# Catalyst Materials Based on $Nb_2O_5$ Supported on $SiO_2-Al_2O_3$: Preparation and Structural Characterization

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Supported niobium pentoxide materials have been effective catalysts for a variety of acid and redox reactions (e.g., dehydration of alcohols, esterifications, etc.). To the best of our knowledge, there are no reports about $Nb_2O_5$ supported on silica−alumina. Catalysts of $Nb_2O_5/SiO_2-Al_2O_3$ were prepared with 2, 5, 10, 15, 20, and 25 wt % of $Nb_2O_5$ by aqueous solution impregnation using ammonium niobium oxalate on silica−alumina. The materials, after being dried at 100 °C, were calcined at 800 °C and characterized by several methods. Investigation through X-ray diffraction showed the typical patterns of crystalline $Nb_2O_5$, which were composed of mixtures of orthorhombic and monoclinic phases (T, M, and H, respectively) present in the materials with content higher than 10 wt %. DTA curves displayed an exothermic peak at 1356 °C (average) without mass loss (confirmed by TG), which may be ascribed to a phase transition (H phase formation) of $Nb_2O_5$ supported on silica−alumina. Pure $Nb_2O_5 \cdot nH_2O$ showed a transition from amorphous to hexagonal or orthorhombic phase (TT or T, respectively) at 567 °C. FTIR and DRIFTS results confirmed the reaction of the niobium oxide with the hydroxyl functionality of silica−alumina. The formation of surface niobium pentoxide species over the support through selective and progressive consumption of hydroxyl groups from the support and the appearance of characteristic niobium hydroxylated species on the surface were demonstrated. Raman spectra attested a two-dimensional overlayer of niobium pentoxide on silica−alumina at contents below 10 wt %. At higher concentrations, the absorptions characterize the formation of phases T and H of bulk $Nb_2O_5$.

## Introduction

Niobium pentoxide is an interesting catalyst because of its high acidity and water-tolerant properties.[1,2] There are many roles for this oxide acting in catalysis, such as promoter, support, acid catalyst, and redox material.[3] Niobium oxide-based materials have lately been pointed out as effective catalysts for many processes (e.g., dehydration of alcohols, oxidative dehydrogenation, esterification, alkylation, polymerization, etc.).[3,4] The catalytic behavior of niobium materials has recently been reviewed, showing the special properties of this element.[5,6]

Niobium pentoxide is the most studied oxide of Nb, and it has been supported on a variety of matrixes (e.g., $SiO_2$, $Al_2O_3$, $TiO_2$, $ZrO_2$). Those niobium oxides supported on silica and alumina are the most studied.[7−18] Different surface species are produced according to the support properties and the niobium content. These species control the structural characteristics of the active sites, and, therefore, the surface species influence the selectivity in the reactions catalyzed by these materials.

Many surface species have been identified on supported $Nb_2O_5$, mostly by Raman and FTIR spectroscopies. For example, the alumina-supported system revealed the presence of $NbO_4$ and $NbO_6$ species, which are dependent on the surface coverage.[19] On the other hand, the silica-supported catalysts showed only isolated $NbO_4$ surface species at very low coverage.[4−19]

Now, to the best of our knowledge, there are no reports about $Nb_2O_5$ supported on $SiO_2-Al_2O_3$. Silica−alumina is an important industrial catalyst for different applications (e.g., support, complement for FCC process, etc.). Therefore, the goal of this work is to prepare and characterize the structure of $Nb_2O_5$ supported on silica−alumina using X-ray diffrac-

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tion (XRD), infrared spectroscopy with Fourier transform (FTIR), diffuse reflectance infrared spectroscopy with Fourier transform (DRIFTS), Raman with Fourier transform (FT-Raman), and thermal analysis (TG, and DTA). Preliminary tests of these materials in our laboratory presented catalytic properties for acid-redox reactions.

## Experimental Section

**Preparation of Supported $Nb_2O_5/SiO_2-Al_2O_3$.** Silica−alumina was purchased from Aldrich (catalyst support grade 135, 12 wt % $Al_2O_3$, >90% AS-100 mesh). Before impregnation, $SiO_2-Al_2O_3$ was activated at 550 °C for 12 h in a muffle furnace for complete transformation from ammoniacal to protonic form. This process was confirmed by TG-DTA and FTIR analysis of the product before and after thermal treatment. Aqueous solutions with adequate amounts of ammonium niobium oxalate, $NH_4[NbO(C_2O_4)_2(H_2O)]\cdot(H_2O)_n$, obtained from Companhia Brasileira de Metalurgia e Mineração (CBMM), were added to a glass round-bottom flask containing activated silica−alumina (as described above) at 1:10 mass/volume ratio of solid to water. Each system was kept under stirring at 80 °C until all of the water evaporated. Next, the solid was removed and dried in air at room temperature for 8 h. Finally, the solid was ground to finer particles and placed in an oven at 100 °C for 2 h, before any further calcination procedure. Niobic acid, $Nb_2O_5\cdot nH_2O$ (HY 340) was supplied by CBMM. The niobium content was checked by ICP-AES. The results are very close (about ±5% difference) to the nominal values mentioned in the paper. Thus, all niobia loadings refer to the nominal values.

**Spectral and Thermal Data.** Sample calcinations were performed in a muffle furnace model FA 1630 (Sybron Thermoline) under static conditions with atmospheric air in porcelain crucibles, and at a heating rate of 10 °C $min^{-1}$. After calcinations, the samples were kept in vials inside a desiccator containing Drierite.

XRD patterns were collected using a Rigaku D/Max-2A/C with Cu Kα radiation of 1.5418 Å (40 kV and 20 mA). A $2\theta$ range from 2° to 60° was scanned at 1.8° $min^{-1}$.

Thermal analysis data were obtained in a simultaneous TG-DSC model SDT 2960 from TA Instruments, with a scan rate of 10 °C $min^{-1}$, from ∼25 °C (room temperature) to 1400 °C under a nitrogen (99.999%) flow of 100 mL $min^{-1}$.

Infrared spectra were recorded at 4 $cm^{-1}$ resolution and 256 scans in dried 1 wt % KBr (Merck) pellets on a Bruker Equinox 55 spectrometer equipped with a DTGS detector. The FTIR spectra of the samples were taken either after preparation (dried in an oven at 100 °C) or after calcination at 800 °C. All FTIR spectra were obtained under ambient conditions.

DRIFTS spectra were collected from 4500 to 3000 $cm^{-1}$ at 25 °C within a Harrick diffuse reflectance accessory (The Praying Mantis), equipped with high-temperature chamber with KBr windows. Before the spectra were taken, each solid was heated at 450 °C under dry nitrogen flow for 30 min and then cooled. Each spectrum was acquired as reflectance against an alignment mirror (256 scans at 4 $cm^{-1}$ resolution) and then converted to Kubelka−Munk units after baseline correction.

FT-Raman spectra of samples previously calcined at 800 °C were obtained under ambient conditions, at room temperature (25 °C), with 256 scans and a resolution of 2 $cm^{-1}$ on a Bruker FRA 106/S module attached to the Equinox spectrometer. The laser excitation (Nd:YAG) and laser power were 1064 nm and 126 mW, respectively. The signal was detected by a liquid $N_2$ cooled Ge detector. The samples were taken from the desiccator and quickly packed into sample cups. Raman spectra were baseline corrected and smoothed using polynomial functions.

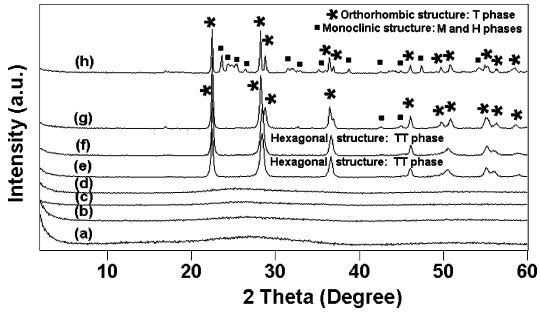


**Figure 1.** XRD pattern of niobic acid treated for 3 h at: (a) 25, (b) 135, (c) 350, (d) 400, (e) 450, (f) 500, (g) 600, and (h) 800 °C.

## Results and Discussion

To understand the effect of thermal treatment under our experimental conditions, first, pure niobic acid was treated at different temperatures for the same time (3 h). The results are presented in Figure 1. A typical amorphous pattern for $Nb_2O_5$ calcined up to 450 °C could be observed. At this temperature, crystalline niobium pentoxide is formed, and, according to the temperature achieved, different phase formations are obtained, as reported in the literature.[20,21] The samples treated at 450 and 500 °C show compatible reflections with the hexagonal phase (TT phase, according to Schäffer notation). Above 500 °C, the spectra give rise to new reflections, which may be attributed to orthorhombic (T) phase at 600 °C and probably a mixture of the orthorhombic (T) and predominantly monoclinic (M and H) phases at 800 °C. These phase assignments were concluded by comparison with PDF files from International Centre for Diffraction Data (ICDD) included in the database of the software JADE 3.0 for XRD analysis. The exact crystallization temperature of $Nb_2O_5$ depends on impurities on the starting materials, rate and time of heating, and interactions with other components (e.g., supports).[20] This is a remarkable effect because, in our laboratory, only the formation of orthorhombic (T) phase when niobium pentoxide was heated at 800 °C for 2 h was observed.

Silica−alumina is amorphous in all ranges of temperature studied. However, when niobium pentoxide was supported on this matrix, only calcinations at or above 800 °C for 3 h started to show crystallite formation on the surface. In addition, the crystallization depends on the niobium content. Figure 2 shows the XRD of supported niobium pentoxide samples calcined at 800 °C for 3 h. The formation of a crystalline phase appears only above 10 wt % of $Nb_2O_5$ supported on silica−alumina. Below or at this level of niobium pentoxide, no defined pattern could be identified. Therefore, a concentration of about 10 wt % may produce the surface monolayer for this support.

Samples containing 15, 20, and 25 wt % $Nb_2O_5$ displayed patterns which had contributions from the predominantly orthorhombic (T) and monoclinic (M and H) phases, while the predominance on pure niobium pentoxide is the monoclinic phase (M and H). This indicates that, under the influence of the silica−alumina support, niobium pentoxide

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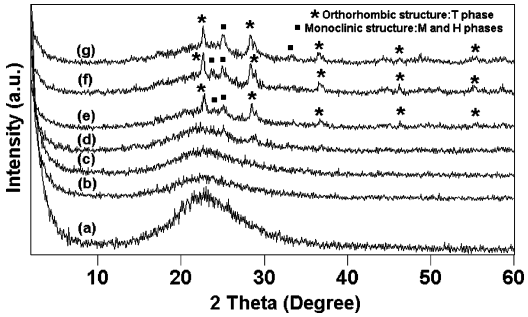


**Figure 2.** XRD pattern of $Nb_2O_5/SiO_2-Al_2O_3$ calcined at 800 °C for 3 h with: (a) $SiO_2-Al_2O_3$; and (b) 2, (c) 5, (d) 10, (e) 15, (f) 20, and (g) 25 wt % loadings of $Nb_2O_5$, respectively.

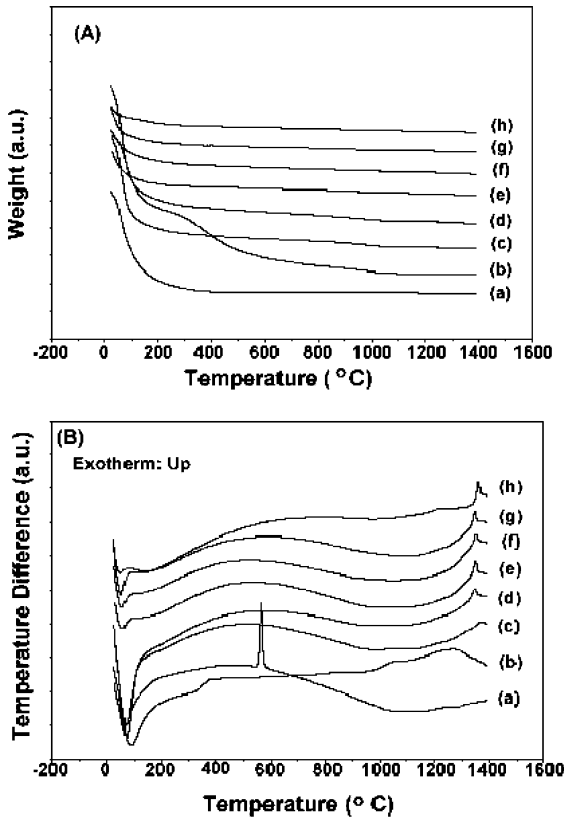


**Figure 3.** (A) TG and (B) DTA curves of: (a) $Nb_2O_5$, (b) $SiO_2-Al_2O_3$, (c) 2, (d) 5, (e) 10, (f) 15, (g) 20, and (h) 25 wt % of $Nb_2O_5/SiO_2-Al_2O_3$, respectively.

has less mobility because of the relative interaction with the support. The reactivity of the niobium pentoxide system has been discussed in terms of formation or not of a specific phase.[20] Thus, the presence of the amorphous pattern (2−10 wt %) and the predominantly T phase at 800 °C (15−25 wt %) shows that the support established a coverage-dependent interaction with niobium pentoxide.

TG-DTA curves for silica−alumina, niobium pentoxide, and the supported catalysts calcined at 800 °C are shown in Figure 3. Silica−alumina presents two thermal events, according to these curves. Centered at about 100 °C is an endothermic peak related to physical desorption of water. A broad peak (250−550 °C) centered at 350 °C is assigned to water release due to dehydroxylation of terminal and bridge OH as well as ammonia decomposition. Also, a third event may be observed at about 550 °C, which is attributed to oxidation of some organic residue that may be sorbed in the silica−alumina.[22] This phenomenon was only observed under air, but not under nitrogen flow.

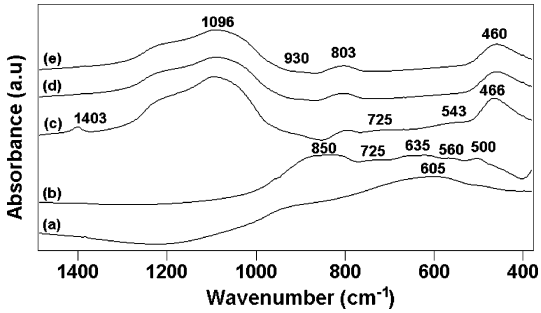


**Figure 4.** FTIR spectra at different calcinations of $Nb_2O_5$ at (a) 25, (b) 800 °C, and $SiO_2-Al_2O_3$ at (c) 25, (d) 550, and (e) 800 °C.

Pure niobium pentoxide shows an endothermic DTA peak about 100 °C related to water desorption. Above 350 °C, no weight loss was observed for the sample. There is a sharp exothermic peak at 567 °C present on the DTA curve that is attributed to an $Nb_2O_5$ phase transition. This phase transition agrees with XRD results, because only after 450 °C was a crystalline phase for $Nb_2O_5$ observed. The difference of temperatures from DTA and XRD experiments for this transition is related to the calcination conditions in both experiments (air versus nitrogen and time of heating). It should be noted that DTA serves only to indicate the latent heat related to the process going from amorphous to crystalline phase, because that phase transition temperature is dependent on the heating rate. This demonstrates how dependent on the experimental conditions is the phase transition for niobium pentoxide. Nevertheless, supported $Nb_2O_5/SiO_2-Al_2O_3$ has a completely different profile. The DTA curves of the samples previously calcined at 800 °C display an endothermic peak at about 100 °C (related to water desorption) and a phase transition at about 1356 °C (average) dependent on the niobium content (1349, 1353, 1354, 1350, and 1362 °C, respectively, for 5, 10, 15, 20, and 25 wt % of $Nb_2O_5$). There is no weight loss associated with this peak, and it is probably related to niobium pentoxide. Samples of supported catalysts heated without previous calcinations, under the same experimental TG-DTA conditions, have shown the same behavior (i.e., phase transition about 1350 °C). It can be concluded that, when the niobium pentoxide is supported on silica−alumina, it becomes more difficult to change its structure, and it remains amorphous under a much higher temperature range under dynamic flow conditions. Considering the range of temperature where the DTA peaks are observed (∼1350 °C), it is most likely that this phase transition is associated with formation of monoclinic (H) phase of $Nb_2O_5$. This phase transition will further be fully investigated.

The interaction of niobium with silica−alumina support was followed by FTIR before and after calcinations. To fully understand the interactions, a clear knowledge of the separated oxides is necessary. Therefore, the spectra of silica−alumina and $Nb_2O_5$ are presented first (Figure 4). The

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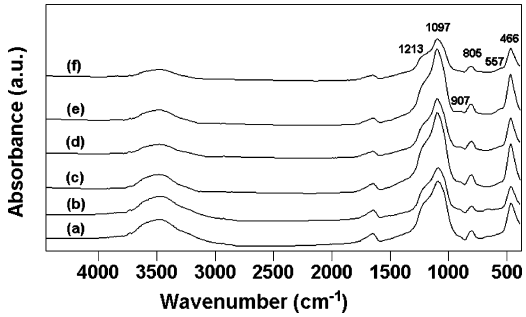


**Figure 5.** FTIR spectra of $Nb_2O_5/SiO_2-Al_2O_3$ calcined at 800 °C with: (a) 2, (b) 5, (c) 10, (d) 15, (e) 20, and (f) 25 wt % loadings of $Nb_2O_5$, respectively.

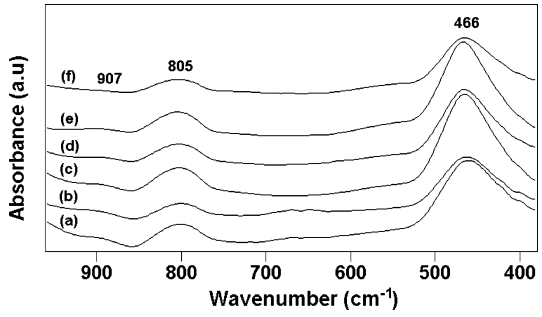


**Figure 6.** Expanded FTIR spectra (950−400 $cm^{-1}$) of $Nb_2O_5/SiO_2-Al_2O_3$ calcined at 800 °C with: (a) 2, (b) 5, (c) 10, (d) 15, (e) 20, and (f) 25 wt % loadings of $Nb_2O_5$, respectively.

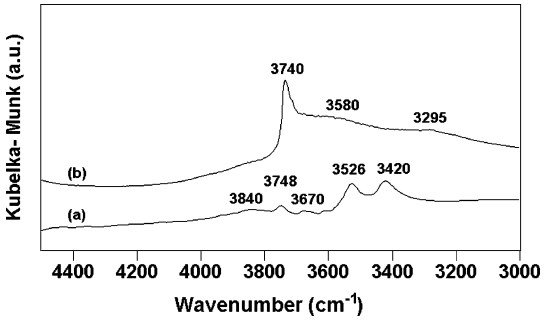


**Figure 7.** DRIFTS spectra of: (a) $Nb_2O_5$ calcined at 800 °C; and (b) $SiO_2-Al_2O_3$ (25 °C).

spectra obtained after different thermal treatments show only a few differences. For silica−alumina, the main peaks are assigned to $\nu_{as}$ (Si−O) ≈ 1100 $cm^{-1}$ (with a shoulder ≈ 1200 $cm^{-1}$), external $\nu$ (Si−$O^-$) ≈ 930 $cm^{-1}$, $\nu_s$ (Si−$O^-$) ≈ 805 $cm^{-1}$, external $\delta$ (Si−$O^-$) ≈ 576 $cm^{-1}$, and $\delta$ (Si−O−Si) ≈ 467 $cm^{-1}$. In addition, the sample not calcined (25 °C) shows a small band due to $\nu$ (Al−O) ≈ 720 $cm^{-1}$, associated with tetrahedral aluminum in the structure, a band at 1409 $cm^{-1}$, assigned to $\nu$ (N−H), and bands at about 3480 and 1650 $cm^{-1}$ related to adsorbed water on hydroxyl groups (−OH−$(H_2O)_n$). Niobium pentoxide hydrated (25 °C) shows three broad bands: ∼900, 605, and a small shoulder at 511 $cm^{-1}$. These bands can be assigned to Nb═O in highly distorted $NbO_6$ groups, symmetric stretching of the niobia polyhedra, and $\nu$ (Nb−O) in slightly distorted $NbO_6$ octahedra, respectively. After heating at 800 °C, $Nb_2O_5$ shows finer characteristics in the same spectral region. There is a large band with a maximum of ∼850, three bands at 725, 635, and 560, and a band at 500 $cm^{-1}$, which are attributed to the main above-mentioned vibrations.

Incorporating niobia on silica−alumina surface gives an IR spectrum resembling that of the support, but with some distinct characteristics. FTIR spectra of the prepared supported samples dried at 100 °C show the presence of niobium precursor through bands in the region 1750−1300 $cm^{-1}$ (1729, 1693, 1407, and 1293 $cm^{-1}$) related to ammonium and oxalate vibrations. These bands disappear after higher temperature calcinations, confirming the thermal decomposition of the starting $NH_4[NbO(C_2O_4)_2(H_2O)]$ forming $Nb_2O_5$ on silica−alumina surface.

Samples calcined at 800 °C (Figure 5) show bands at 1213 (shoulder), 1097, 907, 805, 557, and 466 $cm^{-1}$, which are close to those observed in the silica−alumina. However, some vibration frequency displacements must be considered, and the expanded spectra in the range 950−450 $cm^{-1}$ are provided in Figure 6 to follow a detailed analysis. The original band at 930 $cm^{-1}$ is displaced to 907 $cm^{-1}$, and it might be due to reaction of the niobium precursor with Si−OH forming new surface species containing Si−O−Nb bondings. This is further evidenced because samples with 2 and 5 wt % $Nb_2O_5$ show new absorptions at 670 and 650 $cm^{-1}$, which have been assigned to slightly distorted $NbO_6$ for pure $Nb_2O_5$. The large displacement to lower frequency from the Si−$O^-$ vibrations is indicative that the hydroxyl functionality of silica−alumina has reacted forming a new layer containing niobium oxide species. Actually, this is the main mechanism for anchoring metal oxides on oxide supports of higher surface areas.[23]

The interaction of niobia with silica−alumina was also followed by DRIFTS (Figure 7) in the hydroxyl region (4500−3000 $cm^{-1}$). Silica−alumina in the ammoniacal form shows three absorptions at 3740 $cm^{-1}$ (isolated silanols), 3580 (hydrogen-bonded silanol), and 3295 $cm^{-1}$ (probably due to the presence of $NH_4^+$). Niobium pentoxide displays five absorptions in the same region. The assignment for each band was based upon the conventional establishments.[24,25]

Thus, type I bands are terminal OH groups ($\nu$ higher than 3600 $cm^{-1}$), type II are bridge OH bands (intermediated frequencies), and type III are multicentered OH groups (lower frequencies). The roman number (I, II, and III) indicates the coordination number of the hydroxyl group. Various stretching frequencies of the same type of OH bond in a metal oxide demonstrate the same bond configuration, but a different saturation degree of coordination. Thus, the broad and weak band at 3840 $cm^{-1}$ is probably associated with OH bonded to highly distorted $NbO_6$ or $NbO_7$ and $NbO_8$ species present on the surface of $Nb_2O_5$. This assignment is similar to one reported for alumina,[26] where OH connected to octahedral aluminum is present at about 3800 $cm^{-1}$. This frequency is higher than OH linked to tetrahedral aluminum at 3770 $cm^{-1}$. A second band at 3748 $cm^{-1}$ is assigned to terminal OH bonded to slightly distorted $NbO_6$. The third absorption, also a broad peak with low intensity, occurs at

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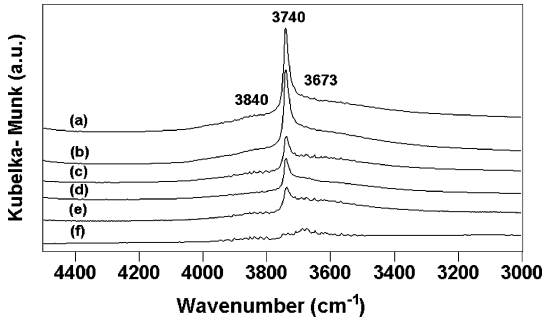


**Figure 8.** DRIFTS spectra of $Nb_2O_5/SiO_2-Al_2O_3$ calcined at 800 °C with: (a) 2, (b) 5, (c) 10, (d) 15, (e) 20, and (f) 25 wt % loadings of $Nb_2O_5$, respectively.

3670 $cm^{-1}$, and it is probably associated with bridge OH (Nb−OH−Nb) connecting $NbO_6$ groups. The last two bands, 3526 and 3420 $cm^{-1}$, are attributed to multicentered OH and hydrogen-bonded OH, respectively, connected to niobium species.

Reaction of niobium precursor followed by calcinations at 800 °C (Figure 8) reveals selective and progressive consumption of silica−alumina OH groups. Isolated silanol (3740 $cm^{-1}$) is the first to be consumed, as expected because of its higher basicity. Besides, there is a new absorption present at 3840 $cm^{-1}$ (similar to bulk $Nb_2O_5$) on the silica−alumina surface, even at lower loadings of niobium pentoxide. Most of the silica−alumina hydroxyls react in the range of 2−10 wt % of $Nb_2O_5$. At about 25 wt % of $Nb_2O_5$ supported on silica−alumina, the DRIFTS spectra resemble that of pure niobium pentoxide, which indicates the formation of its bulk structure over the support. Thus, DRIFTS results confirm the FTIR observations related to reaction of the niobium precursor with hydroxyl functionality of the support.

Raman spectroscopy is a powerful method to identify surface metal oxide species on oxide supports, providing information at the molecular level.[23] Usually, the surface metal oxide species are responsible for the catalytic performance of supported oxide. Raman and IR spectroscopies are complementary because, while in IR the intensity of the band depends on the change in the dipole moment, the intensity in Raman is dependent on the change of polarizability of the vibration.[23] Silica−alumina has weak Raman bands in the region of 400−1000 $cm^{-1}$ due to low polarizability of its light atoms and the relative ionic character of the Si−O and Al−O bonds, in contrast to strong IR absorptions. Major contributions from this support come up with broad absorptions at 1000 and 400 $cm^{-1}$. The same weak absorption effect for $SiO_2$ and $Al_2O_3$ oxides has been reviewed separately.[23]

The Raman spectra of $Nb_2O_5$ have been used either to assign different phases or to identify the species present on the surface of the oxide.[25,27] Figure 9A,B shows the Raman spectra of bulk and supported $Nb_2O_5$ previously calcined at 800 °C, taken under ambient conditions.

Bulk niobium pentoxide presented strong bands at 993, 680, and 630 $cm^{-1}$, in addition to weak bands at 900, 842, 550, and 466 $cm^{-1}$. According to the literature,[28] these bands

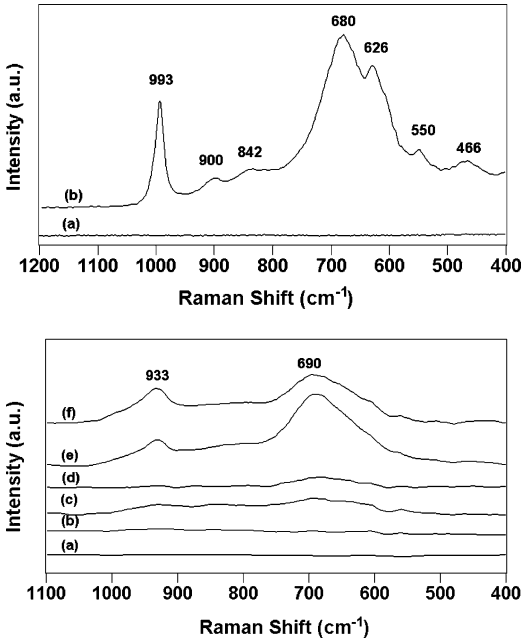


**Figure 9.** Raman spectra of the samples calcined at 800 °C of (A) (a) $SiO_2-Al_2O_3$, (b) $Nb_2O_5$; and (B) $Nb_2O_5/SiO_2-Al_2O_3$ with: (a) 2, (b) 5, (c) 10, (d) 15, (e) 20, and (f) 25 wt % loadings of $Nb_2O_5$, respectively.

may be attributed to the forms T and H. The XRD results, under that condition of calcination, pointed to a mixture of phases T, M, and H. Probably the XRD is more sensitive to the presence of a mixture of different phases, and in addition that no Raman spectrum was found in the literature providing the $M-Nb_2O_5$ vibrations. Thus, this Raman spectrum confirms the presence of mixed phases of $Nb_2O_5$ under our calcination conditions at 800 °C. The 2 and 5 wt % samples showed a very broad absorption with no definite peaks. Actually, even with larger amounts of scans (e.g., 1024 scans), no absorption could be distinguished. This can also be attributed to the available experimental conditions, because the laser source (1064 nm) is not the most adequate for this kind of material. Loadings of 10 and 15 wt % $Nb_2O_5$ on silica−alumina showed broad peaks centered at 950 and 700 $cm^{-1}$. The supported samples with 20 and 25 wt % of $Nb_2O_5$ displayed sharper peaks at 933 and 690 $cm^{-1}$.

The presence of very broad bands in the Raman spectra for the low content samples (2−10 wt %) agrees with XRD results, which have not detected bulk phases of niobium pentoxide (i.e., attributed to the presence of surface niobium oxide species on the support).[29] As the $Nb_2O_5$ content increases (15−25 wt %), the sharper absorption bands can be assigned to the presence of different phases (T and H) on the samples. Niobium pentoxide in the T-phase has a typical absorption at ∼700 $cm^{-1}$, while the H-phase has bands at 993, ∼670, and ∼625 $cm^{-1}$.[27] The different absorption frequencies can be attributed to the interaction of $Nb_2O_5$ with the support including the mixture of phases presents in the material (as observed by XRD) as well as hydration of $Nb_2O_5$ over silica−alumina.

For $Nb_2O_5/SiO_2-Al_2O_3$ materials, the band present at 933 $cm^{-1}$ is related to symmetric stretching of terminal Nb═O

(27) Jehng, J. M.; Wachs, I. E. *Chem. Mater.* **1991**, *3*, 100.
(28) Huang, B. X.; Wang, K.; Church, J. S.; Li, Y.-S. *Electrochim. Acta* **1999**, *44*, 2571.
(29) Burcham, J. L.; Datka, J.; Wachs, I. E. *J. Phys. Chem. B* **1999**, *103*, 6015.

bonds on the surface due to highly distorted $NbO_6$ species, while the band at 690 $cm^{-1}$ is associated with the stretching modes of different niobia polyhedra such as $NbO_6$, $NbO_7$, and $NbO_8$. Therefore, the assignment of molecular species together with different phase formation in supported niobia on silica−alumina show the applicability of Raman spectroscopy in the characterization of this system.

## Conclusions

Catalysts of $Nb_2O_5/SiO_2-Al_2O_3$ prepared in the range 2−25 wt % of $Nb_2O_5$ by aqueous solution impregnation using ammonium niobium oxalate and calcined at 800 °C showed two distinct models. The formation of typical patterns of crystalline $Nb_2O_5$ (mixture of orthorhombic and monoclinic phases) is present in the materials with contents higher than 10 wt %. On the other hand, lower contents (2−10 wt %) displayed the formation of a two-dimensional overlayer on the surface of silica−alumina. XRD and Raman results clearly demonstrated the effects of calcination temperatures and heating times in materials containing niobium pentoxide. TG and DTA data provided evidence of phase transformation differences between pure $Nb_2O_5$ (567 °C) and that supported on silica−alumina (∼1350 °C) under nitrogen flow conditions. FTIR and DRIFTS spectra confirmed the reaction of the niobium oxide with the hydroxyl groups of silica−alumina. The formation of surface niobium pentoxide species over the support through selective and progressive consumption of hydroxyl groups from the support and the appearance of characteristic niobium hydroxylated species on the surface were demonstrated. The higher temperature of $Nb_2O_5$ phase formation on the surface of silica−alumina in relation to pure niobium pentoxide may be attributed to the relative stronger interaction with this support. Nevertheless, once the crystallization started (about 800 °C), the mixture of phases (T, M, and H) in different proportions for both materials indicates the high mobility of niobium oxide species under this condition. Raman spectra agreed with XRD data and showed the formation of a two-dimensional overlayer of niobium pentoxide on silica−alumina at contents below 10 wt %. At higher concentrations, the absorptions characterized the formation of different phases (T and H) of bulk $Nb_2O_5$.

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