Molecular Structures of Supported Niobium Oxide Catalysts under in Situ Conditions

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Supported niobium oxide catalysts were investigated by in situ Raman spectroscopy as a function of Nb2O5 loading and oxide support (MgO, Al2O3, TiO2, ZrO2, and SiO2) in order to determine the molecular structures of the dehydrated surface niobium oxide species. On the SiO2 support, only one dehydrated surface niobium oxide species corresponding to the highly distorted NbO6 octahedral structure at ~980 cm⁻¹ is present. The highly distorted NbO6 octahedra responsible for Raman bands at ~985 and ~935 cm⁻¹ are also observed on the TiO2 and ZrO2 supports at high surface coverages; however, the dehydrated surface niobium oxide phases possessing Raman bands in the 600–700-cm⁻¹ region cannot be directly observed for Nb2O5/TiO2 and Nb2O5/ZrO2 because of the strong vibrations of the oxide supports in this region. Below half a monolayer coverage on the Al2O3 support, two kinds of dehydrated surface niobium oxide species possessing highly and moderately distorted NbO6 octahedra with Nb=O Raman bands at ~980 and ~883 cm⁻¹, respectively, are present. Upon approaching monolayer coverage on the Al2O3 support, additional Raman bands at ~935 and ~647 cm⁻¹ characteristic of highly and slightly distorted NbO6 octahedra are present and are suggestive of a layered niobium oxide structure. Multiple niobium oxide species are present in the Nb2O5/MgO system and are due to the strong acid-base interactions between Nb2O5 and MgO as well as Ca⁺⁺ impurity cations present on the surface. The various dehydrated surface niobium oxide species present in the supported niobium oxide catalysts appear to be related to the oxide support hydroxyl chemistry.

Introduction

Recent studies of supported metal oxide catalysts have revealed that the supported metal oxide phase forms a two-dimensional metal oxide overlayer on oxide supports such as Al2O3, TiO2, and SiO2.¹⁻⁷ These surface metal oxide phases possess different chemical states, which may simultaneously be present on the support surface, than their bulk metal oxide crystallites. The different chemical states of the surface metal oxide phases can be discriminated with Raman spectroscopy because each state possesses a unique vibrational spectrum corresponding to its structure.⁸⁻¹¹ Additional fundamental information about the supported metal oxide catalysts is provided by in situ Raman spectroscopy since this technique provides structural information about the surface metal oxide phases under a controlled environment (temperature and gas-phase composition).⁹⁻¹¹ The molecular structures of supported vanadium oxide on Al2O3, TiO2, and SiO2 supports have been extensively characterized under in situ conditions, where the surface metal oxide phases are dehydrated, with Raman spectroscopy,¹²⁻¹⁵ infrared spectroscopy,¹⁶ and ³¹⁷⁸⁹ V NMR spectroscopy,¹⁷ as well as XANES.¹⁸ Upon dehydration, the surface vanadium oxide Raman bands above 800 cm⁻¹, which are characteristic of the V=O symmetric stretch, split into a sharp Raman band in the 1026–1038-cm⁻¹ region and a broad Raman band at ~900 cm⁻¹. The relative intensity of these two Raman bands varies with surface vanadium oxide coverage on the oxide supports.ⁱ⁰⁻¹²³ However, the V₂O₅/SiO₂ system only possesses one single Raman band at ~1038 cm⁻¹. Raman and ³¹⁷⁸⁹ V NMR studies suggest that the dehydrated surface vanadium oxide phases are present as a mono- or tetrahedral vanadate species (Raman band in the 1026–1038-cm⁻¹ region) and a polymeric tetrahedral metavanadate species (Raman band at ~900 cm⁻¹).⁹ In situ IR studies also suggest that the dehydrated surface vanadium oxide species are present as an isolated vanadate species (IR band in the 1030–1050 cm⁻¹) and a polyvanadate species (expected IR band in the 600–800 cm⁻¹).¹⁶ In addition, in situ Raman studies on Al₂O₃, TiO₂, and SiO₂ supported molybdenum oxide and tungsten oxide catalysts exhibit Raman shifts of the surface molybdenum oxide (from ~950 to 985–1012 cm⁻¹) and the surface tungsten oxide (from ~960 to 1010–1027 cm⁻¹) phases due to hydration of the surface metal oxide phases. In situ XANES/EXAFS studies on SiO₂ and Al₂O₃ supported vanadium oxide catalysts reveal that the hydrated vanadium oxide species on SiO₂ possess a polymeric octahedral structure which transforms into a monoxo tetrahedral vanadate structure upon dehydration, and both hydrated and dehydrated vanadium oxide species on Al₂O₃ possess an isolated tetrahedral structure at low surface coverages.¹⁸ Raman and XPS studies on the supported niobium oxide catalysts under ambient conditions reveal that the surface niobium oxide phase forms a two-dimensional overlayer on oxide supports (MgO, Al₂O₃, TiO₂, ZrO₂, and SiO₂), and the monolayer coverage of supported niobium oxide catalysts is reached at ~19 wt % Nb2O5/Al2O3 ~7 wt % Nb2O5/ZrO2, and ~2 wt % Nb2O5/SiO2 but not for Nb2O5/MgO system due to the incorporation of Nb⁵⁺ into the MgO support.⁷ The molecular structures of the surface niobium oxide phases are controlled by the surface pH of the system. Basic hydrated surfaces result in the formation of highly distorted NbO₆ groups and acidic hydrated surfaces result in the formation of slightly

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distorted NbO₄, NbO₇, and NbO₈ groups (with the exception of the Nb₂O₅/SiO₂ system which forms bulk Nb₂O₅). The molecular structures of the dehydrated surface niobium oxide phases, however, are still not understood and only preliminary in situ XANES studies for silica-supported niobium oxide catalysts have been reported by Yoshida et al. In the present study, the MgO, Al₂O₃, TiO₂, ZrO₂, and SiO₂ supported niobium oxide catalysts will be investigated under in situ conditions with Raman spectroscopy in order to determine the molecular structures of the dehydrated surface niobium oxide phases as a function of Nb₂O₅ loading and the specific oxide support.

Experimental Section

a. Materials and Preparations. Niobium oxalate was supplied by Niobium Products Co. (Pittsburgh, PA) with the following chemical analysis: 20.5% Nb₂O₅, 790 ppm Fe, 680 ppm Si, and 0.1% insolubles. Niobium ethoxide (99.999% purity) was purchased from Johnson Matthey (Ward Hill, MA). The oxide supports employed in the present investigation are MgO (Fluka, ~85 m²/g after calcination at 700 °C for 2 h), Al₂O₃ (Harshaw, ~180 m²/g after calcination at 500 °C for 16 h), TiO₂ (Degussa, ~30 m²/g after calcination at 450 °C for 2 h), ZrO₂ (Degussa, ~39 m²/g after calcination at 450 °C for 2 h), and SiO₂ (Cab-O-Sil, ~275 m²/g after calcination at 500 °C for 16 h).

The TiO₂, ZrO₂, Al₂O₃, and SiO₂ supported niobium oxide catalysts were prepared by the incipient-wetness impregnation method using niobium oxalate/oxalic acid aqueous solutions (aqueous preparation). The water-sensitive MgO support required the use of nonaqueous niobium ethoxide/propanol solutions under a nitrogen environment for the preparation of the Nb₂O₅/MgO catalysts.

For the aqueous preparation method the samples were initially dried at room temperature for 16 h, further dried at 110-120 °C for 16 h, and subsequently calcined at 450 °C (Nb₂O₅/TiO₂ and Nb₂O₅/ZrO₂ 2 h) or at 500 °C (Nb₂O₅/Al₂O₃ and Nb₂O₅/SiO₂ 16 h) under flowing dry air. For the nonaqueous preparation method, the samples were initially dried at room temperature for 16 h, further dried at 110-120 °C for 16 h under flowing N₂, and subsequently calcined at 500 °C for 1 h under flowing N₂ then for 1 h under flowing dry air.

b. In Situ Raman Spectroscopy. The in situ Raman spectrometer consists of a quartz cell and sample holder, a triple-grating spectrometer (SPEx, Model 1877), a photodiode array detector (EG&G, Princeton Applied Research, Model 1420), and an argon ion laser (Spectra-Physics, Model 1420). The sample holder is made from a quartz glass, and a 100-200-mg sample disk is held by a stationary slot in the sample holder. The sample is heated by a cylindrical heating coil surrounding the quartz cell, and the temperature is measured with an internal thermocouple. The quartz cell is capable of operating up to 600 °C, and dry oxygen gas (Linde Specialty Grade, 99.99% purity) is introduced into the cell at a rate of 50-500 cm³/min with a delivery pressure of 150-200 torr.

The Raman spectra are collected for the hydrated sample at room temperature, after heating the sample to 500 °C in flowing oxygen for 30 min, and again after cooling down to 50 °C to avoid the thermal broadening of Raman bands at high temperature. The laser beam 514.5-nm line of the Ar⁺ laser with 10-100 mW of power is focused on the sample disk in a right-angle scattering geometry. An ellipsoid mirror collects and reflects the scattering light into the spectrometer's filter stage to reject the elastic scattering. The resulting filtered light, consisting primarily of the Raman component of the scattered light, is collected with an EG&G intensified photodiode array detector which is coupled to the spectrometer and is thermoelectrically cooled to ~35 °C. The photodiode array detector is scanned with an EG&G OMA III optical multichannel analyzer (Model 1463). The Raman spectrum is recorded only in the high-wavenumber region (600-1100 cm⁻¹) in the present experiments. The overall resolution of the spectra was determined to be better than 1 cm⁻¹.

Results

Nb₂O₅/SiO₂. The in situ Raman spectra of the silica-supported niobium oxide were collected at 25 °C (fresh from the oven) and 500 °C in the closed cell because intense fluorescence occurred after the samples were cooled down to 50 °C in the cell. The hydrated spectra were obtained after exposing the sample to ambient conditions for overnight. The SiO₂ support possesses Raman bands at ~979 and ~812 cm⁻¹ which are characteristic of the Si-OH stretch and Si-O-Si linkages. The hydrated surface niobium oxide phase possessing a weak Raman band at ~960 cm⁻¹ shifts to ~980 cm⁻¹ upon dehydration as shown in Figures 1 and 2. Thus, the Raman spectrum collected at 25 °C

Niobium Oxide Catalysts


Figure 3. In situ Raman spectra of 1 wt % Nb_2O_5/TiO_2: (a) hydrated state (subtracted TiO_2 background in the 750-1100 cm\(^{-1}\) region); (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

Figure 4. In situ Raman spectra of 7 wt % Nb_2O_5/TiO_2: (a) hydrated state (subtracted TiO_2 background in the 750-1100 cm\(^{-1}\) region); (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

Figure 5. In situ Raman spectra of 1 wt % Nb_2O_5/ZrO_2: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

Figure 6. In situ Raman spectra of 5 wt % Nb_2O_5/ZrO_2: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

Figure 7. In situ Raman spectra of 19 wt % Nb_2O_5/ZrO_2: (a) hydrated state; (b) cooled to 50 °C under flowing oxygen.

Figure 8. In situ Raman spectra of 19 wt % Nb_2O_5/ZrO_2: (a) hydrated state; (b) cooled to 50 °C under flowing oxygen.

Figure 9. In situ Raman spectra of 19 wt % Nb_2O_5/ZrO_2: (a) hydrated state; (b) cooled to 50 °C under flowing oxygen.

(fresh from the oven) possessing both a sharp Raman band at ~980 cm\(^{-1}\) and a broad Raman band at ~960 cm\(^{-1}\) indicates that the surface niobium oxide phase is partially dehydrated. For the 4 wt % Nb_2O_5/SiO_2 sample, an additional Raman band is present at ~680 cm\(^{-1}\) and does not shift under the in situ conditions.

Nb_2O_5/TiO_2. The dehydration of the 1 wt % Nb_2O_5/TiO_2 sample reveals that the hydrated supported niobium oxide phase possessing a very weak and broad Raman band at ~895 cm\(^{-1}\) shifts to ~983 cm\(^{-1}\) as shown in Figure 3. The disappearance of the weak Raman band at ~792 cm\(^{-1}\) at 500 °C, the first overtone of the Raman band at ~394 cm\(^{-1}\) of TiO_2, is due to the thermal broadening of the crystalline TiO_2 phase. Upon increasing the Nb_2O_5 loading to 7 wt %, an additional weak and broad Raman band appears at ~935 cm\(^{-1}\) upon dehydrating the supported niobium oxide phase as shown in Figure 4.

Nb_2O_5/ZrO_2. The in situ Raman spectra of the zirconia-supported niobium oxide catalysts are presented in Figures 5 and 6 with different Nb_2O_5 loadings. The ZrO_2 support possesses a weak Raman band at ~756 cm\(^{-1}\) which arises from the first overtone of its strong Raman band at ~380 cm\(^{-1}\). The thermal effect on the Raman scattering cross section of this band is similar to TiO_2. For the 1 wt % Nb_2O_5/ZrO_2 sample, the hydrated supported niobium oxide phase possesses a weak and broad Raman band at ~875 cm\(^{-1}\) which shifts to ~958 and ~823 cm\(^{-1}\) upon dehydration (see Figure 8). For the 5 wt % Nb_2O_5/ZrO_2 sample, the dehydrated surface niobium oxide Raman bands appear at ~988, ~935, and ~823 cm\(^{-1}\).

Nb_2O_5/Al_2O_3. The in situ Raman spectra of the alumina-supported niobium oxide containing 5 and 19 wt % Nb_2O_5 are shown in Figures 7 and 8, respectively. For the 5 wt % Nb_2O_5 loading, a broad and weak Raman band due to the surface niobium oxide phase (since the Al_2O_3 support is not Raman active) appears at ~905 cm\(^{-1}\) under ambient conditions, and shifts to ~980 and ~883 cm\(^{-1}\) upon surface dehydration. For the 19 wt % Nb_2O_5 loading, the hydrated sample exhibits Raman bands at ~890 and ~645 cm\(^{-1}\) due to the hydrated surface niobium oxide phases on the alumina support. Upon dehydration, the Raman band at ~890 cm\(^{-1}\) shifts to ~988, ~935, and ~883 cm\(^{-1}\) and the Raman band at ~645 cm\(^{-1}\), however, remains at the same position.

The Raman spectra of the dehydrated surface niobium oxide phases on alumina are also shown in Figure 9 as a function of Nb_2O_5 loading. For the loadings less than 5 wt % Nb_2O_5, only...

15% Nb2O5/A12O3

(c) 50°C

(a) Hydrated

(b) 500°C

Raman Shift (cm⁻¹)

Relative Intensity (Arbitrary Units)

Figure 7. In situ Raman spectra of 5 wt % Nb2O5/A12O3: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

3% Nb2O5

(c) 50°C

(a) Hydrated

(b) 500°C

Raman Shift (cm⁻¹)

Relative Intensity (Arbitrary Units)

Figure 8. In situ Raman spectra of 19 wt % Nb2O5/A12O3: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

Raman bands at ~980 and ~883 cm⁻¹ are present and their intensity increases with Nb2O5 loading. For the 8 wt % Nb2O5 loading, the Raman band at ~980 cm⁻¹ shifts to ~988 cm⁻¹ and the new Raman bands appear at ~950 and ~630 cm⁻¹. Upon further increasing the Nb2O5 loadings (>8 wt %), the Raman bands originally occurring at ~950 and ~630 cm⁻¹ shift to ~935 and ~647 cm⁻¹, respectively, and their intensity increases with Nb2O5 loading.

Nb2O5/MgO. The in situ Raman spectra of magnesia-supported niobium oxide, with 5 and 10 wt % Nb2O5, are shown in Figures 10 and 11, respectively. The broad Raman band at ~870 cm⁻¹ is associated with the supported niobium oxide phase under ambient conditions since MgO is not Raman active and increases with Nb2O5 loading. The Raman band at ~1085 cm⁻¹ is due to a CaCO3 impurity present in the MgO support. Under in situ conditions, the Raman band originally at ~870 cm⁻¹ splits into bands at ~935, ~892, and ~833 cm⁻¹ for the 5 wt % Nb2O5/MgO sample and into bands at ~985, ~898, and ~834 cm⁻¹ for the 10 wt % Nb2O5/MgO sample. After the sample was exposed to ambient conditions for overnight, the broad Raman band at ~870 cm⁻¹ reappeared due to the hydration of the surface niobium oxide phases by adsorbed moisture (see Figure 11).

Discussion

Raman studies on supported niobium oxide catalysts reveal that niobium oxide is present as a two-dimensional surface overlayer on oxide supports below monolayer coverage.1 The two-dimensional surface niobium oxide overlayer possesses the major Raman bands in the 800-1000 cm⁻¹ region which are different than bulk crystalline Nb2O5 phases (major Raman band at ~690 cm⁻¹). Crystalline Nb2O5 phases are present above monolayer coverage and at elevated temperatures. The molecular structures of the surface niobium oxide phases under ambient conditions, where adsorbed water is present, can be determined by directly comparing their Raman spectra with those of niobium oxide aqueous solutions and are controlled by the surface pH.2,3

Surface pH is determined by the combined pH of the oxide support and the niobium oxide overlayer. The addition of surface niobium oxide (pH ~ 0.5) to oxide supports (2 ≤ pH ≤ 12) will decrease the surface pH, and the decrease will be proportional to the surface niobium oxide coverage. At low surface niobium oxide coverages of supported niobium oxide catalysts, the surface pH under ambient conditions is dominated by the properties of the oxide

support. The basic pH values of the MgO, pH = 12, and Al2O3, pH = 9, supports suggest that hexaniobate species (HxNb6O19-2x), where x = 1, 2, 3) should be present with corresponding Raman bands at ~880 cm⁻¹. The somewhat acidic pH values of the TiO2, pH = 6.0-6.4, and ZrO2, pH = 4-7, supports suggest that Nb2O5·H2O type structures, containing slightly distorted NbO6 as well as Nb2O5 and NbO3 groups, should be present at ~650 cm⁻¹ for Nb2O5/TiO2 and Nb2O5/ZrO2 at low surface coverages. Unfortunately, the strong vibrations of the TiO2 and ZrO2 supports become dehydrated at temperatures due to the slight influence of temperature upon the Nb=O bond lengths. Upon dehydration, the surface niobium oxide Raman bands above 800 cm⁻¹ experience a shift and the surface niobium oxide Raman bands between 600 and 700 cm⁻¹ are not perturbed. Thus, the Raman bands appearing above 800 cm⁻¹ are associated with surface niobium oxide phases and Raman bands appearing between 600 and 700 cm⁻¹ are associated with either bulk niobium oxide phases or surface phases that still possess coordinated moisture as hydroxyl groups. The somewhat acidic pH values of the MgO supports suggest that hexaniobate species also suggest that the dehydrated surface niobium oxide species, which exhibits a sharp Raman band at ~980 cm⁻¹, can only possess one terminal Nb=O bond, because the Nb⁵⁺ atom cannot accommodate two terminal Nb=O bonds and should contain a highly distorted NbO₆ octahedral structure. Consequently, the dehydrated surface Nb₂O₅·H₂O band at ~980 cm⁻¹ is present as the highly distorted NbO₆ octahedron. An additional Raman band at ~680 cm⁻¹ is observed for 4 wt % Nb₂O₅/SiO₂, but this is assigned to a bulk Nb₂O₅ phase because its band position is very close to T-Nb₂O₅ (~690 cm⁻¹) and it readily crystalizes upon heating to elevated temperatures.

A Raman band at ~985 cm⁻¹ is also observed for the dehydrated titania- and zirconia-supported niobium oxide catalysts and is also assigned to the highly distorted NbO₆ octahedra. The somewhat lower Raman band positions of the dehydrated 1% Nb₂O₅/ZrO₂ sample are attributed to the presence of surface Cl and F impurities which were detected with XPS only in this particular sample. Upon approaching monolayer coverage, an additional Raman band at ~935 cm⁻¹ is observed for the dehydrated titania- and zirconia-supported niobium oxide catalysts and is also assigned to a highly distorted Nb₂O₅·H₂O with a slightly longer Nb=O bond.

On the dehydration of the Nb₂O₅·H₂O support, Raman bands at ~980 and ~883 cm⁻¹ are observed for the low Nb₂O₅ loadings (see Figure 5), indicating the presence of two kinds of distorted NbO₆ octahedral structure: one possesses a Nb=O bond length similar to that found in hexaniobate bands, Nb₂O₅·H₂O compounds. At the surface coverage approaching half a monolayer (~8 wt %), the Raman band at ~980 cm⁻¹ shifts to ~988 cm⁻¹ and indicates that the nature of the dehydrated

TABLE I: Raman Bands of Supported Niobium Oxide Catalysts under in Situ Conditions (Dehydrated State)

<table>
<thead>
<tr>
<th>Raman bands, cm⁻¹</th>
<th>5% Nb₂O₅/MgO</th>
<th>10% Nb₂O₅/MgO</th>
<th>5% Nb₂O₅/AI₂O₃</th>
<th>19% Nb₂O₅/AI₂O₃</th>
<th>1% Nb₂O₅/TiO₂</th>
<th>7% Nb₂O₅/TiO₂</th>
<th>5% Nb₂O₅/ZrO₂</th>
<th>5% Nb₂O₅/ZrO₂</th>
<th>2% Nb₂O₅/SiO₂</th>
<th>4% Nb₂O₅/SiO₂</th>
</tr>
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<tbody>
<tr>
<td>930 (w), 892 (m), 833 (s)</td>
<td>985 (m), 898 (s), 834 (s)</td>
<td>980 (s), 883 (m)</td>
<td>988 (m), 935 (s), 883 (w), 647 (s)</td>
<td>983 (m)</td>
<td>985 (s), 935 (m)</td>
<td>956 (s), 823 (s)</td>
<td>988 (s), 935 (m)</td>
<td>980 (s)</td>
<td>980 (s), 680 (m)</td>
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</tbody>
</table>


of CaO decreases with increasing molybdenum oxide loading.

In situ Raman bands are observed at ~950 and ~630 cm\(^{-1}\) and are characteristic of the dehydrated surface 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 one terminal Nb-O bond (34, 35).

In addition, the shifts of Raman bands from ~950 to ~935 cm\(^{-1}\) and from ~630 to ~647 cm\(^{-1}\) upon approaching monolayer coverage also suggest that these two Raman bands arise from the same dehydrated surface niobium oxide species.

An in situ Raman band in present at ~890 cm\(^{-1}\) on the MgO support which reflects the presence of another distorted NbO\(_6\) octahedron that possesses a Nb=O bond length similar to that found in the MgNbO\(_3\) compound. The absence of crystalline NbO\(_3\) formation for NbO\(_2\)/MgO at very high niobium oxide loadings suggests that this species originates from NbO\(_5^+\) incorporated into the MgO support surface due to the strong acid-base interaction between these two oxides. Recent Raman studies on the MgO supported molybdenum oxide catalysts have found that the MgO support contains CaO on the surface, and the amount of CaO decreases with increasing molybdenum oxide loading because of the formation of CaMoO\(_4\). Similar to the MgO/MgO system, the formation of the CaO/MgO compound is due to the reaction of the acidic niobium oxide with CaCO\(_3\) on the MgO surface. The dehydrated NbO\(_2\)/MgO sample also possesses additional Raman bands at ~833 and ~770 cm\(^{-1}\) which coincide with the Raman positions of a distorted NbO\(_6\) octahedral structure present in the CaO/MgO compound.

No Raman feature at ~980 cm\(^{-1}\) for the 5 wt \% NbO\(_2\)/MgO sample indicates that a highly distorted surface NbO\(_6\) species, which was observed in the NbO\(_2\)/SiO\(_2\), NbO\(_2\)/TiO\(_2\), NbO\(_2\)/ZrO\(_2\), and NbO\(_2\)/AlO\(_2\) systems, is not present on the MgO support. However, the Raman features of the supported niobium oxide on MgO are affected by hydration/dehydration procedures due to the hydrophilicity of MgO (the formation of Mg(OH)\(_2\) upon exposure to moisture). XRD does not detect the crystalline MgNbO\(_3\) and CaMgO\(_2\) phases present in the NbO\(_2\)/MgO system. The particle size of the crystalline phases are smaller than 40 Å.

On the dehydrated MgO support, multiple niobium oxide species possessing Raman bands in the 800–900-cm\(^{-1}\) region are present due to the strong acid–base interactions of NbO\(_2\) with the MgO\(^{2+}\) and the Ca\(^{2+}\) surface cations, and their intensity increases with the NbO\(_2\) loading. At high NbO\(_2\) loadings (>10 wt \%), the Raman band at ~985 cm\(^{-1}\) is characteristic of a highly distorted NbO\(_6\) octahedral structure which coexists with the MgNbO\(_3\) and CaMgO\(_2\) compounds (see Figure 11). This suggests that a surface niobium oxide overlayer with a "capping" structure of layered niobium oxide compound is probably formed on the more acidic MgNbO\(_3\) and CaMgO\(_2\) surfaces.

The molecular structures of the dehydrated surface niobium oxide species with their corresponding bond lengths are presented in Table II. The predicted bond lengths of each structure are obtained from empirical Nb–O bond distance/stretching frequency correlation equation which is derived by Hardcastle. Below half monolayer coverage, the highly distorted NbO\(_6\) octahedra, with a Nb=O bond length of 1.71 Å, are present on all the dehydrated oxide supports. On the AlO\(_2\) support, a second dehydrated surface niobium oxide species possessing a moderately distorted NbO\(_6\) octahedral structure, with a Nb=O bond length of 1.76 Å, is also present. As monolayer coverage is approached, additional dehydrated surface niobium oxide species with structures similar to layered niobium oxide compounds, which contain both highly distorted NbO\(_6\) octahedra with a Nb=O bond length 1.73 ± 0.02 Å and slightly distorted NbO\(_6\) octahedra with a Nb=O bond length of 1.92 Å, are present on AlO\(_2\) but not on SiO\(_2\) and MgO. The dehydrated surface niobium oxide phases possessing Raman bands in the 600–700-cm\(^{-1}\) region may be present for NbO\(_2\)/TiO\(_2\) and NbO\(_2\)/ZrO\(_2\), but cannot be determined by Raman spectroscopy because of the strong vibrations of the oxide supports in this region. Layered niobium oxide compounds react with the weak base pyridine, which indicates that these compounds possess strong Brønsted acid sites due to the presence of H\(^+\) protons in the adjacent terminal oxygen layers. Thus, surface acidic studies on TiO\(_2\) and ZrO\(_2\) supported niobium oxide catalysts with FTIR of pyridine adsorption can provide additional information for determining the molecular structures of the dehydrated surface niobium oxide species on these two systems.

In situ XANES/EXAFS studies on the silica-supported niobium oxide catalysts containing different NbO\(_2\) loadings have been reported by Yoshida et al. using YbNbO\(_4\) and KNbO\(_3\) as the reference compounds. They suggest that the dehydrated surface niobium oxide phase possesses a highly distorted NbO\(_6\) tetrahedron at low NbO\(_2\) loadings (<1 wt %) and a square pyramidal structure at high NbO\(_2\) loadings (>7 wt %). The proposed dehydrated surface tetrahedral NbO\(_4\) structure consists of one terminal Nb=O bond, with a bond length of 1.77 Å, and three Nb–O bonds, with a bond length of 1.96 Å, coordinated to the SiO\(_2\) surface. At high NbO\(_2\) loadings (>7 wt %), the proposed dehydrated surface niobium oxide structure consists of one terminal Nb=O bond, with a bond length of 1.79 Å, and four Nb–O bonds, with a bond length of 1.96 Å, coordinated to the SiO\(_2\) surface. The XANES/EXAFS studies on the YbNbO\(_4\) reference compound are in agreement with corresponding Raman studies that YbNbO\(_4\) consists of a tetrahedral NbO\(_4\) structure. KNbO\(_3\) is known as a perovskite structure containing a slightly distorted NbO\(_6\) octahedral structure with Nb–O bond lengths between 1.87 and 2.17 Å. The Raman bands of KNbO\(_3\) occur at ~840, ~601, ~540, and ~285 cm\(^{-1}\). Thus, XANES/EXAFS studies on KNbO\(_3\) are not representative of a dehydrated surface niobium oxide species which possess a highly distorted NbO\(_6\) octahedral structure. Clearly, additional niobium oxide reference compounds XANES/EXAFS studies are required.

The feasibility of Yoshida's model for the dehydrated surface niobium oxide structures is investigated by applying Brown and Wu's valence sum rule. The sum of the valencies, or bond orders, of the individual metal–oxygen bonds should equal the formal oxidation state of the metal cation. The calculated valence state of the Nb\(^{2+}\) atom for the NbO\(_4\) tetrahedron proposed by Yoshida is 4.07 v.u. which is beyond the limit of the 3% relative error allowed for the Nb\(^{2+}\) valence state (5.0 ± 0.16 v.u.), and

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**Table II: A Plausible Model for Molecular Structures of the Dehydrated Surface Niobium Oxide Species**

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Structure</th>
<th>Bond Distances</th>
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<tbody>
<tr>
<td>Below half a monolayer</td>
<td>Highly distorted NbO(_6) octahedra with different Nb–O bond distances</td>
<td></td>
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<tr>
<td>Highly distorted NbO(_6) octahedra coexist in the structure</td>
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</tr>
</tbody>
</table>

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that for the NbO$_2$ square pyramidal also proposed by Yoshida is 4.86 Å which is under the limit of the 3% relative error. The Nb–O bond distance/stretching frequency correlation derived by Hardcastle could also be used to predict the Raman band position of the dehydrated surface niobium oxide on the SiO$_2$ support for the structure proposed by Yoshida. The predicted Nb–O stretching frequency, corresponding to the bond distances of 1.77, 1.79, and 1.96 Å proposed by Yoshida, would appear at ~870, ~840, and ~605 cm$^{-1}$ ($\pm$30 cm$^{-1}$ error). This predicted Raman band is not consistent with the present study in which the dehydrated surface niobium oxide on the SiO$_2$ support is experimentally shown to possess a Raman band at ~980 cm$^{-1}$. The TiO$_2$ and ZrO$_2$ surfaces possess two kinds of surface hydroxyl groups and only one dehydrated surface niobium oxide species (Raman band at ~980 cm$^{-1}$) is present. The TiO$_2$ and ZrO$_2$ surfaces possess two kinds of surface hydroxyl groups and three dehydrated surface niobium oxide species (Raman bands at ~985, ~935, ~880, and ~647 cm$^{-1}$) present. The MgO surface possesses one kind of surface hydroxyl group and only one dehydrated surface niobium oxide species (Raman band at ~980 cm$^{-1}$) is present. The dehydrated surface niobium oxide phases on the SOZ support is experimentally shown to possess a Raman band at ~980 cm$^{-1}$. At high Nb$_2$O$_5$ loading, the predicted Raman bands at ~840 and ~605 cm$^{-1}$ for the structure proposed by Yoshida are consistent with the presence of bulk Nb$_2$O$_5$ (see Figure 2). In addition, the ratio of the NiO$_2$:O$^-$ ionic radius to the O$^-$ ionic radius is too large to fit into a NbO$_4$ tetrahedral structure and a NbO$_6$ octahedral structure is more plausible. Thus, all the theories and experiments indicate that the dehydrated surface niobium oxide phases are not very likely to possess a NbO$_4$ tetrahedral structure.

The various dehydrated surface niobium oxide structures present in supported niobium oxide catalysts appear to be related to the oxide support surface hydroxyl chemistry. The surface niobium oxide phases are formed by reaction of the niobium oxide precursor with the surface hydroxyl groups of the oxide supports which are directly observable with infrared spectroscopy. The SiO$_2$ surface possesses only one kind of surface hydroxyl group and only one dehydrated surface niobium oxide species (Raman band at ~980 cm$^{-1}$) is present. The TiO$_2$ and ZrO$_2$ surfaces possess two kinds of surface hydroxyl groups and two dehydrated surface niobium oxide species (Raman bands at ~985 and ~935 cm$^{-1}$) present. The MgO surface possesses one kind of surface hydroxyl group, but three different niobium oxide species are observed (Raman bands at ~985, ~890, and ~830 cm$^{-1}$) under in situ conditions. The multiple niobium oxide species present in the dehydrated Nb$_2$O$_5$/MgO system are due to the strong acid–base interaction between Nb$_2$O$_5$ and MgO which results in the incorporation of niobium oxide into the MgO support surface and the reaction of Nb$_2$O$_5$ with CaCO$_3$ which is present on the MgO surface. The low surface hydroxyl concentration of the SiO$_2$ support, relative to the other oxide supports, is responsible for the low surface concentration of surface niobium oxide species and the formation of bulk Nb$_2$O$_5$ at very low niobium oxide loadings.

Conclusions

The molecular structures of the dehydrated surface niobium oxide phases were determined in situ Raman spectroscopy by comparing the Raman spectra of the supported niobium oxides with those of solid niobium oxide reference compounds. Under in situ conditions, the adsorbed moisture desorbs upon heating and the surface niobium oxide overlayers on oxide supports become dehydrated. The dehydration process further distorts the highly distorted NbO$_4$ octahedra and shifts the surface niobium oxide Raman bands in the 890–910 cm$^{-1}$ region to 930–990 cm$^{-1}$ region because of the removal of the coordinated water.

A dehydrated surface niobium oxide Raman band is observed at ~985 cm$^{-1}$ on all the oxide supports and reveals that the same surface niobium oxide species possessing a highly distorted NbO$_4$ octahedral structure is present for all the supported niobium oxide catalysts. Below half a monolayer coverage on the Al$_2$O$_3$ support, a second dehydrated surface niobium oxide species possessing a highly distorted NbO$_6$ octahedral structure with a somewhat longer Nb=O bonds (~883 cm$^{-1}$) is also present. Upon approaching monolayer coverage on the Al$_2$O$_3$ support, additional Raman bands at ~935 and ~647 cm$^{-1}$ are observed which are characteristic of highly and slightly distorted NbO$_6$ octahedra similar to those present in layered niobium oxide compounds.

The highly distorted NbO$_6$ octahedra exhibiting a Raman band at ~935 cm$^{-1}$ are also observed on the TiO$_2$ and ZrO$_2$ supports; however, surface niobium oxide phases possessing Raman bands in the 600–700 cm$^{-1}$ region cannot be determined for Nb$_2$O$_5$/TiO$_2$ and Nb$_2$O$_5$/ZrO$_2$ because of the strong vibrations of the oxide supports in this region. On the SiO$_2$ support, only one dehydrated surface niobium oxide species possessing the highly distorted NbO$_6$ octahedral structure is found. The multiple niobium oxide species present in the Nb$_2$O$_5$/MgO system are due to the strong acid–base interaction of Nb$_2$O$_5$ with the Mg$^{2+}$ and the Ca$^{2+}$ cations present on the surface to form MgNb$_2$O$_6$ and Ca$_2$Nb$_2$O$_5$. The various dehydrated surface niobium oxide species present in the supported niobium oxide catalysts appear to be related to the oxide support surface hydroxyl chemistry.

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