Structure of Monolayer Vanadia γ-Alumina Catalysts as Revealed by IR Spectra of Probe Molecules

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IR spectroscopy of NH_3, CO, and CO_2 as probe molecules was used to characterise surface acid and basic sites of vanadia grafted on γ-alumina. NH_4^+ and NH_3 held coordinatively at the surface sites of varying acidity were detected. Two types of acidic alumina sites adsorbing NH_3 coordinatively were postulated. They involve depleted aluminum atoms of free alumina surface and those adjacent to surface clusters of the reduced vanadium oxide. The dependence of the relative amounts of these forms on the surface coverage with vanadia and the reduction degree is described. Reduction is accompanied by coalescence of the vanadium oxide monolayer into small clusters resulting in uncovering of free alumina surface. The adsorption of oxygen on the reduced vanadium atoms modifies the ammonia adsorption considerably. © 1991 Academic Press, Inc.

INTRODUCTION

Considerable research effort has been devoted to the mechanism of the selective catalytic reduction of NO by ammonia due to its importance in the control of environmental pollution. A comprehensive survey of the field was given in a recent work of Bosch and Janssen (*1*). Vanadia supported on titania or alumina has been widely used as the catalyst in this process. The way of preparing the catalyst was found to affect its performance. A monolayer catalyst prepared by grafting technique on alumina proved to be different from the wet-impregnated system (*2*). Also, vanadium monolayer supported on titania was reported to show superior activity compared to the impregnated system (*3*). The vanadia mono-

layer supported on alumina is known to be composed mainly of uniform vanadate-type species in a coherent contact with the support surface (*4–6*). Hence, the vanadia–alumina system is particularly well suited to the investigation of the active sites located at the surface of the support.

Progress of the reaction of NO with ammonia requires activation of the latter on the acid centres of the catalyst. NH_4^+, NH_2 and NH_3 adsorbed forms have been considered in the literature as activated species participating in the reaction (*1, 7–9*).

Very little information has been obtained so far concerning the adsorption of ammonia on the monolayer systems. Hattori *et al.* (*2*) observed for the fully oxidised systems NH_4^+ and coordinatively adsorbed NH_3 species. The vanadia layer is, however, known to be reduced to some extent at catalytic reaction conditions. Thus, experiments en-

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compassing the full range of the surface reduction are necessary to characterise adequately the acid centres of the catalysts and the adsorbed forms of ammonia appearing in the course of the reaction. In particular, intermediate reduction states with oxygen sites partially occupied are of interest as the presence of oxygen in the reactant mixture is known to affect the process strongly.

In this work we used IR spectroscopy of adsorbed NH_3, CO, and CO_2 as probe molecules to characterise the surface sites of vanadia grafted on alumina. Our particular focus was on strongly adsorbed ammonia since such interaction accounts for activation of the molecule in the discussed catalytic process. The investigations were thus carried out after evacuation of the samples at 100°C to remove weakly adsorbed H-bonded forms. The whole range of the reduction degrees and the interaction of the reduced surface with molecular oxygen were studied. Special attention has been paid to the NH bending region of the IR spectrum where the most significant changes were expected.

EXPERIMENTAL

The support used was γ-alumina obtained from Degussa and characterised by surface area of 80 m^2g^{-1}.

The catalyst preparation procedure involved grafting vanadia species on the support through the use of a reaction between $VOCl_3$ and the surface hydroxyls. Details of the preparation method and the chemical analysis of the samples were described earlier (4). Table 1 lists vanadium loadings and surface areas of the samples studied as well as their final degree of reduction expressed in terms of the number of oxygen atoms removed per one vanadium, as determined previously (4).

IR investigations were conducted by using an M80 Zeiss Jena spectrometer. The sample cell with NaCl windows was equipped with a stainless steel holder enabling pretreatment and subsequent infrared transmission measurements of up to six samples in a form of pressed self-supporting wafers (weight about 12 mg cm^{-2}). The cell was connected to the vacuum system. The pretreatment of all the samples at temperatures up to 600°C was carried out at the same time in the upper part of the sample cell. This made possible comparison of the whole set of samples in one experiment.

Four gases were used in the experiments: O_2, NH_3, CO, and CO_2. Oxygen and CO were purified from H_2O and CO_2 by passing them through a liquid N_2 trap. The other two gases were purified by several repeated freeze–pump–thaw cycles.

A standard treatment of every sample investigated involved oxidation in 100 Torr of oxygen at 490°C followed by evacuation at the same temperature. The treatment was repreated until the IR bands due to impurities adsorbed at the surface were no longer observed in the region measured. The sample was then cooled down to the temperature of the reduction and exposed to 100 Torr of ammonia for 30 min. This was followed by evacuation at 490°C for 30 min to 3 h in order to remove all the ammonia adsorbed and water produced during the reduction. The water removal ensured a certain standard dehydroxylation of the sample surface prior to each adsorption experiment.

The reduced samples were cooled down to room temperature and adsorption was carried out by exposure to 50 Torr of NH_3 or 25 Torr of CO, or CO_2. To remove the contribution of the gas phase and physically adsorbed ammonia to the IR spectrum, the samples were evacuated for 30 min at 100°C. As to CO and CO_2, the spectrum was recorded in the presence of the gas phase and then the adsorptions of the gas phase and the support were subtracted by the computer.

The IR spectra of the adsorbed species were measured with an interval of 3.2 cm^{-1} between the measured points. The separation of the overlapping bands was done using a least-squares fit on the assumption of their Gaussian shape.

In one series of experiments, the samples

TABLE 1

Surface Areas, Vanadium Contents, Reducibility, and Oxygen Adsorption on
Vanadia Layers Supported on γ-Alumina

BET surface area $(m^2 \, g^{-1})$	V content $(mol \times 10^{-3} \, g^{-1})$	Average surface coverage $(V \text{ atoms nm}^{-2})$	Number of oxygens removed per V atom on reduction[a]	Oxygen adsorption on reduced samples[b] (O atom per V atom)
80	0.40	3.0	0.49	0.38
79	0.86	6.6	0.60	0.36
70	1.09	9.4	0.64	0.35
70	1.37	11.8	0.72	0.32

[a] In 200 Torr of H_2 at 400°C.
[b] In 100 Torr of NH_3 at 450°C, oxygen adsorption in 100 Torr, at room temperature.

reduced at 450°C were then reoxidised by exposure to 100 Torr of oxygen at various temperatures for 0.5 h. The samples were cooled down to room temperature and evacuated for 30 min; then the adsorption of NH_3, CO, and CO_2 was carried out.

In an additional experiment, the exposure to oxygen was carried out at room temperature as described, the sample was evacuated, and the temperature was increased to 450°C. Then the sample was cooled down to room temperature again and the adsorption of probe gas carried out in a standard way. Contrary to the earlier experiments, gasphase oxygen was absent during pretreatment at higher temperatures.

In order to study the interaction of oxygen with the adsorbed ammonia the sequence of the treatments was reversed. Ammonia was preadsorbed at 150°C on the reduced samples. Then the system was evacuated at 300°C for 30 min and exposed to 50 Torr O_2 for 10 min at various temperatures. Excess oxygen was then removed at 200°C by pumping the system for 10 min. The reason for lower oxygen pressure and shorter interaction time was to preserve as many as possible intermediate oxygen–ammonia species.

RESULTS AND DISCUSSION

1. Adsorption of CO and CO_2

Our earlier redox study of vanadia monolayers on a number of supports showed that

the number of oxygen atoms which can be removed on reduction from a surface V–O complex primarily depends on the nature of the support (4). Vanadia monolayer supported on γ-alumina was found to give off abut 0.5 oxygen atom per vanadium ion.

The detailed picture, however, of this reduction is more complex. Column 1 of Table 1 lists the final degree of reduction attained for vanadia–alumina samples of different vanadia surface content. This degree clearly increases with increasing coverage of the alumina surface, which indicates that a more pronounced reduction is observed even far below the saturation coverage. For the average reduction levels to exceed 0.5 oxygen removed per 1 vanadium, some vanadium ions must be in the V(III) valence state. To get better insight into the reduction of vanadia species on the support, an IR study of adsorbed CO and CO_2 was carried out.

It was suggested by Davydov et al. (10) that the IR band at 2180–2190 cm^{-1}, which appears after CO adsorption on reduced vanadia catalysts, can be attributed to V(III)–CO species. In the present work, the same band was observed for samples reduced at temperatures over 200°C and its intensity increased with the temperature of the reduction (Fig. 1). The band was absent in spectra of oxidised samples.

It has been found that the intensity of the IR band at 2190 cm^{-1} of fully reduced samples increases linearly with vanadia con-
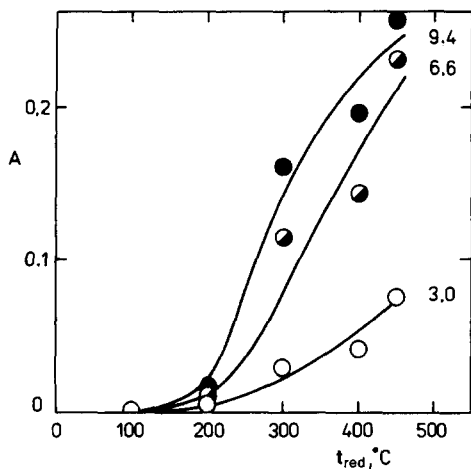
FIG. 1. Intensity of IR band (2190 cm^{-1}) of CO adsorbed on vanadia–alumina catalysts as a function of the temperature of their reduction. The numbers in the figure denote average surface coverage in V atoms nm^{-2}.

tent. Also the quantity of oxygen adsorbed at room temperature on the same samples increases with the content of vanadia, so that the number of oxygen atoms per vanadium atom remains constant (Table 1). When CO is subsequently introduced to these oxygen pretreated samples, its adsorption is practically blocked. This points to the fact that both CO and oxygen adsorb on the same V(III) centres.

The role of basic OH groups in the formation of a catalytic active layer on the oxidic supports has been recently explored by Reddy and Mastikhin using ^{1}H NMR (*11*). The concentration of these species was found to decrease on the alumina surface's being covered with molybdena (*12, 13*) or vanadia (*14*) layers. It has been shown that the basic OH groups of the γ-alumina surface interact selectively with CO$_2$, which leads to the formation of surface bicarbonate species. The species give rise to IR bands at about 1235, 1480, and 1640 cm^{-1} (*15*) which can be used to monitor changes in the number of hydroxyl groups of the alumina support during its being covered with vanadium ions as well as during the subsequent reduction. With

the low transmitting samples the measurements in this spectral region seem to be experimentally easier and even more specific than the direct measurements in the OH stretching region.

On coverage of the support surface with vanadia the amount of basic hydroxyls on the alumina surface, as revealed by the intensity of the 1235 cm^{-1} band, decreases quickly (Fig. 2) so that no more groups are visible at vanadia coverages as low as 6.6 V atoms per nm^2. Figure 3 shows that the surface hydroxyl groups are partially restored in the course of the reduction, which points to an instability of the vanadium oxide monolayer under reducing conditions. The reappearance of free alumina surface in the course of the reduction points to decrease of the dispersion of the surface vanadium phase, i.e., to coalescence of the reduced vanadium oxide monolayer into clusters.

The measurement of the quantity of oxygen adsorbed on the reduced samples, summarized in Table 1, gives further evidence
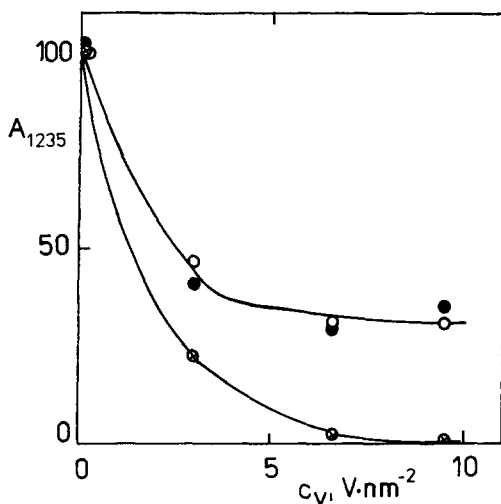

FIG. 2. Intensity of IR band (1235 cm^{-1}) of CO$_2$ adsorbed on vanadia–alumina catalysts: oxidised (O), fully reduced (⊗), and reduced, pretreated in oxygen at room temperature (●), as a function of the vanadia concentration. Band intensity measured for pure alumina is taken as 100%.

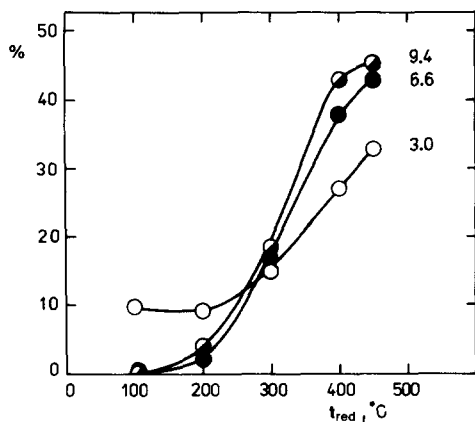FIG. 3. Intensity of IR band (1235 cm^{-1}) of CO_2 adsorbed on vanadia–alumina catalysts, as a function of the temperature of their reduction. Band intensity measured for pure alumina is taken as 100%. The numbers in the figure denote average surface coverage in V atoms nm^{-2}.

of the coalescence of the reduced vanadium phase. Oxygen adsorption probes the number of V(III) ions present at the surface of the system. As the surface coverage of alumina with vanadia increases, an increasing fraction of V ions becomes reduced to oxidation state V(III). However, the number of oxygen molecules adsorbed subsequently per one vanadium ion does not increase correspondingly, but slightly decreases. This clearly points to the fact that with growing surface coverage an increasing fraction of V(III) ions are not available to oxygen adsorption and hence they are probably encapsulated inside small clusters of the reduced oxide.

The coalescence of the monolayer seems to be fully reversible; i.e., free alumina surface is completely re-covered with vanadium species on oxidation of the system at elevated temperatures, as can be monitored by a gradual decrease of the intensity of the 1235 cm^{-1} band indicating the disappearance of the surface OH groups. Figure 2 shows that CO_2 adsorption is not interfered with by oxygen preadsorption at room temperature. Only the increase in temperature brings about the oxidation of the samples

and decreases the CO_2 adsorption to the levels typical of the fully oxidized samples. It is noteworthy that the oxidation can proceed even at the expense of the oxygen adsorbed at the surface, with no oxygen present in the gas phase.

Similar instability of the V_2O_5 monolayer on TiO_2 under reducing conditions was observed by Machej et al. (16) and described in terms of respective lattice energies of the surface phases present (17).

2. Adsorption of Ammonia on Oxidised Samples

Two forms of adsorbed ammonia were observed on the oxidised samples, giving rise to two IR bands in the 1200–1500 cm^{-1} region; one at 1425 and the other at 1250–1260 cm^{-1}. The first band is usually assigned to an ammonium ion, resulting from the adsorption of NH_3 on a Brønsted site. The other band is ascribed to NH_3 coordinatively adsorbed on Lewis acid sites of uncovered surface of the support as its position compares well with the 1280 cm^{-1} band observed after adsorption of ammonia on pure alumina (see below). The shift in the position results apparently from the influence of neighbouring vanadium complexes stabilised on the surface.

The intensity of the band at about 1425 cm^{-1} increases sharply with vanadium content until about 50% of the monolayer coverage is attained. On pure alumina no appearance of NH_4^+ ions was observed. This indicates that NH_4^+ groups are stabilised on vanadium species in agreement with the earlier IR data (18). In contrast, the intensity of the band at 1250–1260 cm^{-1} decreases for more densely covered supports, although the band does not disappear completely even for a sample covered with the amount of vanadia assumed to correspond to a monolayer coverage.

3. Adsorption of Ammonia on Reduced Samples

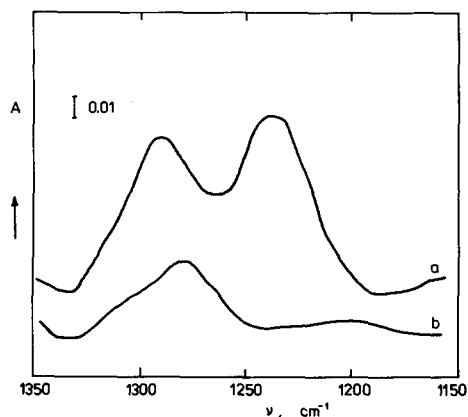The IR spectrum of ammonia adsorbed on the partially reduced samples shows three

FIG. 4. IR spectra of ammonia adsorbed on vanadia–alumina catalyst (6.6 V nm^{-2}) reduced and evacuated at 250°C (curve a). IR spectrum of ammonia adsorbed on pure alumina under the same conditions is given for comparison (curve b).

IR bands in the 1200–1500 cm^{-1} region; one at 1425 cm^{-1} characteristic of NH_4^+ groups, as discussed above, and two others at about 1240 and 1285 cm^{-1} which correspond to the NH_3 molecules held coordinatively by the Lewis acid sites. Figure 4 compares the 1350–1150 cm^{-1} region of the IR spectrum discussed with that of ammonia adsorbed on pure alumina. The comparison allows one to ascribe the band at about 1290 cm^{-1} observed in the spectrum of the reduced vanadia sample to ammonia adsorbed on Lewis acid sites of the uncovered support surface.

The intensity of the bands varies in a characteristic manner with the growing reduction of the surface and in dependence on loading with vanadia. Figure 5 shows the dependence of the band intensities on the temperature of the reduction for the sample containing 9.4 V atoms per nm^2. A decrease of the NH_4^+ absorption observed on the reduction is characteristic of all the samples, irrespectively of the coverage. The amount of ammonia stabilised on Lewis-type acid centres increases with the degree of reduction. For a support covered with only a fraction of the monolayer the 1285 cm^{-1} band dominates the spectrum, the weak 1230

cm^{-1} line appearing for the deep reduction of the vanadia species only.

These observations offer further evidence that the 1285 cm^{-1} feature must be ascribed to ammonia adsorbed on the Lewis acid sites of the free alumina surface. With increasing concentration of vanadia these adsorbed ammonia forms are suppressed on the oxidised samples where vanadium effectively covers the support surface. They reappear, however, when the temperature of the reduction is increased as free alumina surface is uncovered by the coalescence mechanism described earlier.

The other Lewis-type ammonia adsorption site (band 1230 cm^{-1}) must be related in some way to the reduced surface vanadium ions as its concentration increases with vanadium content. Further, the strength of the sites seems to be controlled by the density of adjacent vanadia species. Figure 6 shows the difference between the positions of the two bands corresponding to the two forms of NH_3 species, plotted as a function of the
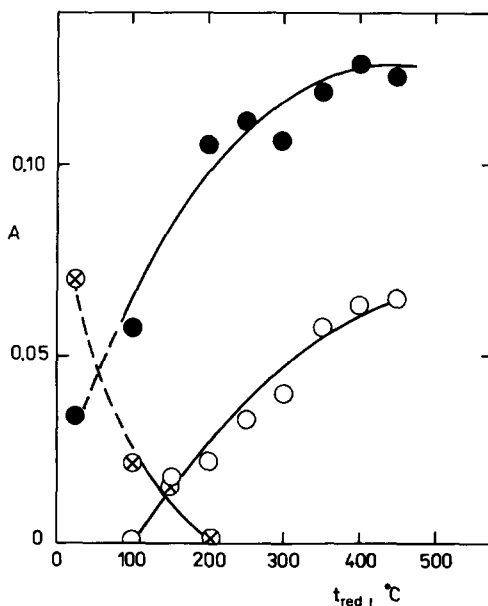

FIG. 5. Changes of IR band intensities of ammonia (1230 (●), 1280 (○), and 1420 cm^{-1} (⊗)) adsorbed on the 9.4 V nm^{-2} sample, as a function of the temperature of the reduction.
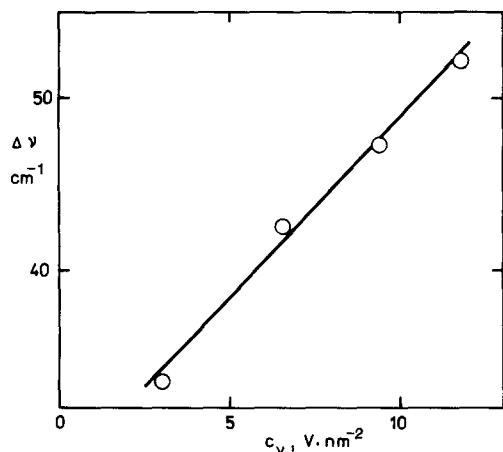
FIG. 6. Shift of the IR bands ($\Delta\nu$) of ammonia adsorbed on Lewis acidic centres of fully reduced catalysts (450°C) as a function of vanadia concentration.

vanadium coverage, as measured for the fully reduced samples. The position of the lower frequency IR band shifts gradually from 1250 to 1230 cm^{-1} with increasing loading of the reduced vanadium surface phase.

The intensity ratio of the two IR bands is changing with the degree of reduction. For the reduction temperatures exceeding about 300°C it attains a constant value (Fig. 7). Thus, this ratio for the fully reduced samples is quantitatively characteristic of the surface state corresponding to a particular vanadia coverage. The intensity ratio of the bands at 1230 cm^{-1} and 1280 cm^{-1} was found to change from nearly zero for coverages below $c_v = 3$ V atoms per nm^2 to about two for the full monolayer coverage. It thus reflects relative amounts of the ammonia adsorption sites present at the free alumina surface and those engendered in the vicinity of the clusters of reduced vanadia.

4. Adsorption of Ammonia on Reduced Samples with Preadsorbed Oxygen

Oxygen interaction with the reduced samples even at room temperatures has a marked effect on ammonia adsorption on the Lewis-type acid sites.

It was found that the position of the 1280

cm^{-1} band does not shift significantly after interaction with oxygen even at higher temperatures. Contrary to this, the lower-frequency IR band shifts to higher frequencies by about 20 cm^{-1}, attaining practically the position characteristic of a fully oxidised sample. The shift is observed even after oxygen pretreatment at room temperature only.

These observations support the earlier finding that oxygen adsorption occurs preferentially at the V(III) Lewis acid sites of the surface. The adsorption sites ascribed to the uncovered surface of alumina remain unchanged in the course of the oxygen pretreatment until the temperature is high enough to bring about the redispersion of the oxidised vanadium monolayer on the support. Intensity changes of the IR bands with increasing temperature of the oxygen interaction are illustrated in Figure 8 for sample with 9.4 V atoms per nm^2. An increase of the IR band characteristic of NH$_4^+$ species is observed with increasing reoxida-
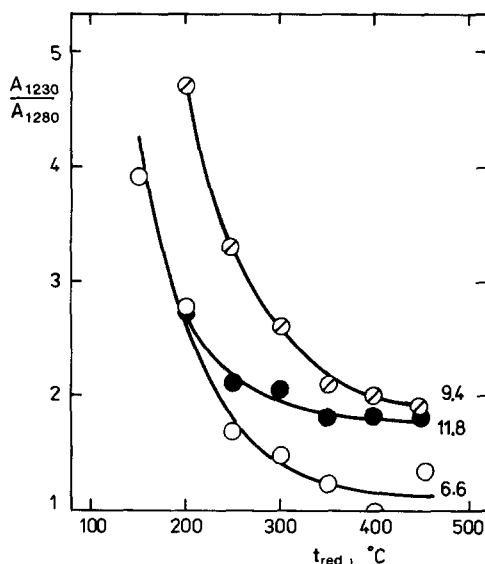

FIG. 7. Ratio of intensities of IR bands of ammonia adsorbed on Lewis type acidic sites (A_{1230}/A_{1280}) of vanadia catalysts as a function of the temperature of reduction. The numbers in the figure denote average surface coverage in V atoms nm^{-2}.
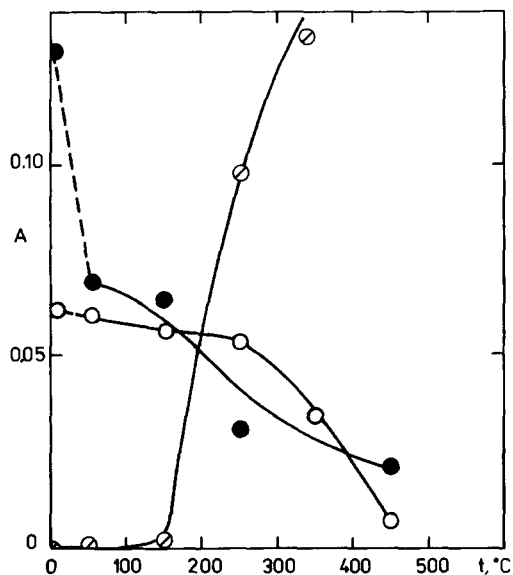
FIG. 8. Changes of IR band intensities of ammonia (1230 (●), 1280 (○), and 1420 cm^{-1} (⊘)) adsorbed on the 9.4 V nm^{-2} sample first fully reduced and then treated in oxygen, as a function of the oxygen treatment temperature.

tion of the samples. In contrast, amounts of both NH_3 species adsorbed coordinatively decrease with the reoxidation.

We performed also a study in the reversed order following the interaction of oxygen with ammonia species adsorbed on the reduced samples.

Reduced samples with adsorbed ammonia were evacuated at 200°C and oxygen was admitted to the systems at temperatures ranging from 100 to 250°C. Two parallel phenomena were observed. First, after oxygen admission the number of coordinatively bound NH_3 was found to decrease strongly, the adsorption form on the free alumina surface (related to the higher-frequency band) being, however, more resistant to the oxygen.

On the other hand, the IR band corresponding to NH_3 species which had remained at the surface was found to shift similarly to what was observed at NH_3 adsorption on the Lewis site containing preadsorbed oxygen. This indicates that an

NH_3–oxygen–vanadium site complex is identical irrespectively of the sequence of the reactant adsorption. A dissociative oxidation of ammonia leading to NH_2–OH pair was mentioned in the literature (19). We found, however, no IR evidence for the formation of NH_2 groups on vanadia catalysts.
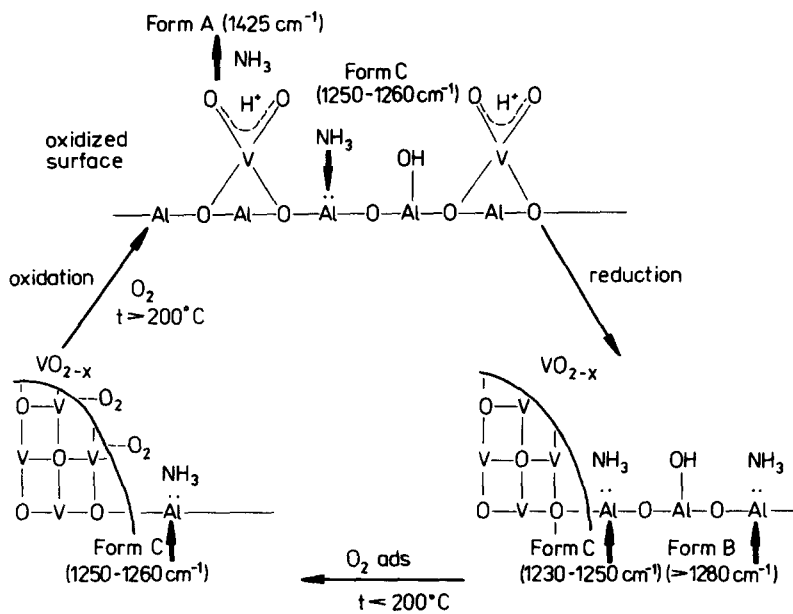
5. Changes in Structure of the Vanadia Layer in the Course of Reduction–Oxidation Cycles

It seems appropriate at this point to discuss the structure of the vanadia species present at alumina surface and the changes it undergoes during the reduction–reoxidation treatments, as monitored by NH_3, CO, and CO_2 adsorption. The previous EXAFS, redox, and radial electron distribution studies (4–6) pointed to polymeric vanadate chains of varying length prevailing at the alumina surface covered with vanadium. On the other hand, this structure proves unstable during the reduction, as discussed in the present work. These observations have led us to put forward the extended scheme of ammonia interaction with the layer reduced to varying extents that is shown in Scheme 1.

Form A. Hydroxylation of the vanadia monolayer was evidenced by a number of authors (20–22). On the oxidised samples, the presence of the protons induces adsorption of ammonia in the form of NH_4^+ ions located on vanadium species and giving rise to the band at 1425 cm^{-1}. The intensity of this band increases with increasing coverage of the alumina surface with vanadia.

Form B and C. The Lewis acidic sites accounting for coordinatively adsorbed ammonia are supposed to be coordinatively unsaturated aluminum atoms. It is evident that the surrounding of these sites must exert a controlling effect on their Lewis acidity. For the system studied in this work, we postulate two types of acidic alumina sites.

The reduction of vanadium oxide monolayer gradually uncovers free alumina surface due to the coalescence of the reduced form of the oxide. Coordinatively unsatu-

Form A (1425 cm^{-1})

↑ NH$_3$

Form C
(1250-1260 cm^{-1})

oxidized
surface

O   H$^+$ O
    V

NH$_3$

OH

O   H$^+$ O
    V

—Al—O—Al—O—Al—O—Al—O—Al—O——

oxidation   O$_2$
              t > 200°C

reduction

VO$_{2-x}$

O—V—O$_2$
V—O—V—O$_2$ NH$_3$
O—V—O—Al—

Form C
(1250-1260 cm^{-1})

VO$_{2-x}$

O—V
V—O—V   NH$_3$ OH   NH$_3$
O—V—O—Al—O—Al—O—Al—

Form C   Form B
(1230-1250 cm^{-1}) (≈1280 cm^{-1})

O$_2$ ads
t < 200°C

SCHEME 1

rated aluminum atoms of strong acidity and basic surface OH groups of pure alumina reappear (see the formation of bicarbonic species on the adsorption of CO_2). The adsorption of ammonia on the former centres gives rise to 1285 cm^{-1} band (Form B). We suppose that these recreated centres are isolated from the surrounding vanadium species at the surface as they are not affected by the degree of reduction and the concentration of vanadium.

Another type of the Lewis acid site is formed by coordinatively unsaturated aluminum atom adjacent to clusters of the reduced vanadium oxide. The adsorption of ammonia on these centres gives rise to 1230–1250 cm^{-1} band (Form C). The sites are strongly affected by the oxidation state of the adjacent vanadium ions. With increasing degree of vanadium reduction, the acidity of these sites decreases due to increasing density of electrons. This is reflected in a gradual shift in the position of ammonia band to a lower wavenumber.

With increasing vanadium loading the fraction of free alumina surface uncovered

on the reduction is decreasing. Hence sites adjacent to vanadium oxide clusters dominate at higher coverages.

These sites are significantly affected by the oxygen adsorption. Their acidity increases due to the electron transfer to O_2 molecules. This was reflected in an abrupt change of the ammonia band position. As long as the vanadium monolayer is not reconstructed by oxidation, the number of adsorption sites present at the free alumina surface remains practically unchanged.

CONCLUSIONS

The main conclusion of this work is that the nature of the adsorbed ammonia strongly depends on the surface coverage of the support with vanadia and the degree of its reduction.

The coalescence of the vanadia monolayer on reduction and its reconstruction by oxidation at higher temperatures were found to account for the changes in the ammonia adsorption.

Two types of the Lewis acid sites on alumina were postulated for the system stud-

ied. They differ in the extent to which their acidity is controlled by their vanadia surrounding.

The proposed complete scheme of ammonia adsorption on vanadia–alumina catalyst is of significance in understanding the mechanism of the selective catalytic reduction of NO by ammonia. Since pure alumina support is inactive in the process, the ammonia activation sites must involve the unsaturated aluminum atoms in the vicinity of surface clusters of vanadium oxide, or hydroxylised vanadium complexes. The relative amounts and the acidity of these sites depend on the vanadium oxide load and its degree of reduction. The presence of oxygen modifies considerably the ammonia adsorption, even at temperteres not high enough to reconstruct the vanadium monolayer.

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