Interactions between Surface Vanadate and Surface Sulfate Species on Metal Oxide Catalysts

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The interactions between surface sulfate and surface vanadate species present on sulfated supported vanadia catalysts under dehydrated conditions have been investigated with infrared and Raman spectroscopies. The surface sulfate species present on sulfated TiO_2, ZrO_2, and Al_2O_3 supports and V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts have identical molecular structures, i.e., $(M-O)_3S{=}O$, where M = Ti, Zr, or Al. Interactions between the surface vanadia and surface sulfate species do not lead to the formation of sulfate−vanadate compounds. The surface sulfate species on the V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts anchor to and displace only the most basic support hydroxyls, while the surface vanadate species titrate both basic and neutral support hydroxyls forming a complete close-packed monolayer. At low V_2O_5 loadings, the surface vanadia species on these catalysts preferentially titrate basic hydroxyls, which consumes the sites capable of sulfate adsorption. Thus, the amount of adsorbed surface sulfate species decreases in an exponential fashion with increasing surface coverage of the vanadia species. Strong interactions between sulfate species and CeO_2 lead to the formation of bulklike cerium−oxy−sulfur compounds. The stable monolayer of VO_4 units present on the surface of a 4% V_2O_5/CeO_2 catalyst was disrupted upon sulfation and lead to the formation of bulklike cerium sulfate and cerium vanadate compounds.

Introduction

Supported vanadia catalysts have found extensive application in air pollution control systems where they are routinely exposed to moderate levels of SO_x (typically 100−1000 ppm). Surface sulfate overlayers may form on these catalysts under reaction conditions owing to strong interactions between SO_x and the oxide supports. During the selective catalytic reduction of NO with NH_3, sulfate overlayers on $V_2O_5/WO_3-MoO_3/TiO_2$ catalysts interact with weakly adsorbed water to form Bronsted acid sites, which promote the adsorption of ammonia.[1] Supported vanadia catalysts, such as Amoco's DeSOx catalyst ($V_2O_5/CeO_2/Mg_2Al_2O_5$), are finding wide acceptance as fluid catalytic cracking unit (FCCU) SO_x transfer additives owing to their ability to (1) oxidize SO_2 to SO_3 in the FCC regenerator, (2) chemisorb the SO_3 in the FCC regenerator, and then (3) release it as hydrogen sulfide in the reducing FCC reactor.[2] In addition, petroleum-refining operations such as FCC and hydroprocessing yield hydrogen sulfide as an undesired product. The hydrogen sulfide is typically concentrated and fed to a Claus plant to produce elemental sulfur. However, owing to equilibrium limitations only 97% of the sulfur is recovered in the Claus plant, and the tail gas, therefore, needs to be treated before release to the atmosphere. The Mobil Oil SO_x treatment (MOST) process involves combusting the Claus tailgas with air, converting all of the sulfur species to SO_2 and SO_3. The SO_x is sorbed onto a $V_2O_5/CeO_2/Mg_2Al_2O_5$ spinel where it is later regenerated to produce concentrated H_2S and SO_2, which is recycled to the Claus plant for further processing.[3] In addition to air pollution control applications, surface sulfates, formed during the oxidative adsorption of SO_2, have been found to restore the catalytic activity of partially deactivated commercial *o*-xylene oxidation catalysts.[4]

Under dehydrated conditions (i.e., catalyst held at 300−700 °C in a flowing oxygen-containing stream), the surface vanadia species on Al_2O_3, TiO_2, ZrO_2, and CeO_2 supports all possess essentially identical molecular structures.[5] The surface vanadia species are primarily present as both isolated (low coverages) and polymerized (high coverages) VO_4 units with similar ratios of the species at any given surface vanadium oxide coverage on the different oxide supports. The molecular structures of the surface vanadia species are tentatively thought to possess a terminal V═O bond and three bridging vanadium−oxygen-support (V−O−M) bonds for the isolated species (tridentate structure), and a terminal V═O bond with one bridging V−O−M and two bridging V−O−V bonds for the polymerized species.

The adsorption and oxidative adsorption of SO_x onto oxide supports (SiO_2, Al_2O_3, TiO_2, ZrO_2, and CeO_2) have been extensively investigated in recent years with numerous spectroscopic (e.g., IR,[6−12] Raman,[13−15] and XPS[15−18]) and thermal (e.g., TGA,[6,9,10,12,14] TPD,[6,14,19] and DTA[20−22]) techniques. The quantity of moderately acidic SO_2 molecules adsorbed by the various supports in the absence of gas-phase oxygen has been used as a measure of the relative basicity of the supports: $CeO_2 \gg ZrO_2 > TiO_2 \sim Al_2O_3 \gg SiO_2$.[6] SiO_2 contains few basic

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surface functionalities and, therefore, cannot form stable surface sulfate overlayers by heating in the presence of sulfur oxides and excess oxygen.[7] More basic supports such as Al_2O_3, TiO_2, and ZrO_2 can form stable sulfate overlayers by heating in the presence of sulfur trioxide or either sulfur dioxide or hydrogen sulfide and excess oxygen. Tridentate SO_4 surface species, i.e., $(Ti-O)_3S{=}O$ and $(Al-O)_3S{=}O$, have been identified on sulfated TiO_2 and Al_2O_3 under dehydrated conditions.[8] In addition, two tridentate SO_4 species and a polymeric S_2O_7 species were also shown to exist on sulfated ZrO_2.[9] Sulfation of the highly basic CeO_2 support produces both surface and bulklike sulfate species. The former is thought to have a tridentate SO_4 structure, i.e., $(Ce-O)_3S{=}O$, while bulklike species have been shown have a more ionic character.[10]

Despite the extensive characterization of both dehydrated supported vanadia catalysts and sulfated metal oxide supports, few fundamental studies have focused on investigating the interactions between the surface sulfate overlayers developed under reaction conditions and the surface vanadate species present in many air pollution control catalysts. The objective of this work is to determine the fundamental interactions that occur between the surface sulfate and surface vanadate species over well-defined catalytic systems, i.e., sulfated V_2O_5/TiO_2, V_2O_5/ZrO_2, V_2O_5/Al_2O_3, and V_2O_5/CeO_2. The molecular structures of the surface sulfate and surface vanadate overlayers will be determined by in-situ infrared and Raman spectroscopy because of the complementary nature of these vibrational spectroscopies.[23]

Experimental Section

Catalyst Preparation. The support materials used in this study were TiO_2 (Degussa P-25, 55 m^2/g), ZrO_2 (Degussa, 39 m^2/g), Al_2O_3 (Harshaw, 180 m^2/g), and CeO_2 (Engelhard, 36 m^2/g). All of the oxide supports were calcined at 120 °C for 4 h and at 450 °C for 2 h prior to impregnation. The vanadium oxide overlayers were prepared on the oxide support by the incipient wetness impregnation method. Vanadium triisopropoxide was used as the vanadium precursor. The air and moisture sensitive nature of the alkoxide precursor required the preparation to be performed under a nitrogen environment and nonaqueous solutions. Solutions of known amounts of vanadium triisopropoxide (Alfa) and 2-propanol (Fisher-certified ACS, 99.9% pure), corresponding to the incipient wetness impregnation volume and the final amount of vanadia required, were prepared in a glovebox and dried at room temperature for 16 h. The impregnated samples were subsequently heated to 120 °C in flowing nitrogen. The final calcination was performed in O_2 (Linde, 99.999% pure) at 450 °C for 2 h.

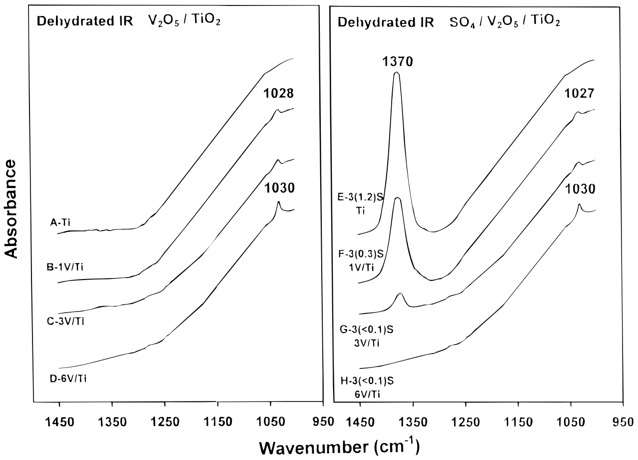

Figure 1. Dehydrated IR spectra of TiO_2 and V_2O_5/TiO_2 catalysts before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading; actual loadings are lower owing to sulfate volatilization and are given in parentheses: A, TiO_2; B, 1% V_2O_5/TiO_2; C, 3% V_2O_5/TiO_2; D, 6% V_2O_5/TiO_2; E, 3% (1.2%) SO_4/TiO_2; F, 3% (0.3%) SO_4/1% V_2O_5/TiO_2; G, 3% (<0.1%) SO_4/3% V_2O_5/TiO_2; H, 3% (<0.1%) SO_4/6% V_2O_5/TiO_2.

It has been demonstrated that the structure and properties of sulfate overlayers are identical regardless of the preparation procedure used to make a sulfate overlayer on TiO_2, ZrO_2, or Al_2O_3 (e.g., impregnation with sulfuric acid or ammonium sulfate, adsorption of SO_3, or oxidative adsorption of either SO_2 or H_2S).[24] Sulfate overlayers were also prepared by the incipient wetness impregnation method using ammonium sulfate as the precursor. Samples requiring both vanadia and sulfate impregnation were first impregnated with vanadium triisopropoxide and calcined as described above before sulfate impregnation took place. Calcination conditions following sulfate impregnation were identical to those following vanadium triisopropoxide impregnation. All samples are reported as weight percent SO_4 or V_2O_5 impregnated in the sample. The actual SO_4 content, as measured by ICP, of the supported vanadia catalysts was less than the impregnated value owing to sulfate volatilization during calcination and is given in parentheses, e.g., 3% (1.2%) SO_4/1% V_2O_5/TiO_2.

Raman Spectroscopy. The laser Raman spectra were obtained with an Ar^+ laser (Spectra Physics, model 2020-50). The incident laser line delivered 10−30 mW of power measured at the sample and was tuned to 514.5 nm. Twenty scans with a resolution of <2 cm^{-1} were averaged to produce the final composite spectra. The scattered radiation from the sample was directed into an OMA III (Princeton Applied Research, model 1463) optical multichannel analyzer with a photodiode array detector thermoelectrically cooled to −35 °C. Approximately 100−200 mg of the pure catalysts were made into wafers and placed in the dehydration cell. The dehydration cell consisted of a stationary holder, which has been described elsewhere.[25] The cell was heated to 300 °C for $^1/_2$ h and then cooled to room temperature before the Raman spectra were obtained. The entire procedure was performed in a stream of flowing oxygen (Linde, 99.999% pure) over the catalyst sample to ensure complete oxidation of the catalysts during the dehydration process. The Raman spectra of the catalysts were also checked under ambient conditions to check for the effect of hydration−dehydration treatments and compound/crystallite formation. However, only the Raman spectra of the dehydrated catalysts are presented in this paper.

Infrared Spectroscopy. Fourier transform infrared (FTIR) spectra were recorded using a Biorad FTS-7 spectrometer (resolution 2 cm^{-1}). The samples were pressed into self-supporting wafers and mounted into a modified in situ cell. The spectra were recorded at room temperature after heating to 400 °C for 1 h.

Results

Sulfated Vanadia−Titania Catalysts. The dehydrated infrared spectra of the TiO_2 support and the 1, 3, and 6% V_2O_5/TiO_2 catalysts (corresponding to 0.16 (~1.5 V atoms/nm^2), 0.5 (~4 V atoms/nm^2), and 1.0 monolayer (~8 V atoms/nm^2) surface vanadia coverages for a Degussa P-25 support with a surface area of ~55 m^2/g), prior to and after sulfation, are presented in Figure 1. The weak IR spectral bands between 1028 and 1032 cm^{-1} are assigned to the terminal $V{=}O$ bond of mono-oxo 4-fold coordinated surface vanadia species. Sul-

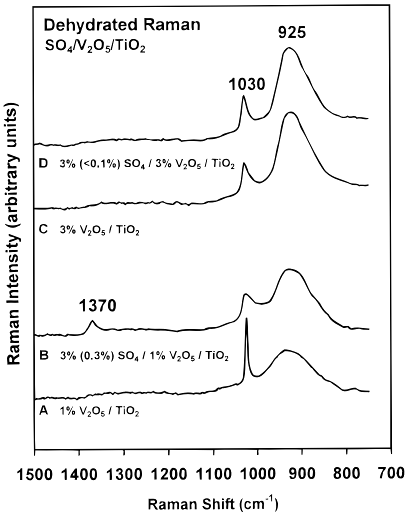

Figure 2. Dehydrated Raman spectra of V_2O_5/TiO_2 catalysts before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading; actual loadings are lower owing to sulfate volatilization and are given in parentheses: A, 1% V_2O_5/TiO_2; B, 3% (0.3%) SO_4/1% V_2O_5/TiO_2; C, 3% V_2O_5/TiO_2; D, 3% (<0.1%) SO_4/3% V_2O_5/TiO_2.

fation of the V_2O_5/TiO_2 catalysts changes neither the intensity nor the vibrational frequency of the $\sim$1030 cm^{-1} IR band.

The infrared spectrum of sulfated TiO_2 (Figure 1e) exhibits an intense band at 1373 cm^{-1}, which was assigned by Saur et al.[8] to the terminal S═O bond of a tridentate surface sulfate species on TiO_2, i.e., $(Ti-O)_3S{=}O$. The infrared spectra of the dehydrated sulfated V_2O_5/TiO_2 catalysts (i.e., spectra f through h in Figure 1) exhibit a single band in the 1100 and 1500 cm^{-1} region centered at 1373 cm^{-1}. The surface concentration of the adsorbed sulfate species, as reflected by the intensity of the 1373 cm^{-1} band, dramatically decreases with increasing coverage of the surface vanadia species. The effect is so pronounced that only negligible amounts of adsorbed sulfate can be detected above half a monolayer coverage of the surface vanadia species. Sulfation of the surface vanadia species was not observed, and no $VOSO_4$ compound was formed (IR and Raman bands at $\sim$1006 cm^{-1} [26]).

The dehydrated Raman spectra of 1 and 3% V_2O_5/TiO_2, prior to and after sulfation, are shown in Figure 2. The bands at 1031 and 925 cm^{-1} have been assigned to terminal V═O bonds and polymerized V−O−V functionalities of mono-oxo VO_4 surface vanadia species, respectively.[27] The presence of the surface sulfate species slightly perturbed the molecular structure of the surface vanadia species by broadening the 1031 cm^{-1} Raman band.

The sulfated samples exhibit only one band in the 1100−1500 cm^{-1} region centered at 1370 cm^{-1}. As observed in the corresponding infrared spectra, the intensity of the 1370 cm^{-1} Raman band dramatically decreases with increasing coverage of the surface vanadia species such that essentially no adsorbed sulfate can be detected above half a monolayer coverage of the surface vanadia species.

The dehydrated Raman spectra of the 1% V_2O_5/TiO_2 catalysts impregnated with variable sulfate loadings are shown in Figure 3. The intensity of the $\sim$1370 cm^{-1} band is approximately constant for all the sulfate loadings tested. A total chemical analysis of the 3, 6, and 12 wt % SO_4 samples showed the actual sulfate loadings of the catalysts to be approximately 1.2 wt % SO_4 ($\sim$1.5 S atoms/nm^2), which is substantially less than a theoretical monolayer ($\sim$4 S atoms/nm^2 or $\sim$3 wt % SO_4 for a 55 m^2/g TiO_2 support; corresponds to that expected for a monolayer of isolated surface SO_4 units).

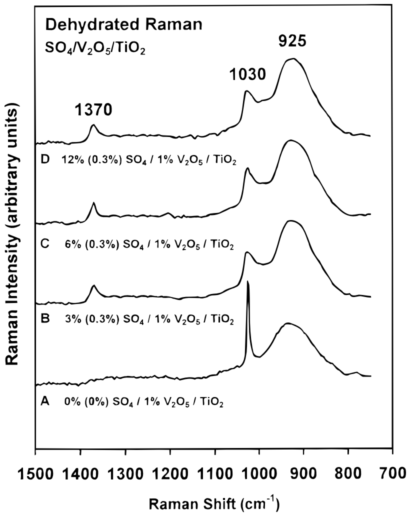

Figure 3. Dehydrated Raman spectra of 1% V_2O_5/TiO_2 catalysts impregnated with aqueous solutions calculated to contain A, 0 wt %; B, 3 wt %; C, 6 wt %; D, 12 wt % SO_4^{2-}.

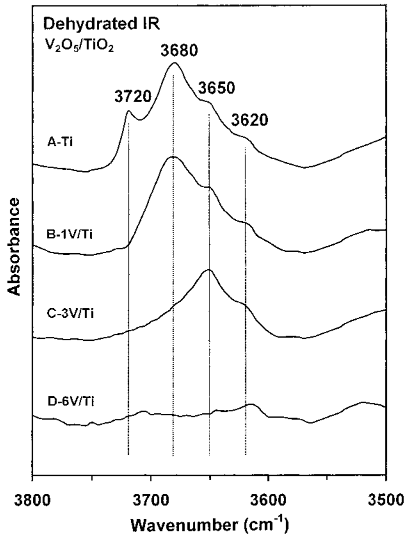

Figure 4. Hydroxyl region of dehydrated IR spectra of TiO_2 and V_2O_5/TiO_2 catalysts: A, TiO_2; B, 1% V_2O_5/TiO_2; C, 3% V_2O_5/TiO_2; D, 6% V_2O_5/TiO_2.

The hydroxyl region (3500−3800 cm^{-1}) of the dehydrated infrared spectra of the TiO_2 support and the 1, 3, and 6% V_2O_5/TiO_2 catalysts are shown in Figure 4. Unpromoted TiO_2 exhibits four distinct IR bands in the hydroxyl region centered at 3720, 3680, 3650, and 3620 cm^{-1}. At low surface vanadia coverage (1% V_2O_5/TiO_2; 0.16 vanadia monolayers or $\sim$1.5 V atoms/nm^2), the surface vanadia species preferentially titrate the surface hydroxyls responsible for the 3720 cm^{-1} band. As the surface vanadia coverage increases to half a monolayer ($\sim$4 V atoms/nm^2), the surface hydroxyls responsible for the 3680 cm^{-1} band have been almost completely titrated. At one monolayer coverage of surface vanadia species ($\sim$8 V atoms/nm^2), the 3650 and 3620 cm^{-1} IR bands also become significantly diminished, indicating that negligible quantities of surface hydroxyls remain on the catalyst surface at monolayer coverage.

In a similar analysis, the IR hydroxyl region of the dehydrated infrared spectra of the TiO_2 support and 3% (1.2%) and 12% (1.2%) SO_4/TiO_2 are presented in Figure 5. As in Figure 4, unpromoted TiO_2 exhibits four distinct bands in the hydroxyl

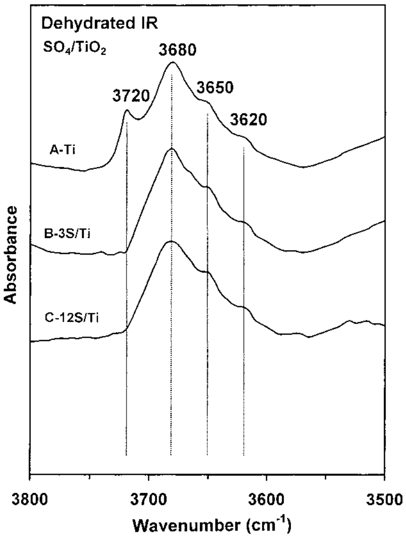

Figure 5. Hydroxyl region of dehydrated IR spectra of TiO_2 impregnated with aqueous solutions calculated to contain A, 0 wt %; B, 3 wt %; C, 12 wt % SO_4^{2-}.

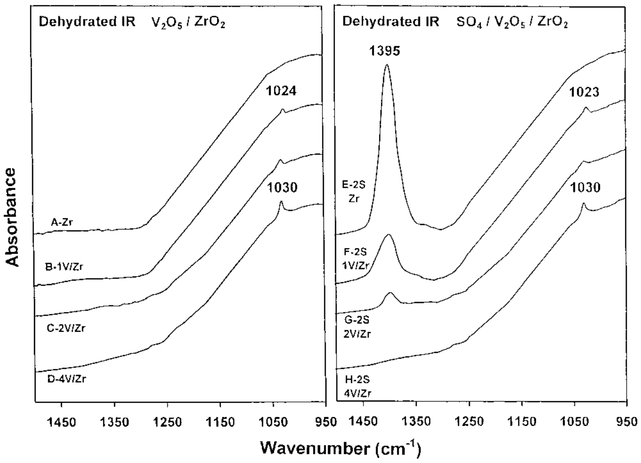

Figure 6. Dehydrated IR spectra of ZrO_2 and V_2O_5/ZrO_2 catalysts before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading: A, ZrO_2; B, 1% V_2O_5/ZrO_2; C, 2% V_2O_5/ZrO_2; D, 4% V_2O_5/ZrO_2; E, 3% SO_4/ZrO_2; F, 3% SO_4/1% V_2O_5/ZrO_2; G, 3% SO_4/2% V_2O_5/ZrO_2; and H, 3% SO_4/4% V_2O_5/ZrO_2.

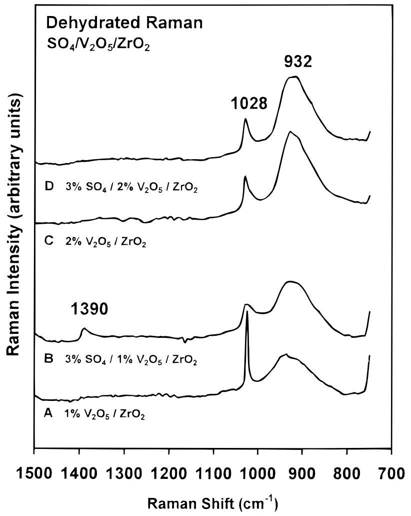

Figure 7. Dehydrated Raman spectra of V_2O_5/ZrO_2 catalysts before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading: A, 1% V_2O_5/ZrO_2; B, 3% SO_4/1% V_2O_5/ZrO_2; C, 2% V_2O_5/ZrO_2; D, 3% SO_4/2% V_2O_5/ZrO_2.

region centered at 3720, 3680, 3650, and 3620 cm^{-1}. Upon sulfation the band at 3720 cm^{-1} is preferentially removed. However, the bands at 3680, 3650, and 3620 cm^{-1} are undisturbed regardless of the amount of sulfate introduced to the sample.

Sulfated Vanadia−Zirconia Catalysts. The dehydrated infrared spectra of the ZrO_2 support and the 1, 2, and 4% V_2O_5/ZrO_2 catalysts (corresponding to 0.25 (~2 V atoms/nm^2), 0.50 (~4 V atoms/nm^2), and 1.0 monolayer (~8 V atoms/nm^2) vanadia coverages for a support with a surface area of 39 m^2/g), prior to and after sulfation, are shown in Figure 6. The weak IR bands between 1024 and 1031 cm^{-1} are assigned to the terminal V=O bond of mono-oxo 4-fold coordinated vanadia surface species. Sulfation of the V_2O_5/ZrO_2 catalysts changes neither the intensity nor the vibrational frequency of the ~1030 cm^{-1} IR band.

The infrared spectrum of sulfated ZrO_2 exhibits only one band in the 1100−1500 cm^{-1} region centered at 1395 cm^{-1}. Benistel et al.[9] demonstrated that this IR band can be attributed to two different surface sulfate species both possessing only one terminal S=O bond and having a tridentate structure. Sulfation of the V_2O_5/ZrO_2 systems does not shift the 1395 cm^{-1} band, nor do any new bands appear between 1100 and 1500 cm^{-1}. However, the surface concentration of the adsorbed sulfate species, as reflected by the intensity of the 1395 cm^{-1} IR band, dramatically decreases with increasing coverage of the surface vanadia species. The effect is so great that only negligible amounts of adsorbed sulfate can be detected above half a monolayer coverage of the surface vanadia species. Owing to the similarities between the IR and Raman spectra of the sulfated V_2O_5/TiO_2 and V_2O_5/ZrO_2 catalysts, verification of the presence of surface sulfates on the V_2O_5/ZrO_2 catalysts by ICP analysis was deemed unnecessary.

The dehydrated Raman spectra of 1 and 2% V_2O_5/ZrO_2, prior to and after sulfation, are presented in Figure 7. The 1390 cm^{-1} Raman band of the sulfated 1% V_2O_5/ZrO_2 essentially coincides with the 1395 cm^{-1} band found in the infrared spectra of sulfated ZrO_2 and is assigned to the terminal S=O of tridentate surface sulfates coordinated to the ZrO_2 support. The surface sulfate species perturbed the molecular structure of the surface vanadia species by broadening the ~1030 cm^{-1} band. Essentially no surface sulfate can be detected above half a monolayer coverage of surface vanadia species. Sulfation of the surface vanadia species was not observed, and no $VOSO_4$ compound was formed.

Sulfated Vanadia−Alumina Catalysts. The dehydrated infrared spectra of the Al_2O_3 support and the 5 and 20% V_2O_5/Al_2O_3 catalysts (corresponding to 0.25 (~2 V atoms/nm^2) and 1.0 monolayer (~8 V atoms/nm^2) vanadia coverages for a support with a surface area of 180 m^2/g), prior to and after sulfation, are shown in Figure 8. The weak IR bands between 1028 and 1032 cm^{-1} are assigned to the terminal V=O bond of mono-oxo 4-fold coordinated surface vanadia species. Sulfation of the V_2O_5/Al_2O_3 catalysts changes neither the intensity nor vibrational frequency of the ~1030 cm^{-1} IR band.

The infrared spectrum of sulfated Al_2O_3 (Figure 8d) exhibits an intense band at 1386 cm^{-1}, which was assigned by Saur et al.[8] to the terminal S=O bond of a tridentate surface sulfate species on Al_2O_3, i.e., $(Al-O)_3S=O$. Sulfation of the V_2O_5/Al_2O_3 systems does not shift the 1386 cm^{-1} band, nor do any new bands appear between 1100 and 1500 cm^{-1}. However, the surface concentration of the adsorbed sulfate species, as

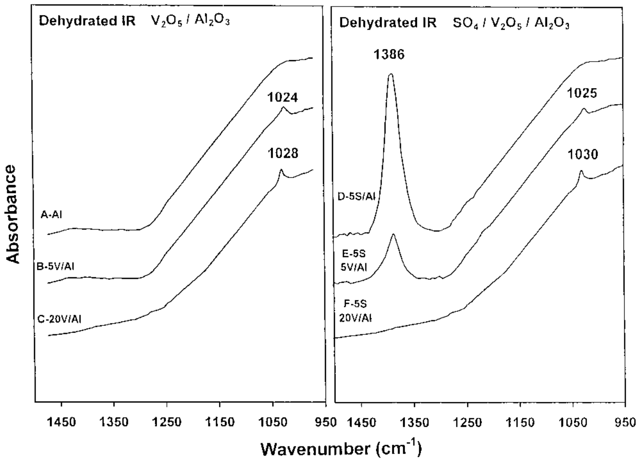

Figure 8. Dehydrated IR spectra of Al_2O_3 and V_2O_5/Al_2O_3 catalysts before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading: A, Al_2O_3; B, 5% V_2O_5/Al_2O_3; C, 20% V_2O_5/Al_2O_3; D, 3% SO_4/Al_2O_3; E, 3% SO_4/5% V_2O_5/Al_2O_3; F, 3% SO_4/20% V_2O_5/Al_2O_3.

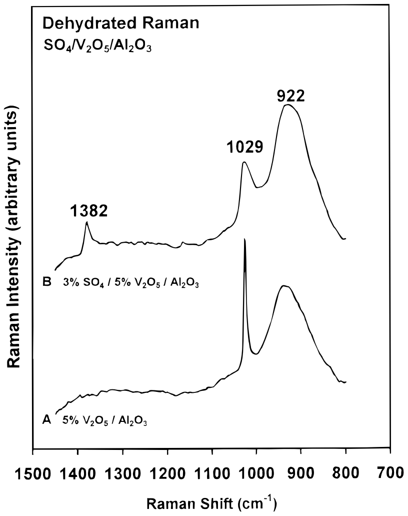

Figure 9. Dehydrated Raman spectra of V_2O_5/Al_2O_3 before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading: A, 5% V_2O_5/Al_2O_3; B, 3% SO_4/5% V_2O_5/Al_2O_3.

reflected by the intensity of the 1386 cm^{-1} IR band, dramatically decreases with increasing coverage of the surface vanadia species.

The dehydrated Raman spectra of 5% V_2O_5/Al_2O_3, prior to and after sulfation, are shown in Figure 9. The 1382 cm^{-1} Raman band of sulfated V_2O_5/Al_2O_3 coincides with the 1386 cm^{-1} IR band found in the infrared spectra of sulfated Al_2O_3 and is assigned to the terminal S=O of tridentate surface sulfates coordinated to the Al_2O_3 support. The surface sulfate species perturbed the molecular structure of the surface vanadia species by broadening the ~1030 cm^{-1} band. Sulfation of the surface vanadia species was not observed, and no $VOSO_4$ compound was formed.

Sulfated Vanadia−Ceria Catalysts. The dehydrated Raman spectra of the CeO_2 support, prior to and after sulfation, are shown in Figure 10. The broad Raman band at 1180 cm^{-1} is due to the CeO_2 support. Upon sulfation of the CeO_2 support, several new Raman bands appear at 975, 995, 1010, and 1120 cm^{-1}, which have been assigned by Twu et al.[13] to bulklike cerium−oxy−sulfur compounds.

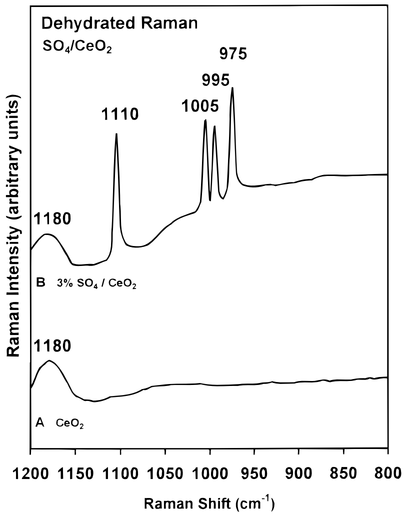

Figure 10. Dehydrated Raman spectra of CeO_2 before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading: A, CeO_2; B, 3% SO_4/CeO_2.

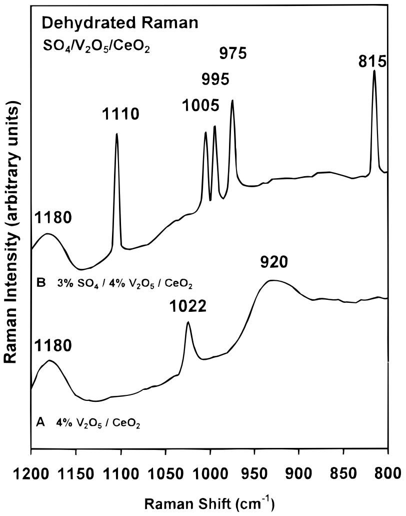

Figure 11. Dehydrated Raman spectra of V_2O_5/CeO_2 before and after sulfation. Sulfate loadings shown represent the calculated impregnation loading: A, 4% V_2O_5/CeO_2; B, 3% SO_4/4% V_2O_5/CeO_2.

The dehydrated Raman spectra of the 4% V_2O_5/CeO_2 catalyst (8 V atoms/nm^2; corresponds to 1.0 monolayer coverage for a 36 m^2/g support), prior to and after sulfation, are shown in Figure 11. The bands at 1022 and 920 cm^{-1} of spectrum (a) have been assigned to terminal V=O bonds and polymerized V−O−V functionalities of mono-oxo VO_4 surface vanadia species, respectively. The Raman spectra of the 4% V_2O_5/CeO_2 catalyst changes drastically after sulfation. The bands at 1022 and 920 cm^{-1} have been removed, and new bands centered at 815, 975, 995, 1005, and 1110 cm^{-1} have appeared. The bands at 975, 995, 1005, and 1110 cm^{-1} are assigned to the same bulklike cerium−oxy−sulfur compound found upon sulfation of the CeO_2 support, while the band at 815 cm^{-1} is characteristic of bulk $CeVO_4$.

Discussion

The similarities between the dehydrated infrared and Raman spectra of the sulfated TiO_2, ZrO_2, and Al_2O_3 supports and V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts lead to the conclusion that the surface sulfate species present on these systems possess identical molecular structures. A mono-oxo assignment for the surface sulfate species appears justified since both the Raman and IR spectra of the sulfated catalysts contain only one

TABLE 1: Effect of Surface Vanadia Coverage on Maximum Obtainable Surface Sulfate Coverage for TiO_2-, ZrO_2-, and Al_2O_3-Supported Catalysts

	surface sulfate coverage (S atoms/nm^2)		
surface vanadia coverage	TiO_2	ZrO_2	Al_2O_3
bare support	2.9[a]	3.0[a]	2.9[a]
0.16 monolayer	1.5		
0.25 monolayer		1.0	1.1
0.50 monolayer	<0.2	<0.2	
1.0 monolayer	0.0	0.0	0.0

[a] Calculated value based on ∼1370 cm^{-1} infrared peak area.

band in the 1100−1500 cm^{-1} region (centered at ∼1370 cm^{-1} for TiO_2, ∼1395 cm^{-1} for ZrO_2, and ∼1386 cm^{-1} for Al_2O_3 supported systems). According to the IR/Raman selection rules this should only occur for a mono-oxo species.[23] Oxygen-18 exchange experiments on the surface sulfates attached to Al_2O_3, TiO_2, and ZrO_2 also support the assignment of a mono-oxo structure under dehydrated conditions.[8,9,12]

The absence of infrared and Raman active spectral features in the 900−1500 cm^{-1} region, with the exception of the ∼1370 cm^{-1} band of the sulfated support and the ∼1030 and ∼930 cm^{-1} bands of the surface VO_4 species, indicates that direct sulfation of the surface vanadia species of the V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts does not readily occur. The difficulties in detecting the sulfation of surface vanadia species have been demonstrated in several recent studies. Following oxidative adsorption of sulfur dioxide at 175 °C on a monolayer V_2O_5/TiO_2 (∼13 μmols V^{5+}/m^2) catalyst, the uptake of sulfur dioxide was undetectable (<0.05 μmol SO_2/m^2).[28] Similarly, sulfur dioxide has been employed as a probe for basic sites present on V_2O_5/Al_2O_3 catalysts at 80 °C.[20−22] As vanadia surface coverage approached a monolayer (∼13 μmol V^{5+}/m^2), the volumetric uptake of sulfur dioxide fell below the limit of detection (<0.09 μmol SO_2/m^2) of the adsorption chamber used in the study. The same studies failed to detect the adsorption of sulfur dioxide onto bulk V_2O_5 and monolayer V_2O_5/SiO_2 catalysts.[21]

Even though sulfation of surface vanadia on V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts does not take place, minor interactions do exist between the surface vanadia and surface sulfate species as evidenced by the broadening of the ∼1030 cm^{-1} Raman band, which has been assigned to the terminal V═O bond of the surface VO_4 units. This signal broadening represents an increase in the structural heterogeneity of the surface VO_4 units most likely due to lateral interactions between the surface sulfate and surface vanadate species.

As shown in Table 1, the amount of adsorbed sulfate present on the TiO_2-, ZrO_2-, and Al_2O_3-supported catalysts appears to decrease in an exponential fashion with coverage of the support by vanadia species, i.e., much more rapidly than one may expect from simple (theoretical) geometrical coverage by vanadate species. This phenomenon was first observed on sulfated MoO_3/Al_2O_3 catalysts and was explained by the observation that while surface sulfate species titrated only the most basic hydroxyls (IR bands at 3785, 3740, and 3705 cm^{-1}), surface molybdate species titrated both basic and neutral hydroxyls (IR bands at 3785, 3740, 3705, and 3590 cm^{-1}) forming a complete monolayer.[15] Similar findings were shown above for sulfated TiO_2 and V_2O_5/TiO_2 catalysts. Surface sulfate species titrated only the most basic hydroxyls (IR band at 3720 cm^{-1}), while surface vanadate species titrated both basic and neutral hydroxyls (IR bands at 3720, 3680, 3650, and 3620 cm^{-1}) forming a complete monolayer. At low MoO_3 and V_2O_5 loadings the molybdena and vanadia surface species preferentially titrate basic hydroxyls, consuming the sites capable of sulfate adsorption. As discussed by Amiridis et al.,[1] this reduction in the number of sites capable of sulfate adsorption implies that only lowly loaded V_2O_5/TiO_2 SCR of NO_x catalysts will experience the beneficial adsorption characteristics provided by the increased Bronsted acidity arising from the interaction of surface sulfates and water vapor. Therefore, catalytic systems using TiO_2, ZrO_2, or Al_2O_3 supports and wishing to benefit from the presence of sulfate overlayers, e.g., SCR $DeNO_x$ catalysts, are restricted to low vanadia loadings owing to vanadia's propensity to occupy the surface sites capable of sulfate adsorption. This lack of adsorption sites explains the observation that regardless of the amount of sulfate introduced to the system, the quantity of stable sulfate species attached to the TiO_2, Al_2O_3, and ZrO_2 supports saturates at less than a theoretical monolayer and then remains constant.

The interaction between the highly basic CeO_2 support and the sulfate species was sufficiently strong to produce bulklike cerium−oxy−sulfur species as opposed to the tridentate surface sulfates present on the TiO_2, ZrO_2, and Al_2O_3 supports and the V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts. The stable monolayer of VO_4 units present on the surface of the 4% V_2O_5/CeO_2 catalyst was destroyed upon sulfation. It was found in a previous study that the 4% V_2O_5/CeO_2 catalyst experiences a drastic (>95%) loss in SO_2 oxidation activity after several hours of exposure to a flowing SO_2 and oxygen containing stream at 400 °C.[29] This loss in catalytic activity can be attributed to the disruption of the highly active vanadia monolayer and formation of less active cerium sulfate and cerium vanadate compounds.

The ability of V_2O_5/CeO_2 catalysts to form bulklike cerium−oxy−sulfur compounds is advantageous in applications such as SO_x transfer additives where the oxidation activity of the vanadia species is secondary to the catalyst's ability to adsorb quantities of sulfates larger than can be provided by monolayer surface coverage (40+ wt % SO_4 vs 3 wt % SO_4[30,31]).

Conclusions

In situ infrared and Raman spectroscopies were employed to investigate the interactions between surface sulfate and surface vanadate species on sulfated supported vanadia catalysts. The surface sulfate species present on sulfated TiO_2, ZrO_2, and Al_2O_3 supports and V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 have identical molecular structures, i.e., $(M{-}O)_3S{=}O$, where M = Ti, Zr, or Al. The mono-oxo assignment for the surface sulfate species is based on coincident IR/Raman bands as well as oxygen-18 exchange studies. The absence of additional spectral features in the 900−1500 cm^{-1} region upon addition of surface sulfate species to the supported vanadia catalysts indicates that direct sulfation of the surface vanadia species is negligible.

The amount of adsorbed sulfate species decreased in an exponential fashion with coverage of the support by vanadia species. It was observed that surface sulfate species present on V_2O_5/TiO_2, V_2O_5/ZrO_2, and V_2O_5/Al_2O_3 catalysts titrate only the most basic support hydroxyls, while surface vanadate species titrate both basic and neutral support hydroxyls forming a complete close-packed monolayer. At low V_2O_5 loadings, the surface vanadia species preferentially occupy the basic surface hydroxyls, consuming the sites capable of sulfate adsorption. This lack of adsorption sites explains the observation that regardless of the amount of sulfate introduced to the system the quantity of stable sulfate species attached to the support becomes saturated at less than theoretical monolayer coverage and then remains constant. This observation has important implications for supported vanadia catalysts employed in air pollution control applications (e.g., SCR of NO_x catalysts and SO_x transfer additives).

Strong interactions between sulfate species and CeO_2 lead to the formation of subsurface cerium−oxy−sulfur compounds. The stable monolayer of VO_4 units present on the surface of a 4% V_2O_5/CeO_2 catalyst was disrupted upon sulfation leading to the formation of bulklike cerium sulfate and cerium vanadate compounds. The ability of CeO_2 supports and V_2O_5/CeO_2 catalysts to form bulklike cerium−oxy−sulfur compounds is advantageous in applications such as SO_x transfer additives where a primary goal is to adsorb quantities of sulfates larger than can be provided by monolayer surface coverage of sulfates.

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