman Bands of Tungsta on Titania with Tungsten Oxide Loading

WO ₃ /TiO ₂ , wt %	peak position, cm ⁻¹	fwhm (Δν), cm ⁻¹
1	942	50
3	952	48
5	962	42
7	966	37
10	972	37

responds to a density of states rather than a transition between two discrete states. The present Raman observations are in excellent agreement with earlier work by Wang and Hall^{21,36} for the rhenia supported on alumina system where the effect of water vapor on the Raman features was first reported. Here the changes could be attributed to hydrolysis of the Al-O-Re bond.

The effect of water coordination to vanadia on silica upon the electron spin-echo modulation spectra was also recently reported by Narayana et al.⁴¹ The surface vanadyl species on SiO₂ appeared to be coordinated to two water molecules which could be removed by heating to 100 °C. The coordination of water molecules to the supported surface oxide species may be a general phenomenon that was not fully appreciated in the past as having a pronounced effect on the Raman bands associated with surface phase oxides. In some cases the interaction may be hydrolysis involving the bound surface phase oxide.

The Raman band of the supported surface oxide species also exhibited a coverage-dependent shift prior to dehydration. This is shown in Table I for a series of tungsta on titania (55 m²/g, 66% anatase) samples. The Raman peak shifts from ~942 to 972 cm⁻¹ with coverage. Similar observations have been made for tungsta on alumina^{11,17} and vanadia on titania³⁹ where the Raman peaks shift ~965–1000 and ~940–1000 cm⁻¹ with coverage of the surface oxide species, respectively. Furthermore, the full width at half-maximum of the Raman band *decreases* as the surface coverage of tungsten oxide *increases*. These shifts have been associated with a distortion of the monolayer species due to lateral interactions and/or the heterogeneity of the adsorption sites of the γ-Al₂O₃ surface.¹⁷ A new explanation is proposed in light of these new observations, namely that water molecules coordinate to the supported surface oxide species and alter the features of the corresponding Raman bands. At lower coverages the surface oxide species may be coordinated to more water molecules than at higher coverages of the surface oxide species because of lateral interactions. The lateral interactions can either sterically or electronically influence the number of water molecules that may be coordinated to the surface oxide species. See for example effects of *gem*-dicarbonyl groups present at the edges of isolated 1.5-nm Rh clusters⁴² and *gem*-dinitrosyl adsorption on the edges of isolated 2.0-nm FeO clusters.³² As the coverage of the supported surface oxide species increases, the extent of hydration of the surface oxide species may be decreased. This would cause the Raman band to sharpen and to shift to a higher wavenumber. Further shifts of the Raman band are achieved by desorbing the remaining water molecules coordinated to the supported oxide species.

Jezirowski and Knözinger⁷ monitored the Raman bands of molybdena on alumina during catalyst preparation. The major Raman band at ~900–1000 cm⁻¹ was found to shift toward higher

frequency during the drying and calcination processes. In light of the present findings, it appears that the shifts observed by Jezirowski and Knözinger are related to two effects. One factor is the decreasing water content of the molybdena on alumina sample, and the other is the decomposition of the oxide precursor with drying and calcination.

The pronounced changes in the Raman spectra of the supported metal oxide phases with extent of hydration further confirm earlier conclusions that the metal oxides are present on the support as surface compounds. The behavior of the Raman bands upon desorption of water could be used as an argument for the coordinative unsaturation of the dehydrated transition-metal oxide centers.^{29–34} The Raman spectra of supported crystalline oxide phases, such as 7% vanadia on titania (8–9 m²/g, anatase), are not affected by the presence of adsorbed water molecules. This new information provides an unambiguous method of distinguishing between surface oxide and crystalline oxide phases (and their corresponding Raman bands) since only the Raman bands of the surface oxide species will respond to changes in extent of hydration.

The coordination of the supported transition-metal oxide surface species has not been completely resolved in the literature. In the case of the tungsta on alumina system it is not clear whether the tungsten oxide surface species is octahedrally or tetrahedrally coordinated to the alumina support.^{14–18} The studies done to date have been performed under ambient conditions where the surface oxide species are coordinated with water molecules. The present findings reveal that, in order to determine the coordination of the supported surface oxide species, the samples must first be dehydrated. This new insight might provide the necessary impetus to employ in situ spectroscopic studies that will allow unambiguous assignment of the coordination state of the supported surface phase oxides.

Conclusion

The in situ laser Raman spectra of crystalline and amorphous supported oxide phases were obtained for a series of oxides (WO₃, MoO₃, and V₂O₅) supported on TiO₂ and Al₂O₃. The changes in the Raman features of crystalline phases at elevated temperatures are due to thermal broadening and are reversed by cooling the sample to ambient temperatures. The Raman bands of the amorphous, supported surface oxide species sharpen and simultaneously shift in frequency at elevated temperatures due to the desorption of water from the surface. The removal of the coordinated water molecules from the supported surface oxide species decreases the degree of disorder (the density of states) and affects the symmetric M=O stretch. This process is reversed by adsorbing water vapor. The shift in the Raman band with coverage of the supported surface oxide species appears to be related to the extent of hydration of the surface oxide species with coverage. This new insight may lead to the unambiguous assignment of the coordination states of the support surface oxide species. The changes in the Raman spectra of the supported metal oxide phases with extent of hydration confirm earlier conclusions that the metal oxides are present on the support as highly dispersed surface oxide species bound to the support surface.

Acknowledgment. The UWM portion of this work was supported by the National Science Foundation under Grant No. CHE-80-19309.

Registry No. WO₃, 1314-35-8; MoO₃, 1313-27-5; V₂O₅, 1314-62-1; TiO₂, 13463-67-7; Al₂O₃, 1344-28-1.

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