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Vanadia/Titania Catalysts for Selective Catalytic Reduction (SCR) of Nitric Oxide by Ammonia

I. Combined Temperature Programmed *in Situ* FTIR and On-Line Mass Spectroscopy Studies[1]

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Combined *in situ* FTIR and on-line mass spectrometric studies have provided simultaneous information of the surface adsorbed species on vanadia/titania catalysts and the composition of reaction products during the selective catalytic reduction (SCR) of NO. The experiments were carried out as temperature programmed surface reaction (TPSR) studies by exposing catalysts with preadsorbed ammonia to either pure NO, pure O_2, or a mixture of NO and O_2. This allowed detailed information to be obtained concerning the changes in the concentrations and the nature of the surface V=O and V–OH species. The TPSR studies in O_2 showed mainly ammonia desorption and some ammonia oxidation at high temperatures. The SCR reaction was observed to take place during the TPSR studies in both NO and NO + O_2, but a greater rate was observed in the latter case. It was found that NH_3 reduces the V=O species and subsequent reaction with NO results in the formation of reduced V–OH species. The results showed that the NO reduction reaction involves the ammonia species adsorbed on V–OH Brønsted acid sites. Evidence for the importance of redox reactions was also found. Separate temperature programmed reduction (TPR) studies in H_2 showed that the surface vanadia layer breaks up while re-exposing TiOH groups. Subsequent temperature programmed oxidation (TPO) studies in O_2 showed this phenomenon to be completely reversible, thus providing direct evidence for spreading/redispersion of vanadia on titania. The TPR/TPO studies also indicated that the Brønsted acid sites essential for the deNO$_x$ reaction are associated with V^{5+}–OH surface sites. © 1995 Academic Press, Inc.

INTRODUCTION

The selective catalytic reduction (SCR) of NO by ammonia has been the most widely adopted process for flue gas cleaning from power plants, despite the recent interests for alternative types of nitric oxide removal processes. The most commonly used catalysts are vanadia/titania type materials (1) due to their thermal stability and their resistance toward sulfur poisoning (2, 3). However, one of the major concerns in this process is the ammonia leakage or the emission of unreacted ammonia which may lead to NO$_x$ again. To understand such phenomena, a detailed knowledge of the reaction mechanism and its dependence on the nature of the surface sites are desired.

Various investigators have studied the adsorption properties of vanadia/titania and found evidence for the presence of both Brønsted and Lewis acid sites on the catalysts (4–10). Our previous IR results (4) have given some indications that the surface Brønsted acid sites are important active sites for the SCR reaction. While this conclusion is in agreement with other earlier work (9, 11, 12), there is still no general agreement on the nature of the active sites, and many different mechanisms are still being considered (13–18). The fact that many of the past studies were not done *in situ* under realistic industrial reaction conditions could be one of the origins of the conflicting conclusions. In view of this situation, we have carried out extensive *in situ* reaction studies under both transient and steady-state conditions. The current paper will present the results from the transient reaction studies and discuss the nature of the surface sites, whereas the following papers in this series will deal with the steady-state reaction studies and the mechanistic and kinetic implications of the different spectroscopic results. A recent report has briefly discussed some of the key findings (19).

EXPERIMENTAL

The series of vanadia/titania samples used in this study contained 0.6, 2, and 6 wt% V_2O_5. These samples were

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prepared by impregnating the titania support (anatase form, surface area of 90 m^2/g) with an oxalic acid solution of ammonium metavanadate, followed by drying at 375 K and calcination at 675 K for 1 h.

The methods used for FTIR measurements have been described previously (20). Briefly, the catalysts were studied as self-supporting wafers (100 mg) in a quartz cell with CaF_2 windows. Catalytic activities measured in this cell were comparable to those obtained in separate reactor studies, thus showing that the cell has only minor bypass and can serve as a catalytic reactor. Spectra were collected on a Digilab FTS80 FTIR spectrometer with an MCT (Mercury–Cadmium–Telluride) detector at a spectral resolution of 4 cm^{-1}.

Prior to all experiments, the samples were oxidized in a flow of 8% O_2/Ar at 675 K for 14 h, followed by cooling to room temperature. At this temperature, the oxygen gas flow was switched to NH_3/Ar to adsorb ammonia. The achievement of saturation coverage of ammonia was checked by monitoring the exit gas composition with the mass spectrometer and saturation was usually achieved within 3 h at a flow rate of 100 N ml/min. Temperature programmed desorption (TPD) and/or temperature programmed surface reaction (TPSR) studies were subsequently carried out by switching to a flow of the desired gas mixture, O_2/Ar, NO + O_2/Ar, or NO/Ar (which has been first stabilized in the bypass with the gas composition checked by the mass spectrometer), while heating at a given temperature ramp (6 K/min). The temperature was held for about 5 min at each 50 K increment to collect FTIR spectra. The temperature was controlled and monitored by a microprocessor (Eurotherm 820).

As described previously (20), the inlet to the *in situ* IR cell/reactor was connected to a gas manifold which allows mixing of gases via electronically controlled mass flow meters (Brooks). Both the gas manifold and the outlet of the IR cell were connected to a Balzers QMG 420 quadrupole mass spectrometer equipped with a heated, continuous gas inlet to permit the analysis of both the reactant and product gas mixtures. Quantitative analysis of the mass spectrometer data was achieved using the fragmentation patterns determined experimentally from calibration gases.

The gases used were mixtures of O_2/Ar (14.8% O_2), NH_3/Ar (3120 ppm NH_3), NO/Ar (3890 ppm NO), and Ar (99.999%), with no additional purification. The H_2 used for the TPR experiment was purified by passage through Pd.

RESULTS

Catalyst Surface Characterization

Figures 1a–1d show IR spectra of the TiO_2 support and the 0.6, 2, and 6% vanadia/titania catalysts after the oxidation pretreatment. The most significant features are the OH region (~3600 cm^{-1}) which shows the interaction of vanadia with the Ti–OH surface groups. Expanded spectra will be discussed further below. Figures 1e–1h compare the IR spectra of TiO_2, 0.6, 2, and 6% vanadia/

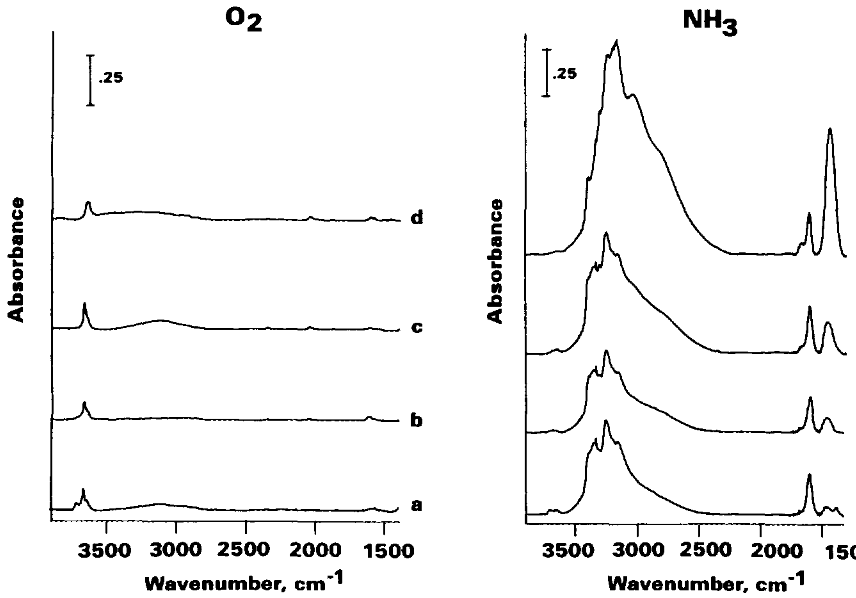

FIG. 1. (a)–(d) IR spectra of TiO_2, 0.6, 2, and 6% V_2O_5/TiO_2, respectively, in flowing O_2/Ar at rt after oxidation pretreatment; (e)–(h) the corresponding spectra of the samples in NH_3/Ar flow at rt.

titania after saturation with NH_3 under a flow of NH_3/Ar flow at room temperature. These spectra in NH_3/Ar flow are similar to those under static adsorption conditions reported earlier (4). O–H and N–H stretching vibration modes are observed in the region between 2800 and 3800 cm^{-1}, and the corresponding deformation modes are seen in the lower frequency region between 1200 and 1700 cm^{-1}. The broad bands at 3020 and 2810 cm^{-1} are due to the stretching vibration of NH_4^+ species, whereas the bands at 3364 and 3334 cm^{-1} are assigned to the asymmetric and symmetric stretching vibration frequencies of coordinated NH_3 (4, 21), respectively. The other bands at 3256 and 3170 cm^{-1} are in accordance with the literature (21) assigned to the split due to Fermi resonance with the overtone of the asymmetric NH_3 deformation. In the N–H bending region, the asymmetric and symmetric bending vibrations of NH_4^+ lie near 1430 and 1670 cm^{-1}, respectively, whereas coordinated NH_3 gives rise to the remaining weaker bands at 1605 and 1220 cm^{-1} (4).

It is seen in Fig. 1 that ammonia adsorbs on the titania surface mainly as coordinated ammonia in agreement with earlier findings (22, 23), reflecting that predominantly Lewis acid (LA) sites are present on pure titania, although the trace of an NH_4^+ band can be detected near 1460 cm^{-1}. For the vanadia/titania catalysts, the amount of ammonium species on the surface increases with vanadia loading, whereas the total amount of Lewis acid sites does not change significantly. It is clear that a main effect of increasing the vanadia loading is to create more Brønsted acid (BA) sites on the surface. Furthermore, the position of the NH_4^+ band is also seen to vary with vanadia loading. Both the 0.6 and 2% samples show an NH_4^+ near 1453 cm^{-1}, whereas the 6% sample shows the band shifted significantly downward to around 1436 cm^{-1}. The 6% vanadia/titania catalyst has a loading corresponding to slightly above monolayer coverage. Thus, the difference in behavior is most likely related to the fact that polymeric species dominate in the catalyst, whereas monomeric species dominate in the lower loading catalysts. Studies using Raman spectroscopy and other techniques have documented such changes in the vanadia structures (14, 24–30) and that they lead to different NH_3 desorption properties (14, 31, 32). Apart from the direct appearance of Lewis and Brønsted ammonia absorption bands, ammonia adsorption is also observed to cause a decrease in the intensity of both the hydroxyl band at around 3640 cm^{-1} and the weak overtone band of V=O at around 2040 cm^{-1} (Figs. 1a–1d). These changes are more clearly seen in spectra discussed in detail below.

Figure 2 shows a plot of the absorbance of the initial V–OH band (~3640 cm^{-1}) prior to ammonia adsorption versus the absorbance of the NH_4^+ band (~1435 cm^{-1}) recorded after ammonia adsorption at room temperature following different pretreatments (both oxidizing and reducing). The observed correlation strongly indicates that the V–OH surface species are the Brønsted acid sites. The same 6% V_2O_5/TiO_2 catalyst was used for these studies to avoid comparing intensities of bands with different frequencies. Also, the low loading catalysts are more difficult to investigate due to overlapping Ti–OH and V–OH bands (discussed further below).

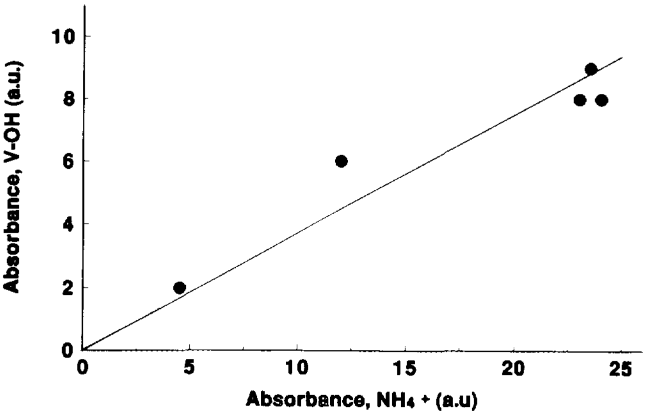

FIG. 2. IR absorbance of the initial V–OH band (at around 3640 cm^{-1}) measured before NH_3 adsorption as function of the absorbance of the NH_4^+ band (at around 1435 cm^{-1}) following NH_3 adsorption at room temperature.

Information regarding the nature of the interaction and coverage of titania with vanadia can be obtained by comparing in Figs. 3a–3d the details of the OH spectra of the different vanadia/titania samples together with that of the TiO_2 support. During the formation of vanadia/titania catalysts, vanadia interacts with the hydroxyl groups on the titania surface (33). In accordance with previous stud-

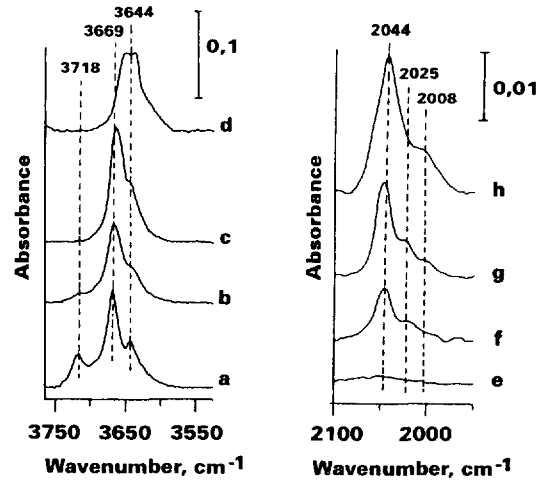

FIG. 3. (a)–(d) IR spectra in the OH stretching region of TiO_2, 0.6, 2, and 6% V_2O_5/TiO_2, respectively, in flowing O_2/Ar (expanded from Figs 1a–1d). The corresponding spectra in the V=O overtone region are shown in (e)–(h).

ies (4), three distinct OH bands at 3718, 3669, and 3644 cm^{-1} can be resolved for the titania support surface (Fig. 3a). Upon adding 0.6% vanadia, the most marked change in the almost complete removal of the 3718 cm^{-1} band with only a small shoulder remaining (Fig. 3b). The fact that the highest frequency Ti–OH band at 3718 cm^{-1} has been removed first shows that the vanadia interacts preferentially with the most basic hydroxyl groups on the titania surface, analogous to the behavior of the Mo/Al$_2$O$_3$ system (34, 35). The frequencies of the OH bands in the 0.6% vanadia/titania (3715, 3667, and 3646 cm^{-1}) (Fig. 3b) are similar to those for the TiO$_2$ support. The spectrum for the 2% vanadia/titania (Fig. 3c) is also similar to that for the 0.6% sample, except that the high frequency shoulder is now completely removed. Also the band maximum has now shifted further downward to 3664 cm^{-1}. The spectrum of the 6% vanadia/titania (Fig. 3d) is quite different from those of the 0.6 and 2% vanadia/titania catalysts. At this high loading, all the Ti–OH groups appear to have been removed and the spectrum shows mainly two V–OH peaks at 3648 and 3636 cm^{-1}. Considering the loading differences of the different catalysts, it appears that the 6% vanadia/titania catalyst has a relatively lower concentration of V–OH groups, suggesting that the vanadia species which dominate at this high loading are more polymeric in nature (i.e., consisting of condensed vanadia structures with few terminal V–OH per vanadia).

Figures 3f–3h show the corresponding spectral region of the first overtone vibration of the V=O for the vanadia/titania catalysts. The TiO$_2$ support (Fig. 3e) does not have any band in this region, and the V=O band intensity increases with increasing vanadia loading, although not quite linearly. Specifically, the intensity increase is small as the loading is increased from 2 to 6% (Figs. 3g and 3h). Furthermore, the band shape and position of the V=O band envelope in this high loading sample (Fig. 3h) (2044 cm^{-1} with shoulder near 2008 cm^{-1}) are somewhat different from the lower loading catalysts (Figs. 3f and 3g) (2046 cm^{-1} with shoulder near 2025 cm^{-1}). This change occurs at the same loading where changes are seen in the V–OH and NH$_4^+$ bands, and these changes are most likely related to a transition to more polymeric vanadia species.

Figure 4 shows the absorbance of the V=O overtone bands (~2045 cm^{-1}) and the NH$_4^+$ species (~1435 cm^{-1}) as functions of the vanadia loading. It is seen that the concentration of BA is roughly proportional to the vanadia concentration. It is difficult to examine the correlation for the surface OH band due to the substantial overlaps from Ti–OH groups for the low loading samples. The concentration of the vanadyl species giving rise to 2045 cm^{-1} band, however, is less sensitive to vanadia loading at higher loadings and is most likely associated with structural changes.

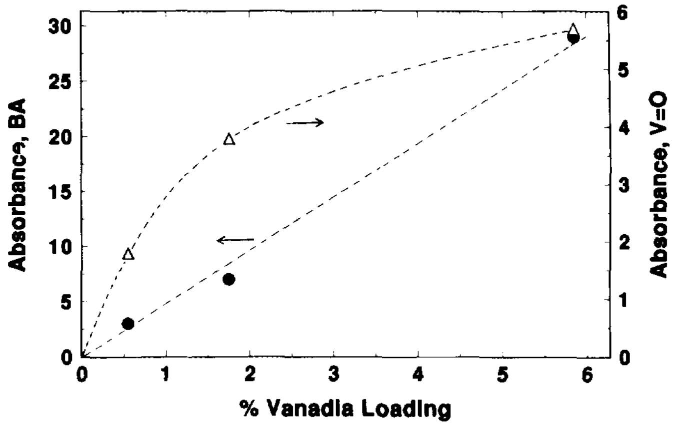

FIG. 4. IR absorbance of BA band (~1435 cm^{-1}) and V=O overtone band (2044 cm^{-1}) as functions of vanadia loading on TiO$_2$.

Under SCR conditions, catalysts are exposed to a mixture containing NH$_3$, NO, and O$_2$. However, it appears that of these gases, NH$_3$ is the only one giving rise to strongly adsorbed species (18, 20, 31). Consequently, experiments were conducted to study the reactivity and reaction products of preadsorbed NH$_3$ upon exposure to different gases (pure NO, pure O$_2$, or a mixture of NO + O$_2$). For comparison, desorption experiments in flowing Ar have also been performed. Figures 5a, 5b, and 5c show IR spectra of 6% vanadia/titania recorded during temperature programmed surface reaction of the preadsorbed ammonia in O$_2$, NO + O$_2$, and NO, respectively. In each figure, the series of spectra starts from the back and the first two spectra are the ones recorded prior to adsorption of ammonia and after saturation ammonia coverage has been achieved. The third spectrum from the back is thus the first one recorded during the TPSR experiments. The subsequent spectra are obtained at 50 K increments in temperature.

In the O$_2$ flow, the intensities of both the Lewis and Brønsted ammonia absorption bands decrease gradually with increasing temperature (Fig. 5a). By analyzing the gases leaving the surface (see below), it can be seen that ammonia desorption dominates, but some surface reactions also take place at the highest temperatures. The disappearance of the ammonia absorption bands is accompanied by the reappearance of the relatively weak V–OH and V=O bands. Traces of adsorbed NH$_3$ can still be detected in these experiments even at the highest temperature.

Figure 5b shows a similar series of ammonia desorption/reaction spectra for the 6% sample in flowing NO + O$_2$ flow (1700 ppm NO, 8% O$_2$ and balance Ar). The TPSR spectra here are significantly different from those obtained in pure O$_2$ (Fig. 5a). Instead of the slow, continuous decrease in the intensity of the NH$_4^+$ band observed in O$_2$, there is a significant enhancement of intensity at

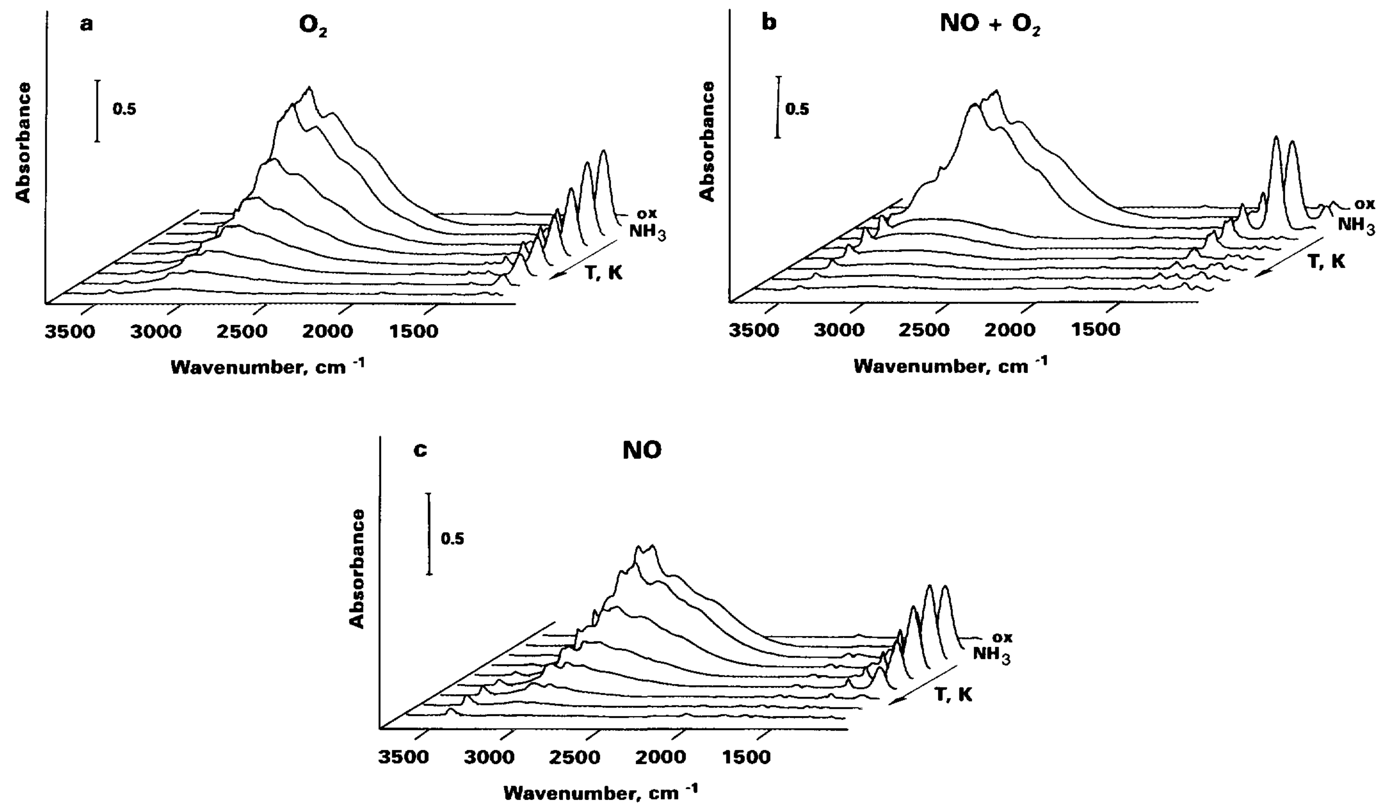

FIG. 5. *In situ* IR spectra of 6% V_2O_5/TiO_2 recorded during TPSR experiments in (a) O_2/Ar, (b) NO + O_2/Ar, and (c) NO/Ar. The first and the second spectra from the rear are obtained at rt in flowing O_2/Ar prior to adsorption and in flowing NH_3/Ar, respectively. The subsequent spectra are obtained in the various gas streams from 375 to 625 K (the front spectra) at 50 K increments.

room temperature in the NH_4^+ band, together with the appearance of H_2O bands (~3450 cm^{-1}, 1630 cm^{-1}). After this initial increase, there is a sharp decrease in band intensity and at 375 K no significant amounts of ammonia on either Lewis or Brønsted acid sites are observed, except for indication of H-bonded water. The initial NH_4^+ band intensity increase is accompanied by a downward frequency shift of the NH_4^+ band from the value of 1437 cm^{-1} observed before TPSR to 1429 cm^{-1}. At 375 K, a new band doublet centered at 1617 cm^{-1} is observed and can be attributed to adsorbed NO_2, as also seen in our adsorption studies on other systems. This band subsequently decreases in intensity with increasing temperature. During TPSR, the V–OH and V=O bands reappear at a lower temperature in NO + O_2 than in pure O_2. At 625 K, no significant amounts of adsorbed surface species remain.

The TPSR experiments in flowing NO (Fig. 5c) show, as also seen in NO + O_2 (Fig. 5b), that the concentration of adsorbed NH_4^+ initially increases to a value greater than that observed in the starting sample. The subsequent decrease in the amount of adsorbed ammonia is more gradual in pure NO than in NO + O_2 (Fig. 5b), but more rapid than in O_2 (Fig. 5a). In addition, the reappearance of the V–OH bands also occurs more readily in NO than in O_2. Adsorbed NO_2 was not detected in TPSR experiments carried out in flowing NO.

Figure 6 summarizes the ammonia reaction results for the V–OH region of the 6% V_2O_5/TiO_2 in the different gases (corresponding to Figs. 5a–5c). The intensity difference in the three V–OH spectra before ammonia adsorption (bottom spectra) is related to slight difference in the length of the O_2 pretreatment. Upon ammonia adsorption, the V–OH bands are removed completely at room temperature. The V–OH band gradually reappears during the TPSR in O_2 (Fig. 6a). A slight upward shift can be seen in spectra up to 475 K, reflecting a stronger O–H bond (or weaker V–O bond) and indicating that some more reduced V species (compared to the initial ones) are being formed by reduction with NH_3. Above this temperature, the band shifts slightly downward again as the surface becomes oxidized.

In view of the apparently quite low intensity of the V–OH band formed at 625 K, experiments were carried out on the oxidized vanadia/titania catalyst to investigate the temperature dependence of the V–OH band intensity. The results are shown in Fig. 7. When the 6% vanadia/titania sample is heated in flowing O_2 (Fig. 7a), the V–OH

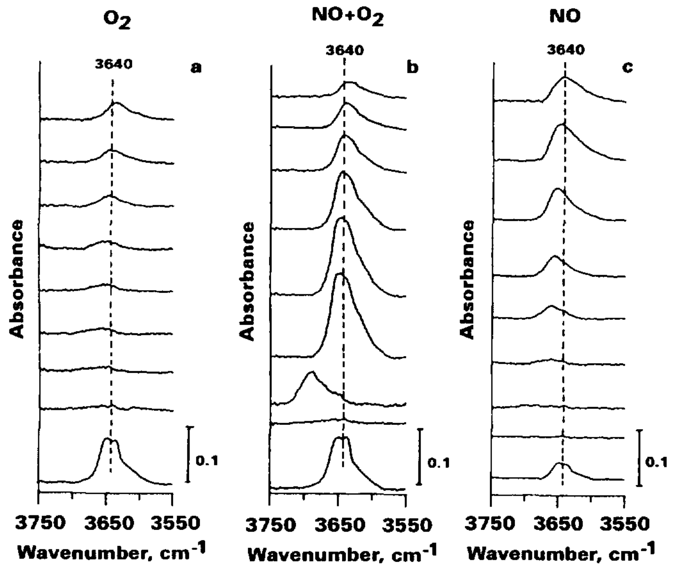

FIG. 6. (a)–(c) IR spectra showing the details of the OH stretching region of the 6% V_2O_5/TiO_2, (shown in Figs. 5a–5c) during TPSR experiments in O_2/Ar, NO + O_2/Ar, and NO/Ar, respectively. The bottom spectra are of the oxidized samples prior to NH_3 adsorption, followed by those after NH_3 saturation at rt and those in the various gas streams from 300 to 625 K at 50 K increments.

band intensity decreases significantly and the band frequency shifts slightly downward (3655 cm^{-1} at room temperature to 3637 cm^{-1} at 625 K). Such changes are seen both in the presence of oxygen and in vacuum and the changes are reversible, as shown in the bottom spectrum which was recorded after cooling to room temperature. Figures 7c and 7d show results from similar experiments in O_2 for 2% V_2O_5/TiO_2 and TiO_2, respectively. It can be seen that the temperature effects on the OH band are much less significant here than the high loading catalysts, again showing the different nature of the OH groups. Taking the temperature effect into consideration for the 6% V_2O_5/TiO_2 catalyst, it can be concluded from the results in Fig. 6a that essentially all the V–OH groups have been regenerated at 625 K in flowing O_2 in agreement with the absence of adsorbed ammonia species.

In contrast to the behavior in O_2, the spectra in Fig. 6b show that a V–OH band reappears at low temperature in NO + O_2. The V–OH band formed initially lies at significantly higher frequency (3690 cm^{-1}) than that prior to ammonia adsorption (3648 cm^{-1}). At 375 K, the band shifts back to 3648 cm^{-1} but with an intensity that is significantly higher than in the oxidized sample. Thus, additional V–OH groups are formed by reaction of preadsorbed ammonia with NO + O_2. At higher temperatures, the band intensity decreases and a downward frequency shift is seen. Finally, the V–OH band at 625 K in NO + O_2 is similar to that in O_2, indicating that the V–OH groups are restored in NO + O_2 and are comparable to those on the original sample. Figure 6c shows that the V–OH band is restored less readily in NO than in NO + O_2 but more readily than in O_2 alone. In NO, the V–OH band at 375 K appears at a higher frequency (3663 cm^{-1}) than in the background spectrum (doublet at 3648 and

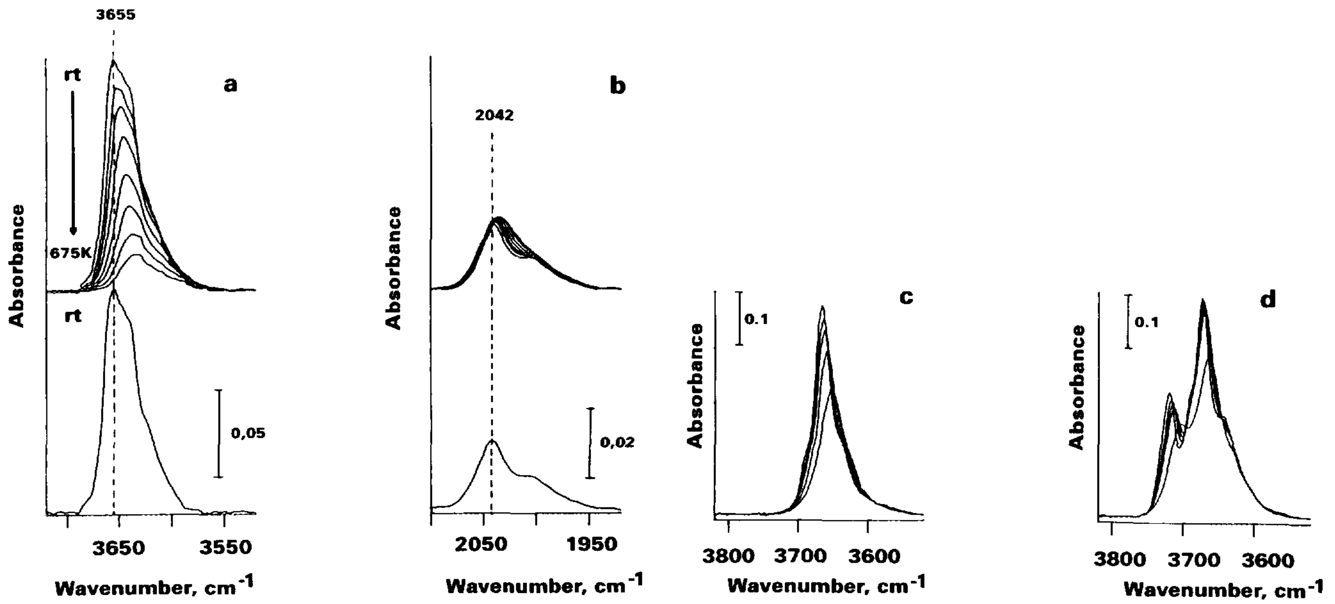

FIG. 7. IR spectra of the (a) V–OH band and (b) V=O overtone band recorded in O_2 flow at rt and 375 to 675 K (start from top, each at 50 K increment). The bottom spectrum is obtained at rt after cooling from 675 K. (c) and (d) show similar spectra sequences of the OH band in 2% V_2O_5/TiO_2 and TiO_2, respectively.

3636 cm^{-1}). The band is seen to shift downward with further increases in temperature. The intensity of the band starts to decrease at temperatures above 575 K. At 625 K, the intensity of the V–OH band is significantly higher in flowing NO than that in the background, especially when one takes into account the temperature effect on the spectral intensity. This result indicates a higher concentration of reduced V–OH species on the surface at this stage as compared to that on the freshly oxidized catalyst (i.e., complete oxidation has not taken place yet, as also seen by the comparatively high frequencies).

The V=O overtone spectral regions are compared in Fig. 8 for the same treatments corresponding to Figs. 5 and 6. In the freshly oxidized catalyst, the V=O overtone region exhibits a main band centered at 2044 cm^{-1} with a shoulder at 2008 cm^{-1}. These bands are replaced by a weak band near 1930 cm^{-1} upon ammonia adsorption at room temperature. In contrast to the behavior of the V–OH bands (Fig. 7a), it is seen in Fig. 7b that the effect of temperature on the spectral intensity of the V=O overtone band is minimal and a downward shift of only 8 cm^{-1} results from an increase in temperature from room temperature to 625 K. The observations that the V=O spectra at the completion of all the TPSR runs are similar to the initial V=O spectrum indicate that the vanadyl structure has been restored in O_2, NO + O_2, and NO. When the temperature is raised to 375 K in O_2 (Fig. 8a), a band near 1970 cm^{-1} is seen with some contribution remaining at 1930 cm^{-1}. Upon increasing the temperature further, the intensity of the 1970 cm^{-1} band increases slightly initially and then decreases slowly. The 1930 cm^{-1} band also decreases quite slowly and a significant band intensity near 1930 cm^{-1} can still be seen even at the highest temperatures. At 475 K, a band around 2035 cm^{-1} starts to appear and it increases in intensity with increasing temperature and becomes the dominant feature at the highest temperatures. This band with a shoulder at 2008 cm^{-1} is, as discussed above, the V=O species present in the catalyst before exposure to ammonia. TPD experiments on the 6% vanadia/titania in flowing Ar give results similar to those in O_2, although the V–OH and V=O bands are regenerated somewhat less readily in Ar.

The IR spectra obtained during the TPSR experiments in flowing NO + O_2 (Fig. 8b) and NO (Fig. 8c) show marked differences to the experiments in flowing O_2. For example, the 1930 cm^{-1} band is almost removed completely at low temperatures in NO + O_2 or NO. Furthermore, the 1970 cm^{-1} band does not become as prominent in these gases. This behavior is especially pronounced for experiments in NO + O_2, where regeneration of original V=O species appears to be almost complete already at 475 K. This regeneration occurs at about 100 K higher temperatures in pure NO without O_2.

Figures 9a and 9b show IR spectra of TiO_2 obtained during reaction of preadsorbed NH_3 in O_2 and NO + O_2, respectively. The bands due to the NH_3 coordinated on Lewis acid sites are seen to be removed progressively with increasing temperature (Fig. 9a). The trace of an ammonium band observed initially also disappears rapidly as the ammonia flow is switched to O_2 at room temperature. In contrast to the 6% vanadia/titania catalyst, some adsorbed ammonia species still remain at the high-

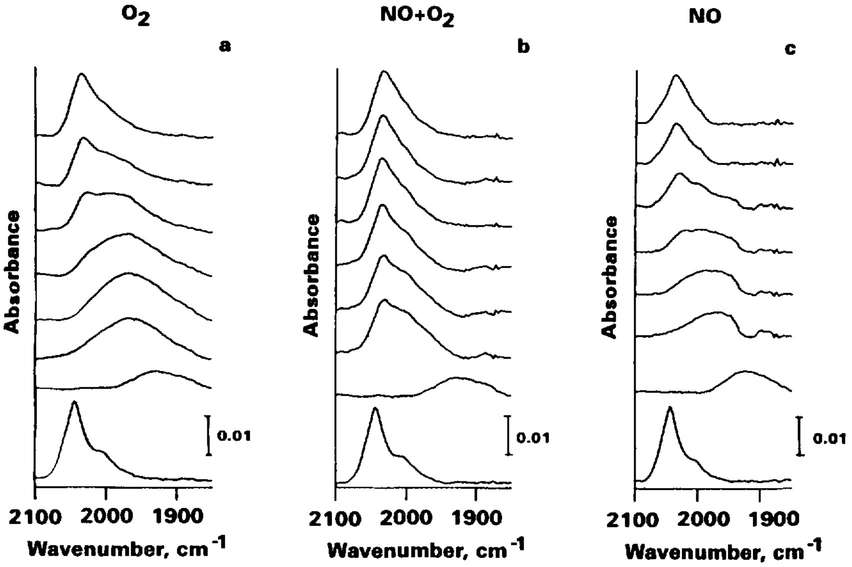

FIG. 8. (a)–(c) IR spectra of the 6% V_2O_5/TiO_2 showing the details of the V=O overtone region during TPSR experiments in O_2/Ar, NO + O_2/Ar, and NO/Ar, respectively. The bottom spectra are the oxidized sample prior to adsorption, followed by the rt spectra in flowing NH_3/Ar and those in the various gas streams from 375 to 625 K at 50 K increments.

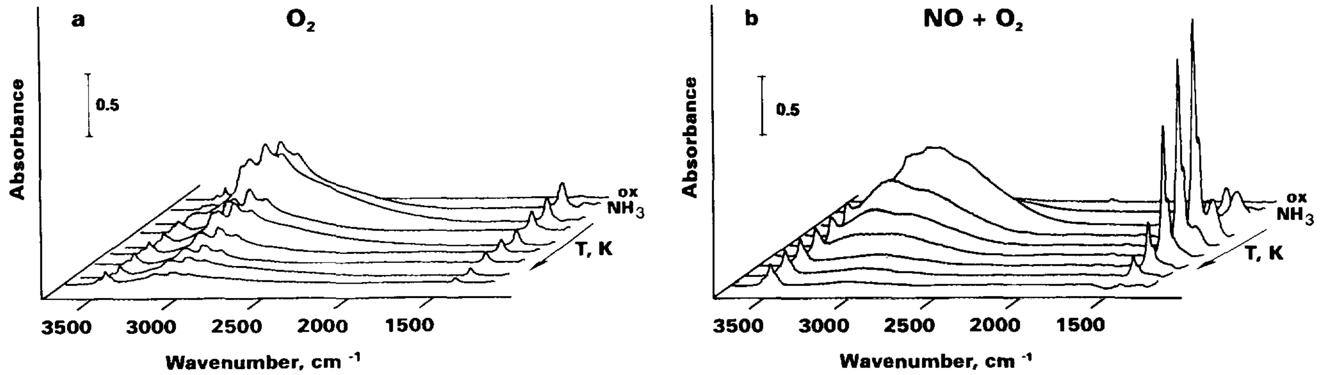

FIG. 9. *In situ* IR spectra of TiO$_2$ recorded during TPSR experiments in (a) O$_2$/Ar and (b) NO + O$_2$/Ar. The first and the second spectra from the rear are obtained at rt in O$_2$/Ar prior to adsorption and in NH$_3$/Ar, respectively. The subsequent spectra are obtained in the various gas streams from 375 to 625 K (the front spectra) at 50 K increments.

est temperature, indicating the presence of strong Lewis acid sites on the titania surface (31).

The results of TPSR experiments for TiO$_2$ in NO + O$_2$ are shown in Fig. 9b. The initial contact with NO + O$_2$ at room temperature (third spectrum from the back), results in a small increase in the weak NH$_4^+$ band (1449 cm^{-1}), accompanied by the appearance of an OH stretching band at 3662 cm^{-1} and a broad band in the high-frequency region indicative of water and H bonding. The NH$_4^+$ deformation band disappears completely with simultaneous appearance of new bands at 375 K. An intense, sharp band characteristic of NO$_2$ is seen at 1617 cm^{-1} with a shoulder at 1587 cm^{-1}. The last spectrum obtained at 625 K looks similar to the spectrum of the freshly oxidized titania prior to contact with NH$_3$, indicating that almost all adsorbed species are removed and the surface has returned to its original state.

The IR spectra during TPSR on the 2% V$_2$O$_5$/TiO$_2$ are shown in Figs. 10a and 10b. It can be seen (Fig. 10a) that significantly fewer NH$_4^+$ species are adsorbed on the surface as compared to the 6% V$_2$O$_5$/TiO$_2$ catalyst. The absorption bands due to coordinated NH$_3$ are, however, relatively more intense in the 2% than in the 6% sample. Similar to the behavior of the pure titania, the bands due to the coordinated ammonia are again observed to be less readily removed in O$_2$ than the bands due to the protonated ammonia species.

The desorption/reaction behavior of the 2% V$_2$O$_5$/TiO$_2$ in NO + O$_2$ (Fig. 10b) is similar to that of titania; however, the initial increase in the concentration of NH$_4^+$ and H$_2$O upon switching to NO + O$_2$ is more pronounced for the 2% sample. This behavior is accompanied by the appearance of an OH band. As in the case of TiO$_2$, bands due to NO$_2$ begin to appear at temperatures above 375 K, and all absorption bands are removed progressively with increasing temperatures.

Similar experiments have also been carried out on a 0.6% V$_2$O$_5$/TiO$_2$. The spectra obtained during the surface

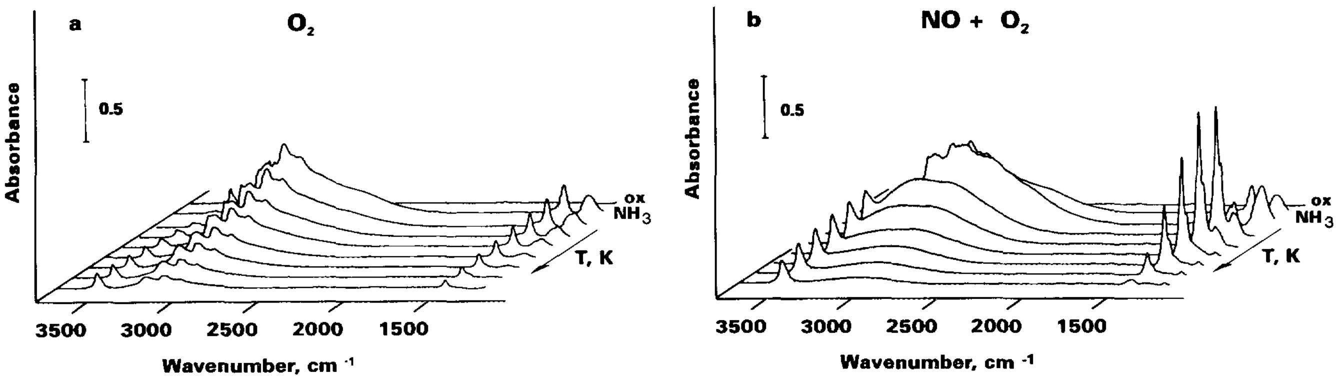

FIG. 10. *In situ* IR spectra of 2% V$_2$O$_5$/TiO$_2$ recorded during TPSR experiments in (a) O$_2$/Ar and (b) NO + O$_2$/Ar. The first and the second spectra from the rear are obtained at rt in O$_2$/Ar prior to adsorption and in NH$_3$/Ar, respectively. The subsequent spectra are obtained in the various gas streams from 375 to 625 K (the front spectra) at 50 K increments.

reaction sequences are intermediate to those of the 2% vanadia/titania and pure titania and will not be shown here.

Throughout all the desorption/reaction studies here, no bands indicative of surface adsorbed NO can be detected. This observation is in agreement with previous findings (4, 5, 13), where strongly adsorbed NO species were observed only on extensively reduced surfaces.

Gas Analysis during Desorption/Surface Reaction

On-line mass spectrometry was used to monitor the reaction gas compositions simultaneously with the recording of all the aforementioned FTIR spectra. Figures 11a, 11b, and 11c show the gas compositions as a function of reaction temperature for the 6% V_2O_5/TiO_2 catalyst in O_2, NO + O_2, and NO, respectively. Significant amounts of NH_3 are detected initially in flowing O_2 (Fig. 11a), while no N_2, H_2O, or NO_2 can be observed at temperatures below 375 K. Thus, simple desorption dominates here. The continued release of NH_3 over a wide temperature range suggests the presence of a broad distribution of ammonia adsorption sites, in agreement with previous results (31). Water and small amounts of N_2 can be seen at higher temperatures. The H_2O/N_2 ratio is significantly greater than one, implying the presence of ammonia oxidation. No formation of N_2O, NO, or NO_2 is observed.

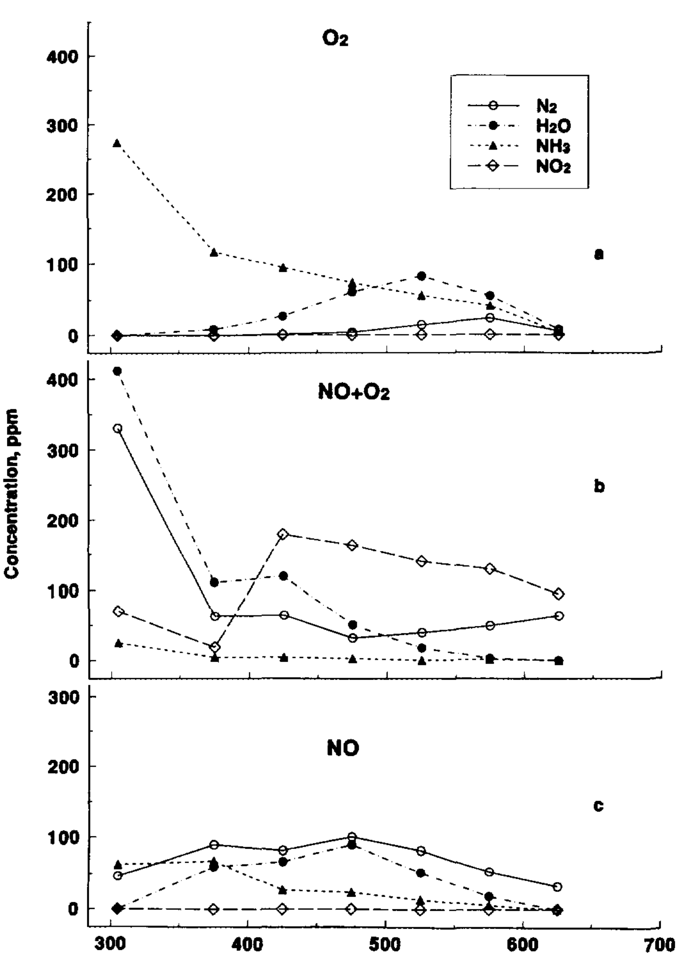

FIG. 11. On-line mass spectrometry results on the 6% V_2O_5/TiO_2 presented as concentrations vs temperature from the TPSR experiments in (a) O_2/Ar, (b) NO + O_2/Ar, and (c) NO/Ar.

The reaction behavior during TPSR experiments in NO + O_2 (Fig. 11b) is quite different. Negligible amounts of ammonia are desorbed but NH_3 is consumed in a surface reaction even at the lowest temperatures. Significant amounts of N_2 and H_2O are produced, initially with a ratio of H_2O/N_2 slightly above unity. These results suggest that the SCR reaction is occurring. The almost complete absence of gaseous NH_3 over the entire temperature range indicates that the rate of the SCR reaction is higher than the rate of NH_3 desorption. Figure 11b also shows the formation of significant amount of NO_2 at temperatures above 375 K. NO_2 was not formed in experiments with pure O_2 (Fig. 11a) or pure NO (Fig. 11c). The formation of NO_2 is attributed to gas-phase reaction between NO and oxygen, and separate experiments without catalyst have confirmed this assignment.

The TPSR experiments in NO (Fig. 11c) show the presence of the SCR reaction. However, a major difference from the behavior in NO + O_2 (Fig. 11b) is the significant amount of NH_3 desorbed over a wide temperature range. This suggests that the rate of the SCR reaction is considerably slower in pure NO than in NO + O_2 mixtures, as also seen by the lower concentration of N_2 and H_2O formed initially in NO. The greater concentration of N_2 and H_2O formed around 475 K in NO compared to NO + O_2 is related to the fact that the SCR reaction in NO + O_2 has already consumed most of the adsorbed ammonia at lower temperatures. This behavior is directly observed in the IR studies (compare Figs. 5b and 5c).

Figures 12a and 12b show mass spectrometric analysis results during the TPSR experiments for the 0.6% V_2O_5/TiO_2 catalyst in O_2 and NO + O_2, respectively. In comparison to the 6% sample (Fig. 11a), much less NH_3 is desorbed from the 0.6% sample in O_2 (see Fig. 12a). The lower loading sample has relatively fewer of the weak adsorption sites and it apparently also contain sites stronger than those in the 6% vanadia/titania catalyst, in accordance with the FTIR results and earlier TPD experiments (31). The TPSR experiments in NO + O_2 (Fig. 12b) show significant SCR reactivity (production of H_2O and N_2 in close to 1 : 1 ratio), in agreement with the behavior of the 6% vanadia/titania sample (Fig. 11b). Also, for the 0.6% vanadia/titania catalyst, the rate of the SCR reaction is apparently faster than the rate of NH_3 desorption over the entire temperature range. Compared to the 6%

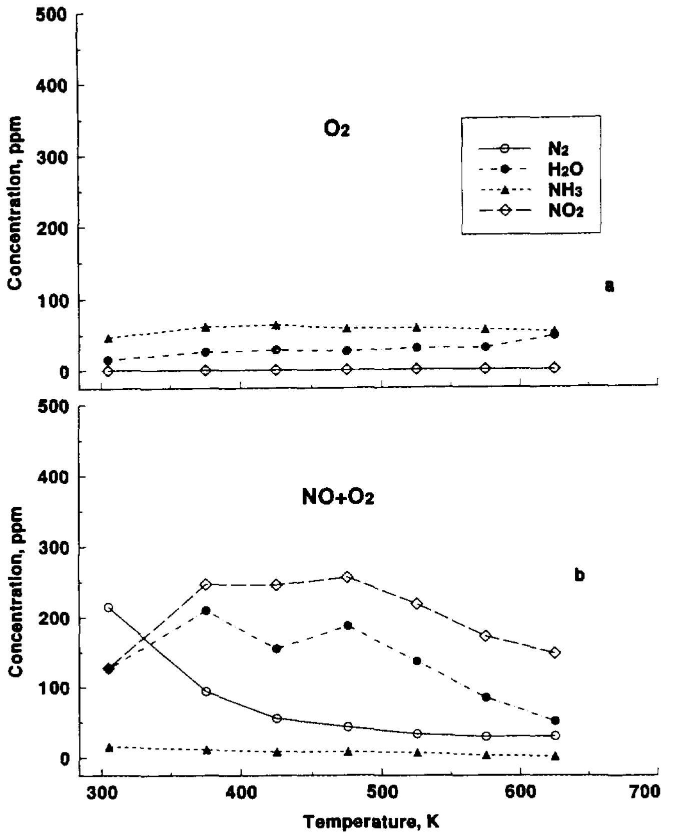

FIG. 12. On-line mass spectrometry results on the 0.6% V_2O_5/TiO_2 presented as concentrations vs temperature from the TPSR experiments in (a) O_2/Ar and (b) NO + O_2/Ar.

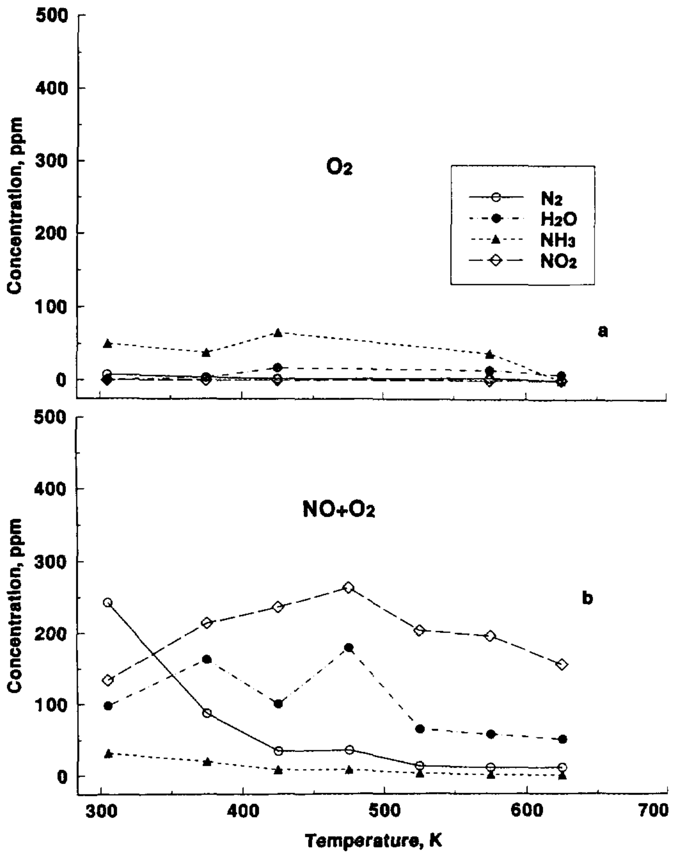

FIG. 13. On-line mass spectrometry results on the TiO_2 presented as concentrations vs temperature from the TPSR experiments in (a) O_2/Ar and (b) NO + O_2/Ar.

vanadia/titania catalyst, the rate of the SCR reaction for the 0.6% vanadia/titania does not decrease as much at higher temperatures. This behavior may be related to the stronger adsorption and more NH_3 remaining on the surface at these temperatures for reaction to take place. Significant amounts of NO_2 are detected already at 375 K for the low loading catalyst, whereas correspondingly much less NO_2 was detected in the high loading sample. The water concentration here is seen to follow that of NO_2 rather than N_2.

The mass spectroscopic data obtained for the TiO_2 support are similar to those of the 0.6% V_2O_5/TiO_2 and are shown in Figs. 13a and 13b. It can be seen that the reaction products are dominated by NO_2 and H_2O at temperatures above 375 K.

Temperature Programmed Reduction/Oxidation Studies

Temperature programmed reduction/oxidation studies were carried out on the 6% V_2O_5/TiO_2 catalyst to elucidate possible surface vanadia structural changes which may take place under oxidizing and reducing atmosphere. Figure 14a shows the OH region for the freshly oxidized catalyst at room temperature (bottom), while the next seven spectra are obtained during reduction in flowing H_2 at increasing temperature. The decreases in the band intensity and frequency upon temperature increase to 575 K are the same as those observed in O_2 (Fig. 7a) or vacuum. Thus, the results show no significant effects of H_2 reduction below 575 K. The OH spectrum, however, changes significantly at 625 K from the broadened at 3648 cm^{-1} (observed at 575 K) to two bands at 3665 and 3706 cm^{-1}. These bands are similar to the characteristic Ti–OH bands seen for the titania support and they become more distinct and shift to slightly higher frequencies as expected (compare with Fig. 7d) upon cooling to room temperature. Subsequent TPSR experiments in O_2 are carried out. The surface changes observed are the reverse of those in H_2. At 425 K, the Ti–OH contribution is significantly reduced and a large contribution of V–OH is noted. This latter contribution dominates above 575 K and the last spectrum (top spectrum) obtained at room temperature following heating in O_2 to 625 K is similar to the freshly oxidized sample before TPR. These results show that the structural

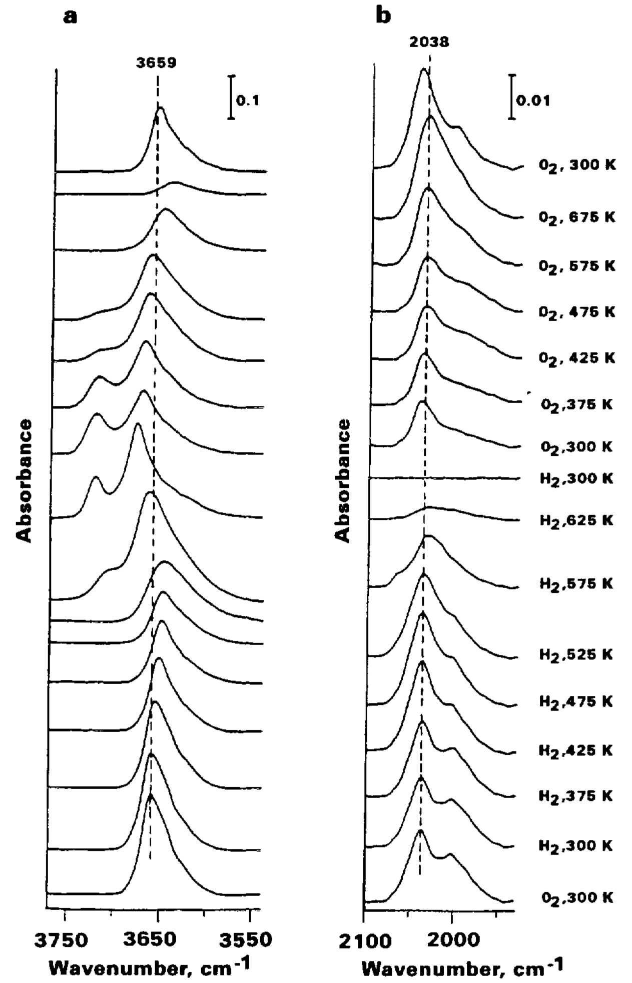

FIG. 14. *In situ* IR spectra of 6% V_2O_5/TiO_2 recorded during TPR/TPO experiments. (a) and (b) show the OH stretching and the V=O overtone regions, respectively. The bottom spectra are obtained at rt after oxidation in flowing O_2 at 675 K for 14 h. Subsequent spectra are recorded during H_2 TPR and TPO (as designated). The last spectra at the top are obtained at rt after TPO.

changes occurring on the surface during H_2 reduction are reversible upon oxidation.

The corresponding spectra in the V=O overtone region are shown in Fig. 14b. The shoulder band at 1998 cm^{-1} is mostly removed in H_2 at 575 K, and the V=O band has essentially completely disappeared at 625 K. Upon switching to flowing O_2, the 2038 cm^{-1} band reappears readily with increasing temperature, whereas the lower frequency shoulder is apparently regenerated less readily. After oxidation to 675 K, a spectrum very similar to the original one is regenerated.

The disappearance of the V–OH band V=O structures on the surface in flowing H_2, together with the appearance of the Ti–OH structures, can be interpreted as a breaking up of the vanadia monolayer structure which had initially formed via interaction with Ti–OH groups.

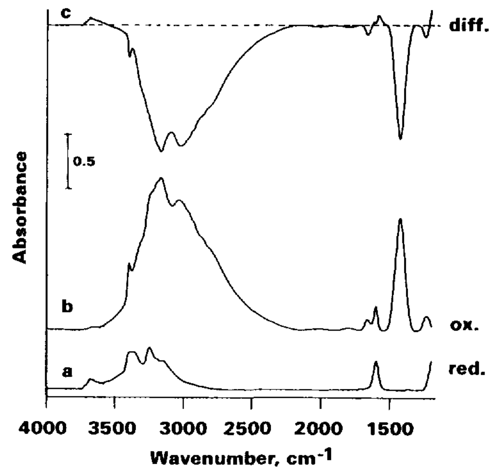

FIG. 15. IR spectra of NH_3 adsorbed at rt on the (a) H_2-reduced and (b) O_2-oxidized surface of 6% V_2O_5/TiO_2. The difference spectrum is shown in (c).

This breakup thus re-exposes the titania surface and Ti–OH groups. Upon reduction of the support interactions, the vanadia structures apparently agglomerate and very few V–OH and V=O groups are seen. The reversed behavior in O_2 indicates that the vanadia can be redispersed on the titania, providing direct evidence that spreading of vanadia can occur on titania.

Figure 15 shows IR spectra after ammonia adsorption on the oxidized 6% sample and following treatment in H_2 flow for 14 h at 625 K. It can be seen that only coordinated ammonia and no NH_4^+ bands can be detected on the reduced surface, indicating that all the Brønsted acid sites have been removed by reduction leaving only Lewis acid sites. Therefore, it can be concluded that Brønsted acid sites are associated with V^{5+}–OH.

DISCUSSION

From examination of the hydroxyl region of the IR spectra for the vanadia/titania catalysts, it can be seen that vanadia interacts with surface Ti–OH groups and that the vanadia species formed have associated V–OH groups (4, 33). For low loading catalysts, the surface hydroxyl structure thus contains both V–OH and Ti–OH and depends on the vanadia concentration. The hydroxyl structure in the high loading sample (6% vanadia/titania) shows that essentially all the Ti–OH groups have disappeared and the surface hydroxyls are dominated by V–OH species. Thus, "complete" coverage of the TiO_2 surface has been achieved. In view of recent results for other systems, it is very likely that the vanadia monolayer structures will not be evenly distributed over the whole titania surface but are predominantly located at the part initially covered by Ti–OH groups. The V–OH species of the different loading catalysts have different frequencies and the adsorptive and reaction properties are also observed to depend on vanadia coverage (or loading).

As reported previously (4–10), both BA and LA sites are present on the surface of vanadia/titania catalysts, and ammonia adsorbs both as protonated and coordinated ammonia. The Brønsted acid sites are seen to be associated directly with the surface V–OH species and the concentration of these sites is found to be roughly proportional to the vanadia loading (Fig. 4). However, the surface chemistry varies with the surface vanadia coverage, as seen by the differences in the V–OH and NH_4^+ band positions as well as in the relative concentration of BA to LA sites. The small amount of BA sites in TiO_2 gives rise to a weak band at 1460 cm^{-1}, whereas both the 0.6 and 2% samples show a NH_4^+ band at 1453 cm^{-1}, and a band position of 1436 cm^{-1} is seen for the 6% sample. These frequency differences reflect the presence of the weakest N–H bond in the ammonium adsorption complex (or the strongest surface O–H bond) for the highest loading vanadia/titania.

Besides the variation in the hydroxyl groups, differences in the vanadyl structures for the catalysts also show that the vanadia structures change with loading (Figs. 3f–3h and 4). Such vanadia structural changes with loading have been reported in the literature by different techniques and for several different types of catalysts (14, 24–30, 36, 37). Our results agree with, for example Went *et al.* (24), who found that mainly monomeric vanadyls are present on the surface of low loading V_2O_5/TiO_2 catalysts, whereas polymeric vanadates predominate on high loading catalysts. Above monolayer coverage, bulk V_2O_5 structures also appear (24).

The nature of the reactions taking place on vanadia/titania can be understood by comparing the results from TPSR studies carried out in either pure O_2, pure NO, or a mixture of the two gases. A number of reactions could possibly take place. For example, besides the SCR reaction, NH_3 and NO oxidation should be considered. It is furthermore possible that products other than N_2 and H_2O could be formed. Some of the overall ammonia oxidation (reactions [1]–[4]), SCR (reactions [5], [6]), and NO oxidation reactions (reaction [8]) are as follows:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad [1]$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad [2]$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad [3]$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \qquad [4]$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad [5]$$

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad [6]$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad [7]$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad [8]$$

$$2NO \rightarrow N_2 + O_2 \qquad [9]$$

$$2NH_3 + NO + 4O_2 \rightarrow 3NO_2 + 3H_2O. \qquad [10]$$

Thermodynamically, both NO oxidation (reaction [8]) and decomposition (reaction [9]) are favored below 675 K, although the latter is seldom observed to take place.

When oxygen was passed at increasing temperatures over the 6% vanadia/titania catalyst with preadsorbed ammonia, analysis of the gas mixture shows that desorption of ammonia dominates at low temperatures (at 375 K or lower) with little evidence of any reaction. At higher temperatures, ammonia desorption continues to take place, but nitrogen and water are also formed at a relative concentration ratio of about 3 : 1, reflecting the presence of ammonia oxidation to N_2 (reaction [1]). Since N_2O, NO, and NO_2 are not observed at these temperatures, oxidation to higher oxidation states (e.g., reactions [2] and [3]) is apparently negligible. The release of NH_3 observed with increasing temperature in O_2 was similar to that observed in flowing Ar, confirming that NH_3 desorption dominates at low temperatures. The absence of N_2 in the product stream in the Ar experiments shows that gas-phase oxygen is involved in the ammonia oxidation observed at higher temperatures in flowing O_2. The IR spectra obtained in the TPSR experiments in O_2 shows that the NH_4^+ bands are removed more readily than the bands due to coordinated NH_3. This observation is in agreement with several previous findings (31) which have shown that the heat of adsorption of NH_3 on LA sites is generally higher than on BA sites. The present observation of a wide distribution of adsorption sites is also consistent with quite broad IR bands and the results of separate TPD studies (31) and reflects the coexistence of a distribution of different structures. The apparent presence of a larger concentration of weaker NH_3 adsorption sites in the high loading catalyst agrees well with the higher concentration of BA sites observed on the surface.

When the 6% vanadia/titania catalyst with preadsorbed ammonia is exposed to flowing NO + O_2, significant amounts of nitrogen and water are produced already at room temperature (Fig. 11b). This result shows the occurrence of the SCR reduction reaction (reaction [5]). The presence of this reaction is also confirmed by the H_2O/N_2 ratio determined in the product mixture. This ratio is much smaller than that found during the ammonia oxidation observed at higher temperatures in O_2. Simultaneously with the SCR reaction, the IR spectrum shows a significant increase in the concentration of NH_4^+ species (Fig. 5b) and the production of V–OH species (Fig. 6b) upon the initial contact of preadsorbed ammonia with

NO + O_2 at room temperature. It appears that this increase in the V–OH and Brønsted acid sites at room temperature can be most reasonably attributed to some rehydration of the surface by water formed via the reduction of NO. The decrease accompanying the SCR reaction in the intensity of the absorption band due to coordinated ammonia seems to suggest some migration (or desorption/readsorption) from Lewis acid sites to the newly formed Brønsted acid sites. Alternatively, the Lewis ammonia may also be involved in a stoichiometric SCR reaction without necessarily playing an important catalytic role (38).

When the temperature was raised above 375 K, the adsorbed ammonia species disappeared together with the reappearance and production of V–OH species. The concentration of reaction products decreases with further increases in temperature as the surface becomes depleted of adsorbed ammonia reactants. The fact that essentially no ammonia is observed in the products over the entire temperature range indicates that the rate of the SCR reaction is faster than the net rate of ammonia desorption.

The apparent correspondence between the consumption of the more weakly held ammonia (the NH_4^+ species) and the N_2 production, as seen in the simultaneous IR and MS results, suggests that ammonia on the Brønsted acid sites is predominantly involved in the SCR reaction. Furthermore, the fact that no adsorbed NO has been observed on the surface suggests that the reaction occurs between gaseous or weakly adsorbed NO and some species related to NH_4^+. The significant amount of NO_2 produced at temperatures above 375 K can be attributed to gas-phase reaction of NO with O_2. The fact that no N_2O can be observed throughout the TPSR experiments is expected, since reaction [6] is known (39) to be significant only at higher temperatures where the NH_3 coverage has become very low. The observation of larger amounts of N_2 than H_2O at the highest temperatures may be attributed to small amounts of direct NO decomposition.

The TPSR results for the 0.6% vanadia/titania catalyst are quite similar to those obtained on the titania support. When NH_3 preadsorbed on titania is contacted with NO + O_2, some N_2 is formed initially. The combined IR and MS results show the reaction to be associated with the presence of small amounts of Brønsted acidity. However, this reaction discontinues when all the NH_4^+ species have reacted. Subsequent reaction on titania and the low loading catalysts is then dominated by the production of NO_2 and H_2O (reaction [10]). Although the mass spectrometric results show the formation of NO_2 in the TPSR in NO + O_2 for 6% V_2O_5/TiO_2, 0.6% V_2O_5/TiO_2, and TiO_2 (see Figs. 11b, 12b, and 13b), the corresponding IR spectra (shown for 6% V_2O_5/TiO_2, 2% V_2O_5/TiO_2, and TiO_2 in Figs. 5b, 10b, and 9b, respectively) show increasing amounts of adsorbed NO_2 species at lower vanadia loadings. Therefore, it appears that these adsorbed NO_2 species are especially associated with titania.

The TPSR experiments in pure NO show some important differences from the experiments in NO + O_2. For the 6% vanadia/titania catalyst, only small amounts of SCR reaction products are formed initially at room temperature in pure NO (Fig. 11c). Accordingly, preadsorbed NH_3 is not consumed as rapidly by the surface reaction and significant amounts are desorbed. Also, at higher temperatures, where the rate of the SCR reaction increases, NH_3 is still observed in the gas phase, in contrast to experiments with NO + O_2. Due to the lower SCR rate in the NO TPSR experiments, the corresponding IR spectra show a much slower decrease of the amount of adsorbed ammonia with increasing temperature. However, due to the presence of the SCR reaction, the TPSR experiments in pure NO are very different from the TPSR in O_2, where NH_3 desorption and oxidation dominate.

Since both the surface hydroxyl groups and the V=O groups are involved in NH_3 adsorption, it is important to examine how these groups change upon NH_3 adsorption and subsequent TPSR experiments. In flowing, O_2 adsorbed ammonia mainly desorbs as NH_3 from the 6% sample (besides some NH_3 oxidation at higher temperatures). The IR spectra (Figs. 6a and 8a) show that both the initial V–OH and V=O groups which were removed upon NH_3 adsorption are slowly restored in the TPSR experiments in oxygen. For TiO_2 and low vanadia loading catalysts, the MS results show that most of the ammonia is strongly held on the surfaces. The broad distribution of ammonia adsorption sites indicated by the temperature desorption data shows a rather inhomogeneous surface energetically, despite the fact that Lewis acid sites predominate on these surfaces.

The ammonia adsorbed on the high loading catalyst reacts with NO rapidly in flowing NO + O_2. Surface vanadyl groups are seen to be restored more rapidly than in flowing O_2. The initial increase followed by a decrease in surface V–OH concentration indicates the formation of new OH species during the NO reduction reaction. The higher OH stretching frequency upon contacting with NO + O_2 reflects a stronger O–H bond of these species. Thus, these species are apparently associated with more reduced vanadium centers (e.g., V^{4+}–OH).

The slower rate of the SCR reaction in NO without the presence of oxygen makes these experiments well suited for obtaining information about the nature of the surface interactions and the corresponding surface changes. The intensity increase and the upward frequency shift of the V–OH band during TPSR in NO relative to those features of the freshly oxidized catalyst indicate that new OH species are formed as a result of reaction of NO with preadsorbed NH_3 reaction. The observation that the V–

OH band shifts upward initially and subsequently returns to its original position as the temperature is raised further is evidence for the presence of a surface redox reaction. The fact that such large changes are not seen in flowing O_2 suggests that the redox reaction is associated with the SCR reaction and the production of reduced V species.

Previous authors (24) have used TPR/TPO experiments to infer information about redox reactions occurring in the surface vanadia structures. The present TPR/TPO experiments (Fig. 14), however, show that the major effects are dramatic morphological changes. H_2 reduction leads to breakup of the monolayer structures, agglomeration, and re-exposure of the titania surface. Upon subsequent high-temperature oxidation, the vanadia structures spread (redisperse) and the original monolayer-type structures are regenerated. Thus, the effects mainly involve wetting/nonwetting or disperson/agglomeration transitions and appear analogous to those observed in other systems (40).

The observed changes in the surface vanadyl species upon NH_3 adsorption and TPSR experiments indicate important interactions of these species with ammonia. It is seen that ammonia adsorption shifts the vanadyl band to a significantly lower position than that of the original band. This lowering in frequency can be attributed to a weakening of the V=O bond associated with interaction with the adsorbate. A similar phenomenon was observed by Busca and co-workers (21, 26) upon adsorption of acetonitrile, pyridine, and ammonia. Went *et al.* (27, 32) also reported lowering of the V=O band frequency in their Raman spectroscopy studies on the adsorption of H_2O or C_2H_5OH on vanadia/titania. At increasing temperatures in O_2, NO, and NO + O_2, the frequency of this vanadyl species shifts progressively upward again and eventually the original V=O band is restored. This behavior indicates that all these gases can gradually restore the surface back to its original oxidized state prior to ammonia adsorption. A comparison of the TPSR results shows, however, that the original V=O is restored at a lower temperature in NO + O_2, at higher temperature in NO, and at the highest temperature in O_2. This trend in chemical changes is similar to that seen for the surface V–OH species.

CONCLUSIONS

The present studies show that the surface structures in vanadia/titania catalysts may change depending on the vanadia concentration and the pretreatment. Such changes will lead to variations in both the nature and concentration of Brønsted acid sites (associated with the surface V–OH groups) and surface vanadyl groups. The TPSR studies in either NO or NO + O_2 show that SCR reaction occur between preadsorbed NH_3 on Brønsted acid sites and NO with a higher rate in the latter gas mixture. TPSR in pure O_2 leads predominantly to ammonia desorption and ammonia oxidation. The TPSR studies in NO or NO + O_2 have also provided evidence for redox reactions occurring during the SCR reaction involving the formation of new OH groups on a more reduced vanadium center. Attempts to further elucidate the nature of the redox reactions by separate H_2 TPR/O_2 TPO experiments proved to be not very informative. This is attributed to the occurrence of large morphological changes involving breakup of the monolayer with subsequent agglomeration in H_2 and redispersion in O_2. The TPR/TPO experiments do, however, support the fact that the Brønsted acid sites are predominantly associated with V^{5+}–OH groups. The present TPSR studies carried out in a transient fashion have provided insight into different possible surface reactions. The role of such surface reactions and surface sites during steady-state reaction conditions will be discussed in the following paper.

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