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UV Raman spectroscopy of adsorbed SO_x on γ-alumina and Pt/γ-alumina catalysts

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Raman spectra of SO_x adsorbed on γ-alumina and Pt/γ-alumina model catalysts have been obtained with a 244 nm Raman spectrometer. Strong peaks in the 980–1380 cm^{-1} region characteristic of adsorbed sulfates are clearly portrayed in the spectra, which contrast with fluorescence-dominated scans obtained using visible excitation. Broad bands are also observed in the 3500–3700 cm^{-1} O–H stretch region on the γ-alumina, which belong to weakly-bound physisorbed water and more strongly-bound surface hydroxyls. These features are monitored as the samples are heated up to 600 °C in the presence of nitrogen. The sulfate peaks vary in position depending on whether or not the γ-alumina is loaded with platinum, hydrated, or dehydrated. Platinum appears to inhibit the physisorption of water and the formation of hydroxyls on the γ-alumina surface, as evidenced by the absence of O–H stretch vibrations on the Pt-loaded sample. Our spectral data demonstrate that UV Raman spectroscopy is a useful technique for analytical studies of adsorbed SO_x on γ-alumina, and holds promise for future *in situ* investigations of other adsorbed species on catalytic substrates of automotive interest.

Keywords: UV Raman, sulfates, SO_x, γ-alumina, Pt/γ-alumina, catalysts, hydroxyls, adsorbed species

1. Introduction

Sulfur exists as a trace impurity in most petroleum-based fuels. During the combustion process sulfur-containing hydrocarbons are converted to SO_2, which can then react further on the catalyst used for exhaust-gas treatment. Although reactions of SO_2 in the exhaust-gas environment are slow, they occur more quickly on the catalyst surface, where their products can build up over time. The accumulation of SO_x species on the catalyst surface can lead to significant degradation in catalyst performance. For example, in automotive exhaust catalysts, surface sulfur compounds on the precious metals can block their catalytic activity, and such compounds on the supports can contribute to H_2S emissions and reduce oxygen storage capacity. Gamma-alumina is widely used as a support in exhaust-gas catalysts, and a better microscopic understanding of the SO_x species formed on this material is key to the development of more sulfur-tolerant catalysts.

The purpose of this work is to use UV Raman spectroscopy to study the formation of surface oxysulfur species on model γ-alumina catalysts with and without Pt. We also demonstrate the advantages of UV excitation compared with conventional visible excitation for Raman studies of γ-alumina-based catalysts. We observe strong features, with little or no fluorescence interference, for adsorbed SO_x, water, and surface hydroxyls, and we are able to follow the evolution of these species as the samples are heated in different environments.

In the past two decades, a host of studies have examined the adsorption of SO_2 on alumina and Pt/γ-alumina surfaces. We cite here infrared and Raman studies only. The earliest infrared investigation on various alumina and zeolite surfaces showed that SO_2 was both physisorbed and chemisorbed, depending on the temperature [1]. Chang [2] studied SO_2 adsorption on γ-alumina as a function of temperature and showed that both sulfite and sulfate species are formed. Datta et al. [3] identified five possible types of adsorbed SO_x species, where the strengths of adsorption depended on the nature of the adsorption sites. Lavalley et al. [4–10] have performed the most extensive studies on the sulfation of alumina and have proposed a kinetic model for the SO_2 adsorption process in their most recent study [10]. They have also identified the formation of a single tridentate surface sulfate species on the alumina, of the form $(Al–O)_3S{=}O$ [6]. Other more recent infrared work has focused on the interaction of surface sulfate and vanadate species on alumina and other metal oxides catalysts [11], the interaction of SO_2 with H_2S on alumina [12], the interaction of SO_2 on alumina and sodium-impregnated alumina [13] and the generation of acidity on sulfur-promoted alumina and other oxides [14]. Raman studies [15–17] have observed spectra similar to those seen in infrared absorption. There have also been previous UV Raman studies of adsorbed SO_x, but these works have concentrated on zirconia supports [18–20].

2. Experimental

The Raman spectra were obtained with a Renishaw 1000 Raman microscope using 244 nm excitation from a Lexel frequency-doubled argon ion laser. The microscope employed the usual 180° backscattering geometry. Stacked dielectric filters were used to attenuate the Rayleigh scattering, since the holographic notch filters commonly used in visible Raman microscopes cannot withstand exposure to 244 nm radiation. These filters have much broader stop bands than the holographic ones; thus, they prevented us from obtaining spectra closer than about 500 cm^{-1} from the laser line. The light was dispersed by a single-stage spectrometer with a 3600 groove/mm grating. The detector was a CCD array optimized for UV collection efficiency with a lumogen coating, and the instrument was controlled by Grams/32 software from Galactic Industries Corporation. The spectra were recorded in an extended-scan mode in which the grating is stepped in synchronous with the shifting of charge in the CCD array. Long spectral scans are obtained, and there are no systematic errors due to pixel-to-pixel variability, since each spectral point is averaged over all the active pixels in the array.

The γ-alumina samples were obtained by hydrolysis of aluminum alkoxide, followed by drying and calcination for 6 h each at 600 and 800 °C. Powder of mesh size 100/120, corresponding to an average particle size of 120 μm, was selected, and the surface area, as measured by gas adsorption, was found to be 144 m^2/g before platinum loading. Platinum-containing γ-alumina samples were prepared by impregnation to incipient wetness using an aqueous solution of H_2PtCl_6 followed by drying at 100 °C, three successive times, to yield a Pt loading of 1 wt%. The samples were then calcined for 4 h at 600 °C and reduced in 5% H_2/N_2 at 400 °C for 3 h. Before exposure to SO_2, the samples were pretreated by heating up to 800 °C in a flowing N_2/10% O_2 stream at a rate of 10 °C/min. The sulfur exposure was done at 500 °C by flowing a N_2 stream at atmospheric pressure containing 800 ppm SO_2 and 10% O_2 over the catalysts for 12 h. Further details on the treatment and thermogravimetric characterization of the samples will be reported elsewhere [21].

For the Raman measurements the samples were loaded into a temperature-controlled chamber from Linkam Scientific that allowed optical access through a thin fused silica window. Spectra were recorded first at ambient temperature and then at temperatures up to 600 °C, to assess the thermal stability. The above-ambient measurements were done in a 50 sccm flow of dry N_2, while the samples were heated in 50–100 °C increments at 50 °C/min. At each set temperature the samples were allowed to sit for 20 min before spectra were acquired. The UV beam was focused onto the sample with a 15× objective. The power reaching the sample was 2–3 mW with a spot size of 10 μm. The laser power was purposely kept low to avoid doing chemistry on the sample. Spectra were accumulated with 450 s/pixel exposure times from 500 to 3900 cm^{-1} and intensity corrected for the transmission characteristics of the stacked dielectric filters. The spectrometer calibration was adjusted each day using the single-crystal graphite peak at 1582 cm^{-1}, and the resolution was $\sim$8 cm^{-1}. The incident beam was linearly polarized, and a polarizer could be inserted between the spectrometer and the dielectric filter in order to measure the polarization properties of the lines.

The superiority of the UV Raman system over a visible laser system for bringing out the Raman features in our samples is demonstrated in figure 1, in which we compare spectra of sulfated γ-alumina obtained in ambient air at room temperature using the UV spectrometer (a) and a 633 nm HeNe laser (b). Whereas the UV-excited spec-

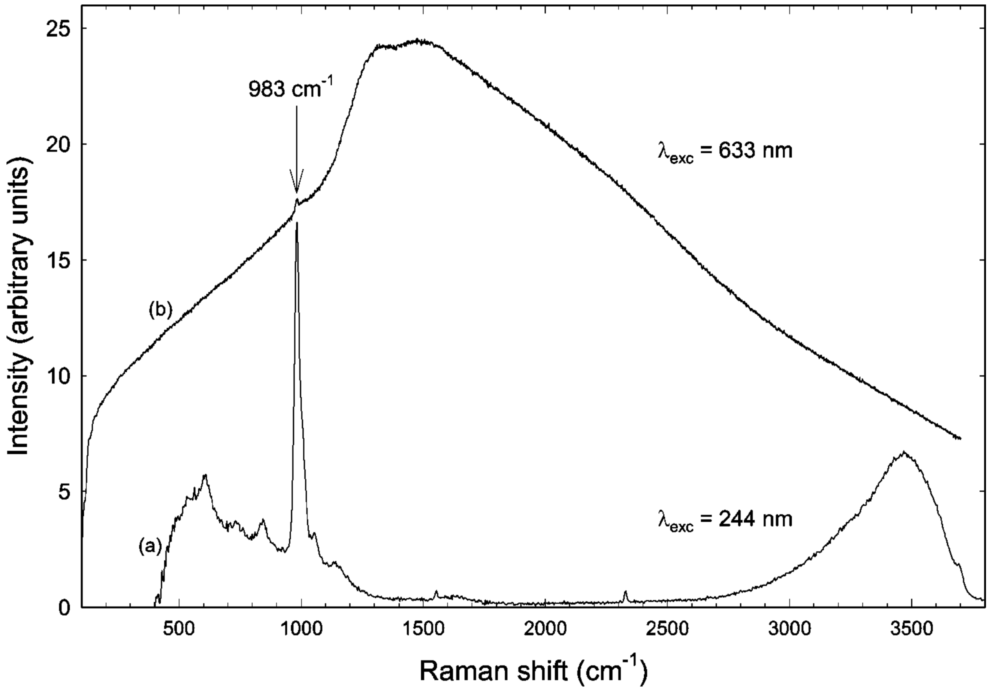

Figure 1. Comparison between UV (244 nm) and visible (633 nm) Raman spectra of sulfated γ-alumina (3.3 wt% SO_x) illustrating the superiority of the UV system for bringing out Raman features.
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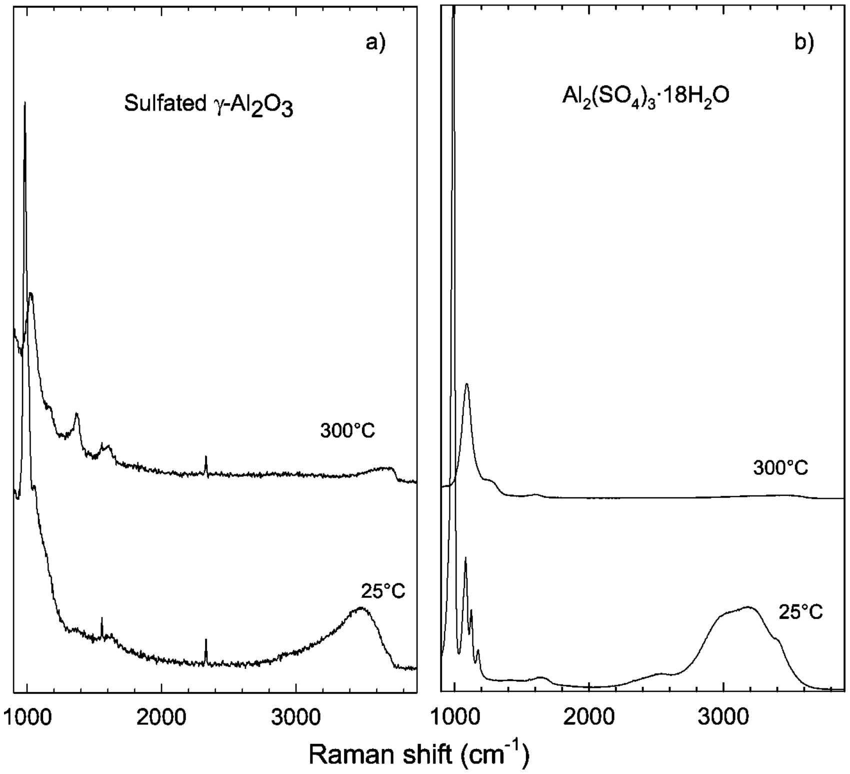

Figure 2. Sulfated γ-alumina (a) and $Al_2(SO_4)_3{\cdot}18H_2O$ (b) at room temperature and 300 °C. As the temperature increases, the sharp sulfate peak at 980–990 cm^{-1} in both samples shifts to higher frequencies and broadens, while the broad O–H band weakens.

trum shows several peaks due to various species to be discussed later, a broad fluorescence background dominates the HeNe-laser-excited spectrum [22]. Fluorescence is still excited by the UV laser, but its Stokes shift is so large that it no longer interferes with the Raman spectrum. The only feature that the two spectra have in common is the small peak at 983 cm^{-1} in (b), which exactly matches the strong line in (a). This peak arises from a sulfate species, and its appearance in both spectra indicates that the UV light is not perturbing the SO_x chemistry on the sample. Further evidence of this can be seen in section 3, where the individual peaks are discussed and compared with previous infrared and Raman work. Note also that the O–H stretch band near 3500 cm^{-1} is quite strong in the UV spectrum, but unobservable in the visible spectrum, which suggests that this band may be resonantly enhanced by the use of UV excitation. These O–H stretch vibrations are generally difficult to see with visible Raman excitation, and our ability to measure them is important in these experiments, since many of the changes in the adsorbed SO_x spectra are accompanied by changes in the hydroxyl region.

3. Results and discussion

3.1. Sulfated γ-alumina without Pt

At elevated temperatures and under oxidizing conditions, SO_2 tends to form as $Al_2(SO_4)_3$ on alumina [23], which hydrates under exposure to a humid environment. This tendency is found in our γ-alumina samples without Pt, as shown in figure 2. Here we compare spectra from a γ-alumina sample, sulfated with 3.3 wt% of SO_x, with spectra from a reagent-grade hydrous aluminum sulfate, $Al_2(SO_4)_3{\cdot}18H_2O$. In both samples the room-temperature spectra are dominated by a strong, sharp line at ~980–990 cm^{-1}, due to the sulfate complex, and broad bands peaked at around 3500 or 3200 cm^{-1}, due to the O–H stretch. When the samples are dehydrated by heating to 300 °C in flowing N_2, they behave in a similar fashion: the sharp, strong line near 1000 cm^{-1} shifts up in frequency and broadens, and the O–H stretch band shifts up and nearly disappears.

Figure 3 shows a series of spectra obtained *in situ* at the indicated temperatures for the sulfated γ-alumina sample without platinum. The prominent peaks, which carry the most interest for us, occur in the vicinity of 1000 cm^{-1}, and also near 1370 cm^{-1} at higher temperatures. These lines are seen to shift slightly towards higher frequencies as the γ-alumina becomes more dehydrated. At 200 and 300 °C an additional line at 1600 cm^{-1} appears. On all the traces, three peaks at 835, 1555, and 2330 cm^{-1} appear consistently. The latter two belong to unresolved Q-branch vibrations of oxygen and nitrogen in air, respectively (see, for instance, [24]). The O_2 signal gets much weaker when N_2 is flowed through the cell, but it is still detectable due to the beam path in air just above the window. The line at 835 cm^{-1} is due to the bare alumina sample, most likely to

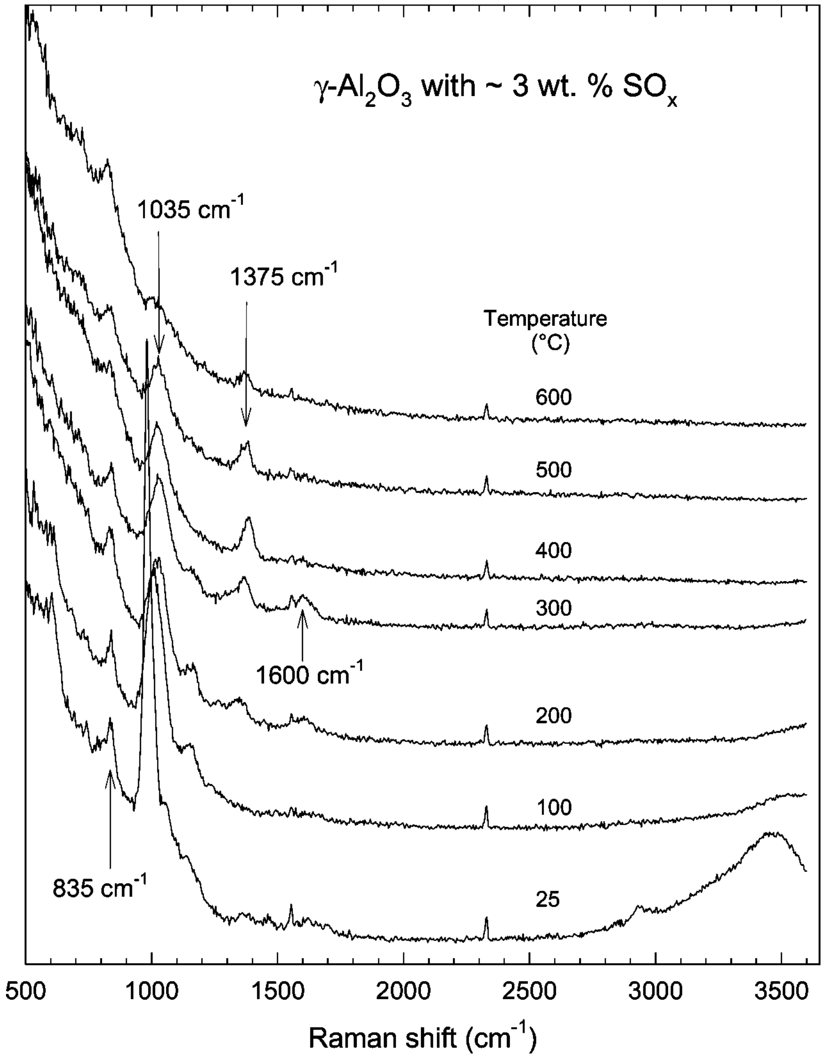

Figure 3. Sulfated γ-alumina at different temperatures under flowing dry nitrogen. Adsorbed sulfates exhibit peaks at around 1000 and 1370 cm^{-1}; the O–H band due to physisorbed water appears at 3470 cm^{-1}.

one of the other transitional aluminas θ- or δ-Al_2O_3, a small amount of which can be formed during the high-temperature treatments [25]. We also observe it in the Raman spectrum of the unsulfated sample, and it has been observed by others [17]. Finally, the room-temperature spectrum shows a broad band at 3470 cm^{-1}. It is due to physisorbed water, since it disappears upon heating the sample above 100 °C. Water readily physically and chemically adsorbs on the surface of γ-Al_2O_3, and furthermore, there are studies that support the existence of hydrogen in the bulk structure of γ-Al_2O_3 [26–28]. The O–H stretches for the more strongly bound surface hydroxyls are observed in our Raman spectra near 3700 cm^{-1}, as will be discussed in section 3.3, and are seen in the same spectral region by infrared absorption studies [29–31].

The ambient-temperature peaks at 983 and 616 cm^{-1} are assigned to an aqueous (SO_4^{2-}) complex with T_d symmetry [32]. This is consistent with previous observations of a strong, sharp peak at 983 cm^{-1} associated with a totally symmetric stretch vibration in Raman spectra of aqueous solutions of oxosulphuric ions [33–36]. Molecules adsorbed onto solid surfaces are expected to exhibit spectra similar to those in solution [37]. The 983 cm^{-1} line is the $\nu_1(a_1)$ vibration while the line at 616 cm^{-1} is the $\nu_4(f_2)$ vibration [32,38]. Normally, the T_d-symmetry $\nu_3(f_2)$ antisymmetric stretch appears at 1100 cm^{-1} [32]; adsorption has shifted it to 1150 cm^{-1} [38–40]. The 983 cm^{-1} line is strongly polarized, as expected for a totally symmetric vibration.

As the sulfated γ-alumina sample is heated, the 983 cm^{-1} peak broadens and shifts to higher frequencies. Frequency shifts of sulfate peaks have been observed previously depending on the amount of water present [2,41,42]. These shifts correspond to the transformation from the tetrahedral, hydrated form of the sulfate to a structure that is more dehydrated and more directly bonded to the alumina surface. We found that we could recover the room-temperature spectrum in figure 3 by flowing “wet” nitrogen over the dehydrated sample. The small peak at 1050 cm^{-1} is the $\nu_2(a_1)$ vibration of (HSO_4^-) [15,33,34,38].

The two peaks at 1035 and 1375 cm^{-1} that appear at higher temperatures ($T > 300\,^\circ C$) have previously been observed in infrared and Raman studies of sulfated γ-alumina [6,11,17]. Similar peaks have also been seen in the same frequency region for other sulfated oxides such as CeO_2 [43,44], ZrO_2 [45,46], and Fe_2O_3 [47]. These peaks have mostly been attributed to surface sulfates, except those of CeO_2, which contained “bulk” sulfates as well.

For sulfated Fe_2O_3, Yamaguchi [47] determined by XPS that the surface sulfur species giving the 1375 cm^{-1} band had an oxidation number of 6+. A comparison of their spectra with S–O stretching frequencies of various sulfur-containing compounds allowed them to conclude that the four peaks they observe on their dehydrated samples (from ∼960 to 1375 cm^{-1}) closely resemble those of organic compounds with a bidentate sulfate having two covalent S=O bonds [48–50]. Whereas the other metal oxides may contain a surface sulfate of this form, Lavalley and co-workers [6] have ruled out this structure for the adsorbed sulfate on the γ-alumina from isotopic studies, and have instead proposed a tridentate species of the form $(Al–O)_3$–S=O. They attribute the higher frequency vibration (1375 cm^{-1}) to the S=O stretch, and the lower one to a stretch of the Al–O–S moiety. They note that the symmetric and antisymmetric stretch vibrations of an SO_2 group are typically separated by ∼200 cm^{-1}, which is less than the >340 cm^{-1} difference between the observed peaks on the γ-alumina. Dunn et al. [11] have adopted the same structure in their IR and Raman study of the interactions between surface vanadate and sulfate species on various metal oxide catalysts. Riemer [46] and Spielbauer [17] have assigned the 1375 and 1035 cm^{-1} lines to S=O and S–O stretches, respectively, thus also indirectly supporting Lavalley’s postulated surface sulfate structure. While it is convenient and reasonable to attribute the surface sulfate peaks to the tridentate structure proposed by Lavalley, especially in the light of his isotopic studies, we hesitate at this point to definitively adopt this structure. The surface of γ-alumina is poorly characterized and not well understood [26,29,51], compared to those of other metal oxides or even α-alumina [52]. To determine more conclusively the structure of the surface sulfate species requires a knowledge of the mechanism of sulfate bonding to the variously coordinated surface aluminum atoms, the classification of structures that satisfy valence requirements, and the calculation of vibrational frequencies (infrared and Raman) for the proposed structures. Additionally, a comparison with other surface science techniques such as XPS would give a more complete picture.

The 1600 cm^{-1} peak appearing in the 200–300 °C range of figure 3 may belong to an olefinic C=C stretch [50], probably from an organic impurity acquired during handling or treatment. This line has been previously seen in UV Raman spectra of diamond-like carbon films [53] and coke formed on various metal oxide catalysts [18]; it has also been seen in visible Raman spectra of particulate carbon in exhaust gas [54] and hydrocarbon deposits on sulfated zirconia [55]. The weak band at 2950 cm^{-1} in the room-temperature spectrum of figure 3 is also likely from a C–H stretch band of an organic impurity. However, it is difficult to reconcile the assignment of the 1600 cm^{-1} band to an olefinic C=C stretch with its disappearance simply by heating above 300 °C. An alternative explanation is that this line is the bending vibration of chemisorbed H_2O coordinated on Lewis acid sites [51]. This alternative assignment is consistent with the temperature dependence of the line, which follows that of the O–H stretch band of the surface hydroxyls, as will be discussed in section 3.3.

3.2. Sulfated Pt/γ-alumina

Figure 4 shows a series of spectra obtained for a Pt/γ-alumina sample with 5.9 wt% SO_x at different temperatures. It is qualitatively similar to figure 3 in that both contain the signature of adsorbed sulfates. However, unlike figure 3, the peak at 983 cm^{-1} for the ambient-temperature spectrum is missing. This peak is the signature for the aqueous T_d-symmetry sulfate. Also missing is the broad O–H band at 3470 cm^{-1}. These missing features indicate the absence of physisorbed water on the sample. The strong ambient-temperature sulfate peak now appears at 1014 cm^{-1} (accompanied by a barely discernible bump at 1158 cm^{-1}) and shifts to slightly higher frequencies at progressively higher temperatures, until it disappears altogether at 600 °C. The other surface sulfate peak at 1375 cm^{-1} only makes an appearance at ∼300–400 °C, and is also gone at 600 °C.

We note that although the O–H band characteristic of the physisorbed water on the γ-alumina surface has largely disappeared from the spectrum, the surface may still contain some physisorbed water, since the sulfate peak appears at 1014 cm^{-1} rather than the value 1035 cm^{-1}, which corresponds to the completely dehydrated sulfate peak in figure 3 (at 500 °C). These O–H stretches are simply not seen in our Raman spectra.

The SO_x concentration in the Pt-impregnated sample is higher by about a factor of two compared with the pure γ-alumina sample, although both samples have undergone the same SO_2 exposure. This is due to the fact that Pt is known to catalyze sulfate formation [41,56]. Surprisingly, the sulfate peaks in the Pt-impregnated sample of figure 4 are generally weaker than the corresponding peaks in figure 3, in spite of the higher SO_x concentration. This intensity difference is likely caused by the reduced penetration depth of the laser beam in the Pt-loaded sample, which has a dark gray appearance compared to the pure white appearance of the plain γ-alumina. Another factor affecting the intensity may be the tendency of some of the sulfur to bind directly to the Pt, rather than to form a surface sulfate [42,57,58].

The more rapid disappearance of the sulfate peaks at high temperature shown in figure 4, compared with the same peaks in figure 3, indicates that the surface sulfate on Pt/γ-alumina can be more readily thermally decom-

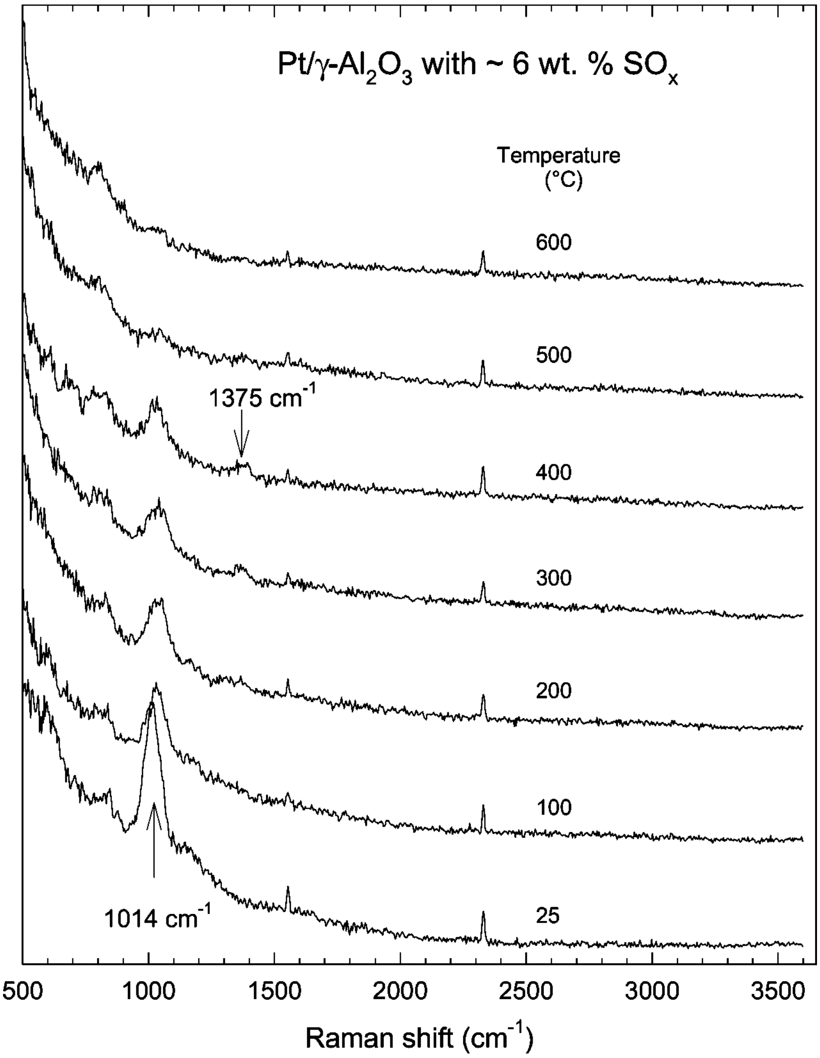

Figure 4. Sulfated Pt/γ-alumina at different temperatures under flowing dry nitrogen. Adsorbed sulfates show peaks at around 1000 and 1370 cm^{-1} similar to the γ-alumina sample without Pt. Note, however, the absence of the physisorbed water peak.

posed than the same species on γ-alumina. When the sulfated Pt/γ-alumina sample is cooled, the sulfate peaks are still missing from the spectrum obtained the following day. However, when N_2 bubbled through water is flowed across the sample during the cool down, a peak at 1005 cm^{-1}, indicative of a partially hydrated surface sulfate, is recovered the following day. The intensity of this peak is about a factor of two lower than the original peak, indicating that some of the SO_x has been permanently lost, most likely through conversion to SO_2, which is then desorbed. Thus, heating to 600 °C in dry N_2 volatilizes some of the surface sulfate and converts the rest to a form that is not detectable by Raman scattering. These sulfur species can then be transformed back into detectable sulfates by heating at lower temperatures in a moist environment.

3.3. Hydroxyls on γ-alumina and Pt/γ-alumina

From the above results, it is clear that Pt loading of the catalyst inhibits physisorption of water (or the observation of physisorbed water) on the γ-alumina. This is true whether or not the sample has been sulfated. It also appears to block surface hydroxyl sites. Figure 5 shows results illustrating this point. The O–H stretch region for the pure γ-alumina sample in figure 5(a) exhibits the broad 3500 cm^{-1} band from physisorbed H_2O and the expected hydroxyl bands, which peak near 3700 cm^{-1} and are mostly gone by 600 °C. The sample with platinum does *not* have either of these bands even at room temperature. After heating the samples to 600 °C, they were cooled back to ambient in the presence of “wet” flowing nitrogen. The topmost traces in figure 5 illustrate spectra of the samples obtained the following day. While the pure γ-alumina sample once again shows a band due to the physisorbed water, the Pt/γ-alumina sample still has none. The weak O–H bending mode of adsorbed water is observed in the room-temperature spectrum of γ-alumina at 1640 cm^{-1} after heating to 600 °C and rehydrating. A similar peak is seen in the bulk aluminum sulfate octadecahydrate spectrum, figure 2(b).

It is interesting to speculate on the effect the Pt has on the apparent OH content of the sample. At a 1 wt% Pt loading

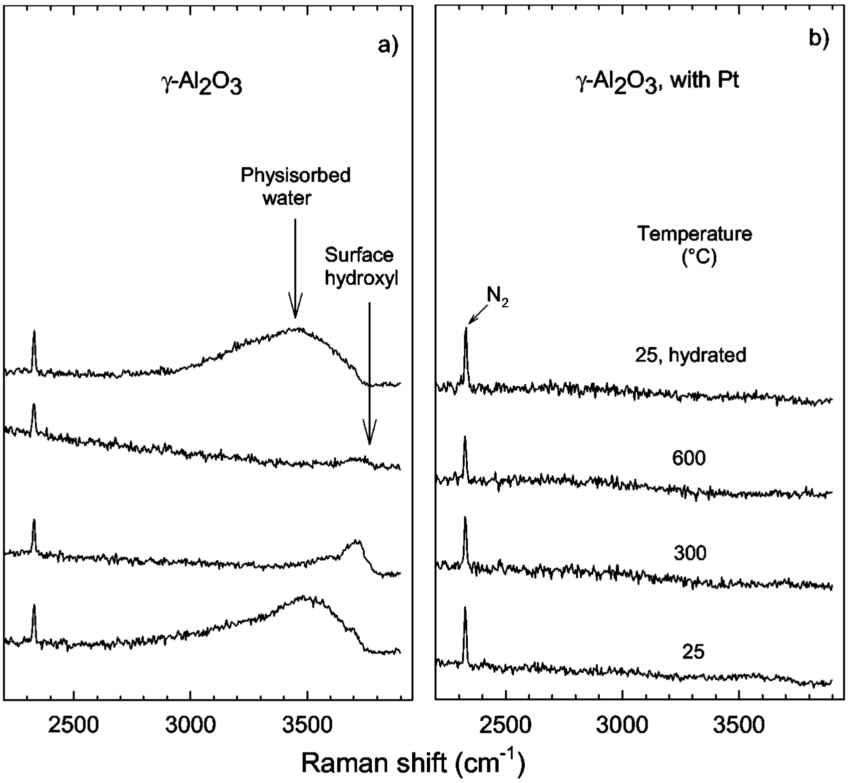

Figure 5. Unsulfated γ-alumina (a) and Pt/γ-alumina (b) showing the O–H stretch region at 25, 300 and 600 °C under flowing dry nitrogen (lower three traces), and at 25 °C after the heating followed by cooling and hydrating with flowing wet nitrogen (top traces). The pure γ-alumina sample shows the O–H stretch due to physisorbed water at 25 °C, and the O–H stretch due to the hydroxylated surface at 300 and 600 °C. The sample with Pt shows neither band.

there is one Pt atom for every 200 Al_2O_3 units. With a surface area of 144 m^2/g, this translates into a rather low average coverage of one Pt for every 500 $Å^2$ of surface. How can this small amount of Pt completely block the adsorption of H_2O? It has been shown by Alexeev et al. [59] that Pt reduces by about a factor of three the ability of γ-alumina to physisorb H_2O. They studied Pt/γ-alumina samples that had been prepared and reduced in a fashion similar to ours. In our case *no* physisorbed H_2O is detectable on the Pt/γ-alumina sample. A possible explanation for this result is that we are seeing only a fraction of the adsorbed waters and surface hydroxyls on the γ-alumina sample, those that are in sites whose Raman spectra are resonantly enhanced with the 244 nm excitation. These same sites are then the ones that the Pt binds to, thus blocking the adsorption of water and formation of surface hydroxyls at sites that lead to a strong Raman signal.

Other studies on γ-alumina may shed more light on this matter. Scanning transmission electron microscope (STEM) Z-contrast images of platinum ultradispersed on γ-alumina have shown that Pt atoms form dimers and trimers on its surface, though their exact positions relative to the surface could not be determined [60]. Density functional calculations have also addressed the role of H in the structure of γ-alumina, and they have determined densities and vibrational frequencies of bulk hydroxyls [26]. It would be extremely interesting if calculations can verify that Pt atoms reside on sites that would normally contain surface hydroxyls or physisorbed water, particularly sites that may show resonantly-enhanced Raman spectra with UV excitation.

4. Conclusion

We have shown that UV Raman spectroscopy is useful for characterizing adsorbed SO_x on γ-alumina-based catalysts. Our results are consistent with previous infrared and Raman work, demonstrating that UV radiation does not affect SO_x surface chemistry. The nature of the sulfates adsorbed on γ-alumina with and without Pt is the same; however, we find systematic differences between them, apparently related to physisorbed water and surface hydroxyls. Further experimental and computational studies that specifically address the structure of adsorbed sulfates and the role of Pt on water adsorption and surface hydroxyls on γ-alumina are needed to completely understand these issues.

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