In Situ Raman Spectroscopy of Alumina-Supported Metal Oxide Catalysts

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The molecular structures of the surface overlayers of rhenium(VII) oxide, molybdenum(VI) oxide, tungsten(VI) oxide, chromium(VI) oxide, vanadium(V) oxide, niobium(V) oxide, and titanium(IV) oxide on γ-alumina were determined by in situ Raman spectroscopy under dehydrated conditions. It was found that the dehydrated surface metal oxide structures of all the systems under study, except for supported titanium oxide, are different from those under ambient condition where moisture is present on the surface. Supported molybdenum oxide, tungsten oxide, vanadium oxide, and niobium oxide show the presence of a highly distorted mono-oxo species (one M=O bond) at all loadings. At higher surface coverage these supported systems also reveal the presence of M=O–M linkages which are indicative of polymeric structures. Above ~20% metal oxide loading, monolayer coverage is exceeded and crystalline MoO3, WO3, V2O5, and Nb2O5 particles are found on the alumina surface together with the dehydrated surface species. Crystalline Re2O7 is not formed at high loadings and two slightly different surface rhenium oxide species are observed as a function of surface coverage. Both possess three terminal Re=O bonds and one bridging Re=O–Al bond. Polymeric chromium oxide surface species are observed at all loadings, 0.5–5% Cr2O3/Al2O3, as well as for titanium oxide which also forms a surface metal oxide overlayer of polymeric species up to a loading of 17%.

The polymeric titanium oxide surface species are, however, not sensitive to moisture and only possess Ti=O–Ti bonds and not Ti=O bonds. Crystalline TiO2 (anatase) is found to be present at the alumina surface in the 17% TiO2/Al2O3 sample.

Introduction

Supported metal oxides are extensively used as heterogeneous catalysts in numerous chemical processes ranging from, e.g., hydrodesulfurization, cracking, polymerization, and partial oxidation of hydrocarbons to the selective reduction of nitrogen oxides.1 Knowledge of the local structure of the catalyst surface and insight into the factors which determine the surface structure play an important role in the further development and optimization of supported metal oxide heterogeneous catalytic systems. Characterization of the molecular structure of the supported metal oxides, however, is complicated since the supported metal oxide phase can simultaneously possess several different molecular structures as well as chemical states. Thus, useful characterization techniques, which can provide detailed information about the molecular structure of the surface metal oxide, must be capable of discriminating between these different states. To date, the characterization techniques which can provide such detailed molecular information are extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge spectroscopy (XANES), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and recently 51V solid-state NMR.

Raman spectroscopy has proved to be a very powerful characterization technique for obtaining detailed information about the molecular structure of the metal oxide overlayer on oxide supports. The reason is that each molecular state possesses a unique vibrational spectrum that is related to its structure. Furthermore, Raman spectroscopy is ideally suited for in situ studies because there are inherent limitations on the temperature, pressures, or the presence of reaction gases during investigations. Recent improvement of Raman instruments through the use of triplemate spectrometers coupled to multichannel detectors and improved software has significantly enhanced the quality of the measurements.2,3 The various types of structural information which can be obtained from Raman spectroscopy about supported metal oxides was reviewed by Wachs et al. in 1986,4 and more recently by Stencel in a book entitled Raman Spectroscopy for Catalysts which gathers literature acquired from 1975 to 1988.4

Most of the previously reported Raman studies on supported metal oxide catalysts, however, were performed under ambient conditions, where moisture is present on the oxide support surface. The first in situ Raman study on supported metal oxides was reported by Wang and Hall for supported rhenium oxide5 and

by Schrader and Cheng for sulfided molybdenum oxide in 1983.6 Subsequent to these studies several in situ Raman studies have been reported,7-26 however, the influence of hydration/dehydration still remains a source of confusion and has hampered progress in the understanding of supported metal oxide catalysts. The supported metal oxide systems studied to date in situ Raman spectroscopy include molybdenum oxide,6,7,10,11,12,14,15 tungsten oxide,6,7,11,12,14,15,16-22 vanadium oxide,6,7,11,12,14,15,16-22 rhenium oxide,5,7,23 niobium oxide5,24,25 and nickel oxide.6,26 Except for the supported nickel oxide system, all of these in situ studies showed a drastic change in the Raman spectra upon dehydration. Generally, it was observed that the symmetric stretching frequency of the M=O bonds shifts upward upon dehydration. Except for the supported vanadium oxide system, which has recently been studied in detail under dehydrated conditions,7,8,11,13,16-22 the upward shift of the symmetric stretching mode is not well understood and has been attributed to an increase in metal oxide–support interaction and not to a change in structure. Thus, most studies concluded that the same surface metal oxide species is present under hydrated and dehydrated conditions and that under dehydrated conditions simply the water molecules are removed.

This article deals with the determination of the molecular structures of several metal oxides (rhenium(VII) oxide, chromium(VI) oxide, molybdenum(VI) oxide, tungsten(VI) oxide, vanadium(V) oxide, niobium(V) oxide, and titanium(IV) oxide) supported on γ-alumina by in situ Raman spectroscopy. The purpose of this work is to reveal the drastic structural change of the dispersed metal oxides upon dehydration and to show the effect of loading upon the dehydrated surface metal oxide structures. This study is part of a larger investigation to determine the molecular structures of supported metal oxides under dehydrated conditions as a function of oxide support, loading, presence of promoters, as well as a second surface metal oxide species.

Experimental Section

Sample Preparation. Most of the supported metal oxide catalysts were prepared by the incipient-wetness impregnation method on γ-alumina (Harshaw, ~180 m2/g). Aqueous solutions of ammonium metatungstate ((NH4)2H2W12O40), ammonium heptamolybdate ((NH4)6Mo7O24·4H2O), chromium nitrate ([Cr(NO3)3·6H2O]), perbenzic acid (HReO4), and niobium oxalate/oxalic acid were used for the preparation of the corresponding supported metal oxide samples. After the impregnation step, the samples were dried at room temperature overnight, at 110 °C overnight and finally calcined in dry air at 500 °C. The vanadium oxide samples were prepared by impregnation with a vanadium triisopropoxide (VO(OCH3)3) solution in methanol. Due to the

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Results

The in situ Raman spectra of the supported metal oxide systems are presented in Figures 1–9. γ-Alumina does not show any Raman features in the 100–1100-cm⁻¹ region and, therefore, all the observed Raman bands are assigned to metal oxide vibrations. At very low metal oxide loadings (0.7–5 wt % metal oxide), however, additional weak Raman bands are observed at ~650, ~480, and ~400 cm⁻¹ in the in situ Raman spectra of all supported metal oxide samples under study which are attributed to detector noise.

Re₂O₇/Al₂O₃. The in situ Raman spectra of the Re₂O₇/Al₂O₃ catalysts as a function of rhenium oxide surface coverage are presented in Figure 1. To underline the spectral differences with increasing loading, the Raman spectra of the 1.3 and 16.9% Re₂O₇/Al₂O₃ samples are shown enlarged in the 1100–700-cm⁻¹ range in Figure 2. One surface species, observed at all coverages, possesses bands at 1004, 889, and 340 cm⁻¹ (with a shoulder at ~310 cm⁻¹). A second surface species is present at higher loadings with bands at 1015 and ~980 cm⁻¹ and probably the same mode at 340 cm⁻¹ (with a shoulder at ~310 cm⁻¹) since no changes are observed in the low-wavenumber range with increasing loading.

Cr₂O₇/Al₂O₃. The in situ Raman spectra of a series of chromium oxide on alumina are presented in Figure 3 as a function of the chromium oxide coverage. All samples (0.5–5% Cr₂O₇/Al₂O₃) reveal the same Raman bands at 1005, ~935 (shoulder), 880,
stretching mode of the Mo-O-Mo bonds. Comparing the intensity ratio of the 960-cm⁻¹ band relative to the 870-cm⁻¹ mode in the spectrum of crystalline (NH₄)₆Mo₇O₂₄·4H₂O versus the intensity ratio in the spectrum of the hydrated 20% sample, however, shows that the 870-cm⁻¹ band is too intense to be attributed to the asymmetric stretching mode only. Upon dehydration the broad 870-cm⁻¹ band does not change and is therefore assigned to a molybdate species that is not influenced by the presence of moisture. The in situ Raman spectra of the 10, 15, and 20% MoO₃/Al₂O₃ samples reveal the existence of a third surface molybdate species due to the presence of additional weak bands at ~940, ~580, ~360, and ~208 cm⁻¹. Above 20% MoO₃/Al₂O₃, monolayer coverage has been exceeded and crystalline MoO₃ particles are present on the dehydrated alumina surface (major bands at 815, 663, 335, and 281 cm⁻¹) together with the dehydrated surface molybdate species.

WO₃/Al₂O₃. The in situ Raman spectra of the WO₃/Al₂O₃ catalysts, as a function of tungsten oxide loading are presented in Figure 6. All spectra reveal a sharp band in the W=O stretching region, which shifts from 1004 to 1020 cm⁻¹ with increasing surface coverage, together with a broad band in the bending region at ~300 cm⁻¹. This band is not related to any other bands in the 800-1000-cm⁻¹ region since the intensity ratio of these bands changes with increasing loading, while on silica the sharp band has been observed without the presence of any other bands. A second vanadium oxide species possesses a broad band at 885 cm⁻¹, together with a shoulder at 845 cm⁻¹, and becomes more pronounced with increasing surface coverage. At 15% V₂O₅/Al₂O₃ and above, the 885-cm⁻¹ band shifts to ~925 cm⁻¹ and additional bands at ~770, ~620, ~560, ~340, and ~250 cm⁻¹ show up. Above 20% V₂O₅/Al₂O₃, monolayer coverage has been exceeded and crystalline V₂O₅ particles are also present on the dehydrated alumina surface (not shown in Figure 6).

Nb₂O₅/Al₂O₃. The in situ Raman spectra of Nb₂O₅/Al₂O₃ as a function of niobium oxide coverage are presented in Figure 8. The 3% Nb₂O₅/Al₂O₃ sample shows broad bands at 980, 940, 880, 630, and ~300 cm⁻¹. With increasing loading, the 980-cm⁻¹ band shifts to 988 cm⁻¹, while the 940- and 630-cm⁻¹ bands shift to ~950 and ~645 cm⁻¹, respectively, and become more pronounced.
TABLE I: Raman Band Positions (in cm⁻¹) of Several Rhenium Oxide Reference Compounds

<table>
<thead>
<tr>
<th>Rhenium Oxide Reference Compound</th>
<th>Raman Band Positions (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO₂ (aq)</td>
<td>971, 916, 332, 332</td>
</tr>
<tr>
<td>NaReO₄</td>
<td>963, 980, 403, 321</td>
</tr>
<tr>
<td>ReO₂F³⁻</td>
<td>1009, 980, 293, 344</td>
</tr>
<tr>
<td>ReO₂Cl⁺</td>
<td>1001, 961, 350, 332</td>
</tr>
<tr>
<td>ReO₂Br⁻</td>
<td>997, 963, 370</td>
</tr>
<tr>
<td>ReF₃Oₓ</td>
<td>1026, 680, 360, 456</td>
</tr>
<tr>
<td>α-Li₆ReO₂₆</td>
<td>1004, 980, 341, 456</td>
</tr>
<tr>
<td>Re₄O₇(gas)</td>
<td>1015, 980, 322, 185</td>
</tr>
</tbody>
</table>

*Only the rhenium oxide vibrations are shown. *Wagging and rocking modes are omitted.

Discussion

Recently, Deo and Wachs proposed a model to predict the molecular structures of surface metal oxide species on different oxide supports (MgO, Al₂O₃, ZrO₂, TiO₂, and SiO₂) under ambient conditions. It was found that under ambient conditions the support surface is hydrated and that the surface metal oxide becomes dehydrated. As a consequence of the model proposed by Deo and Wachs, the molecular structures of the surface metal oxide phases must generally be altered upon dehydration since the surface pH can only exert its influence via an aqueous environment. This has been experimentally confirmed by the present in situ Raman investigation as will be discussed below for the supported systems under study.

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Figure 8. In situ Raman spectra of Nb₂O₅/Al₂O₃. The niobium oxide loading increases from 3 to 19%.

relative to the 988-cm⁻¹ band. The intensity changes of the Raman bands suggest that different surface niobium oxide species are present as a function of the loading. Above 19% Nb₂O₅/Al₂O₃, the monolayer has been exceeded and crystalline Nb₂O₅ is present on the surface (major band at 680 cm⁻¹, not shown in Figure 8 but presented in refs 24 and 25).

TiO₂/Al₂O₃. Figure 9 shows the in situ Raman spectra of titanium oxide supported on alumina as a function of the surface coverage. The Raman spectra of the 5 and 13.5% TiO₂/Al₂O₃ samples exhibit a broad band in the 800-900-cm⁻¹ region and two bands at ~710 and ~600 cm⁻¹. At 17%, the monolayer has been exceeded and crystalline TiO₂ (anatase) particles are present on the alumina surface (major bands at 643, 520, 394, 199 and 144 cm⁻¹).

surface independent of loading or support type. However, the present Raman study reveals that two surface rhenium oxide species are present under dehydrated conditions. One species is observed at all coverages and possesses bands at 1004, 890, and 340 cm⁻¹ (with a shoulder at ~310 cm⁻¹), while a second species is present at higher loadings with bands at 1015 and ~980 cm⁻¹ and probably the same mode at 340 cm⁻¹ (with shoulder at ~310 cm⁻¹). These findings are consistent with an earlier in situ Raman study by Wang et al. and are also supported by in situ IR spectroscopy.

The Raman spectra of various rhenium oxide compounds have been reported in the literature and are summarized in Table I. The table shows characteristic bands for ReO₂ (aq), NaReO₄, α-Li₆ReO₂₆, Re₂O₇, ReO₃Z⁻ (with Z is F, Cl, Br), and ReO₂F₃. The high-wavenumber positions of the 1004- and 1015-cm⁻¹ bands in the spectra of the supported rhenium oxide catalysts reveal a tetrahedral coordination of the rhenium cation in both surface species since vibrations of octahedrally coordinated rhenium oxides are found at much lower frequencies (see Table I). The tetrahedral coordination of the rhenium cation at low surface coverage is further supported by an earlier in situ XANES study. For a tetrahedrally coordinated rhenium oxide, the symmetric stretching mode is always observed as a sharp and intense band in the Raman spectrum and is found at higher frequency than the weak and broad asymmetric mode. Accordingly, the intense band at 1004 cm⁻¹ and weak broad band at 890 cm⁻¹ are assigned to the symmetric and asymmetric stretching modes of the first surface rhenium oxide species, while the 1015- and ~980-cm⁻¹ bands are assigned to the symmetric and asymmetric stretching modes of the second surface species, respectively.

The two 1004- and 1015-cm⁻¹ bands are both Raman active and IR allowed (see ref 5) which indicates a symmetry lower than Tₐ (e.g., C₃ᵥ or C₂ᵥ symmetry). For a surface rhenium oxide species with three equivalent terminal Re=O bonds and one bridging Re-O-Al bond the symmetry should be C₃ᵥ. Rhenium oxide reference compounds with C₃ᵥ symmetry are, e.g., ReO₂Z⁻ (with Z is F, Cl, Br) (Table I). When two oxygen atoms bridge
Dehydration transforms these different hydrated surface species into one type of chromium(VI) oxide species which possesses Raman bands at 1005, 935 (shoulder), 880, ~760 (shoulder), ~600, 400, and ~300 cm⁻¹.

Chromium(VI) oxide compounds prefer a tetrahedral coordination of the Cr⁴⁺ cation and various types of tetrahedrally coordinated chromium oxide compounds are known.¹³ The tetrahedral coordinated chromium cation can be monomeric (CrO₄²⁻), dimeric (Cr₂O₇⁻), trimeric (Cr₃O₁₀⁻), and tetrameric (Cr₄O₁₃⁻) both in aqueous solution and in a crystalline lattice. The chromate ion has regular tetrahedral symmetry (T₄) in aqueous solution but in a crystalline lattice the symmetry is lower than T₄ (usually C₄ site symmetry). The dichromate ion contains one oxygen bound to two CrO₃ groups while in the trichromate structure two terminal CrO₃ groups are linked together by a Cr₂O₇ unit. The tetrachromate ion possesses two terminal CrO₃ units linked together by a Cr₂O₇ unit and crystalline CrO₃ has a chain structure of CrO₃ tetrahedra with two terminal Cr₆⁺ and two bridging Cr-O bonds for each Cr⁴⁺ cation.⁴⁴ When one oxygen atom is substituted (e.g., CrO₃Br⁻) and three equivalent CrO₃ bonds remain, the symmetry becomes C₃ᵥ. Substitution of two oxygen atoms lowers the symmetry to C₂ᵥ for which CrO₂Cl₃ is an example.⁴⁶ The characteristic Raman bands of these reference chromium(VI) oxide compounds are summarized in Table II. These Raman spectra reveal that the band position of the symmetric stretching mode (and consequently the bond strength) increases in the following order: \( \nu_3(\text{CrO}_2\text{Cr}) < \nu_3(\text{CrO}_3) \) < \( \nu_3(\text{CrO}_4) \). Furthermore, the \( \nu_3(\text{CrO}_3) \) shifts to higher wavenumber on passing from trichromate to crystalline CrO₃ (945-975 cm⁻¹, respectively) which reflects the increase in bond strength of the CrO₃ groups with polymerization. A similar effect is observed for the bridging CrO₄Crs groups since its intense asymmetric stretching mode shifts from 818 cm⁻¹ for \( K_2\text{Cr}_3\text{O}_10 \) to 894 cm⁻¹ for crystalline CrO₃.

Comparing the Raman spectra of CrO₃/Al₂O₃ with those of chromium oxide reference compounds reveals that under dehydrated conditions the surface chromium oxide possesses a polymeric structure. The very high frequency position of the 1005 cm⁻¹ band reflects a very short chromium–oxygen bond distance and is only consistent with the symmetric stretching mode of CrO₃ units. The asymmetric stretching mode of the Cr₂O₇ group could not be resolved in these Raman spectra, but was observed at 1030 cm⁻¹ in the in situ Raman spectra of CrO₃/ZrO₂ and CrO₃/TiO₂.⁴⁷ The shoulder at ~930 cm⁻¹ is assigned to the stretching mode of the terminal CrO₃ groups while the very intense 880 cm⁻¹ band together with the ~760 cm⁻¹ band are assigned to the stretching modes of the bridging CrO₄Cr units. The weak broad band at ~600 cm⁻¹ belongs to the symmetric stretching mode of the CrO₄Cr units, the 390 cm⁻¹ band to the Cr₂O₇ bending mode, and the weak 300 cm⁻¹ band to the CrO₃ bending mode.
The wavenumber position of the stretching mode of the bridging CrOOCr groups at 880 cm\(^{-1}\) indicates that the surface chromium oxide species possesses a rather long chain structure since this position is comparable with the \(\nu_{\text{as}}(\text{CrOOCr})\) of crystalline CrO\(_2\) (observed at 894 cm\(^{-1}\) in its IR spectrum \(^{44}\)).

\(\text{MoO}_3/\text{Al}_2\text{O}_3\). The \(\text{MoO}_3/\text{Al}_2\text{O}_3\) system has been studied extensively under ambient conditions and it is now generally accepted that at low loadings a hydrated tetrahedrally coordinated \(\text{MoO}_3\)\(^{2+}\) species and at higher surface coverage hydrated hepta- or octo-molybdate cluster are present.\(^{45,46}\) The Raman spectra reveal that under dehydrated conditions several surface molybdate species are present on the alumina surface up to monolayer coverage (\(\geq0.05\)).

One surface species is observed at all loadings and possesses one sharp band at \(\sim1000\) cm\(^{-1}\) and a weak band at \(\sim300\) cm\(^{-1}\). The absence of bands in the Mo-O-Mo bending region (<250 cm\(^{-1}\)) in the spectrum of the 0.7% \(\text{MoO}_3/\text{Al}_2\text{O}_3\) sample indicates that this species is isolated. The presence of only one sharp band shows that this species possesses one short terminal M-O bond since a species with two equivalent M-O bonds would show at least two bands in the stretching region (symmetric stretch and antisymmetric stretch) and two inequivalent M-O bonds would yield at least two Mo-O stretching modes.\(^{40}\) Wang et al. reported an IR band at \(\sim1008\) cm\(^{-1}\) together with its overtone at 2008 cm\(^{-1}\) for a 4.6% \(\text{MoO}_3/\text{Al}_2\text{O}_3\) sample under dehydrated conditions.\(^{7}\) The coincidence of the Raman band and the IR band reveals an increase of Bronsted acid sites with increasing surface coverage. Hardcastle et al. proposed the following structure for this species based upon their diatomic approximation method: a molybdenum oxide with one short M-O bond, one long opposing M-O bond, and four M-O bonds.\(^{45}\) The slight shift of the Mo-O stretching mode of this species from 993 to 1002 cm\(^{-1}\) with increasing loadings can be caused by a decrease in the bond angle or in the bond strength of the Mo-O group. A decrease of the bond angle can be the result of crowding on the surface at higher surface coverage. A similar shift has been reported for bridging Si-(OH)-Si groups upon a decrease in the Si-O-Si angle.\(^{49}\) A decrease of the bond strength can be due to the presence of protons coordinated to the bridging Mo-O-support oxygen atoms at higher surface coverage. The presence of such protons is supported by pyridine adsorption studies which revealed an increase of Bronsted acid sites with increasing surface coverage.\(^{40}\)

The second surface species, present at \(\geq5\%), possesses a broad band at \(\sim880\) cm\(^{-1}\) and is not affected by moisture. Hardcastle et al. argued that a band at 870 cm\(^{-1}\) is only consistent with a regular \(\text{MoO}_3\) tetrahedron and that this band may be due to microcrystalline molybdates formed from small amounts of cationic impurities (such as K\(^+\), Na\(^+\), Ca\(^{2+}\), Sr\(^{2+}\), or Ba\(^{2+}\)).\(^{48}\) The third molybdate surface species (bands at \(\sim940, \sim580, \sim360, \sim210\) cm\(^{-1}\)) shows up at \(\geq15\%) and has a three-dimensional structure which best matches the octahedrally coordinated hepta- or octamolybdate cluster. This dehydrated surface cluster is slightly different from the hydrated cluster, present under ambient conditions (bands at 960, \(\sim870, 360, 220\) cm\(^{-1}\)), which is most probably due to the absence of coordinated water molecules.

Stencel et al. reported for the first time in situ Raman spectra of a 5 and 15% \(\text{MoO}_3/\text{Al}_2\text{O}_3\) sample.\(^{1}\) They found a sharp band at 986 cm\(^{-1}\) and a broad band at 870 cm\(^{-1}\) for the 5% sample while the 15% sample showed a sharp band at 1006 cm\(^{-1}\) and a broad band at 870 cm\(^{-1}\). Also Payen et al. reported a sharp band at 1000 cm\(^{-1}\) and a broad band at \(\sim840\) cm\(^{-1}\) for a 14% sample.\(^{11,12}\) Both studies, however, assigned the sharp and broad band to the same surface molybdate species, while this study shows that the sharp and the broad band belong to different surface molybdate species. Moreover, due to the poor signal to noise ratio in the Raman spectra of these early studies, the bands of the dehydrated molybdate cluster could not be resolved. Chan et al. also reported an in situ Raman spectra of a 4.6% \(\text{MoO}_3/\text{Al}_2\text{O}_3\) sample.\(^{2}\) This spectrum reveals basically the same bands as the present study (bands at 1012, 950, 872, 320, and 210 cm\(^{-1}\)) but no assignment of these bands were given.

\(\text{WO}_3/\text{Al}_2\text{O}_3\). Under ambient conditions two hydrated surface tungsten oxide species have been reported to exist on the alumina surface.\(^{45,46}\) At low loadings a hydrated \(\text{WO}_3\) species and at higher surface coverage a hydrated octahedrally coordinated cluster, which best matches the structure of \(\text{WO}_4^{2-}\), is present on the alumina surface. The Raman spectra reveal that under dehydrated conditions several surface tungsten oxide species are present with different structures than those under ambient conditions. At all loadings a tungsten oxide species is observed which exhibits a sharp band in the 1004-1020 cm\(^{-1}\) region. The presence of a single sharp band is consistent with a monooxo (one \(\text{W}=\text{O}\) bond) species as discussed above for the \(\text{MoO}_3/\text{Al}_2\text{O}_3\) system. The upward shift of the 
\(\text{W}=\text{O}\) stretching mode with increasing surface coverage is similar as observed for the monooxo molybdate species.\(^{80}\) Wang et al. reported an IR band at \(\sim1018\) cm\(^{-1}\) together with its overtone at 2008 cm\(^{-1}\) for a 4.8% \(\text{WO}_3/\text{Al}_2\text{O}_3\) sample under dehydrated conditions, and the coincident of the IR and Raman band further supports the monooxo model.\(^{7}\) Hardcastle et al. argued, based upon the diatomic approximation method, that this monooxo species is only consistent with a highly distorted octahedral coordination of the \(\text{W}^{6+}\) cation.\(^{52}\) A structure was proposed with one short \(\text{W}=\text{O}\) bond, one long opposing \(\text{W}=\text{O}\) bond and four \(\text{W}=\text{O}\) bonds which bridge to the alumina surface. A highly distorted octahedral tungsten oxide structure is also in agreement with an in situ XANES study by Horsley et al.\(^{51}\) A significant increase in the intensity of the pre-edge feature was reported on heating a 10% \(\text{WO}_3/\text{Al}_2\text{O}_3\) sample. Generally, the pre-edge feature increases by any distortion of a regular octahedral environment since the center of inversion symmetry is removed and consequently the transitions from the 2s core orbital are no longer forbidden.

The broad band at \(\sim880\) cm\(^{-1}\), assigned to a second tungsten oxide species, is not affected by moisture since the Raman spectra of \(\text{WO}_3/\text{Al}_2\text{O}_3\) shows the same broad band at \(\sim880\) cm\(^{-1}\) and the band position is similar to the one observed by Horsley et al.\(^{51}\) The position of this broad band at \(\sim880\) cm\(^{-1}\) is too low for the symmetric stretching mode of a tetrahedrally coordinated tungstatem\(^{52}\) and, therefore, the second surface tungstate species must have a octahedral coordination.

At higher tungsten oxide loadings (15 and 20% \(\text{WO}_3/\text{Al}_2\text{O}_3\)), the Raman spectra reveal additional weak bands at \(\sim940, \sim590, \) and 215 cm\(^{-1}\) which are indicative of a third surface species. Tungsten oxide reference compounds which possess bridging \(\text{W}-\text{O}-\text{W}\) groups, such as \(\text{Na}_2\text{WO}_4, \text{K}_2\text{[W}_2\text{O}_7\text{(OH)}_4\text{]}_2\), or \((\text{NH}_4)_6\text{H}_4\text{W}_{12}\text{O}_{40},\) reveal bands in the 900-1000 cm\(^{-1}\) region (symmetric stretch), 800-900 cm\(^{-1}\) region (asymmetric stretch), 500-650 cm\(^{-1}\) region (\(\text{W}-\text{O}-\text{W}\) symmetric stretch), 300 cm\(^{-1}\) region (bending), and 150-250 cm\(^{-1}\) region (\(\text{W}-\text{O}-\text{W}\) bending).\(^{51}\) Thus, especially the bands at \(\sim590\) and \(\sim215\) cm\(^{-1}\), present in the Raman spectra of the 15 and 20% \(\text{WO}_3/\text{Al}_2\text{O}_3\) samples, are diagnostic of \(\text{W}=\text{O}-\text{W}\) linkages and indicate the presence of polytungstate species on the alumina surface at higher surface coverages. The Raman spectra do not reveal if this polymeric tungsten oxide is octahedrally or tetrahedrally coordinated since both polymeric tetrahedral and octahedral tungsten oxide reference compounds possess bands in the same region.\(^{51}\) However, the in situ XANES study by Horsley et al. demonstrated that the L\(_2\) pre-edge is less pronounced at monolayer coverage (high loadings) than at low surface coverage where a highly distorted octahedrally coordinated species is present as discussed above.\(^{55}\) A decrease in pre-edge intensity indicates that a less distorted octahedrally coordinated tungsten oxide species becomes more abundant with
increasing coverage and, therefore, it is suggested that the polymeric species has a slightly distorted octahedral coordination.

In situ Raman spectra of the $\text{WO}_3/\text{Al}_2\text{O}_3$ system have been reported before by Payen et al. and Stencel, which are consistent with our data. However, Payen and Chan did not disclose the structures of the dehydrated oxide species or the influence of surface coverage, while Stencel used a model in which only isolated, tetrahedrally coordinated tungsten oxide species were considered. Such species are, as the current data shows, not present on the dehydrated alumina surface.

$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. Recently, Deo et al. revealed that under ambient conditions hydrated metavanadate species, (VO)$_n$, are present on the alumina surface at low surface coverage, while hydrated decavanadate clusters, V$_{10}\text{O}_{28}$, are observed at higher surface coverage. Under dehydrated conditions also several surface vanadium oxide species are identified as a function of the surface coverage, but with different structures than their hydrated counterparts. One species is present at all loadings and possesses sharp Raman band at ~1015 cm$^{-1}$. The presence of a single band indicates that this species has one short V=O bond (mono-oxo) as discussed for the molybdate system. Wang et al. also found an IR band at 1030 cm$^{-1}$ for a 10% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample under dehydrated conditions, which supports a mono-oxo model. The high-frequency position reflects the extreme short V=O bond distance which shows that the monooxo vanadate species must have a highly distorted structure, while the absence of bands in the V=O-V bending region (200-300 cm$^{-1}$) in the Raman spectrum of the 1% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample further indicates that this highly distorted vanadium oxide species is isolated. The upward shift from 1015 to 1025 cm$^{-1}$ is similar as observed for the monooxo molybdate species. The isolated structure of this species is in agreement with an in situ EXAFS study by Yoshida et al. which showed that the V=O distance is too large for V=O-V linkages. In situ $^{31}$V NMR measurements further suggested a tetrahedral coordination of the V$^{5+}$ cation at low surface coverage. Thus, this surface monooxo species is best represented as an $\text{O}_5-\text{V}=\text{O}$ species with three oxygen atoms bridging to the support and one terminal oxygen covalently bonded to the vanadyl cation. The same monooxo structure has been proposed by other authors for the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system, and has also been identified on the surface of silica, titania, niobia, and zirconia under dehydrated conditions.

A second surface vanadium oxide with a band at 885 cm$^{-1}$ and a shoulder at ~845 cm$^{-1}$ becomes more abundant at higher coverage as has also been found for the $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{ZrO}_2$. The two Raman bands closely match those of crystalline $\text{ZnV}_2\text{O}_4$ (major bands at ~880 and 850 cm$^{-1}$) and, therefore, it is suggested that this second surface vanadium oxide species has a dimeric vanadate-type structure. This second surface vanadate oxide species becomes more polymerized at higher surface coverage as revealed by the shift of the symmetric stretching mode to 925 cm$^{-1}$ and the appearance of additional bands at ~770, ~620, ~560, ~340, and ~250 cm$^{-1}$ which are characteristic for V=O-V stretching (500-800 cm$^{-1}$) and V-O-V bending modes (150-300 cm$^{-1}$), respectively. The presence of polyvanadate species at higher surface coverage has also been concluded by Wint et al. on basis of their in situ Raman spectra, although they argued that the average coordination of vanadium changes from 4-fold to 6-fold with increasing chain length. This is not in agreement with recent in situ $^{31}$V NMR studies which suggested a tetrahedral coordination up to high surface coverage.

$\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$. The supported niobium oxide system has recently been studied by Jehng et al. in detail as a function of support type, calcination temperature, loading and dehydration. It was found that under ambient conditions hydrated hexaniobate-like surface species are present on the alumina support at low surface coverage, while Nb$_5$O$_{10}$H$_x$ containing slightly distorted Nb$_6$O$_{16}$ as well as Nb$_6$O$_4$ and Nb$_5$O$_{12}$ groups, are present at higher surface coverage.

Raman studies on various bulk niobium oxide compounds show that highly distorted tetrahedrally coordinated NbO$_4$ structures are not known while for regular tetrahedral NbO$_4$ structures (such as YNbO$_4$, YNb$_2$O$_7$), the major Raman frequencies appear in the 790-830-cm$^{-1}$ region. In slightly distorted octahedral NbO$_6$ structures the major Raman frequencies appear in the 500-700-cm$^{-1}$ region, while highly distorted octahedral NbO$_6$ structures show their major bands in the 850-1000-cm$^{-1}$ region.

Under dehydrated conditions, the present study shows that several surface species are present as a function of the loading as indicated by the intensity changes of the Raman bands at 980, 940, 880, and 630 cm$^{-1}$. The sharp band at ~980 cm$^{-1}$, present at all loadings is assigned to a highly distorted Nb$_6$O$_{16}$ octahedron. This surface species has recently also been observed on silica, titania, and zirconia under dehydrated conditions. On the basis of the diatomic approximation method, Hardcastle et al. argued that this niobium oxide species possesses one terminal Nb=O cation, since the Nb=O bond cannot accommodate two terminal Nb=O bonds and contain a highly distorted NbO$_6$ octahedral structure. The monoxo model is further supported by recent Raman studies on layered niobium oxide compounds which possess layers of regular Nb$_6$O$_{16}$ octahedra but terminate in highly distorted monoxo octahedron. These compounds also exhibit a Raman band at ~985 cm$^{-1}$ under dehydrated conditions similar to the monoxo surface species.

A second niobium oxide surface species also possesses a highly distorted octahedral coordination of the Nb$^{5+}$ cation since its symmetric stretching mode at ~880 cm$^{-1}$ is similar to that found in hexaniobate compounds such as H$_2$Nb$_7$O$_{12}$($\text{a-x}$)$^\text{2+}$ and Nb$_7$O$_{12}$($\text{a-x}$)$^\text{2+}$. This species is only slightly affected by moisture since under ambient conditions a similar surface hexaniobate have been identified with a Raman band at ~900 cm$^{-1}$. The two Raman bands at ~940 and ~630 cm$^{-1}$ are assigned to a third surface species and are characteristic of a dehydrated niobium oxide species containing both highly and slightly distorted NbO$_6$ octahedral structures. These Raman bands are also observed for layered niobium oxide compounds which consist of both highly and slightly distorted NbO$_6$ octahedral structures connected by sharing corners. In addition, the shifts of Raman bands from ~940 to ~950 cm$^{-1}$ and from ~640 to ~650 cm$^{-1}$ upon approaching monolayer coverage also suggest that these two Raman bands arise from the same dehydrated surface niobium oxide species. The increase of the 650-cm$^{-1}$ band relative to the 950-cm$^{-1}$ band with increasing surface coverage is due to the increasing background at lower wavenumbers.

$\text{TiO}_2/\text{Al}_2\text{O}_3$. Solid titanium(IV) oxo complexes are rarely found to exhibit a true Ti=O moiety. Some exceptions, however, exist such as TiO(porphyrin), TiO(phthalocyanine), TiO(edta $\text{H}_2$)$\text{H}_2$O, and salts containing TiOF$_5$. These complexes show broad bands near 900 cm$^{-1}$ which are indicative of a Ti-O-Ti chain network. This is the situation in all oxohalides of the type $\text{TiX}_2\text{O}_3$ (X = F, Cl, Br, or I) and also in complexes such as TiOF$_2$H$_2$O, TiOCl$_2$2py, and KTiO(FQ$_4$). Bridged Ti-O-Ti moieties were also observed in acidic aqueous solution of $\text{TiCl}_4$ by Reichmann et al. They reported Raman bands at 395 and 910 cm$^{-1}$ which were assigned to the symmetric and anti-symmetric stretches of Ti-O-Ti bonds. When the acid concentration was increased, new Raman bands at ~480, 650, and ~930 cm$^{-1}$ showed up which were also assigned to Ti-O-Ti vibrations. At extremely high HCl concentrations a titanium containing oligomer, [Ti$_3$O$_2$H$_2$O$_{24}$Cl]$_2$HCl$\text{H}_2$O, was identified which revealed bands at 350, 480, and 910 cm$^{-1}$. The in situ Raman spectra of the 5 and 13.5% $\text{TiO}_2/\text{Al}_2\text{O}_3$ samples do not reveal bands in the 950-1000-cm$^{-1}$ region and this suggests that the surface titanium oxide species do not contain Ti-O-Ti moieties. The broad band in the 500-900 cm$^{-1}$ region of $\text{TiO}_2/\text{TiO}_2$ and $\text{TiO}_2$-TiO$_2$ moieties and so are the bands at 710 and 460 cm$^{-1}$. Thus, it is concluded that below a surface coverage of 17%, the titanium oxide forms a surface layer on alumina which has a polymeric titanium oxide structure.
These polymeric surface species differ from the other surface metal oxides discussed in this article in two ways. First, they do not possess short terminal Ti=O bonds but only Ti-O-Ti bonds while all the other surface metal oxide species do show the presence of short M=O bonds as discussed above. Second, supported metal oxides with a high oxidation state (Re⁷⁺, Cr⁶⁺, Mo⁶⁺, W⁶⁺, V⁵⁺) are all influenced by hydration/dehydration while the TiO₂/AI₂O₃ system is not affected by moisture since the same Raman bands have been observed under ambient conditions.²³ Other supported metal oxides with a low oxidation state such as Ni²⁺, Co²⁺, Fe⁺⁺, Mn⁴⁺ also reveal the same Raman bands under ambient and dehydrated conditions, demonstrating the insensitivity of these supported systems upon the presence of moisture.²⁶,²⁶

**Monolayer Coverage.** The in situ Raman spectra further show that, above 20% MoO₃/AI₂O₃, 20% WO₃/AI₂O₃, 20% V₂O₅/AI₂O₃, 19% Nb₂O₅/AI₂O₃, and 13.5% TiO₂/AI₂O₃, the monolayer coverage has been exceeded and crystalline MoO₃, WO₃, V₂O₅, Nb₂O₅, and TiO₂ particles, respectively, are present on the dehydrated alumina surface. The same results have been obtained under ambient conditions which demonstrates that crystalline metal oxide particles are not affected by moisture in contrast to the surface metal oxide species and consequently the monolayer coverage is the same under ambient and dehydrated conditions. Crystalline Re₂O₇ is not stable at high temperatures but leaves the surface as gaseous Re₂O₇ during calcination and is, therefore, not present above monolayer coverage (<17% Re₂O₇/AI₂O₃).²⁷

Crystalline Cr₂O₃ is also not found above monolayer coverage due to its instability at high temperatures but is reduced to Cr₂O₃. Monolayer coverage, however, is reached at much higher surface coverage (~12% Cr₂O₃/AI₂O₃) than employed in this study.²⁸,²⁸

**Models.** Thus, it is demonstrated that different surface species are present on the alumina surface under ambient and dehydrated conditions and the question remains if there is a general correlation between the hydrated and dehydrated surface structures. For the V₂O₅/AI₂O₃ system this correlation would result in a model that at low surface coverage the hydrated metavanadate species, (VO₃)ₙ convert into highly distorted monooxo O₃-V=O species while at higher loading hydrated decavanadate species, V₁₀O₃⁴⁻18H₂O, convert into dimeric and polymeric surface vanadate species upon dehydration. On silica, however, it has been reported that the vanadate oxide only forms a surface overlayer at very low loadings and under ambient condition hydrated decavanadate clusters are found on the silica surface.²⁹ Upon dehydration these clusters convert into highly distorted O₃-V=O species.²⁸,²⁹ Thus, simply correlating hydrated and dehydrated surface structures is not correct. This correlation also does not apply for the other supported metal oxide systems discussed in the present study. The MoO₃/AI₂O₃ system, for example, reveals the presence of hydrated MoO₃⁴⁻ species at low molybdenum oxide coverage under ambient conditions,²⁹,³⁰,³¹ while under dehydrated conditions a highly distorted monooxo species is observed on the alumina surface. The same monooxo molybdate is also observed in situ in the Raman spectroscopy on the dehydrated silica surface, while under ambient conditions only hepta- or octamolybdate clusters are present.⁶⁹,⁷⁰

Another model is to correlate the surface metal oxide structures with the support hydroxyl chemistry. IR studies have revealed that alumina possesses five different types of surface hydroxyl groups.³² For the MoO₃/AI₂O₃, WO₃/AI₂O₃, V₂O₅/AI₂O₃, and Nb₂O₅/AI₂O₃ systems it has recently been demonstrated that the so-called “basic hydroxyl groups” are titrated at low surface coverage, while at higher loadings the neutral and acid OH₃ groups are consumed.⁷² The Raman spectra show that these four supported systems possess a highly distorted monooxo structure (one short M=O bond) at low loadings and polymeric structures at higher surface coverages. Therefore, it is suggested that the highly distorted monooxo species are associated with the replacement of the basic hydroxyl groups and the polymeric species are associated with the titration of the other alumina hydroxyl groups. Direct information about the interaction between the metal oxide species and the alumina surface, however, cannot be obtained from Raman spectroscopy since none of the Raman spectra reveal bands of these bridging M-O-Al bonds. The absence of these bands which are expected below ~700 cm⁻¹ (or anywhere in the spectrum) could be due to a (partly) ionic character of the bridging M-O-Al bond. It is also possible that the M-O-Al bonds are delocalized over the alumina surface.⁵⁶ The hydroxyl chemistry of the Re₂O₇/AI₂O₃ system is the same as for the four supported systems discussed above.²³,²⁷ However, titration of the neutral and acidic hydroxyl groups at higher surface coverage does not result in the formation of polymeric rhenium oxide species but leads to the presence of a second isolated rhenium oxide species which possesses a weaker Re-O-Al bond.³³ Interestingly, silica only possesses one major surface hydroxyl group and recently it has been revealed that up to monolayer coverage only one isolated surface metal oxide species (Re³⁺, Cr⁶⁺, Mo⁶⁺, W⁶⁺, V⁵⁺) is present on the dehydrated silica surface.

**Conclusions.** The in situ Raman spectra reveal that the dehydrated surface metal oxide structures of all the systems under study, except for supported titanium oxide, are different from those under ambient condition where moisture is present on the surface. Supported molybdenum oxide, tungsten oxide, vanadium oxide, and niobium oxide show the presence of highly distorted monooxo species (one M-O bond) at all loadings. At higher surface coverage these supported systems also reveal the presence of M-O-M linkages which are indicative of polymeric structures. Above ~20% metal oxide loading, monolayer coverage is exceeded and crystalline MoO₃, WO₃, V₂O₅, and Nb₂O₅ are found on the alumina surface together with the dehydrated surface species. These metal oxide crystallites are not sensitive to moisture in contrast to the surface metal oxide species. Crystalline Re₂O₇ is not formed at high loadings and two slightly different surface rhenium oxide species are observed as a function of surface coverage. Both are isolated and possess three Re=O bonds and one bridging Re-O-Al bond. The polymeric chromium oxide surface species are observed at all loadings, 0.5–5% Cr₂O₃/AI₂O₃, as well as for titanium oxide which also forms a surface metal oxide overlayer of polymeric species up to a loading of 17%. The polymeric titanium oxide surface species are, however, not sensitive to moisture and only possess Ti-O-Ti bonds and not Ti=O bonds. Crystalline TiO₂ (anatase) is found to be present at the alumina surface in the 17% TiO₂/AI₂O₃ sample. Combining the present investigation under dehydrated conditions with earlier characterization studies under ambient conditions shows that a simple correlation between dehydrated and dehydrated metal oxide species does not exist. Correlating the surface structure of metal oxides under dehydrated conditions with the support hydroxyl chemistry seems to be a better model to explain the results, although more work needs to be done to prove this model unambiguously.

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**Registry No.** Al₂O₃, 1344-28-1; Re₂O₇, 1314-68-7; Cr₂O₃, 1333-82-0; MoO₃, 1331-27-5; WO₃, 1314-35-8; V₂O₅, 1314-62-1; Nb₂O₅, 1313-96-8; TiO₂, 13463-67-7.

**References and Notes**


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