Characterization of the Nature of Surface Sites on Vanadia–Titania Catalysts by FTIR

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With the aim of understanding the vanadia–titania catalysts used for selective catalytic reduction of NO by NH_3 in the SCR $DeNO_x$ process, the surface structure of vanadia, titania, and vanadia supported on titania catalysts were studied by FTIR. The interactions of NO, NH_3, and NO + NH_3 with the catalysts in different states of oxidation/reduction have also been investigated. Vanadia was found to be highly dispersed on the TiO_2 as a result of interaction with Ti–OH. This interaction phase also exhibited new V–OH bands not observed on V_2O_5. The nature of the titania and vanadia surface hydroxyl groups was observed to be very sensitive to sample pretreatment in that oxidation enhanced their concentration whereas reduction removed these OH groups. Extensive reduction in H_2 of the vanadia–titania sample broke up the surface vanadia structure, eliminated the V–OH species, and reexposed the surface Ti–OH groups. Adsorption of NH_3 on the surface demonstrated the presence of both Brønsted and Lewis acid sites on the vanadia–titania catalysts, while Brønsted and Lewis acid sites were observed to dominate on V_2O_5 and TiO_5, respectively. The ratio of Brønsted to Lewis acid sites on the vanadia–titania catalysts was found to depend on the number of V–OH and V=O groups, the vanadia loading, or the vanadia coverage, as well as the oxidation state of vanadia. No adsorption of NO was evidenced on the oxidized or the NH_3-reduced surface of vanadia–titania and adsorption occurred only on the H_2-reduced samples. On a partially reduced catalyst with preadsorbed NH_3, NO was observed to oxidize the surface at room temperature accompanied by a transformation of Lewis to Brønsted acid sites. The redox properties of these catalysts were found to play an essential role in the surface adsorption/reaction process. Evidence of interaction of NO with surface NH_4^+ species further suggested the importance of Brønsted acid sites and thus also the V–OH groups in the SCR $DeNO_x$ reaction mechanism. © 1991 Academic Press, Inc.

INTRODUCTION

The increasing problem of air pollution by nitrogen oxides (NO_x) has resulted in more stringent emission regulations in many countries and a great increase of interest in the development of effective $DeNO_x$ catalysts. One of the most important $DeNO_x$ processes is the so-called Selective Catalytic Reduction (SCR) process where the NO_x is reduced by NH_3 to form N_2 and H_2O (see, e.g., Ref. (*1*)). Many different types of catalyst have been used for this process but vanadia–titania based catalysts are probably the most commonly used. Despite the various studies made on this system (*2–14*), there is still no general agreement on the nature of the surface ac-

tive sites and the reaction mechanism. For example, Inomata *et al.* (*3*) from their studies on vanadium oxide catalyst concluded that the site responsible for the NO–NH_3 reaction was the V^{5+}=O species and they later extended this conclusion to vanadia–titania (*4*) and vanadia–alumina catalysts (*5*) where they have found the number of vanadyl species to correlate with the activity. Bond *et al.* (*6*) proposed oxohydroxy species, VO_x, bonded to two surface oxygens as the important sites present on the surfaces of vanadia–titania catalysts. Later, Gasior *et al.* (*7*) concluded from their studies on V_2O_5 that the active sites could not be V^{5+}=O but were acidic hydroxyl groups on the vanadia surface. This view was recently shared by Rajadhyaksha

et al. (8, 9) from their ammonia adsorption investigation on vanadia supported on titania–silica catalysts.

In view of the outstanding problems, we have carried out a series of physical and catalytic investigations on the vanadia–titania system employing a variety of techniques. This paper will present and discuss the results of FTIR studies on the surface structures and on the adsorption properties of these catalysts. In order to simulate the different states of the catalyst which may be present during a catalytic cycle, the catalysts have been investigated both in oxygen (the SCR reaction takes place in an excess oxygen environment) and after exposure to the reactants NO and NH$_3$ alone or together. The catalysts have also been studied after more extensive prereduction in hydrogen. The present results will form a basis for our combined FTIR and activity studies which will be discussed in a subsequent publication.

EXPERIMENTAL

The vanadia–titania catalysts, with either 0.6 or 6 wt.% V$_2$O$_5$, were prepared by impregnating TiO$_2$ in an oxalic acid solution of ammonium metavanadate followed by drying at 100°C and calcination at 400°C. V$_2$O$_5$ was prepared by heating ammonium metavanadate at 450°C for 1 h and the phase purity of the resulting structure was verified by X-ray diffraction: the oxide had a BET surface area of 7 m^2/g. The titania support used was anatase with a surface area of 90 m^2/g. For the FTIR measurements, the samples were ground and pressed into self-supporting wafers and mounted into an IR cell which allowed *in situ* measurements of the samples during pretreatments, as well as during adsorption or desorption in vacuum at various temperatures.

The effects of different oxidation pretreatments were investigated. However, if not specified, "oxidized" samples refer to samples evacuated for 1 h at 400°C and subsequently oxidized in 400 Torr of O$_2$ for 2 h at 400°C. The resulting samples were then cooled in O$_2$ and evacuated at room temperature (RT) before adsorption of gases at the same temperature. This pretreatment was used in most cases since the resulting samples gave the highest concentration of sites for ammonia adsorption. The other oxidation treatments used will be described together with the results in later section. The NH$_3$-"reduced" surfaces were obtained after NH$_3$ adsorption at RT and subsequent TPD up to 400°C during 3 h followed by further evacuation at 400°C for $\frac{1}{2}$ h. FTIR spectra were recorded during the TPD. The H$_2$-reduced surface was obtained after flowing H$_2$ over the sample at 400°C for 2 h and subsequently evacuating at RT. The infrared spectra were recorded on a Digilab FTS80 FTIR spectrometer equipped with a MCT (mercury–cadmium–telluride) detector at a spectral resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

I. Surface Hydroxyl Structure

Oxide surfaces are in general covered by hydroxyl groups to various extents. The degree of surface hydroxyl coverage depends greatly on the sample pretreatments. For example, evacuation at progressively increasing temperatures will first remove the hydrogen-bonded hydroxyls of the physisorbed water and will then remove the surface hydroxyl groups of the oxide. An examination of the surface hydroxyl structure of an oxide catalyst can therefore provide useful information on the nature of the oxide surface and its interaction with surface metal atoms, which often involves surface OH groups. In view of this, an investigation was made on the surface hydroxyl structure of TiO$_2$, 0.6 and 6% vanadia–titania. The OH stretching regions of these samples after the standard oxygen pretreatment are shown in Figs. 1a–c. For TiO$_2$ (Fig. 1a), the OH stretching region consists of a series of bands dominated by a sharp band positioned at 3675 cm^{-1} and a weak shoulder at 3718 cm^{-1} which are characteristic of the two different types of hydroxyl groups on
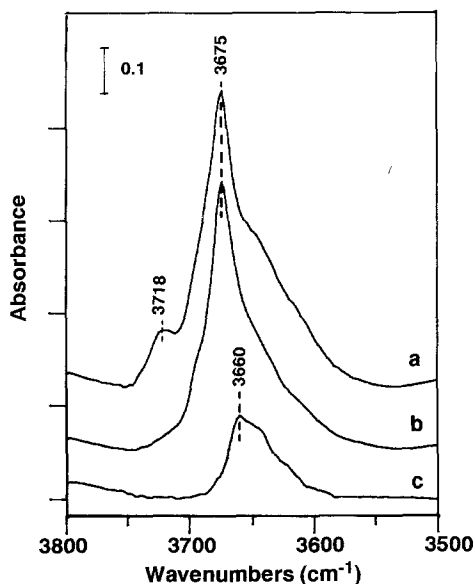
FIG. 1. Infrared spectra of the hydroxyl structure of (a) TiO_2, (b) 0.6% vanadia–titania, and (c) 6% vanadia–titania.

the surface of anatase (*11*). The intensity of these hydroxyl stretching bands, especially those of the shoulder bands, is seen to decrease upon addition of vanadia to titania (Fig. 1b). When the vanadia loading was increased to 6% vanadia on titania, the sharp OH stretching band typical of anatase was replaced by a broader band at 3660 cm^{-1}. This downward frequency shift of 15 cm^{-1} indicates that the OH groups on the 6% V_2O_5/TiO_2 are now bonded to more electronegative surface metal atoms than Ti^{4+}. These hydroxyl groups are attributed to V^{5+}-OH, in agreement with earlier assignments (*2*). Thus, these results show that vanadia is highly dispersed on the titania surface (approx. 40–50% coverage of TiO_2 at 6% V_2O_5). The gradual disappearance of the Ti–OH groups upon addition of vanadia suggests that vanadia interacts with the titania surface mainly via bonding with the surface Ti–OH groups, forming new V–OH species. The absence of crystalline vanadia phases in the XRD pattern on the vanadia–titania samples further confirms the high dispersion of vanadia.

As expected, the nature of these surface OH groups is found to be sensitive to the sample pretreatment. Figure 2 shows how the surface hydroxyl structure of TiO_2 is affected by different pretreatment conditions. The OH stretching band at 3675 cm^{-1} observed in the initially oxidized sample (Fig. 2a) decreased in intensity upon reduction by NH_3 (Fig. 2b). The slight downward frequency shifts of the OH stretching bands observed in the reduced sample reflect an increase of electron density at the metal atom due to reduction. This was only partially regenerated, as shown in Fig. 2c, upon reoxidation (as with the initial O_2 pretreatment). Similar irreversible behavior was observed for the vanadia–titania samples.

Figure 3a shows the surface hydroxyl structure of the oxidized vanadia–titania. Fig. 3b and c shows that NH_3 reduction (Fig. 3b) and H_2 reduction (Fig. 3c) affect the OH region quite differently. Upon NH_3 reduction (Fig. 3b), the V–OH band at 3659 cm^{-1} has decreased in intensity but remains at the same position, whereas after H_2 reduction (Fig. 3c), a new OH band at 3678
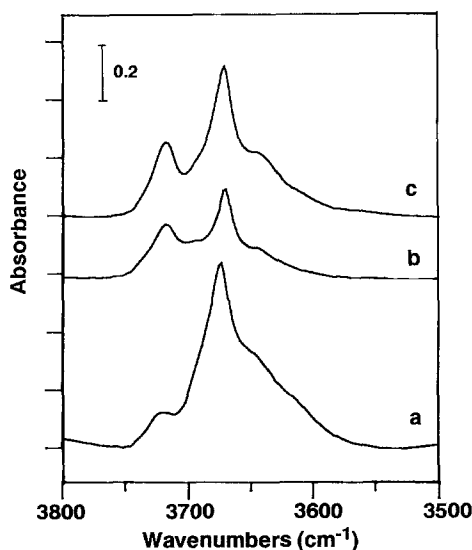

FIG. 2. Infrared spectra of the hydroxyl structure of TiO_2 (a) after "oxidation," (b) after "reduction," and (c) after reoxidation.
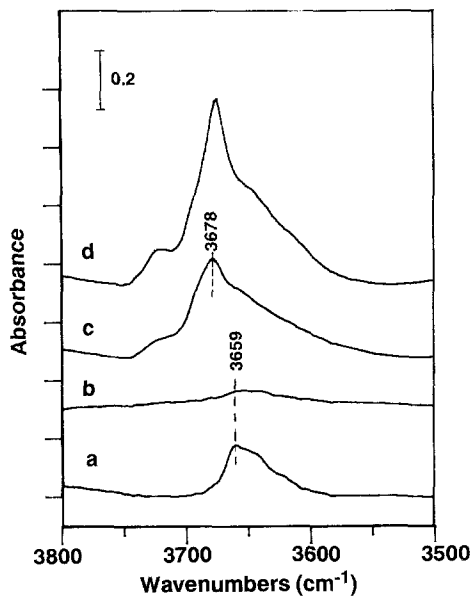
FIG. 3. Infrared spectra of the OH structure of the 6% vanadia–titania (a) after oxidation in 200 Torr O_2 at 400°C for 2 h, (b) after NH$_3$ reduction, (c) after H$_2$ reduction, as compared to (d) TiO$_2$ after oxidation.

cm^{-1} was observed, which is the band position of Ti–OH as discussed above for the pure TiO$_2$ sample (Fig. 3d). Thus, the results indicate that the H$_2$ reduction treatment not only removed the V–OH groups and created coordinatively unsaturated sites but also regenerated the Ti–OH by reexposing the support surface. This indicates that the surface vanadia phase is not stable under such severe reduction conditions and that the highly dispersed vanadia phase is at least partially destroyed by H$_2$ reduction. It is noteworthy that NH$_3$ reduction was apparently not sufficient to remove all the OH bonded to V and to regenerate the Ti–OH, as in the H$_2$ reduction. Thus, the vanadate structure is not destroyed by exposure to NH$_3$. This stability is no doubt an important feature for the application of these catalysts for SCR operation. These changes in surface hydroxyl structure due to variations in vanadia concentration and state of oxidation affect the

different adsorption properties as will be discussed below.

II. Surface Vanadyl Structure

Besides the hydroxyl band structure, bands are also observed for the vanadia samples around 2000 cm^{-1} attributed to the first overtone vibration of the V=O group (2). The oxidized 0.6% vanadia–titania sample shows the V=O overtone band at 2038 cm^{-1} (Fig. 4a). The intensity of this band is enhanced over a broad shoulder at around 2002 cm^{-1} when the vanadia loading was increased to 6% (Fig. 4b). The pure V_2O_5 shows V=O overtones at 2021 cm^{-1} and 1972 cm^{-1} (Fig. 4c). The higher V=O overtone band frequency observed when vanadia is supported on TiO$_2$ as compared to that of the pure V_2O_5 indicates a support interaction which strengthens the V=O bond on the surface and that the nature of the surface vanadia species differs from that of the bulk V_2O_5. Upon NH$_3$ reduction, upward shifts to 2050 and 2044 cm^{-1} are observed for both the 0.6% and 6% vanadia, respectively, with a simultaneous intensity enhancement (Figs. 4d,e), whereas a slight intensity increase is seen for V_2O_5 with, however, no band shifts. The increase in frequency which reflects a strengthening of the V=O bond upon NH$_3$ reduction, in view of above results, is likely to be associated with a decrease in V–OH concentration on the surfaces. Such strengthening of the V=O bond has also recently been reported in the literature (15) as due to surface dehydration. From the differences observed in the V=O band behavior on the bulk V_2O_5 and supported vanadia, one would expect a difference in surface adsorption properties. These properties would in turn depend on the nature of the support and sample pretreatments.

III. Nature of NH$_3$ Adsorption

Since ammonia is one of the reactants in the SCR reaction, it is important to understand the nature of ammonia interactions with the catalyst surface. The nature of
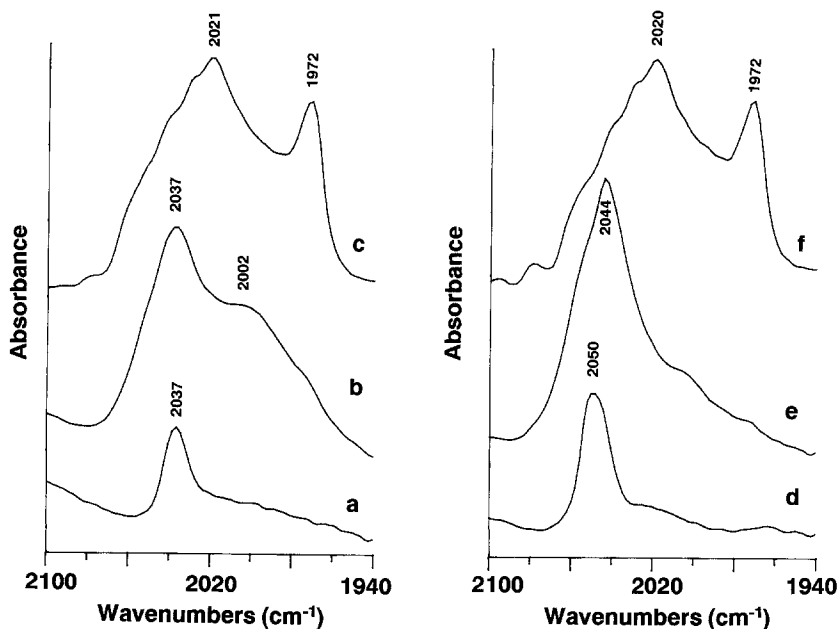
FIG. 4. Infrared spectra of the V=O overtone region of oxidized (a) 0.6% vanadia–titania, (b) 6% vanadia–titania, (c) V_2O_5, and (d), (e), (f) are those of the same samples but after NH_3 reduction.

NH_3 adsorption was studied systematically on the titania support, the V_2O_5 model compound, and the two vanadia–titania catalysts. In order to understand the effects of sample pretreatment and surface oxidation states, NH_3 adsorption after different pretreatments was investigated.

TiO₂. Ammonia adsorbed readily at RT on the TiO_2 surface after all the various pretreatments. The resulting changes due to the NH_3 adsorption are clearly seen in the IR spectra, especially in the region of the OH and NH stretching vibrational modes. The room temperature IR difference spectra (with the TiO_2 background spectrum subtracted) of NH_3 adsorbed on TiO_2 after oxidation, NH_3 reduction, and reoxidation treatments are compared in Fig. 5. The positive band area shows the ammonia species adsorbed on the surface whereas the negative band area shows the disappearance of some surface hydroxyl groups upon NH_3 adsorption. The bands at 3398 cm^{-1} and 3350 cm^{-1} are assigned to the asymmetric and symmetric stretching frequencies, re-

spectively, of NH_3 chemisorbed on the surface (*16*). The other bands at 3256 cm^{-1} and 3156 cm^{-1} are according to Busca (*2*) assigned to the $\nu_s(NH_3)$ split due to a Fermi resonance with the overtone of the asymmetric NH_3 deformation. The intensity of these bands was seen to decrease gradually after desorption by evacuation at increasing temperatures but some traces of these bands can still be detected at 300°C. Thus, these results show that the NH_3 is chemisorbed on the surface by coordination of its lone-pair electrons to surface titanium sites, thereby indicating the presence of Lewis acid sites (LA). In the NH_3 bending region, no distinct band around 1400 cm^{-1} due to the deformation vibrational mode of NH_4^+ is observed, showing the absence of distinct surface Brønsted acidity (BA) on this sample. The broad band region around 3000 cm^{-1} shows, however, some hydrogen bonding between NH_3 and surface Ti–OH groups. It can also be seen from these three spectra that the oxidized sample (spectrum a) adsorbs the most NH_3, mostly in the
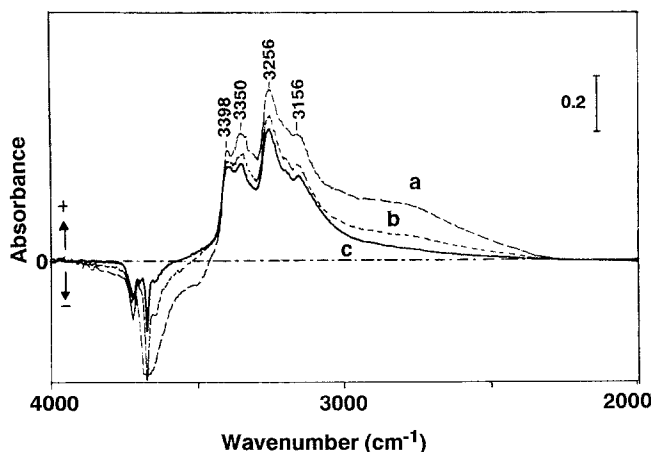
FIG. 5. Infrared spectra of NH_3 adsorption on TiO_2: (a) after "oxidation," (b) after reoxidation, and (c) after "reduction." The spectrum of the TiO_2 sample prior to adsorption has been subtracted in all cases.

form of H-bonded NH_3, whereas the reduced sample (spectrum c) shows the least adsorption. The fact that the oxidized sample also shows the largest negative OH band area confirms that the increased amount of NH_3 adsorbed is mainly due to H-bonding to NH_3 to the surface Ti–OH species. Furthermore, it is seen from the NH_3 adsorption on the reoxidized TiO_2 that the adsorption is not completely reversible. This is also evidenced in the desorption spectra, where the disappearance of adsorbed NH_3 was not accompanied by any appreciable regeneration of Ti–OH groups.

This regeneration will presumably require the presence of H_2O. In summary, ammonia can both bond coordinatively to surface Lewis acid sites (most probably coordinatively unsaturated Ti^{3+} ions) and hydrogen bond with Ti–OH. Furthermore, ammonia is seen to reduce the surface and deplete the surface hydroxyl groups.

V_2O_5. Figure 6 shows the IR spectra of ammonia adsorbed on V_2O_5 in its oxidized (Fig. 6a) and reduced (Fig. 6b) states. On the oxidized sample, a distinct band at 1417 cm^{-1} and weak bands at 1670, 1609, and 1242 cm^{-1} are observed. The 1417 and 1670 cm^{-1} bands are attributed to the asymmetric and symmetric bending vibration of

NH_4^+ (2), whereas the two remaining weak bands are due to the asymmetric and symmetric bending modes of coordinated NH_3. These results show that, in contrast to TiO_2, predominantly Brønsted acid (BA) sites are present on the surface of oxidized V_2O_5. However, after reduction treatment,
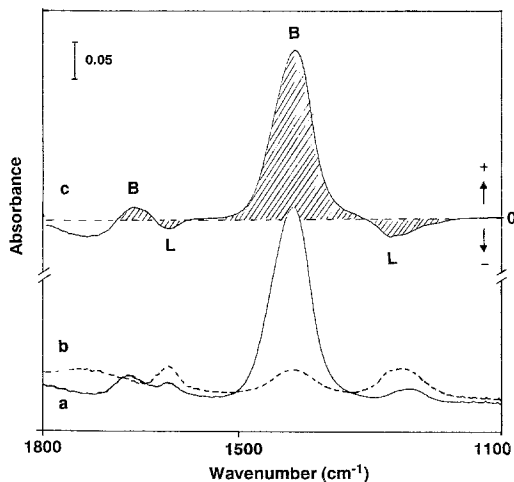

FIG. 6. Infrared spectra of NH_3 adsorption on V_2O_5. (a) "Oxidized," (b) "reduced," (c) the difference spectrum between the "reduced" and the "oxidized" spectra. (The symbols B and L represent NH_3 adsorbed on Brønsted and Lewis acid sites, respectively).
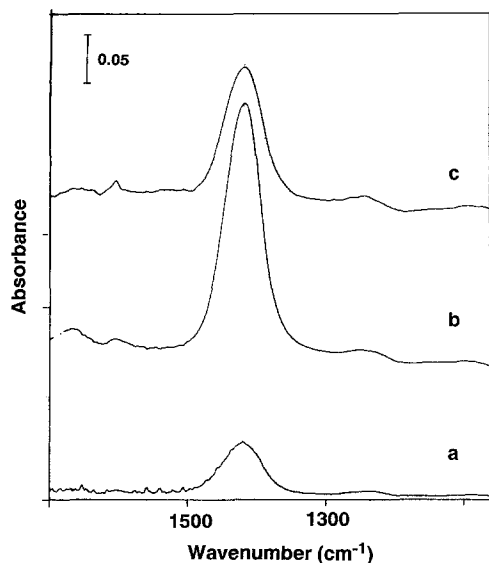
FIG. 7. Infrared spectra (background subtracted) of NH_3 adsorbed on V_2O_5: (a) after oxidation in 90 Torr of O_2 at 400°C for 1 h, (b) after oxidation in 200 Torr of O_2 at 400°C for 2 h, and (c) after oxidation in O_2 flow at 400°C for 10 h.

the intensity of the NH_4^+ band decreases drastically, whereas that of the coordinated NH_3 increases slightly, indicating that the number of BA sites greatly decreased on the reduced sample, while more LA sites were formed due to more anion vacancies created during reduction (see the difference spectrum, Fig. 6c).

In view of the sensitivity to sample pre-treatment, the effects of different oxidation procedures were also investigated. Figure 7 shows the spectra of ammonia adsorbed on the same vanadia sample wafer after three different oxidation procedures. Figure 7a shows NH_3 adsorption after the vanadia has been oxidized in 90 Torr of O_2 at 400°C for 1 h, whereas Fig. 7b shows that of the sample after oxidation in 200 Torr of O_2 at 400°C for 2 h and Fig. 7c is that after an oxidation in O_2 flow at 400°C for 10 h. These results clearly show that the degree of oxidation affects the extent of NH_3 ad-sorption. The largest NH_4^+ band intensity is seen for the sample shown in Fig. 7b. The

low NH_4^+ band intensity seen in Fig. 7a indicates that this oxidation treatment is apparently not sufficient to oxidize the surface completely. The decrease seen in the number of NH_4^+ species on the sample subjected to lengthy oxidation (Fig. 7c) is not clear at this point but it could be due to a slight sintering of the vanadia.

V_2O_5/TiO_2. When 0.6 wt.% V_2O_5 was im-pregnated onto TiO_2, the OH structure of TiO_2 was seen to change only slightly (Fig. 1b) and the nature of the interaction with NH_3 was found to be not too different from that of TiO_2. This indicates that a large frac-tion of TiO_2 surface is exposed. Figure 8 compares the spectrum of NH_3 adsorbed on the 0.6% vanadia–titania after oxidation (Fig. 8a) with that after reduction (Fig. 8b). As seen in the case of TiO_2, the reduced sample shows less ammonia adsorption and also fewer OH groups consumed as also in-dicated in the difference spectrum, Fig. 8c. Although there seems to be indication for NH_4^+ species, the sample shows mostly co-ordinated and hydrogen bonded NH_3 on the surface as in TiO_2.

The sample with the higher vanadia cov-erage was also investigated. Figure 9 shows the IR spectra of the oxidized 6% vanadia–titania before (Fig. 9a) and after (Fig. 9b)
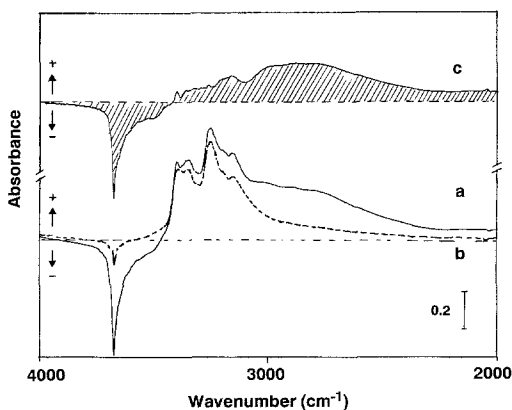

FIG. 8. Infrared spectra (background subtracted) of NH_3 adsorbed on the 0.6% vanadia–titania. (a) "Oxi-dized," (b) "reduced," and (c) the difference spec-trum between the "oxidized" and "reduced" sample.
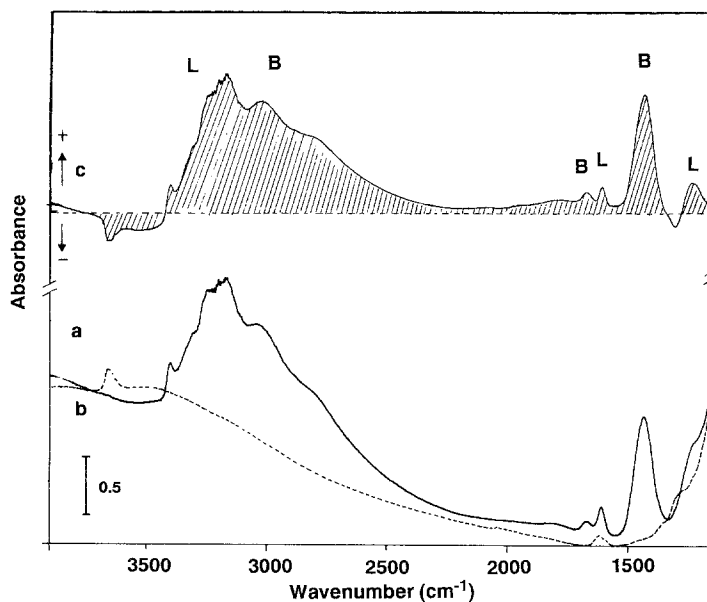
FIG. 9. Infrared spectra of the 6% vanadia–titania (a) before and (b) after NH_3 adsorption, and (c) the difference spectrum showing changes occurred upon NH_3 adsorption. (B and L represent NH_3 adsorbed on Brønsted and Lewis acid sites, respectively.)

ammonia adsorption. The V–OH band is seen to disappear upon ammonia contact (Fig. 9b). The background-subtracted spectrum (Fig. 9c) shows more clearly the formation and removal of the surface species due to the adsorption process. In the high-frequency spectral region, one observes an intense band envelope consisting of the same NH_3 stretching bands as seen in TiO_2 overlapped with strong bands at 3019 and 2808 cm^{-1} due to the stretching vibration of NH_4^+ species. This adsorption was also accompanied by a depletion of the surface hydroxyls, especially the band at 3652 cm^{-1} due to V–OH. In the lower-frequency region, one sees the intense band at 1430 cm^{-1} and a weaker band at 1669 cm^{-1} attributed to NH_4^+ adsorbed on the surface. The frequency of this NH_4^+ band at 1430 cm^{-1} has shifted upwards by 13 cm^{-1} as compared to that on pure V_2O_5. This indicates a stronger N–H bond strength in the NH_4^+ species and a slightly weaker bonding of the NH_4^+ to the vanadia supported on titania than to an unsupported vanadia. Thus, the

acid strength of BA sites of vanadia is apparently enhanced by supporting on TiO_2, most probably through the interaction of the V–OH species with titania. Such enhancement of Brønsted acidity of vanadia-titania is in agreement with the observations of Busca (2). Besides the BA sites, a pair of bands at 1605 and 1229 cm^{-1} due to the coordinated NH_3 is also observed. These results show that both BA and LA sites are present on the surface of the oxidized 6% vanadia/titania sample where BA sites, however, seem to dominate. Figure 10 compares the NH_3 adsorption on this sample in its oxidic (Fig. 10a) and reduced (Fig. 10b) states. The number of BA sites is seen to decrease drastically while the number of LA sites is seen to increase somewhat upon reduction (Fig. 10c). Thus, reduction treatment has created more anion vacancies and transformed some BA sites into LA sites. Upon heating, as was found for the TiO_2, NH_3 started to desorb substantially already at 100°C and was practically all removed at around 300°C.
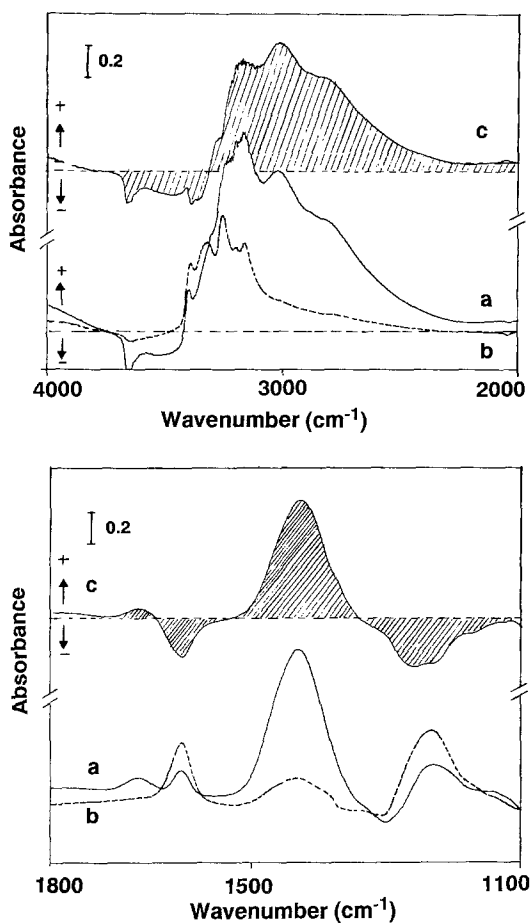
FIG. 10. Infrared spectra (background subtracted) showing both high and low frequency regions of NH_3 adsorbed on 6% vanadia–titania (a) after "oxidation," and (b) after "reduction." The shaded spectra in (c) are the difference spectra.

Besides the changes observed in the V–OH bands, the V=O overtone bands are completely removed upon NH_3 adsorption. The fact that the intensity of the V=O band increases with reduction, thus following the same trend as the coordinatively bonded NH_3, suggests that the coordinatively unsaturated vanadyls contribute to Lewis acidity in the vanadia–titania samples, as also found by Busca (2). The result that pure V_2O_5 displays very few LA sites indicates that the vanadyl groups without titania do not lead to significant Lewis acidity.

IV. Effects of H_2O

Since water is usually present in the flue gas in the SCR process, it is also important to understand how water affects the adsorption properties of the catalyst. Ammonia adsorption on the vanadia–titania catalyst with preadsorbed H_2O (5 Torr H_2O at RT, subsequent evacuation at RT) showed essentially the same IR band position and LA band intensity but slightly higher NH_4^+ band intensity than the fully oxidized sample without water. This observation indicates that water does not block BA sites, or in other words that NH_3 is a stronger base than H_2O.

V. NO Adsorption

The adsorption properties of NO, one of the reactants in the $DeNO_x$ reaction, were studied on the catalysts under various conditions. On an oxidized surface of the 6% vanadia–titania, no NO adsorption was observed. Similarly, no NO adsorbed species were found on the NH_3-reduced surface. These observations agree with those reported in the literature (4, 10). However, in contrast to results reported by Takagi et al. (10) who also failed to see any NO adsorption on a H_2-reduced V_2O_5 (100 Torr of H_2, 400°C, 2 h), we observed extensive adsorption of NO on the vanadia–titania after the sample was reduced in H_2 flow at 400°C for 2 h and subsequently evacuated at RT (Fig. 11). The spectrum displays a series of bands in the region of 1600–1900 cm^{-1}. These are probably due to the NO stretching vibrations of mononitrosyl and dinitrosyl surface complexes and possibly also adsorbed NO_2 (at 1616 cm^{-1}) on the coordinatively unsaturated sites at the surface. Some gaseous N_2O (2224 cm^{-1}, 1286 cm^{-1}) was also detected. This adsorption behavior is not surprising since it has been observed in many instances that NO adsorption occurs on reduced oxide surfaces (17–19). Also, the (d^0) configuration of the V^{5+} ions does not allow the accommodation of the antibonding electron in the NO mole-
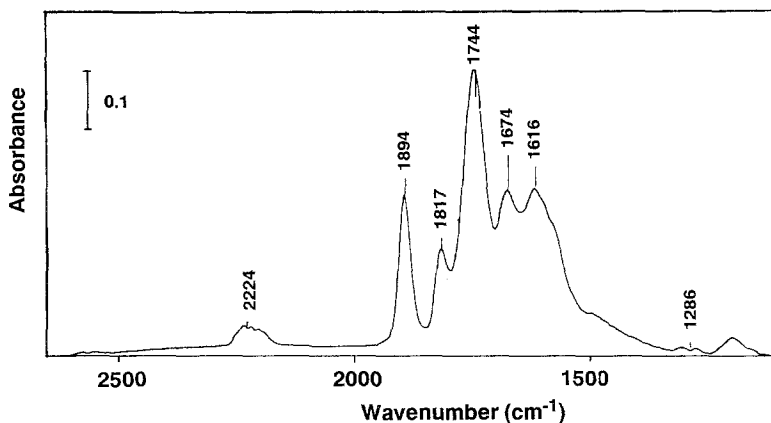
FIG. 11. Infrared spectrum of NO adsorbed on 6% vanadia–titania after reduction in H_2 flow at 400°C for 2 h.

cule upon chemisorption in contrast to vanadium ions at lower valences. Such behavior was also observed for Mo^{6+} vs. reduced molybdenum ions (20).

As mentioned above, V–OH groups on the surface of the 6% vanadia–titania are removed upon severe reduction in H_2 while reexposing the surface Ti–OH species. Upon adsorption of NO, this Ti–OH band is observed to disappear completely, indicating that NO must have interacted with these hydroxyls. These results show that NO does not chemisorb on an oxidized vanadia–titania surface but it does interact with a strongly reduced surface, most probably with vanadium ions at lower valences than 5+ and with Ti–OH species.

VI. NH₃ + NO Adsorption

Since NO does not interact with either the oxidized or the NH_3-reduced surfaces directly as discussed above, it is important to study if NO may interact with surfaces containing preadsorbed NH_3. In view of the variations seen in the nature of the surface OH species and adsorbed NH_3 species with different pretreatment, studies were performed both on the catalyst reoxidized after NH_3 reduction and the initially oxidized catalyst. The results on the initially oxidized surface will be discussed first.

In order to avoid reactions with gas phase NH_3, excess NH_3 was removed before NO adsorption. As found for the initially oxidized and NH_3-reduced surface, no NO adsorption species could be detected at RT on the initially oxidized surface of the 6% vanadia–titania with NH_3 preadsorbed. A quite similar result was reported for a pure vanadia catalyst by Inomata et al. (3) and Takagi et al. (10) who reported a similar lack of adsorption of NO on surfaces with preadsorbed NH_3. Also, we observed no NO_2 arising from oxidation of NO by surface oxygen. Furthermore, very little change in the surface adsorbed ammonia species was seen upon NO contact. However, at around 100°C, gaseous NO began to disappear, and both the adsorbed NH_3 and NH_4^+ species also started to decrease, accompanied by a release of gaseous NH_3. These observations strongly suggest that an NO–NH_3 reaction has taken place or that NO has replaced NH_3 at the surface. However, in view of the previous results of NO adsorption, the latter process is not likely. Also, an analogous experiment under the same conditions but in the absence of gaseous NO showed that the intensity decrease of the surface ammonia species (due to desorption in this case) was much less than that in the presence of NO.
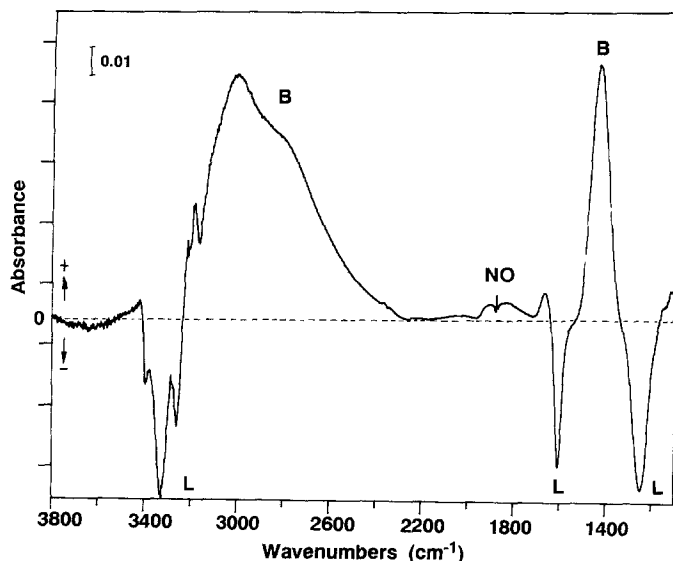
FIG. 12. Infrared spectrum (background of sample with preadsorbed NH_3 subtracted) of adsorption of NO on 6% vanadia–titania with preadsorbed NH_3. (B and L represent NH_3 adsorbed on Brønsted and Lewis acid sites, respectively.)

Furthermore, it was seen that in the presence of NO, NH_4^+ species were preferentially removed indicating that the reaction is predominantly between NO and surface NH_4^+ species. At above 250°C, traces of N_2O could be detected, possibly due to NH_3 oxidation.

The surface reactions of NO with the reoxidized 6% vanadia–titania sample containing preadsorbed NH_3 are shown in Fig. 12. As seen above, no distinct NO adsorption species could be detected at RT. However, in contrast to the initially oxidized catalyst, the BA band intensity is seen to increase significantly at RT, while that of the LA is seen to decrease with a simultaneous release of N_2O. This trend is observed to continue to a maximum at a temperature around 125°C. Above this temperature, a decrease in the intensity of both BA and LA bands is seen together with the release of gaseous NH_3. These results can be explained by the observations that the reoxidized surface is not completely oxidized (as in the case of the initially oxidized sample) and that these

surfaces with preadsorbed NH_3 can be oxidized by NO at room temperature to form N_2O. Since N_2O was not detected on the NH_3-reduced surface without preadsorbed NH_3, the present result suggests that the BA or LA sites can assist or are directly involved in the surface oxidation reaction. The observation that the BA/LA ratio increased during this process could be due to NH_3 desorption and readsorption on the more oxidized surface which is known to give higher BA/LA. The observation that the surface reaction occurs on a surface which has been reoxidized with O_2 indicates that NO is a better oxidizing agent than O_2 for these samples. Besides the above special features of the reoxidized sample, it was observed that at higher temperatures (above 100°C), NO starts to react with surface NH_3, most likely forming N_2 as in the case of the initially oxidized sample. It is very likely that this step is the step producing N_2 during the SCR reaction.

The above reactions are much less evident for the 0.6% vanadia–titania sample and negligible on TiO_2. Also, no evidence

of any surface reaction or N_2O production can be detected on the V_2O_5. Thus, surface reactions leading to the SCR reaction appear to be directly related to the vanadia layer and the special BA sites and surface V–OH species.

CONCLUSIONS

The present studies have shown that the vanadia is highly dispersed on the TiO_2 surface in a vanadia–titania catalyst. Vanadia interacts with Ti–OH to form V–OH species which are found to be important adsorption sites for NH_3. The nature of the surface sites and the surface adsorption properties are very sensitive to the pretreatment of the catalyst. There are mostly Brønsted acid sites on V_2O_5 and Lewis acid sites on TiO_2, whereas both Brønsted and Lewis acid sites are present on vanadia-titania catalysts. The relative amounts of these sites are highly dependent on the oxidation state of the catalyst. An oxidized vanadia–titania has considerably more Brønsted acid sites than a reduced catalyst, whereas the reverse is true for Lewis acid sites. The results indicate some interconversion between BA and LA on the vanadia–titania surface or a transformation of V–OH to V=O due to dehydroxylation during NH_3 reduction treatment. No direct adsorption of NO was seen on the type of surface expected during the SCR reaction. NO adsorbs only on H_2-reduced vanadia-titania surface interacting with both the vanadia and Ti–OH. However, significant NO reaction/adsorption was seen in the presence of preadsorbed NH_3.

On a partially oxidized surface of vanadia–titania with preadsorbed NH_3, NO can oxidize the surface at room temperature to forming N_2O while transforming Lewis acid sites to Brønsted acid sites. This does not occur in the fully oxidized surface. The fact that NO is a better oxidizing agent than O_2 could suggest a possible role of NO in the SCR reaction. Such a reaction step may be the route for N_2O formation observed in some cases and it appears to be related to insufficient surface oxidation by oxygen. The failure to observe any NH_4^+ perturbations or NH_4^+–NO complexes may indicate that these species, once formed, are depleted from the surface via a fast subsequent reaction. Reaction between NO and NH_4^+ on the vanadia–titania surface was evidenced at above 100°C. This may well be the important N_2 formation step in the SCR reaction. In fact, the results indicate that the Brønsted acid sites on the vanadia–titania catalyst or the acidic V–OH groups are the principal reaction sites in DeNO$_x$, in agreement with the proposal of Gasior et al. (7). The fact that the nature of the V=O species is seen to differ between the bulk V_2O_5 and the titania-supported vanadia indicated a support interaction and that the vanadia phase present on the titania surface is not bulk-like V_2O_5. As for the V–OH groups, the V=O groups are also found to be sensitive to sample pretreatment and they disappear upon NH_3 adsorption, suggesting that they are also involved in the reaction. Furthermore, since NO is not seen to interact directly (i.e., without adsorbed NH_3) with the typical surfaces of vanadia or titania (surfaces likely to be present to some extent in a DeNO$_x$ catalyst), the results do not support the mechanism suggested by Odriozola et al. (13) involving mainly reaction of NH_3 with adsorbed NO on TiO_2. The present findings also do not give evidence for reaction between NO_2 and surface NH_4^+ as postulated by Takagi et al. (10). The sensitivity of the surface sites and the adsorption behavior with sample pretreatment found in this study reveal the importance of the redox properties of these catalysts and their possible influence on DeNO$_x$ activity. Thus, the activity of these catalysts would undoubtedly depend greatly on the local gas composition and the reaction condition. The mechanistic aspects will be discussed further in a subsequent paper.

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