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Reactivity of V_2O_5 Catalysts for the Selective Catalytic Reduction of NO by NH_3: Influence of Vanadia Loading, H_2O, and SO_2

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A systematic investigation of the selective catalytic reduction (SCR) of NO by NH_3 over V_2O_5/TiO_2 catalysts of variable vanadia loading has been carried out at 623 K. Kinetic studies were conducted both in the presence and in the absence of H_2O and SO_2. The structure of the various catalysts, as well as adsorbed species present on their surface, was characterized by *in situ* Raman and infrared spectroscopies. Under dry and SO_2-free conditions, the turnover frequency of the SCR reaction was found to go through a maximum with vanadia surface coverage at approximately half a monolayer. The observed decrease in the SCR turnover frequency at vanadia surface coverages exceeding half a monolayer can be attributed to the loss of strong acid sites which are associated with the TiO_2 support. Addition of H_2O to the reacting gas mixture results in a decrease in the SCR turnover frequency of approximately 40–50%, which is independent of the vanadia surface coverage. *In situ* Raman results suggest that such a decrease can be attributed to the competitive adsorption of H_2O on the active vanadia sites. The presence of SO_2 in the gas phase during the SCR reaction results in a significant increase of the turnover frequency at low vanadia surface coverages, while it has no effect at vanadia surface coverages above half a monolayer. Raman and infrared results suggest that the effect of SO_2 can be attributed to the formation of surface sulfate species, which are only present on the titania surface below half a monolayer coverage due to repulsive interactions between the surface vanadia and sulfate species.

INTRODUCTION

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by ammonia (NH_3) represents today the state of the art among NO_x emission control technologies for stationary sources, despite some recent advances at the research level with alternative control strategies. Transition metal oxides are the most active SCR catalysts in the temperature range between 573 and 723 K, which is frequently encountered in commercial installations of SCR technology. Among such catalysts, V_2O_5/TiO_2-based materials are the most commonly used, due to their high activity, thermal stability, and resistance to poisoning by SO_2 (1, 2). An extensive body of literature exists on both the reactivity and the characterization of V_2O_5/TiO_2-based SCR catalysts (see Ref. 1 for a review of the early literature).

Significant advances have been made in both the resolution and the availability of surface characterization techniques since the first reports on SCR over V_2O_5/TiO_2 catalysts appeared in the literature in the late 1970s and early 1980s. As a result, some of the conclusions of the early work in SCR have been revised, and some new questions need to be addressed. Both vibrational (Raman and infrared) (3–5) and NMR spectroscopies (6), for example, have demonstrated the presence of multiple structures of vanadium oxide on the titania surface. Monomeric and polymeric surface vanadyl species have been observed below monolayer coverages of surface vanadia. The relative distribution of these different types of surface vanadia structures has been shown to vary with the surface vanadia coverage. The reactivity of these species for SCR has been examined in previous reports (7–9). All of these studies, however, were conducted at temperatures significantly lower (120 K or more) than the average temperature of maximum SCR activity (623 K) which is frequently selected for commercial SCR applications and/or at NO concentrations of an order of magnitude higher than the ones encountered in a typical flue gas. Furthermore, the vast majority of SCR studies available in the literature has been conducted, for simplicity, in the absence of H_2O and SO_2. Although there are reports that these two components of the flue gas significantly affect the activity of V_2O_5/TiO_2-based SCR catalysts (10, 11), we are not aware of any study that systematically examines their effect over catalysts with different vanadia loadings.

In this work, we systematically investigated the reactivity of V_2O_5/TiO_2 catalysts of variable vanadia loading for the SCR reaction, under conditions frequently encountered in commercial applications. These included higher temperatures (i.e., 623 K) than the ones previously reported

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and gas streams containing H_2O and SO_2. Results from Raman and infrared spectroscopic studies were combined with the kinetic measurements to help us gain a better understanding of the effect of these two gases on the surface structures and reactivity of the V_2O_5/TiO_2 catalysts.

EXPERIMENTAL

Catalyst preparation. The catalysts used in this study were prepared by the incipient wetness impregnation method. Degussa P-25 TiO_2 (approximately 50 m^2/g) was used as the support, and vanadium triisopropoxide (Alfa, 95–98% purity) was used as the precursor for the vanadium oxide. Because of the air and moisture sensitivity of the vanadium triisopropoxide, the preparation was performed in a nitrogen environment, using methanol (Fisher-certified ACS, 99.9% purity) as the solvent. The TiO_2 support was impregnated with the vanadium triisopropoxide–methanol solution to incipient wetness and allowed to remain under nitrogen atmosphere for 16 h. The catalysts were then subjected to various heat treatments in nitrogen (12) followed by a final calcination at 723 K. Sulfated V_2O_5/TiO_2 samples were prepared by impregnating the V_2O_5/TiO_2 catalysts with aqueous solutions containing 3, 6, and 12 wt% of SO_4^{2-}. The precursor used for the sulfate preparation was $(NH_2OH)_2 \cdot H_2SO_4$, which was dissolved in distilled water. Final calcination of the sulfate-doped catalysts was performed at 773 K.

Raman spectroscopy. Raman spectra of supported vanadium oxide catalysts were acquired using a specially designed *in situ* cell. The details of the cell have been outlined elsewhere (13). The 514.5-nm line of an argon–ion laser (Spectra Physics, Model 165) was used as the excitation source. For all of the studies reported in this paper, the laser power was 50–100 mW when measured at the sample. The Raman-scattered light from the sample was collected at right angles to the laser beam and directed into an OMA III (Princeton Applied Research, Model 1463) optical multichannel analyzer with a photodiode array detector thermoelectrically cooled to 238 K. For all of the scans, the spectral resolution and reproducibility was less than 2 cm^{-1}. About 0.2 g of each supported vanadium oxide catalyst was pressed into a thin wafer of about 1 mm thickness. Each sample was then heated to 673 K for 30 min and finally cooled to room temperature. The entire procedure was performed in flowing oxygen. Raman spectra of the catalysts were also collected under ambient conditions and confirmed that the hydration–dehydration procedure did not result in the formation of any new compounds. For the collection of the *in situ* spectra in the presence of moisture, pure oxygen flowing at 100 scc/min was bubbled through a flask of water to produce a mixture containing approximately 7–8% H_2O.

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 collected at room temperature after heating to 673 K for 1 h.

Activity tests. The activity tests for the selective catalytic reduction of NO by NH_3 were carried out in a stainless-steel one-pass flow reactor. The reacting gasses were mixed and preheated prior to the reactor entrance. Analyzed certified mixtures (Matheson) of 12% NO in N_2, 5% NH_3 in N_2, and 2% SO_2 in N_2 were used as the sources of the flue gas components. Air was mixed in as the source of O_2, and N_2 was used as the carrier gas. Water was introduced into the system through a high-performance pump (Shimadzu). The catalyst temperature was measured through a thermocouple projecting into the center of the catalyst bed. The NO concentration at both the inlet and the outlet of the reactor was analyzed by the use of a chemiluminescent analyzer (Thermo Electron).

Each run utilized approximately 0.1 g of catalyst in the form of 40/60 mesh spherical particles. The total flow rate over the catalyst was controlled at approximately 3300 scm^3/min (200 SL/h). Reaction rates were calculated by treating the reactor as a plug flow or integral reactor, according to the equation

$$r = -F_{\mathrm{NO}}/m_{\mathrm{cat}} * \ln(1 - x),$$

where r is the observed reaction rate, F_{NO} is the molar feed rate of NO to the reactor, m_{cat} is the mass of the catalyst in the reactor, and x is the fractional conversion of NO across the reactor. This equation assumes a first-order dependence on NO and zero-order dependence on NH_3, in agreement with numerous published results over V_2O_5-based SCR catalysts (14).

Under these conditions, internal diffusion limitations were important for some of the catalysts tested. Therefore, intrinsic rates were calculated according to standard correction methods (15). In particular, the model of Wakao and Smith (16) was used to calculate the effective diffusion coefficients. For similar catalysts, coefficients thus obtained were found to be within 10% of the experimentally measured values (17). Experiments repeated with similar catalysts using different particle sizes have shown that the intrinsic rates can be reproduced within 10%, validating this correction method (18). The observed conversions in this study varied between 8 and 50%, while the calculated effectiveness factors varied between 0.6 and 0.9.

RESULTS AND DISCUSSION

Vanadia structure. Previous studies have shown that depending on the vanadia loading, two surface vanadia species

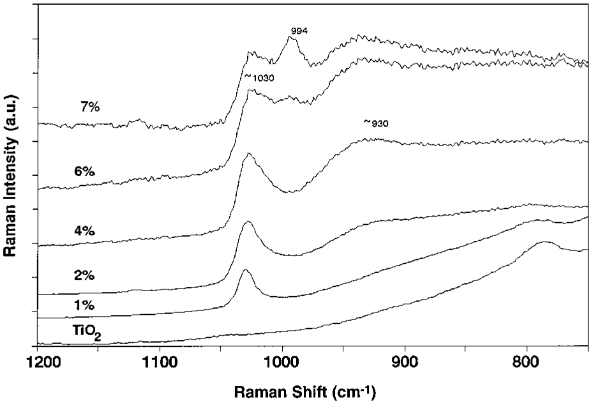

FIG. 1. Raman spectra of dehydrated V_2O_5/TiO_2 catalysts as a function of vanadia loading.

and microcrystalline phase V_2O_5 particles can be present on the surface of V_2O_5/TiO_2 catalysts (4–6). In brief, at low vanadia loadings vanadia exists on the titania surface primarily as an isolated, tetrahedrally coordinated, surface vanadyl species (Raman band at approximately 1027 cm^{-1}). At higher vanadia loadings, the surface vanadyl species polymerize on the titania surface (Raman band at 1027 cm^{-1} shifts to 1030 cm^{-1}, and a new Raman band appears at approximately 930 cm^{-1}). At coverages exceeding a monolayer (approximately 13 μmol V^{5+}/m^2) microcrystalline V_2O_5 particles are formed as a separate phase on the two-dimensional surface vanadia overlayer (major Raman band at 994 cm^{-1}). The relative concentrations of these species depend on the surface vanadia coverage as shown in Fig. 1. Raman spectra of the catalysts prepared for this work are in agreement with those previously reported in the literature.

For the present catalysts, monolayer coverage corresponds to approximately 6% V_2O_5/TiO_2, where a trace of crystalline V_2O_5 can be detected. Higher vanadia loadings give rise to a strong Raman band at 994 cm^{-1} due to the formation of crystalline V_2O_5. Density calculations for vanadia crystals yield a surface density of approximately 9.5 V^{5+}/nm^2 (19). For a catalyst with a surface area of 50 m^2/g this would correspond to a monolayer vanadia loading of 7%. Given that the dispersed vanadia is expected to have a somewhat lower density than the crystal, this value can be viewed as the upper limit for the monolayer, with the Raman results providing the more accurate estimate.

Effect of vanadia surface coverage. The activity of V_2O_5/TiO_2 catalysts of variable vanadia loading was determined at 623 K. Experiments were initially conducted in the presence of equimolar amounts of NO and NH_3 and excess O_2. In subsequent experiments, H_2O and SO_2 were also added to the reacting gas mixture. A detailed listing of the various conditions employed in these experiments is shown in Table 1. Each catalyst was tested under all three sets of conditions, with the results reported in Table 2 and plotted as a function of vanadia surface coverage in Fig. 2.

TABLE 1

Concentrations of Flue Gas Components for the Various Kinetic Runs

Components	Set 1	Set 2	Set 3
NO	400 ppm	400 ppm	400 ppm
NH_3	400 ppm	400 ppm	400 ppm
O_2	4%	4%	4%
H_2O	—	8%	8%
SO_2	—	—	800 ppm

The results in Fig. 2 show that, in the absence of H_2O and SO_2, the turnover frequency of the V_2O_5/TiO_2 catalysts (expressed in units of moles of NO reacted per mole of V per second) initially increases with the vanadia surface coverage, reaches a maximum at coverages corresponding to approximately half a monolayer, and then decreases at higher coverages. Previous studies of the activity of V_2O_5/TiO_2 catalysts, conducted at lower temperatures, have also shown an increase in the rate of the SCR reaction with vanadia surface coverage (7–9). Such an increase has been attributed to a higher specific activity of the polymeric vanadate species (9), or the accompanying increase of Brønsted acid sites with vanadia surface coverage (20).

The same studies, however, have reported that the increase of the turnover frequency in the submonolayer region is monotonic, and in only one case was a plateau reached at surface coverages between half and one monolayer coverage (8). The lower turnover frequencies

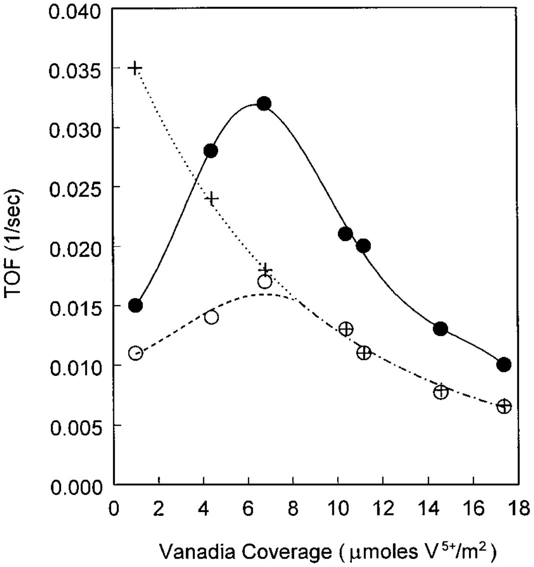

FIG. 2. Effect of surface vanadia coverage on SCR activity of V_2O_5/TiO_2 catalysts (Conditions: ●, Set 1; ○, Set 2; +, Set 3).

TABLE 2

SCR Activity of Various V_2O_5/TiO_2 Catalysts at 623 K

V_2O_5 loading			Set 1			Set 2			Set 3		
wt%	BET SA (m^2/g)	(μmol V^{5+}/m^2)	R_{obs}[a]	R_{int}[b]	TOF[c]	R_{obs}[a]	R_{int}[b]	TOF[c]	R_{obs}[a]	R_{int}[b]	TOF[c]
0.5	56	1.0	0.8	0.8	15	0.5	0.6	11	1.6	2.0	35
2.0	49	4.4	4.1	6.1	28	2.4	3.0	14	3.6	5.2	24
3.0	49	6.8	7.0	10.5	32	4.3	5.6	17	4.6	5.9	18
4.0	42	10.4	6.1	9.3	21	4.2	5.7	13	4.2	5.7	13
5.0	49	11.2	6.6	10.8	20	4.6	6.3	11	4.5	6.2	11
6.0	45	14.6	6.3	8.3	13	4.2	5.1	7.7	4.3	5.2	7.9
7.0	44	17.4	5.7	7.8	10	4.0	5.0	6.5	4.0	5.1	6.6

[a] Observed rate [(μmol NO)/(g-catalyst)(s)].
[b] Intrinsic rate [(μmol NO)/(g-catalyst)(s)].
[c] Turnover frequency [(mol NO)/(mol V^{5+})(s)] $\times 10^{-3}$.

observed at coverages exceeding one monolayer are due to the presence of microcrystalline V_2O_5 particles which are not 100% dispersed as assumed in the turnover frequency calculations (this is the case in this study as well, with the 6% and especially the 7% V_2O_5/TiO_2 catalysts). The observed maximum, and the subsequent decrease of the SCR turnover frequency at coverages between half and one monolayer under our conditions, can be attributed to the loss of strong acid sites at high vanadia surface coverages. Acid sites are expected to be involved in the adsorption and subsequent activation of NH_3 for the SCR reaction. Temperature-programmed desorption studies of NH_3 over V_2O_5/TiO_2 catalysts of variable vanadia loading have indeed shown that the fraction of acid sites capable of adsorbing NH_3 at 623 K is significantly reduced as the surface vanadia coverage is increased to levels between half and one monolayer (21). In contrast, the number of acid sites capable of adsorbing NH_3 at temperatures between 370 and 520 K appears to be approximately the same regardless of vanadia loading. As a result, a decrease in activity, due to the reduction in the number of acid sites, is observed under our conditions at surface vanadia coverages between half and one monolayer, while the activity increases slightly or remains almost constant in the previous studies conducted at lower temperatures.

Furthermore, the effect of the surface vanadia coverage on the SCR turnover frequency appears to be significantly higher at the lower temperatures. The data of Baiker *et al.* (8), for example, show that the turnover frequency for the SCR reaction at 423 K increases by a factor of 20–30 when the surface vanadia coverage increases from 2 to 6 μmol V^{5+}/m^2. A similar increase in surface vanadia coverage under the conditions utilized in the current study, however, results in an increase in the turnover frequency of only a factor of 2. We have previously reported that the activation energy of the SCR reaction decreases significantly with the vanadia loading (18). When the different activation energies are used to extrapolate our results to lower temperatures a good agreement is achieved with the previously reported data.

Effect of H_2O. Addition of 8% H_2O to the reacting gas mixture resulted in a decrease in the SCR turnover frequency of approximately 40–50% (Fig. 2). This decrease appears to be uniform for all different surface vanadia coverages examined. *In situ* Raman spectra of a 1% V_2O_5/TiO_2 catalyst collected at temperatures ranging from 723 to 393 K in a gas stream containing 8% H_2O are shown in Fig. 3. Significant changes are observed in these spectra, while no such changes are observed in the corresponding spectra collected under dry conditions. In particular, the Raman

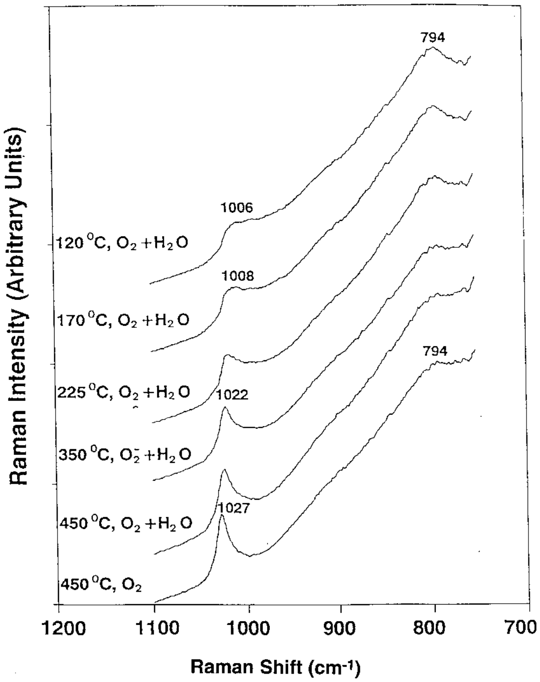

FIG. 3. *In situ* Raman spectra at different temperatures of a 1% V_2O_5/TiO_2 catalyst in a gas stream containing 8% H_2O.

band at 1027 cm^{-1} appears to be broadened and shifted toward lower wavenumbers. The effect is more pronounced at lower temperatures (the band eventually shifts to 1006 cm^{-1} at 393 K) and suggests that adsorption of H_2O (hydration) is taking place on the vanadyl species. At the reaction temperature (623 K), the effect is already detectable (i.e., the vanadyl band has shifted to 1022 cm^{-1}), but not as pronounced as at the lower temperatures. This suggests a picture of the catalyst surface at 623 K that has H_2O molecules adsorbed on it, but is not "flooded" by them. Such a picture is consistent with the kinetic results which show a 40–50% decrease in the SCR turnover frequency. The Raman spectra suggest that this decrease can be attributed to the competitive adsorption of H_2O on the vanadia sites, and hence, a reduction in the number of the sites available for the adsorption and reaction of NH_3 and NO. Similar results were also obtained with a series of Raman spectra collected with a 5% V_2O_5/TiO_2 catalyst in the presence of water, in agreement with the kinetic observations which suggest that the effect of H_2O is independent of the surface vanadia coverage.

Effect of SO_2. Addition of 800 ppm SO_2 to the reacting gas mixture resulted in an increase in the SCR turnover frequency at low surface vanadia coverages. In contrast, the presence of SO_2 did not have any effect on the turnover frequency of catalysts with surface vanadia coverages exceeding half a monolayer. As a result, the SCR turnover frequency in the presence of H_2O and SO_2 no longer presents a maximum, but decreases monotonically with the surface vanadia coverage (see Fig. 2).

Differences were also observed in the transient behavior of the low V_2O_5 loading catalysts following the addition of H_2O and SO_2 in the reacting gas mixture. While the catalytic activity reached steady state within a few minutes following the addition of H_2O, it took approximately 2 h to reach steady state following the addition of SO_2. Similarly, the initial activity was recovered within minutes following removal of the H_2O from the reacting gas mixture, while overnight treatment at elevated temperatures was required for the catalysts to return to their previous steady states following removal of the SO_2.

This behavior is consistent with the formation of a stable surface sulfate species during the exposure of the V_2O_5/TiO_2 catalysts to SO_2. The kinetic results further suggest that such a species is formed in significant amounts only on the catalysts with surface vanadia coverages below half a monolayer, indicating that it is associated with the TiO_2 support. Thermogravimetric analysis and infrared and X-ray photoelectron spectroscopies have been used previously by Chen and Yang (11) to confirm the formation of surface sulfate species on TiO_2 surfaces under SCR reaction conditions, in agreement with our observations.

We further explored this behavior by impregnating two of the V_2O_5/TiO_2 catalysts, containing 1 and 3% V_2O_5, respectively, with an aqueous solution containing 3% SO_4^{2-}. FTIR spectra of the resulting catalysts were collected following calcination at 773 K and are shown in Fig. 4. The

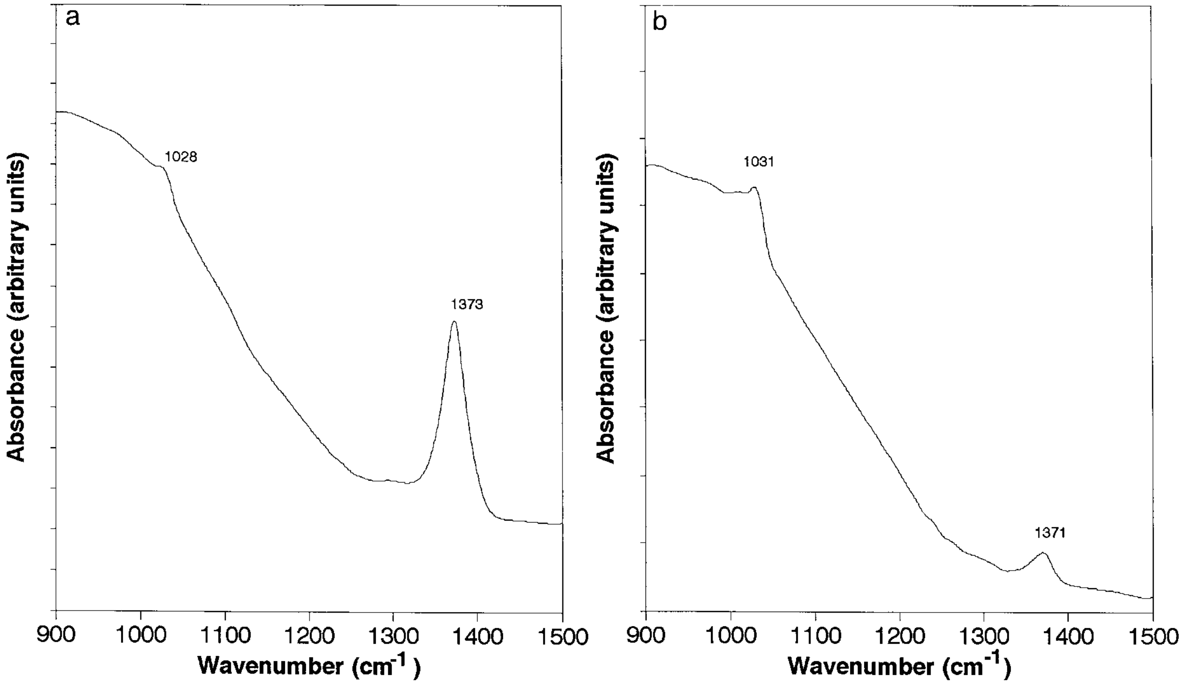

FIG. 4. FTIR spectra obtained under dehydrated conditions of (a) 1% and (b) 3% V_2O_5/TiO_2 catalysts impregnated with an aqueous solution containing 3% SO_4^{2-}.

strong peak at 1370–1375 cm^{-1}, present in the spectrum of the catalyst containing 1% V_2O_5, has been previously observed in the infrared spectra of sulfated metal oxides and has been assigned to the stretching frequency of a terminal S=O bond (11). Its presence is consistent with the formation of a surface sulfate species. More importantly, the intensity of this peak is significantly lower in the spectrum of the catalyst containing 3% V_2O_5, in agreement with the kinetic results, which suggest that the promoting effect of SO_2, and hence, the concentration of surface sulfates, is significantly decreased on V_2O_5/TiO_2 catalysts containing more than half a monolayer of surface vanadia. ICP analysis supports these results, since it revealed that following the impregnation with the solution containing 3% SO_4^{2-}, the 1 and 3% V_2O_5/TiO_2 samples contained 1.2 and less than 0.2% sulfur, respectively. As to the reasons for this behavior, currently, we can only offer speculations regarding the competition for the same TiO_2 sites by both the vanadyl and sulfate species or a possible repulsive interaction between these species.

Raman spectra of the 1% V_2O_5/TiO_2 catalyst following impregnation with aqueous solutions containing 3, 6, and 12% SO_4^{2-}, and calcination at 773 K, are shown in Fig. 5. In agreement with the FTIR spectra, a band is observed at approximately 1370 cm^{-1} corresponding to the stretching frequency of a terminal S=O bond. The intensity of this band appears to remain constant with increasing sulfate concentration above 3 wt% in the impregnating solution, suggesting that a maximum amount of surface sulfate species has been reached. ICP analysis supports this conclusion, since all three samples were found to contain approximately the same amount of sulfur (1.1–1.2%) regardless of the concentration of sulfates in the impregnating solutions (3, 6, or 12%). In addition, the presence of the sulfate species appears to have an effect on the spectrum of the vanadyl species. In particular, the sharp Raman band at 1026 cm^{-1} shifts to 1031 cm^{-1} and the broad Raman band increases in relative intensity and shifts from 880 to 910 cm^{-1}. These changes suggest that the ratio of the polymeric to the isolated vanadyl species is increased in the presence of the surface sulfates and are consistent with a model in which the formation of the sulfate species "crowds" the vanadyl species together and leads to their polymerization.

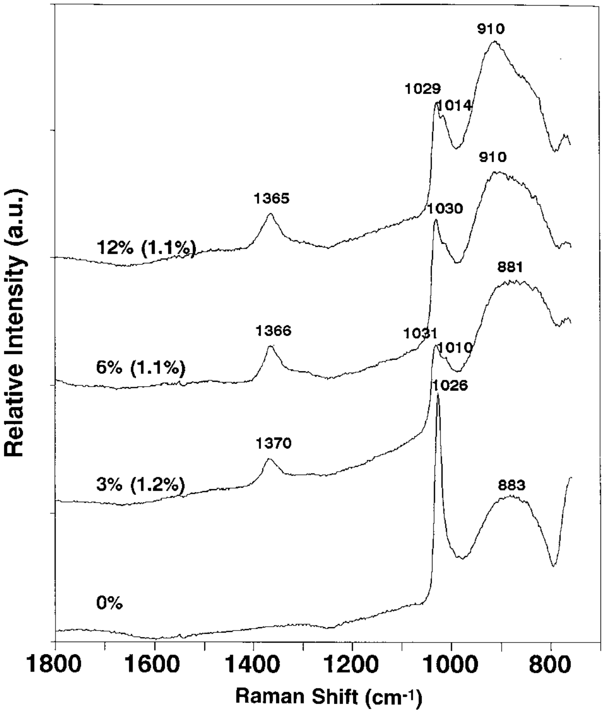

FIG. 5. *In situ* Raman spectra of a 1% V_2O_5/TiO_2 catalyst impregnated with aqueous solutions containing 3, 6, and 12% SO_4^{2-} (final SO_4^{2-} concentrations on the catalyst are noted in parentheses).

Reaction mechanism. The mechanism of the SCR reaction has been extensively debated in the literature. Both Langmuir–Hinshelwood (9, 22, 23) and Eley–Rideal (24–27) models have been proposed, since NO is not known to adsorb strongly on the V_2O_5/TiO_2 surface (24, 28–31). Recently, Topsøe *et al.* (27) demonstrated that the plethora of available kinetic and spectroscopic data can be explained by a relatively simple catalytic cycle which includes the adsorption and activation of ammonia on a Brønsted acid site, the reaction of the activated ammonia with gaseous or weakly adsorbed NO, and the reoxidation of the active vanadia site by molecular oxygen. The data collected in this work cannot add to or resolve the controversy about the reaction mechanism, since our observations appear to be related to changes in the number of available active sites and do not directly probe the reaction step between NO and the active ammonia species. Indeed, the effects of both H_2O and SO_2 on the turnover frequency can be explained by a decrease and increase, respectively, in the number of available active sites for the SCR reaction. Such an explanation is also supported by observations that the overall activation energy for the reaction remains the same both in the presence and in the absence of H_2O and SO_2 (18), which indicates that there is no significant change in the form of the overall rate expression caused by the presence of these two components of the flue gas.

Our kinetic and spectroscopic data suggest that the effect of H_2O, can be attributed to the competitive adsorption between water and ammonia (and even possibly NO) on the vanadia sites. Such a competition is expected to decrease the number of sites available for reaction and hence decrease the SCR turnover frequency. The presence of large amounts of H_2O in the reacting gas mixture may also lower the rate of the SCR reaction by slowing the reoxidation of vanadia, since H_2O is a product of this reaction. The formation of a surface sulfate species was found in this work to be responsible for the effect of SO_2 on the rate of the SCR reaction. Such a species, has been shown previously to become a strong Brønsted acid site in the presence of H_2O (11) and is, therefore, expected to increase the number of available sites for the adsorption and activation of the ammonia, and hence, increase the SCR rate. From this point of view, our data appear to support previous claims that ammonia adsorbed on a Brønsted acid site is the active SCR intermediate (11, 24, 27, 30, 32).

CONCLUSIONS

Kinetic measurements performed at 623 K show that the turnover frequency of the SCR reaction goes through a maximum with surface vanadia coverage at approximately half a monolayer. The decrease in the SCR turnover frequency at higher surface vanadia coverages is due to the loss of strong acid sites which are associated with the TiO_2 support. Addition of H_2O to the reacting gas mixture results in a decrease in the SCR turnover frequency of approximately 40–50%. This decrease is independent of the surface vanadia coverage and can be attributed to the competitive adsorption of H_2O on the surface vanadia sites. The presence of SO_2 in the gas phase during the SCR reaction results in a significant increase of the turnover frequency at low surface vanadia coverages, but it has no effect at surface vanadia coverages exceeding half a monolayer. The effect of SO_2 can be attributed to the formation of a surface sulfate species which in the presence of H_2O represents a strong Brønsted acid site. The concentration of these species decreases with increasing vanadia loading.

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