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 Nb_2O_5 loading and oxide support (MgO, Al_2O_3, TiO_2, ZrO_2, and SiO_2) in order to determine the molecular structures of the dehydrated surface niobium oxide species. On the SiO_2 support, only one dehydrated surface niobium oxide species corresponding to the highly distorted NbO_6 octahedral structure at ~980 cm^{-1} is present. The highly distorted NbO_6 octahedra responsible for Raman bands at ~985 and ~935 cm^{-1} are also observed on the TiO_2 and ZrO_2 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 Nb_2O_5/TiO_2 and Nb_2O_5/ZrO_2 because of the strong vibrations of the oxide supports in this region. Below half a monolayer coverage on the Al_2O_3 support, two kinds of dehydrated surface niobium oxide species possessing highly and moderately distorted NbO_6 octahedra with Nb=O Raman bands at ~980 and ~883 cm^{-1}, respectively, are present. Upon approaching monolayer coverage on the Al_2O_3 support, additional Raman bands at ~935 and ~647 cm^{-1} characteristic of highly and slightly distorted NbO_6 octahedra are present and are suggestive of a layered niobium oxide structure. Multiple niobium oxide species are present in the Nb_2O_5/MgO system and are due to the strong acid–base interactions between Nb_2O_5 and Mg^{2+} as well as Ca^{2+} 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 surface 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 Al_2O_3, TiO_2, and SiO_2.[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.[8,9] 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).[8-11]

The molecular structures of supported vanadium oxide on Al_2O_3, TiO_2, and SiO_2 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 ^{51}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.[10,12,13] However, the V_2O_5/SiO_2 system only possesses a single Raman band at ~1038 cm^{-1}.[12] Raman and ^{51}V NMR studies suggest that the dehydrated surface vanadium oxide phases are present as a monoxo tetrahedral vanadate species (Raman band in the 1026–1038-cm^{-1} region) and a polymeric tetrahedral metavanadate species (Raman band at ~900 cm^{-1}).[19] 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 Al_2O_3, TiO_2, and SiO_2 supported molybdenum oxide and tungsten oxide catalysts also exhibit Raman shifts of the surface molybdenum oxide (from ~950 to 985–1012 cm^{-1})[10,20-22] and the surface tungsten oxide (from ~960 to 1010–1027 cm^{-1})[8,10,20,23-25] phases due to dehydration of the surface metal oxide phases. In situ XANES/EXAFS studies on SiO_2 and Al_2O_3 supported vanadium oxide catalysts reveal that the hydrated vanadium oxide species on SiO_2 possess a polymeric octahedral structure which transforms into a monoxo tetrahedral vanadate structure upon dehydration, and both hydrated and dehydrated vanadium oxide species on Al_2O_3 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, Al_2O_3, TiO_2, ZrO_2, and SiO_2), and the monolayer coverage of supported niobium oxide catalysts is reached at ~19 wt % Nb_2O_5/Al_2O_3, ~7 wt % Nb_2O_5/TiO_2, ~5 wt % Nb_2O_5/ZrO_2, and ~2 wt % Nb_2O_5/SiO_2, but not for the Nb_2O_5/MgO system due to the incorporation of Nb^{5+} 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 NbO_6 groups and acidic hydrated surfaces result in the formation of slightly

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distorted NbO_6, NbO_7, and NbO_8 groups (with the exception of the Nb_2O_5/SiO_2 system which forms bulk Nb_2O_5). 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.[26]. In the present study, the MgO, Al_2O_3, TiO_2, ZrO_2, and SiO_2 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 Nb_2O_5 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% Nb_2O_5, 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, ~80 m^2/g after calcination at 700 °C for 2 h), Al_2O_3 (Harshaw, ~180 m^2/g after calcination at 500 °C for 16 h), TiO_2 (Degussa, ~50 m^2/g after calcination at 450 °C for 2 h), ZrO_2 (Degussa, ~39 m^2/g after calcination at 450 °C for 2 h), and SiO_2 (Cab-O-Sil, ~275 m^2/g after calcination at 500 °C for 16 h).

The TiO_2, ZrO_2, Al_2O_3, and SiO_2 supported niobium oxide catalysts were prepared by the incipient-wetness impregnation method using niobium oxalate/oxalic acid aqueous solutions (aqueous preparation).[27] The water-sensitive MgO support required the use of nonaqueous niobium ethoxide/propanol solutions under a nitrogen environment for the preparation of the Nb_2O_5/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 (Nb_2O_5/TiO_2 and Nb_2O_5/ZrO_2, 2 h) or at 500 °C (Nb_2O_5/Al_2O_3 and Nb_2O_5/SiO_2, 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 N_2, and subsequently calcined at 500 °C for 1 h under flowing N_2 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 171). 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 cm^3/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 spec-
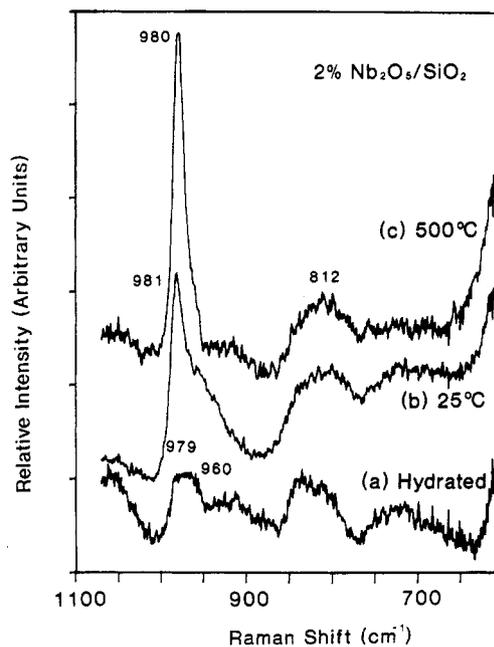
Figure 1. In situ Raman spectra of 2 wt % Nb_2O_5/SiO_2: (a) hydrated state; (b) collected at 25 °C (fresh from the oven at 500 °C); (c) heated at 500 °C under flowing oxygen.
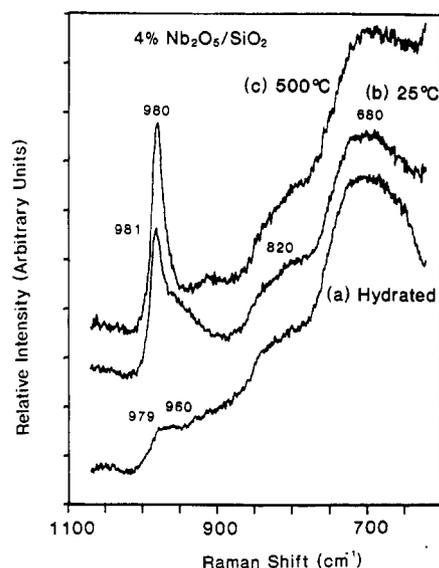
Figure 2. In situ Raman spectra of 4 wt % Nb_2O_5/SiO_2: (a) hydrated state; (b) collected at 25 °C (fresh from the oven at 500 °C); (c) heated at 500 °C under flowing oxygen.

trum 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

Nb_2O_5/SiO_2. 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 SiO_2 support possesses Raman bands at ~979 and ~812 cm^{-1} which are characteristic of the Si–OH stretch and Si–O–Si linkages.[28] 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

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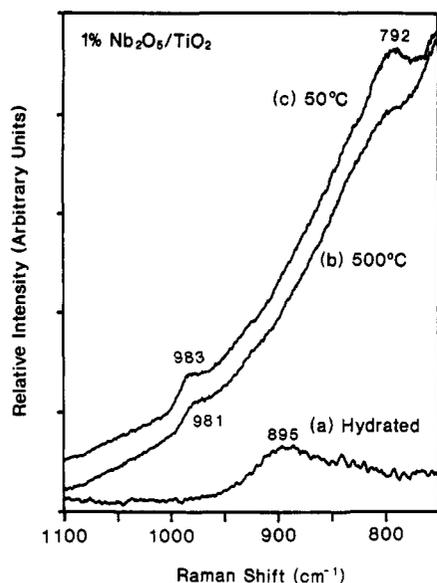
Figure 3. In situ Raman spectra of 1 wt % Nb_2O_5/TiO_2: (a) hydrated state (subtracted TiO_2 background in the 750–1100-cm^{-1} region); (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.
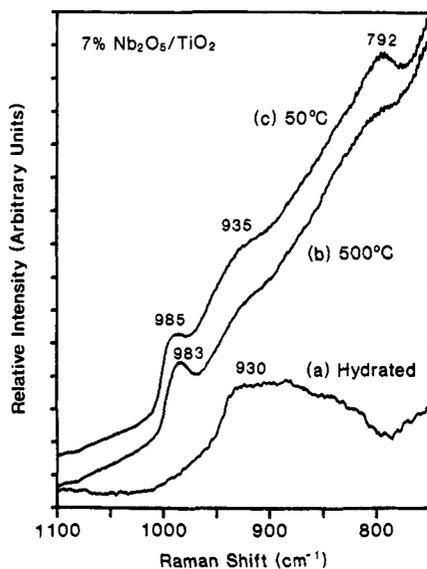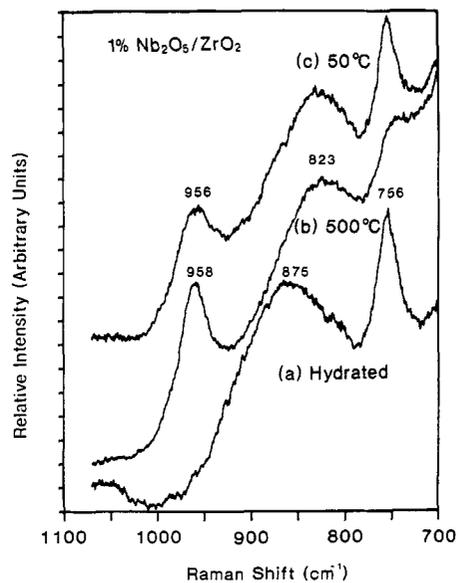

Figure 4. In situ Raman spectra of 7 wt % Nb_2O_5/TiO_2: (a) hydrated state (subtracted TiO_2 background in the 750–1100-cm^{-1} region); (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

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.
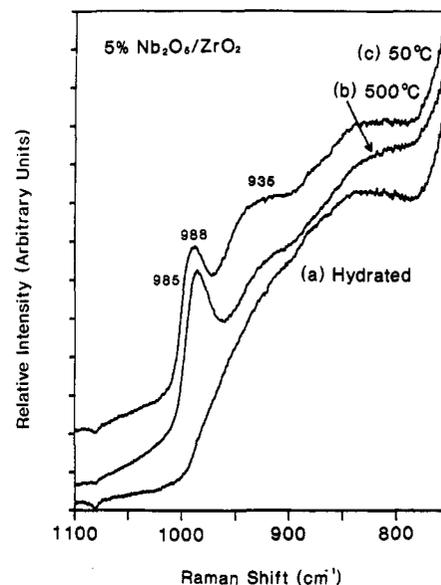
(fresh from the oven) possessing both a sharp Raman band at ~980 cm^{-1} and a broad Raman band at ~960 cm^{-1} indicates that the surface niobium oxide phase is partially dehydrated. For the 4 wt % Nb_2O_5/SiO_2 sample, an additional Raman band is present at ~680 cm^{-1} and does not shift under the 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$^-$ 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
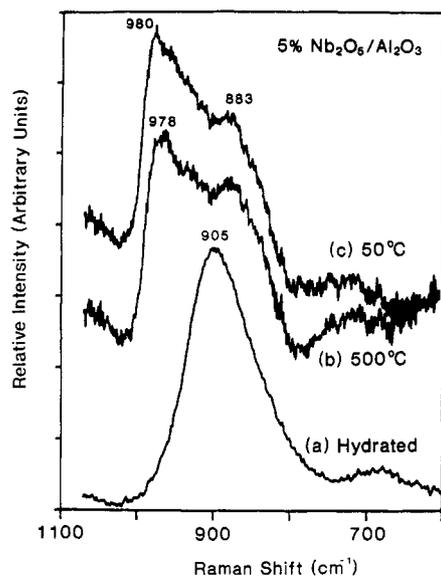
Figure 7. In situ Raman spectra of 5 wt % Nb_2O_5/Al_2O_3: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.
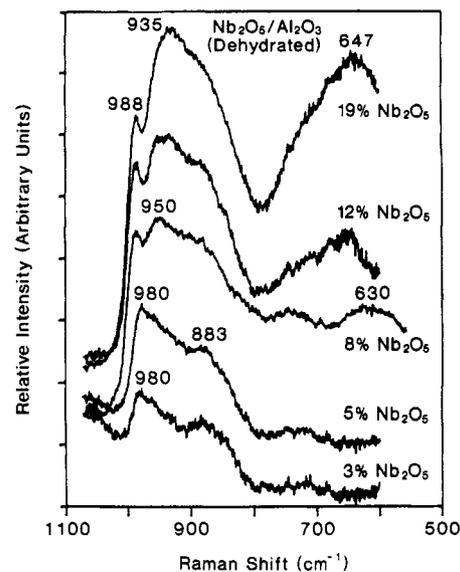
Figure 9. In situ Raman spectra of the Nb_2O_5/Al_2O_3 system as a function of Nb_2O_5 loading.
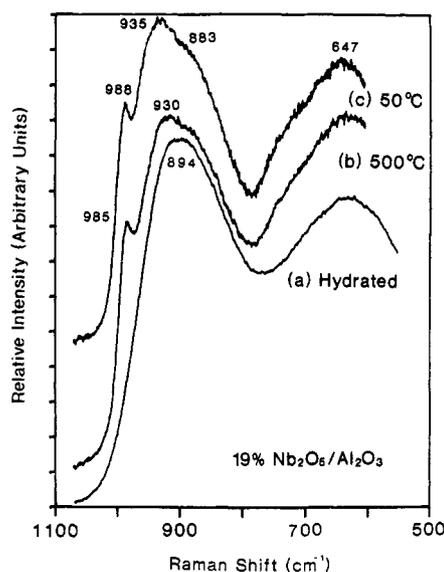
Figure 8. In situ Raman spectra of 19 wt % Nb_2O_5/Al_2O_3: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

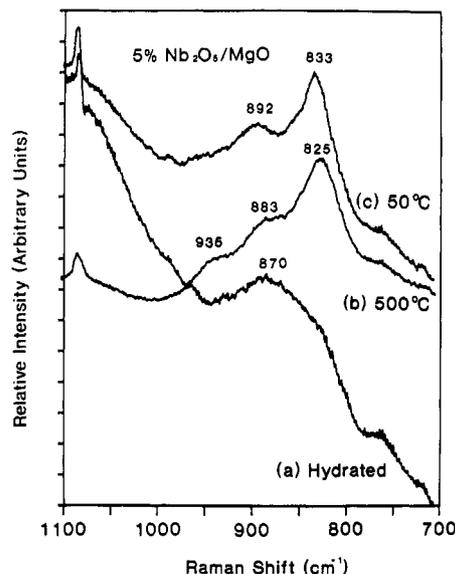**Figure 10.** In situ Raman spectra of 5 wt % Nb_2O_5/MgO: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen.

Raman bands at ~980 and ~883 cm^{-1} are present and their intensity increases with Nb_2O_5 loading. For the 8 wt % Nb_2O_5 loading, the Raman band at ~980 cm^{-1} shifts to ~988 cm^{-1} and new Raman bands appear at ~950 and ~630 cm^{-1}. Upon further increasing the Nb_2O_5 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 Nb_2O_5 loading.

Nb_2O_5/MgO. The in situ Raman spectra of magnesia-supported niobium oxide, with 5 and 10 wt % Nb_2O_5, 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 Nb_2O_5 loading. The Raman band at ~1085 cm^{-1} is due to a $CaCO_3$ 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 % Nb_2O_5/MgO sample and into bands at ~985, ~898, and ~834 cm^{-1} for the 10 wt % Nb_2O_5/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.[7] The two-dimensional surface niobium oxide overlayer possesses the major Raman bands in the 800–100-cm^{-1} region which are different than bulk crystalline Nb_2O_5 phases (major Raman band at ~690 cm^{-1}). Crystalline Nb_2O_5 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.[7,29] The 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

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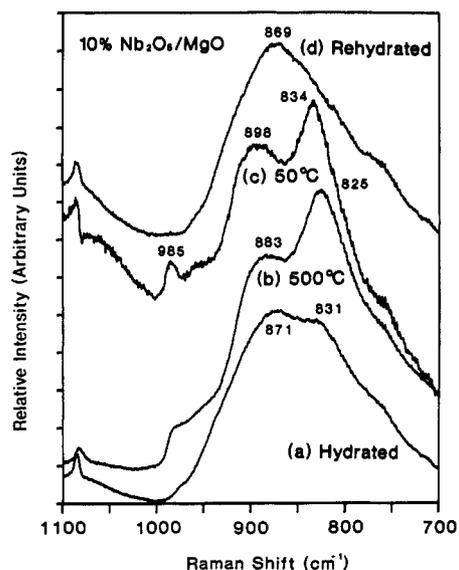
Figure 11. In situ Raman spectra of 10 wt % Nb_2O_5/MgO: (a) hydrated state; (b) heated at 500 °C under flowing oxygen; (c) cooled to 50 °C under flowing oxygen; (d) readsorbed water molecules under ambient conditions.

support. The basic pH values of the MgO, pH = 12, and Al_2O_3, pH = 9, supports suggest that hexaniobate species $(H_xNb_6O_{19}^{(8-x)}$, where x = 1, 2, 3) should be present with corresponding Raman bands at $\sim$880 cm^{-1}.[29] The somewhat acidic pH values of the TiO_2, pH = 6.0–6.4, and ZrO_2, pH = 4–7, supports suggest that $Nb_2O_5 \cdot nH_2O$ type structures, containing slightly distorted NbO_6 as well as NbO_7 and NbO_8 groups, should be present at $\sim$650 cm^{-1} for Nb_2O_5/TiO_2 and Nb_2O_5/ZrO_2 at low surface coverages. Unfortunately, the strong vibrations of the TiO_2 and ZrO_2 supports in this region do not allow direct confirmation of such niobium oxide species. However, the rather weak Raman bands for Nb_2O_5/TiO_2 and Nb_2O_5/ZrO_2 at $\sim$895 and $\sim$875 cm^{-1} (see Figures 3a and 5a), respectively, are consistent with this conclusion. For the acidic SiO_2 support with a pH value of $\sim$3.9, $Nb_2O_5 \cdot nH_2O$ type structures with Raman band at $\sim$650 cm^{-1} would be expected, but a weak and broad Raman band appearing at $\sim$960 cm^{-1} instead of $\sim$650 cm^{-1} is observed (see Figure 1a). This indicates that the surface niobium oxide phase on silica after treatment at 500 or 600 °C calcination contains a highly distorted NbO_6 octahedron which is similar to the "capping" structure of layered niobium oxide reference compound.[30] The transformation of the structure of the surface niobium oxide phase, from a slightly distorted NbO_6 octahedron to a highly distorted NbO_6 octahedron, on SiO_2 under high-temperature treatments is probably due to the weak interaction between the surface niobium oxide phase and the SiO_2 support, and the hydrophobicity of SiO_2. At high surface coverages on basic (Al_2O_3) and acidic (TiO_2 and ZrO_2) oxide supports, hydrated niobium oxide type surface species $(Nb_2O_5 \cdot nH_2O)$ are also present. The hydrated niobium oxide type surface species contain slightly distorted NbO_6 octahedra as well as slightly distorted NbO_7 and NbO_8 structures. In addition, bulk Nb_2O_5 Raman band at $\sim$680 cm^{-1} was observed for 4 wt % Nb_2O_5/SiO_2, indicating that a monolayer coverage had been exceeded.

Under in situ conditions the adsorbed moisture desorbs upon heating and the surface metal oxide overlayers on the oxide supports become dehydrated.[8–10,30] The molecular structures of the surface metal oxide phases are generally altered upon dehydration because the surface pH can only exert its influence via an aqueous environment. Consequently, Raman shifts upon dehydration constitute direct proof of a two-dimensional surface metal oxide phase and the removal of coordinated water.[8–10,30]

The Raman band positions of the supported niobium oxide catalysts under in situ conditions (spectra were taken at 50 °C

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

	Raman bands, cm^{-1}
5% Nb_2O_5/MgO	930 (w), 892 (m), 833 (s)
10% Nb_2O_5/MgO	985 (m), 898 (s), 834 (s)
5% Nb_2O_5/Al_2O_3	980 (s), 883 (m)
19% Nb_2O_5/Al_2O_3	988 (m), 935 (s), 883 (w), 647 (s)
1% Nb_2O_5/TiO_2	983 (m)
7% Nb_2O_5/TiO_2	985 (s), 935 (m)
1% Nb_2O_5/ZrO_2	956 (s), 823 (s)
5% Nb_2O_5/ZrO_2	988 (s), 935 (m)
2% Nb_2O_5/SiO_2	980 (s)
4% Nb_2O_5/SiO_2	980 (s), 680 (m)

in a closed cell after being heated to 500 °C in flowing oxygen with the exception of the Nb_2O_5/SiO_2 spectra which were taken at 500 °C) are presented in Table I. The Raman positions of the surface niobium oxide phases at 50 °C usually occur at 2–3 cm^{-1} higher than at 500 °C 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. Multiple dehydrated surface niobium oxide species with Raman bands in the 800–1000-cm^{-1} region are present in the supported niobium oxide catalysts.

On the SiO_2 support, only one dehydrated surface niobium oxide species with a sharp Raman band at $\sim$980 cm^{-1} is observed, and no additional surface niobium oxide phases possessing Raman bands in the 880–950-cm^{-1} region are present. A Raman band at $\sim$980 cm^{-1} is generally observed for highly distorted NbO_6 octahedra[30] and is also present at the interfaces of layered niobium oxide compounds.[30,31] Recent structural studies of the supported niobium oxide catalysts also suggest that the dehydrated surface niobium oxide species, which exhibits a sharp Raman band at $\sim$980 cm^{-1}, can only possess one terminal Nb=O bond, because the Nb^{5+} atom cannot accommodate two terminal Nb=O bonds and should contain a highly distorted NbO_6 octahedral structure.[32] Consequently, the dehydrated surface niobium oxide phase on SiO_2 is present as the highly distorted NbO_6 octahedron. An additional Raman band at $\sim$680 cm^{-1} is observed for 4 wt % Nb_2O_5/SiO_2, but this is assigned to a bulk Nb_2O_5 phase because its band position is very close to T-Nb_2O_5 ($\sim$690 cm^{-1}) and it readily crystallizes upon heating to elevated temperatures.[7]

A Raman band at $\sim$985 cm^{-1} is also observed for the dehydrated titania- and zirconia-supported niobium oxide catalysts and is also assigned to the highly distorted NbO_6 octahedra. The somewhat lower Raman band positions of the dehydrated 1% Nb_2O_5/ZrO_2 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 $\sim$935 cm^{-1} is observed for the dehydrated titania- and zirconia-supported niobium oxide catalysts and is also assigned to a highly distorted NbO_6 octahedron with a slightly longer Nb=O bond.

On the dehydrated Al_2O_3 support, Raman bands at $\sim$980 and $\sim$883 cm^{-1} are observed for the low Nb_2O_5 loadings (see Figure 5), indicating the presence of two kinds of distorted NbO_6 octahedral structure: one possesses a Nb=O bond length similar to layered niobium oxide compounds and the other possesses a Nb=O bond length similar to that found in hexaniobate, $Nb_6O_{19}^{8-}$, compounds.[30] At the surface coverage approaching half a monolayer ($\sim$8 wt %), the Raman band at $\sim$980 cm^{-1} shifts to $\sim$988 cm^{-1} and indicates that the nature of the dehydrated

(31) Jacobson, A. J.; Lewandowski, J. T.; Johnson, J. W. *J. Less-Common Metals* **1986**, *116*, 137.

(32) Hardcastle, F. D. Ph.D. Dissertation, Lehigh University; University Microfilms International: Ann Arbor, MI 1990.

surface niobium oxide species changes with surface coverage. New 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 structure connected by sharing corners.[30,31] 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 $MgNb_2O_6$ compound.[33,34] The absence of crystalline Nb_2O_5 formation for Nb_2O_5/MgO at very high niobium oxide loadings suggests that this species originates from Nb^{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 $CaCO_3$ on the surface, and the amount of $CaCO_3$ decreases with increasing molybdenum oxide loading because of the formation of $CaMoO_4$.[35] Similar to the MoO_3/MgO system, the formation of the $Ca_2Nb_2O_7$ compound is due to the reaction of the acidic niobium oxide with $CaCO_3$ present on the MgO surface. The dehydrated Nb_2O_5/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 $Ca_2Nb_2O_7$ compound.[36] No Raman feature at ~980 cm^{-1} for the 5 wt % Nb_2O_5/MgO sample indicates that a highly distorted surface niobium oxide NbO_6 species, which was observed in the Nb_2O_5/SiO_2, Nb_2O_5/TiO_2, Nb_2O_5/ZrO_2, and Nb_2O_5/Al_2O_3 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 $MgNb_2O_6$ and $Ca_2Nb_2O_7$ phases present in the Nb_2O_5/MgO system suggest that 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 Nb_2O_5 with the Mg^{2+} and the Ca^{2+} surface cations, and their intensity increases with the Nb_2O_5 loading. At high Nb_2O_5 loadings (>10 wt %), the Raman band at ~985 cm^{-1} is characteristic of a highly distorted NbO_6 octahedral structure which coexists with the $MgNb_2O_6$ and $Ca_2Nb_2O_7$ compounds (see Figure 11). This suggests that a surface niobium oxide overlayer with a "capping" structure of layered niobium oxide compound[30] is probably formed on the more acidic $MgNb_2O_6$ and $Ca_2Nb_2O_7$ 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 an empirical Nb-O bond distance/stretching frequency correlative equation which is derived by Hardcastle.[32] 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 Al_2O_3 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

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(35) Williams, C. C.; Ekerdt, J. G.; Jehng, J. M.; Hardcastle, F. D.; Wachs, I. E., submitted to J. Phys. Chem.
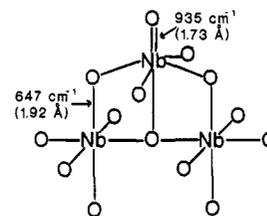
(36) Jehng, J. M.; Wachs, I. E., unpublished work.

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

• Below half a monolayer coverage:
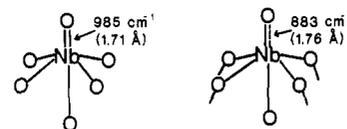
Highly distorted NbO_6 octahedra with different Nb-O bond distances

• Approaching monolayer coverage:

Highly and slightly distorted NbO_6 octahedra coexist in the structure

of 1.73 Å and slightly distorted NbO_6 octahedra with a Nb-O bond length of 1.92 Å, are present on Al_2O_3 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 Nb_2O_5/TiO_2 and Nb_2O_5/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.[31] 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 Nb_2O_5 loadings have been reported by Yoshida et al. using $YbNbO_4$ and $KNbO_3$ as the reference compounds.[26] They suggest that the dehydrated surface niobium oxide phase possesses a highly distorted NbO_4 tetrahedron at low Nb_2O_5 loadings (<1 wt %) and a square pyramidal structure at high Nb_2O_5 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 Nb_2O_5 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.[30] $KNbO_3$ 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.[30,32] The Raman bands of $KNbO_3$ occur at ~840, ~601, ~540, and ~285 cm^{-1}.[30] 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 compound 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.[37] 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^{5+} 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^{5+} valence state (5.0 ± 0.16 v.u.), and

(37) Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1976**, *B32*, 1957.

that for the NbO_5 square pyramidal also proposed by Yoshida is 4.86 v.u. which is under the limit of the 3% relative error. The Nb–O bond distance/stretching frequency correlation derived by Hardcastle[32] can 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 $\sim$870, $\sim$840, and $\sim$605 cm^{-1} ($\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 $\sim$980 cm^{-1}. At high Nb_2O_5 loading, the predicted Raman bands at $\sim$840 and $\sim$605 cm^{-1} for the structure proposed by Yoshida are consistent with the presence of bulk Nb_2O_5 (see Figure 2). In addition, the ratio of the Nb^{5+} ionic radius to the O^{2-} ionic radius is too large to fit into a NbO_4 tetrahedral structure and a NbO_6 octahedral structure is more plausible.[38] 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.[39] 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.[40,41] The SiO_2 surface possesses only one kind of surface hydroxyl group and only one dehydrated surface niobium oxide species (Raman band at $\sim$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 band at $\sim$985 and $\sim$935 cm^{-1}) are present. The Al_2O_3 surface possesses at least four different surface hydroxyl groups and three dehydrated surface niobium oxide species (Raman bands at $\sim$985, $\sim$935, $\sim$880, and $\sim$647 cm^{-1}) present. The MgO surface possesses one kind of surface hydroxyl group, but three different niobium oxide species are observed (Raman bands at $\sim$985, $\sim$890, and $\sim$830 cm^{-1}) under in situ conditions. The multiple niobium oxide species present in the dehydrated Nb_2O_5/MgO system are due to the strong acid–base interaction between Nb_2O_5 and MgO which results in the incorporation of niobium oxide into the MgO support surface

and the reaction of Nb_2O_5 with $CaCO_3$ which is present on the MgO surface. The low surface hydroxyl concentration of the SiO_2 support,[39] relative to the other oxide supports, is responsible for the low surface concentration of surface niobium oxide species and the formation of bulk Nb_2O_5 at very low niobium oxide loadings.

Conclusions

The molecular structures of the dehydrated surface niobium oxide phases were determined with 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_6 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 $\sim$985 cm^{-1} on all the oxide supports and reveals that the same surface niobium oxide species possessing a highly distorted NbO_6 octahedral structure is present for all the supported niobium oxide catalysts. Below half a monolayer coverage on the Al_2O_3 support, a second dehydrated surface niobium oxide species possessing a highly distorted NbO_6 octahedral structure with a somewhat longer Nb=O bonds ($\sim$883 cm^{-1}) is also present. Upon approaching monolayer coverage on the Al_2O_3 support, additional Raman bands at $\sim$935 and $\sim$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 $\sim$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_2O_5/TiO_2 and Nb_2O_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_2O_5/MgO system are due to the strong acid–base interaction of Nb_2O_5 with the Mg^{2+} and the Ca^{2+} cations present on the surface to form $MgNb_2O_6$ and $Ca_2Nb_2O_7$. 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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