Mechanism of the Selective Catalytic Reduction of NO with NH_3 over MnO_x/Al_2O_3

II. Reactivity of Adsorbed NH_3 and NO Complexes

W. Sjoerd Kijlstra, Danny S. Brands, Hendrik I. Smit, Eduard K. Poels, and Alfred Bliek[1]

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

The mechanism of the selective catalytic reduction of NO with NH_3 over low loaded MnO_x/Al_2O_3 catalysts has been investigated using TPRD, FTIR, and step-response studies with labelled components. Attention has been focused on the reactivity of the adsorbed NO and NH_3 complexes, identified in the preceding paper, at reaction temperatures below 473 K. FTIR shows that the reaction starts with adsorption of NH_3 on Lewis acid Mn^{3+} sites and its subsequent transformation to NH_2 species; NH_4^+ ions, formed at Brønsted acid sites, hardly participate in the reaction. The NH_2 species can react with both gas phase NO (Eley–Rideal mechanism) and reactive nitrite intermediates (Langmuir–Hinshelwood mechanism). Bridged nitrites and monodentate nitrites are able to react at these low temperatures. The role of O_2 cannot simply be explained by reoxidation of the surface to close the catalytic cycle; O_2 appears to be important both for H-abstraction from adsorbed NH_3 and in assisting in the formation of reactive nitrites. Bidentate nitrates are formed at a slow rate in a $NH_3/NO/O_2$ mixture and partly deactivate the catalysts at temperatures below 500 K. In contrast, they serve as reactive intermediates for the SCR reaction at higher temperatures. On the basis of these results, a reaction scheme in elementary steps is proposed for this type of catalyst.   © 1997 Academic Press

INTRODUCTION

In part I of this study (1) the necessity for a detailed, systematic study on the mechanism of the SCR reaction of NO with NH_3 over low-loaded MnO_x/Al_2O_3 catalysts was outlined. Subsequently, the adsorption properties of these catalysts with respect to the single reaction components NO, NH_3, and O_2 were examined. This study resulted in an overview of the surface complexes that can be formed at the reaction temperature (383–473 K), the thermal stability of these complexes, and their location on Mn and/or Al sites. An important point discussed in (1)

was that the NH_3–Mn–NO species, previously proposed as active species by Kapteijn *et al.* (2), according to FTIR studies in the absence of O_2, does not exist in the presence of O_2 due to the instability of nitrosylic species in oxidising atmospheres. Hence, further mechanistic research in the presence of O_2 is necessary. Recently, a characterisation study (3) on these low-loaded Mn/Al_2O_3 catalysts turned out that manganese is mainly present as isolated Mn^{3+} ions in octahedral coordination, which results in a very high selectivity towards N_2 production. Therefore, N_2O formation is not further addressed here. In this paper we will evaluate which of the complexes, observed in the preceding paper (1), is present under reaction conditions and whether they play a role in the SCR reaction mechanism. Attention is focused on the next four questions.

First, the nature of the active NH_3 species has not been clarified so far. In the preceding paper (1) it was shown that NH_3 is adsorbed on both Brønsted and Lewis acid sites and that these adsorption modes have comparable thermal stabilities. Besides, amide species are present at the surface, mainly on Mn sites. The question whether the SCR reaction requires Brønsted or Lewis acid sites is discussed extensively in literature. For V_2O_5/TiO_2 catalysts, several authors point, based on FTIR results, towards the necessity of a Brønsted acid site next to a redox site (4–6), whereas other authors propose Lewis bound NH_3, followed by dissociation to amide species and recombination to N_2H_4 species to be the key route towards N_2 production (7, 8). For CuO/Al_2O_3 a reaction mechanism *via* amide species was also proposed (9), whereas for CuO/TiO_2 significant SCR activity is shown without any Brønsted acidity at the catalyst surface (10). In this paper, the reactivity of the observed three NH_3 adsorption modes on low loaded MnO_x/Al_2O_3 will be determined by means of FTIR experiments.

Second, it is not clear whether the reaction proceeds *via* a Langmuir–Hinshelwood (LH) mechanism or an Eley–Rideal (ER) mechanism. Previously published TPD results

on higher loaded catalysts (2) point towards an instantaneous reaction of gas phase NO with preadsorbed NH_3. On the other hand, the preceding paper (1) very clearly shows that a variety of nitrite and nitrate complexes are thermally stable at the reaction temperature in the presence of O_2. Moreover, kinetic studies reveal that the reaction order with respect to NO is significantly lower than one (11), which means that reaction of gas phase NO with preadsorbed NH_3 cannot be the only reaction in which NO is involved. The controversy whether the SCR reaction proceeds *via* an ER mechanism or a LH mechanism is discussed abundantly for most other SCR catalysts, with contradictory conclusions. The reaction between adsorbed NH_3 and gas phase NO was reported for V_2O_5/TiO_2 catalysts (4–6, 10, 12–18) and Cu(II)-exchanged zeolite Y (19). On the other hand, the reaction between adsorbed NH_3 and a NO-containing surface complex was reported, *also* on V_2O_5/TiO_2 catalysts (20–24), as well as on Cu-ZSM-5 (25), CuO/Al_2O_3 (26), CrO_x/TiO_2 (27), unsupported CrO_x (28), and Ce-MOR (29). Nitrosyls (2), nitrosonium ions (29), linear nitrites (28), monodentate nitrites (26), and several nitrates (22, 25) are proposed as reactive intermediates. As several of these species can be formed on the surface of 2 wt% Mn/Al_2O_3 at 423 K in the absence of NH_3 (1), their role with respect to the SCR reaction will be determined by means of FTIR, TPRD, and step response techniques.

Third, the role of gas phase O_2 in the reaction cycle has to be elucidated, Kinetic studies (11) show that the reaction order with respect to O_2 is positive up to an O_2 concentration of 10 vol%. Four mechanistic roles of O_2 are conceivable. In the preceding paper (1) it was shown that one of these roles, oxidation of gas phase NO, is not significant at these low temperatures and concentrations. Moreover, a second role, the need for oxidised sites for H-abstraction, could not be confirmed as gas phase O_2 does not enhance the reaction from coordinated NH_3 to NH_2 species after an inert pretreatment. The third role, creation of a more oxidised surface to enhance NO adsorption, remains plausible according to the adsorption studies (1), but it can only be relevant if a LH mechanism is operative. Finally, O_2 could simply act to close the catalytic cycle. These latter three roles of O_2 will be investigated in this paper by FTIR and step response experiments.

The fourth question to answer is the unexplained long-term deactivation, observed during the first 200 h under reaction conditions (with diluted SCR reactants) at 423 K. Possibly, one of the reactants or products of the SCR reaction blocks active sites at low temperatures (<473 K). Transient experiments will be used to reveal the nature of this deactivation.

After addressing these four questions an attempt is made to construct a catalytic cycle which can serve for further kinetic modelling and reactor design.

EXPERIMENTAL

Catalysts

The catalyst was prepared by incipient wetness impregnation of a Ketjen CK300 γ-Al_2O_3 support ($S_{BET} = 192 \, m^2 \, g^{-1}$, pore volume 0.5 $cm^3 \, g^{-1}$ and particle size 150–250 μm) with an aqueous solution of $(CH_3COO)_2Mn \cdot 4H_2O$. Subsequently, the catalyst was dried in stagnant air overnight at 383 K, followed by calcination in O_2 at 573 K for 1 h and at 773 K for 3 h. Due to the limited solubility of the precursor the impregnation was performed in two steps with drying in-between. In this way, a 2 wt% manganese loading was established. A more detailed characterisation of this catalyst was reported previously (3, 30).

Gases

The following gases, 0.40 vol% NO/He, 0.75 vol% ^{15}NO/He (99% isotopically pure), 0.40 vol% NH_3/He, O_2 (99.6% purity), 3.5 vol% $^{18}O_2$/He (99% isotopically pure), and He (99.996%), were used during the flow reactor studies (UCAR). The O_2 was dried before use by molecular sieves (5 A, Janssen Chimica). For *in situ* FTIR experiments pure NO (99.9%), NH_3 (99.998%), and O_2 (99.6%) were used (UCAR).

Temperature Programmed Reaction and Desorption (TPRD)

The TPRD experiments were performed in a setup described elsewhere (31) containing a flow reactor connected on-line with a mass spectrometer (UTI 100C). Fragmentation patterns of N_2O ($m/e = 44$) on the NO and N_2 signals, as well as fragmentation of H_2O on the NH_3 signal were determined. The MS was sampled twice a minute in the experiments of Figs. 2–8, and four times a minute in the experiment of Fig. 9. The connecting tubing was heated at 385 K to avoid adsorption on the walls. The experiment started with a pretreatment in 2 vol% O_2/He or He up to 773 K. Subsequently, the sample, containing 100 mg of 2 wt% Mn/Al_2O_3, was cooled down to 323 K in the same atmosphere and purged with He to remove any physisorbed O_2. After this pretreatment a gas mixture containing 1000 ppm NO and 1 vol% O_2 or 1000 ppm NH_3 in He was passed over the catalyst until saturation of the catalyst surface was reached, as apparent from the MS data. Subsequently, the sample was purged in He for about 60 min to remove all physisorbed species. Finally, TPRD was carried out in 500 ppm NH_3 or 500 ppm NO and 1 vol% O_2 in He at a heating rate of 5 K min^{-1} up to 773 K, followed by a 1-h isothermal period. The experiments are always denoted as follows: pretreatment/adsorption/desorption. All flow rates were 50 cm^3 min^{-1}. ^{15}NO and $^{18}O_2$ were used to reveal the origin of the reaction products.

Step-Response Experiments

Step-response experiments were all carried out with 80 or 100 mg 2 wt% Mn/Al$_2$O$_3$ in the same equipment as the TPRD studies. In general, the following procedure was performed. First, the catalyst was pretreated in 2 vol% O$_2$/He at 673 K for 1 h and subsequently cooled down to the reaction temperature, 423 K. Second, a mixture containing 450 ppm NO, 500 ppm NH$_3$, and 2 vol% O$_2$ was supplied to the catalyst during 9 h to reach a pseudo steady state (less than 0.5% conversion loss per hour). This mixture will be referred to as *standard reaction mixture*. Third, one of the three reactants was cut from the feed stream until all concentrations reached a new, stable level, as apparent from the MS data (0.5–6 h). Then, the missing reactant was resupplied to the feed stream, and the concentrations were monitored until a new steady state situation was established. All flow rates were 50 cm^3 min^{-1}. In some of the experiments ^{15}NO and ^{18}O$_2$ were used to reveal the origin of the reaction products.

Fourier Transform Infrared Spectroscopy (FTIR)

Typically, 15–20 mg of material was pressed in self-supporting discs. A detailed description of the *in situ* infrared transmission cell is given elsewhere (32). Spectra were recorded with a Biorad FTS 45 A spectrometer; 64 scans were averaged to obtain a spectrum with 2 cm^{-1} resolution over the spectral range 4000–1000 cm^{-1}. Samples were *in situ* pretreated *in vacuo* at 673 K for 1 h and subsequently cooled down to 323 K. At this temperature, two types of experiments were performed. The first one started by adsorption of 2 mbar NO and 5 mbar O$_2$ during 30 min, followed by evacuation. Then, increasing amounts of NH$_3$ were adsorbed on the surface. The second experiment started by adsorption of 2 mbar NH$_3$ during 15 min, followed by evacuation. Then, increasing amounts of NO were adsorbed in the presence of 5 mbar O$_2$. In both cases, the adsorption was followed by heating up to 673 K; during heating, spectra were recorded at increments of 25 K.

RESULTS

Stability Test

In the introduction, the need for an explanation for the long-term deactivation of a 2 wt% Mn/Al$_2$O$_3$ catalyst in a standard reaction mixture at 423 K was outlined. The stability of the catalyst is shown in Fig. 1. Clearly, it takes a long period to reach a stable activity. The NO conversion decreases slightly but progressively during the first 150 h down to a stable level of about 38% at the given space velocity. Afterwards, no changes in activity are observed.

Temperature Programmed Reaction and Desorption

In part I of this study (1) it was shown that, after adsorption of NO and O$_2$, the surface is covered by NO complexes
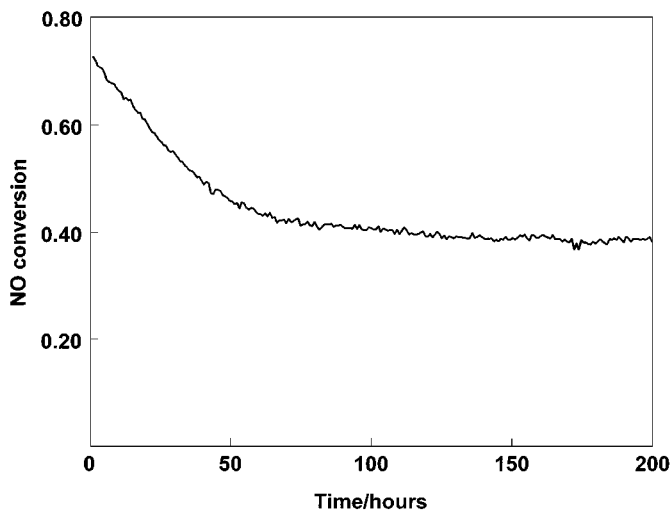

FIG. 1. NO conversion as function of time in a standard reaction mixture at 423 K; VHSV = 31.000 h^{-1}; 2 wt% Mn/Al$_2$O$_3$.

(NO/Mn $\approx$ 1), which can roughly be divided in weakly adsorbed (desorption at 323–500 K during TPD in He) and strongly adsorbed (desorption 500–700 K) surface species. The TPRD profile for the O$_2$/^{15}NO + ^{18}O$_2$/NH$_3$ experiment is shown in Fig. 2. The temperature program is started immediately after introduction of the NH$_3$/He flow. Clearly, NH$_3$ is able to remove weakly adsorbed NO from the surface as ^{15}NO desorption directly starts upon NH$_3$ admission. At 385 K, the production of N^{15}N starts, formed from one ^{15}NO and one NH$_3$ molecule, whereas the ^{15}NO desorption decreases concurrently. At 473 K, no desorption of ^{15}NO is observed anymore, while a strong peak of N^{15}N becomes visible from that temperature, accompanied by minor N^{15}NO desorption. The desorption of produced H$_2$O
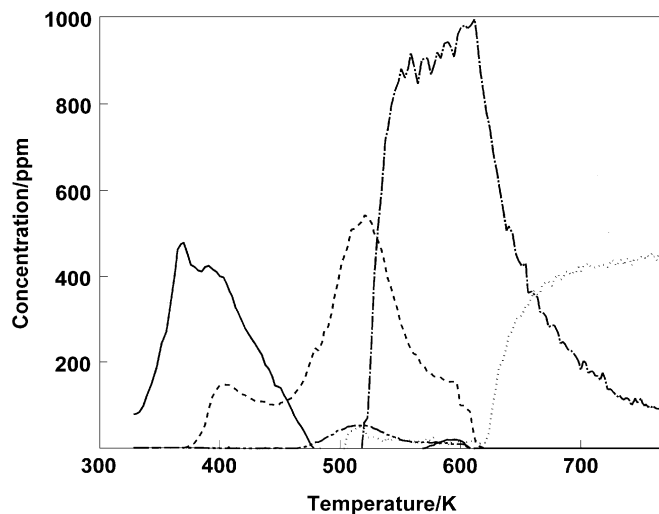

FIG. 2. TPD in 500 ppm NH$_3$ after adsorption 1000 ppm ^{15}NO and 2 vol% ^{18}O$_2$ at 323 K; ^{15}NO (———), N^{15}N (– – –), NH$_3$ (ıııııııı), N^{15}NO (—··—) and H$_2$O (– ·· –); 2 wt% Mn/Al$_2$O$_3$.

TABLE 1

Molar Uptake (Positive) and Desorption (Negative), Normalised per Mole of Manganese, during TPD Experiments after Adsorption at 323 K, 2 wt% Mn/Al$_2$O$_3$

TPD	NO	N$_2$	NH$_3$	H$_2$O	N$_2$O
NO + O$_2$/NH$_3$	−0.38	−0.52	+1.08	−1.09	−0.04
NH$_3$/NO + O$_2$	+0.99	−0.95		−0.22	−0.02

does not begin before the temperature is raised up to 525 K, and continues at high rate up to 625 K, the temperature at which the adsorbed ^{15}NO is exhausted and above which no further N^{15}N production takes place. Apparently, NO complexes that are thermally stable up to 600–650 K (1) can react with adsorbed NH$_3$ at considerably lower temperature, 500–525 K. Breakthrough of NH$_3$ does not start before 625 K. The amounts of desorbed NO, produced N$_2$, and adsorbed NH$_3$ are reported in Table 1, according to appropriate mass balances. By consequence, the correct NH$_3$ uptake is obtained after subtraction of the amount of N ^{15}N produced. When a summation is made of all products (both desorption and reaction) originating from ^{15}NO, a NO/Mn ratio of 0.94 is obtained, which is close to the ratio of approximately one that was reported after NO adsorption in the presence of O$_2$ (1). Besides, a large amount of NH$_3$ is adsorbed on the surface in the course of the temperature program (NH$_3$/Mn > 1).

The O$_2$/NH$_3$/NO + O$_2$ experiment provides a completely different picture. As N$_2$ production starts immediately upon introduction of the reactants at 323 K, it was chosen not to initiate the temperature program before the N$_2$ production decreased to zero. The concentrations as a function of time are shown in Fig. 3. The instantaneous formation of N$_2$ up to 150 ppm is followed by a gradually increasing N$_2$ production during 35 min. The breakthrough of NO corresponds with the maximum in N$_2$ production, which subsequently decreases very gradually to zero. Table 1 reports the NO uptake and the amounts of reaction products. In the preceding paper (1) it was shown that after NH$_3$ adsorption the NH$_3$/Mn ratio is slightly higher than one. The amount of N$_2$ produced proves that the major part of the adsorbed NH$_3$ species is able to react at these low temperatures. The surface sites which are liberated as a consequence of reaction are filled up by both NO (NO/Mn ≈ 1) and H$_2$O, which is supposed to be formed 1.5 times the N$_2$ production, but which is held on the surface in a ratio H$_2$O/Mn = 1.21 (= 0.95 ∗ 1.5 − 0.22; see Table 1). These ratios show that additional surface sites, probably located on the support, must be involved in the NO and H$_2$O adsorption. During the subsequent heating program (not shown), these high amounts of H$_2$O and NO desorb, together with some N$_2$ resulting from the reaction between adsorbed NO and a minor fraction of NH$_3$, which did not react at 323 K.
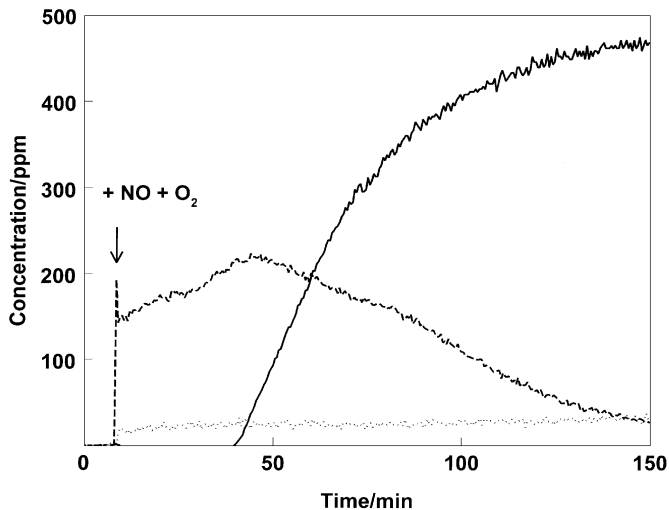

FIG. 3. Isothermal period at 323 K before start TPD: addition 500 ppm NO + 2 vol% O$_2$ after adsorption 1000 ppm NH$_3$ at 323 K; NO (———), N$_2$ (– – –) and H$_2$O (⫶⫶⫶⫶); 2 wt% Mn/Al$_2$O$_3$.

Step-Response Studies

Step-response studies are all performed starting from a pseudo steady state (reached after 8–10 h) at 423 K in a *standard reaction mixture* with a 2 wt% Mn/Al$_2$O$_3$ catalyst. Upon replacing ^{14}NO by ^{15}NO the concentration of both ^{14}NO and ^{14}N$_2$ decreases rapidly to zero while the concentrations of ^{15}NO and N^{15}N increase correspondingly (Fig. 4). Within 15 min the original NO conversion and N$_2$ production are restored. Moreover, the $m/e = 30$ signal (^{14}NO or ^{15}N$_2$) does not exceed the value of the isotopic impurity, showing that in the standard reaction mixture at 423 K all N$_2$ produced results from the reaction between one molecule
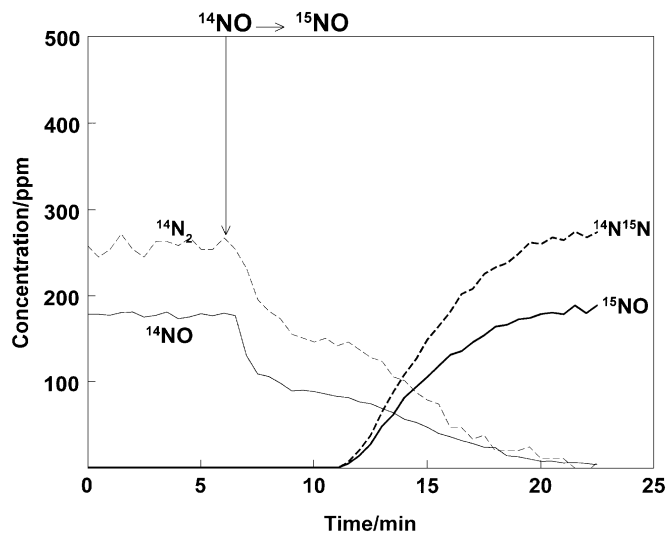

FIG. 4. Switch at 423 K: 500 ppm NH$_3$, 450 ppm NO, 2 vol% O$_2$ ⇒ 500 ppm NH$_3$, 450 ppm ^{15}NO, 2 vol% O$_2$; 2 wt% Mn/Al$_2$O$_3$.

FIG. 5. Switch from *standard reaction mixture* at 423 K: NO off/NO on; 2 wt% Mn/Al$_2$O$_3$.
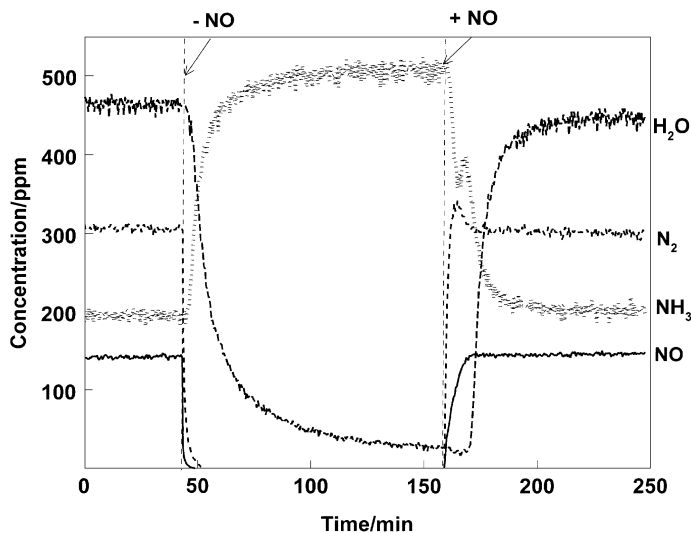

FIG. 6. Switch from *standard reaction mixture* at 423 K: NH$_3$ off/NH$_3$ on; 2 wt% Mn/Al$_2$O$_3$.

NO and one molecule NH$_3$. This result is used to calculate accumulation and desorption of reactants and products in the following step-response experiments.

Switch NO off/on. Upon the removal of NO from the gas stream (Fig. 5) the signals of both NO and N$_2$ instantaneously drop to almost zero in a few minutes, indicating that both the rate of NO desorption and SCR reaction become negligible. Apparently, hardly any reactive NO complexes are present at the surface under reaction conditions at 423 K. The withdrawal of NO results in an NH$_3$ uptake and concurrent H$_2$O desorption, suggesting a new surface equilibrium between both compounds due to the termination of H$_2$O production by the SCR reaction. The amounts of adsorbed/desorbed compounds are presented in Table 2. It is assumed that all N$_2$ produced desorbs instantaneously into the gas phase. Uptakes and desorption of NO and NH$_3$ are corrected for the produced N$_2$ in the corresponding period. Upon reintroduction of NO to the reaction mixture, the production of N$_2$ starts again and the exit concentration regains its original level within 10 min. The conversion of NO during the first 10 min is higher than expected on the basis of reaction stoichiometry, indicative for a small NO uptake in that period. The concentration of NH$_3$ does not

drop directly to the original level upon reintroduction of NO, but it shows a desorption maximum after a few minutes. Probably, the coverage of NH$_3$ is lowered by the competitive adsorption of H$_2$O, the production of which restarts simultaneously with the production of N$_2$. The time it takes for NH$_3$ to reach its original concentration coincides with the breakthrough of H$_2$O. The adsorbed/desorbed quantities upon the introduction of NO are also presented in Table 2. The overall amount of adsorbed NO and NH$_3$ has not changed significantly after the entire step-response experiment. Correspondingly, the NO conversion is comparable before and after the two switches.

Switch NH$_3$ off/on. Upon withdrawal of NH$_3$ from the reaction mixture, the NO concentration drops slightly for about 5 min after which a gradual increase is observed (Fig. 6). This means that NO and NH$_3$ adsorb competitively on at least part of the surface sites. The increase of the NO concentration is accompanied by a very slow decrease in the N$_2$ production; the SCR reaction proceeds until about 1 h after the removal of NH$_3$ from the gas stream, resulting in a N$_2$/Mn ratio of 0.84 (Table 3). This means that under reaction conditions the majority of the Mn sites are able to coordinate a NH$_3$ molecule that can react with NO and O$_2$

TABLE 2

Molar Uptake (Positive) and Desorption (Negative), Normalised per Mole of Manganese, upon Removal and Reintroduction of NO from the Standard Reaction Mixture at 423 K, 2 wt% Mn/Al$_2$O$_3$

	NO	N$_2$	NH$_3$	H$_2$O
NO off	−0.004	−0.003	+0.25	−0.65
NO on	+0.03		−0.29	

TABLE 3

Molar Uptake (Positive) and Desorption (Negative), Normalised per Mole of Manganese, upon Removal and Reintroduction of NH$_3$ from the Standard Reaction Mixture at 423 K, 2 wt% Mn/Al$_2$O$_3$

	NO	N$_2$	NH$_3$	H$_2$O
NH$_3$ off	+1.00	−0.84	−0.10	−1.33
NH$_3$ on	−0.17		+1.12	

after switching off NH_3. The removal of NH_3 from the gas stream reduces the desorption rate of H_2O, probably due to competitive adsorption between these compounds (11), resulting initially in an instantaneous decrease in H_2O concentration. Subsequently, the H_2O concentration decreases very gradually due to the slowly stopping SCR reaction. The NO concentration, which is apparently stable after 170 min, does not reach the entrance concentration, indicating that some uptake of NO continues for a very long period. It must be noted that the reported NO uptake in Table 3 concerns the amount determined until the NH_3 was reintroduced to the reaction mixture. Upon switching on the NH_3, a part of the weakly adsorbed NO is removed from the surface, as can be observed from the NO concentration which exceeds the feed concentration during 15 min. Subsequently, the NO concentration reaches a steady state value which is higher than the steady state value before switching off the NH_3. Hence, the catalyst is deactivated considerably during the previous period of $NO + O_2$ supply. Note that the extent of deactivation is comparable to the long term deactivation under standard conditions (Fig. 1). The amount of NO adsorbed after switching off the NH_3 only partly desorbs or reacts after the reintroduction of NH_3, suggesting that the amount of nitrites and/or nitrates on the surface has increased considerably after the two switches (Table 3). Upon reintroduction of NH_3 the production of N_2 immediately restarts; after a sharp increase, the production progressively increases to a steady state value. The production of H_2O is observed significantly later, suggesting that large amounts of freshly produced H_2O remain adsorbed on the surface before desorption starts. The breakthrough of NH_3 is only observed 35 min after its reintroduction. Even after subtraction of the produced N_2 the uptake of NH_3 amounts to 1.12 mole per mole of Mn (Table 3). This means that the amount of NH_3 that desorbed or reacted after NH_3 is removed from the gas stream is more than completely readsorbed after switching on the NH_3. The distribution of adsorbed species after this step response experiment was evaluated by TPD (Fig. 7). A strong N_2 production peak with a maximum at 510 K is observed, together with a NO desorption peak at 630 K, accompanied by desorption of O_2, confirming the formation of stable nitrates during the absence of NH_3 in the gas stream. The N_2 production at 510 K (compare Fig. 2) confirms that stable nitrates are able to react with adsorbed NH_3 at temperatures higher than 500 K. Both peaks are absent in the TPD pattern of the catalyst operating at high NO conversion (11), at the start of the step-response experiment. When the experiment shown in Fig. 6 is repeated at 523 K, the NO conversion reaches its original value after the two switches. Hence, stable nitrates which are bidentate or bridged coordinated (1) do not deactivate the catalyst at that temperature.

Switch $^{18}O_2$ on/off. In Fig. 8 the response to the instantaneous addition and removal of O_2 from the reaction mix-
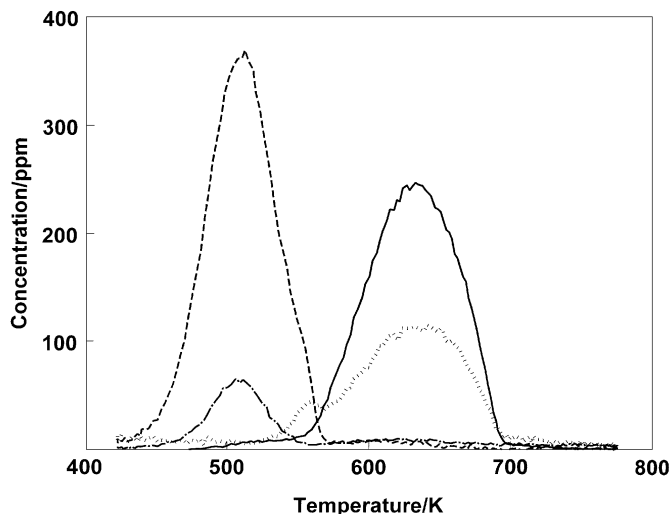
FIG. 7. TPD after the step-response experiment of Fig. 5; NO (———), N_2 (– – –), N_2O (— – —) and O_2 (⋯⋯); *not shown*: H_2O; 2 wt% Mn/Al_2O_3.

ture is shown. Clearly, the SCR reaction immediately starts upon the addition of O_2, and a constant reaction rate is attained in less than 2 min. Upon removal of O_2 the NO conversion drops directly, although it reaches a zero value only after 20 min. The N_2 production exactly matches this trend. The calculated N_2 production after switching off the O_2 remains very low: $N_2/Mn = 0.03$. This means that lattice oxygen of the catalysts does not participate significantly in the reaction upon removal of O_2 from the gas stream at this temperature. The fact that the response to the reintroduction of $^{18}O_2$ is so rapid indicates that the necessary oxidised sites are easily formed by O_2 and not by NO. Besides, the
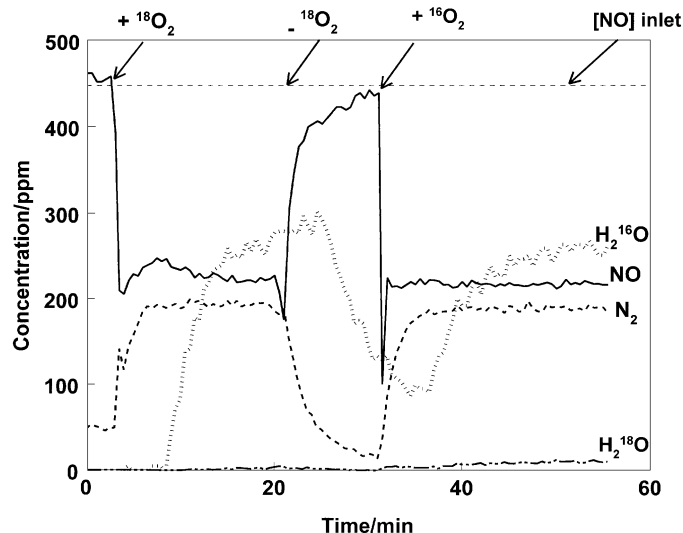
FIG. 8. Switch from *standard reaction mixture* at 423 K: $^{18}O_2$ on/off; $^{16}O_2$ on; 2 wt% Mn/Al_2O_3.

experiment shows that produced H$_2$^{18}O, containing oxygen originating from gas phase ^{18}O$_2$, only becomes visible after a long time, indicative for a large reservoir of OH groups on the surface.

Switch NO + O$_2$ ⇒ ^{15}NO + NH$_3$ + O$_2$. Finally a transient isotopic labelling experiment is carried out which is comparable to the NH$_3$ off/on experiment (Fig. 6), but the reintroduction of NH$_3$ is accompanied by a switch ^{14}NO ⇒ ^{15}NO. The experiment is considered as decisive whether a Langmuir–Hinshelwood or an Eley–Rideal mechanism is operative for this catalyst system. At the point prior to the switch the surface is covered by nitrates and nitrites (see Table 3). Upon introduction of NH$_3$ and ^{15}NO, NH$_3$ adsorbs on the surface (compare Figs. 5 and 6). Subsequently, it can react with adsorbed NO complexes or gas phase ^{15}NO. In Fig. 9, the switch NO + O$_2$ ⇒ ^{15}NO + O$_2$ is shown. Immediately after this step N^{15}N production starts, indicative for an Eley–Rideal mechanism. The production gradually increases to a steady state value 50 min after the step. However, also a minor amount of ^{14}N$_2$ is formed upon switching. This ^{14}N$_2$ production continues at a low rate during the entire experiment, which suggests that a minor part of the adsorbed NH$_3$ reacts *via* a Langmuir–Hinshelwood mechanism under reaction conditions at this temperature. The concentration of ^{14}NO strongly drops upon the switch, subsequently increases slightly to a maximum 15 min after the step, and then progressively decreases to zero. The remarkable increased desorption of NO after 15 min is accompanied by enhanced ^{15}NO adsorption in the same period. The breakthrough of both NH$_3$ and H$_2$O is comparable to the responses observed in Fig. 6.
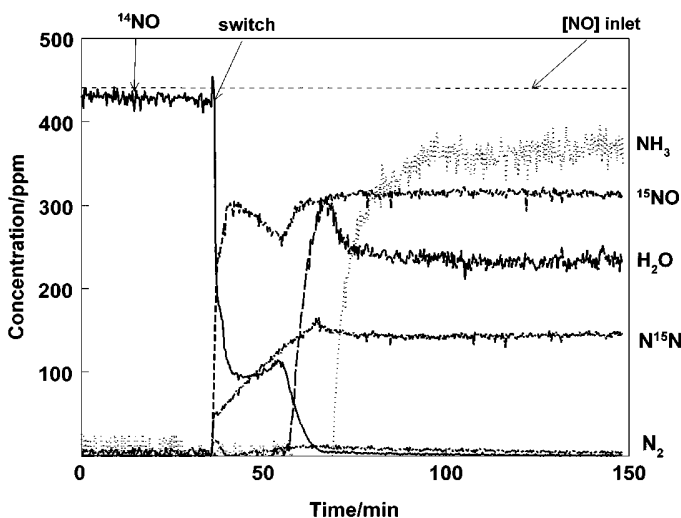

FIG. 9. Switch at 423 K: 450 ppm NO, 2 vol% O$_2$ ⇒ 500 ppm NH$_3$, 450 ppm ^{15}NO, 2 vol% O$_2$; 2 wt% Mn/Al$_2$O$_3$.
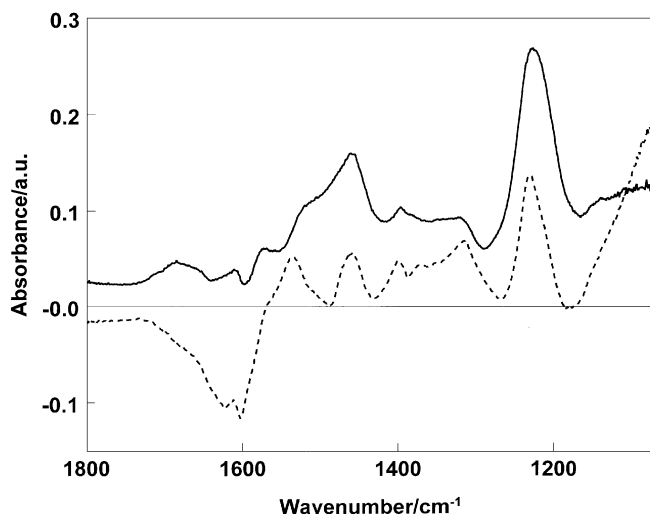

FIG. 10. Adsorption of 3 mbar NO + 2 mbar O$_2$ at 323 K on a sample precovered with NH$_3$ (———), followed by heating to 423 K (– – –); 2 wt% Mn/Al$_2$O$_3$. Spectra after NH$_3$ adsorption and subsequent evacuation are subtracted.

Infrared Spectroscopy

In order to determine the nature of the reacting species at low temperatures, IR spectra are recorded of successive adsorption of NO and NH$_3$ and *vice versa*, both in the presence of O$_2$. The sequence of adsorption and reaction steps and the corresponding partial pressures are comparable to those of the TPRD studies. In part I of this study (1) we showed that the surface complexes formed upon both NH$_3$ and NO adsorption show several IR vibrations in the spectral range 1000–1900 cm^{-1}. By consequence, overlapping bands are expected upon sequential adsorption. Therefore, the spectra of the preadsorbed compounds are subtracted for the sake of clarity. After preadsorption of NH$_3$ and O$_2$ the spectrum of a 2 wt% Mn/Al$_2$O$_3$ catalyst is characterised by bands due to both NH$_4^+$ ions (1479 (ν_{as}) and 1690 (ν_s) cm^{-1}) and coordinated NH$_3$ (1603 (ν_{as}) and 1190–1220 (ν_s) cm^{-1}), as well as some amide species (1511 cm^{-1}). Upon NO adsorption in the presence of O$_2$ at 323 K (Fig. 10), a sharp peak arises at 1231 cm^{-1}, together with some weak peaks at 1321, 1398, 1574, and 1612 cm^{-1}, and two stronger bands at 1459 and 1685 cm^{-1}. The latter two bands, as well as the band at 1398 cm^{-1}, are attributed to additional NH$_4^+$ ions, formed due to the H$_2$O production of the SCR reaction. A comparable shift in the distribution of adsorbed NH$_3$ species by the presence of additional hydroxyls was observed on both CuO/Al$_2$O$_3$ (9) and V$_2$O$_5$/TiO$_2$ (33) catalysts. Enhanced IR absorption in the 3400–3600 cm^{-1} range due to hydrogen-bridged hydroxyls (not presented) confirms that H$_2$O production indeed takes place. At this point, it is not easy to determine whether coordinated NH$_3$ or NH$_4^+$ ions preferentially react with NO. The bands at 1231 cm^{-1} (bridged nitrites) and 1320 cm^{-1} (monodentate nitrites) show that even weakly adsorbed NO complexes are

formed to some extent on a surface precovered by NH_3. The more stable bidentate nitrates (1579 cm^{-1}) and bridged nitrates (1612 cm^{-1}) are also formed in small amounts. Upon heating to the reaction temperature (423 K), significant changes in the spectrum are observed due to the SCR reaction. A strong negative band is visible at 1603 cm^{-1}, accompanied by significantly decreased IR-absorption at 1180–1200 cm^{-1}, attributed to coordinated NH_3 at Mn^{3+} sites (1, 30). Moreover, a substantial band grows at 1533 cm^{-1}, showing that coordinated NH_3 is transformed to NH_2 species to a large extent. In contrast, the bands due to NH_4^+ ions even remain positive, which may be partly due to the formation of linear nitrites (absorbing at 1466 cm^{-1}) on the liberated surface sites. Another explanation is that the formation of additional Brønsted acid sites still overrules the consumption of NH_4^+ ions by the SCR reaction. The intensities of the bands due to bridged and monodentate nitrites are reduced with respect to the spectra recorded at 323 K, showing that these surface species are able to react with coordinated NH_3 at the reaction temperature.

Upon NH_3 adsorption on a surface precovered by NO ($+O_2$), shown in Fig. 11, the spectra are overruled by the bands due to adsorbed NH_3. After subtraction the spectra remain positive, except for the band at 1070 cm^{-1} due to Al-coordinated linear nitrite (1) which is probably removed from the surface by NH_3. Bands are observed due to NH_4^+ ions (1400, 1456, 1488, and 1687 cm^{-1}) and amide species (shoulder 1500–1530 cm^{-1}), together with some bands of bidentate nitrates (shoulder 1555 cm^{-1}) and bridged nitrates (1623 cm^{-1}) which still grow as a function of time due to surface transformation from less stable nitrites (1). The fact that hardly any coordinated NH_3 is observed at the surface provides additional evidence that these species are
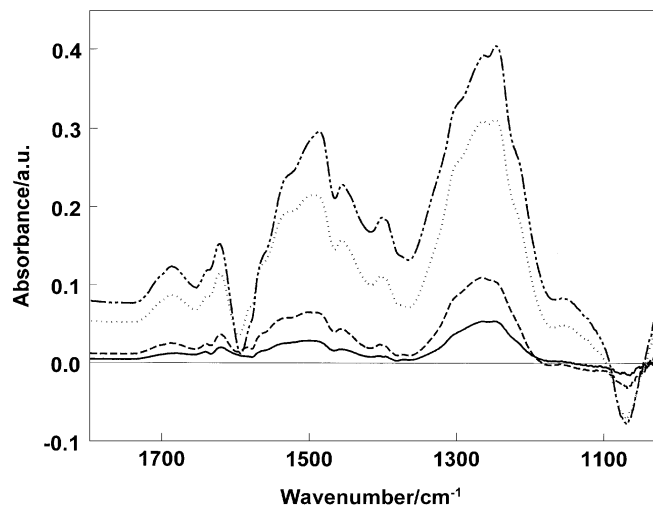
the first to react in the SCR reaction with unstable surface nitrites.

DISCUSSION

Nature of the Active NH_3 Species

In the preceding paper (1) it was shown that NH_3 adsorbs on both Lewis acid and Brønsted acid sites on low loaded Mn/Al_2O_3 catalysts at 323 K, resulting in coordinated NH_3 and NH_4^+ ions, respectively. Moreover, NH_2 species are present due to H-abstraction from coordinated NH_3. The coordinated NH_3 and NH_2 species are present both at Mn^{3+} and Al^{3+} sites, whereas the NH_4^+ ions are predominantly observed on the Al_2O_3 support (1). The FTIR results presented above clearly show that upon admission of O_2 and NO at the reaction temperature (423 K) coordinated NH_3 species react to form NH_2 species. In contrast, the amount of NH_4^+ ions even increases during the course of the reaction; therefore, a SCR pathway starting from these species is very unlikely. The increase of the amount of NH_4^+ may be due to the formation of additional surface hydroxyls as result of H_2O production by the SCR reaction. Interestingly, H-abstraction is hardly observed at 323 K, although the SCR reaction proceeds at a significant rate upon $NO + O_2$ adsorption on a sample precovered with NH_3, as demonstrated by both TPRD (Fig. 3) and FTIR (Fig. 10). Apparently, H-abstraction is difficult at low temperatures, but amide species react readily, once formed. On the other hand, at 423 K the relative amount of NH_2 increases considerably (as observed by IR), showing that H-abstraction is an activated process. At this temperature the reaction of amide species to N_2 and H_2O is no longer faster than the formation of amide species. As a result, the amide species are more clearly detected in IR. The results agree with the picture of NH_3 adsorption and reaction on CuO/Al_2O_3 by Centi *et al.* (9). These authors also propose the SCR reaction to proceed *via* an amide intermediate, but the activated formation of this species is only observable in IR at higher temperatures. On CuO/TiO_2 systems, studied by Ramis *et al.* (10), NH_3 transformation to NH_2 is hardly observable at 323 K, whereas a strong NH_2 peak in IR is found at 423 K. The fact that these catalysts do not exhibit any Brønsted acidity was used as evident proof that a SCR reaction pathway starting from coordinated NH_3 is plausible.

Our results indicate that on the surface of MnO_x/Al_2O_3, where both coordinated NH_3 and NH_4^+ ions with comparable thermal stabilities are present, a SCR reaction pathway starting from coordinated NH_3 is operative in the low temperature range.

SCR Reaction via Langmuir–Hinshelwood (LH) vs Eley–Rideal (ER) Mechanism

There is general agreement that the SCR reaction starts with NH_3-adsorption; the adsorption is very strong

FIG. 11. Adsorption of 0.5 mbar (———), 1 mbar (– – –), 2 mbar (⸱⸱⸱⸱⸱⸱⸱⸱⸱) and 3 mbar (— – –) NH_3 at 323 K on a sample precovered with NO and O_2; 2 wt% Mn/Al_2O_3. Spectra after $NO + O_2$ adsorption and subsequent evacuation are subtracted.

compared to the adsorption of both NO and the reaction products and, as a result, the reaction order with respect to NH$_3$, determined in kinetic studies, is zero for most SCR catalysts. In contrast, there is no agreement on the way the reaction continues: by (1) reaction of gas phase NO with (activated) NH$_3$ to an activated transition state and subsequent decomposition in N$_2$ and H$_2$O, or (2) adsorption of NO on adjacent sites, followed by reaction to an activated transition state and decomposition to the reaction products.

In part I of this study (1) it was shown that at 423 K, NO adsorbs in the presence of O$_2$ on MnO$_x$/Al$_2$O$_3$ as linear, bridged, and monodentate nitrites and bridged and bidentate nitrates. The TPRD in NH$_3$ after adsorption of NO and O$_2$ (Fig. 2) shows that the SCR reaction starts as soon as part of the weakly adsorbed NO species (nitrites) has been desorbed. The N$_2$ produced below 470 K originates from weakly adsorbed NO, but it is difficult to determine whether reaction takes place from the gas phase after forced desorption or directly from an adsorbed state. On the other hand, the fact that strongly bound NO complexes (bridged and bidentate nitrates) which decompose at 600 K (1), can react with adsorbed NH$_3$ to N$_2$ at 500 K (Fig. 2) provides evidence that these nitrates react *via* a LH mechanism.

If it is assumed that the SCR reaction proceeds at one type of Mn^{3+} site, the instantaneous N$_2$ production upon NO and O$_2$ admission on a surface saturated by NH$_3$ (Fig. 3) strongly suggests a reaction of gas phase NO. If the reaction proceeds exclusively by a LH mechanism the initiation of the SCR reaction would require some NH$_3$ desorption, which is not observed. Moreover, a gradually increasing reaction rate is expected due to the increasing NO coverage until exhaustion of adsorbed NH$_3$ species becomes rate limiting. On the other hand, if only an ER mechanism is operative, one expects that the N$_2$ production rate reaches a maximum directly upon NO and O$_2$ admission (when both concentration of adsorbed NH$_3$ and gas phase NO are maximal) and declines monotonically as adsorbed NH$_3$ species become exhausted. In contrast, after a sharp initial rise the *observed* reaction rate increases gradually for a significant period before slowing down. Based on this "one site assumption" the observed response to NO + O$_2$ admission is clearly *in-between* the expected response for a LH and an ER mechanism, suggesting that both are operative at this low temperature. However, if it is assumed that the sites at which NH$_3$ and NO adsorb are (partly) different, the observed response in Fig. 3 can be completely explained by a quick adsorption of NO on sites which are unoccupied by NH$_3$, followed by a rapid reaction to N$_2$, thus only *via* a LH mechanism.

The step-response experiment presented in Fig. 9 is considered to be decisive whether an ER mechanism is operative or not. At the point prior to admission of NH$_3$ and ^{15}NO, the surface is completely covered by ^{14}NO; all types of nitrites and nitrates reported in the previous paper (1)

are expected to be present. Upon admission of NH$_3$ and ^{15}NO, NH$_3$ is expected to be able to remove some ^{14}NO containing nitrites from the surface as it is the stronger adsorbent (compare Figs. 2, 5, and 6). ^{15}NO is not expected to adsorb at the surface; some exchange with adsorbed ^{14}NO may be possible, but only at a slow rate ($T = 423$ K). The fact that an instantaneous reaction to N^{15}N is observed at a significant rate is considered to provide conclusive evidence for an ER reaction pathway. As a result, there is no need to assume two different active species to explain the N$_2$ production in Fig. 2. ^{14}N$_2$ is produced as well upon the switch NO + O$_2$ $\Rightarrow$ ^{15}NO + NH$_3$ + O$_2$, be it in lower amounts. Part of the produced ^{14}N$_2$ can result from ^{14}NO that is forced to desorb upon NH$_3$ addition. However, the fact that the production continues for several hours is indicative for a continuous contribution of a LH reaction pathway to the total N$_2$ production. These results are in agreement with the reaction order with respect to NO smaller than one, as determined from kinetic studies (11). The fraction of adsorbed NO reacts quickly *via* a LH mechanism as the coverage of reactive NO species is low under standard reaction conditions (see Fig. 5).

Interestingly, a previous study (11) showed that the formation of nitrites is strongly inhibited by the adsorption of H$_2$O and that the reaction order in NO changes from 0.8 under "dry" conditions to about one in the presence of H$_2$O. These results can nicely be explained by blocking of the LH pathway by chemisorbed H$_2$O.

The infrared experiments did not unequivocally point towards one reactive nitrite intermediate at low temperatures. Linear nitrites disappear upon adsorption of NH$_3$ (Fig. 11), but in the preceding paper (1) it was shown that these nitrites are only present at the Al$_2$O$_3$ area of low loaded Mn/Al$_2$O$_3$ catalysts. The fact that bridged nitrites can be formed on the surface at 323 K aside NH$_3$ species (Fig. 10) and react upon heating up to 423 K strongly suggests that this species is reactive under standard reaction conditions.

The occurrence of a LH mechanism has been previously shown on a α-Cr$_2$O$_3$ catalyst (28) on the basis of TPD after co-adsorption of ^{15}NO and NH$_3$ at room temperature. The production of high amounts of N^{15}N during heating demonstrated adsorbed NO to be a reactive intermediate. Kantcheva *et al.* (22) for their V$_2$O$_5$/TiO$_2$ catalysts came to the conclusion that a LH mechanism was operative in the NH$_3$–NO$_2$ reaction on the basis of IR results. However, most of the SCR studies on V$_2$O$_5$/TiO$_2$ catalysts propose a reaction between adsorbed NH$_3$ and gaseous, or very weakly bound NO (4–7, 10, 12–16, 18). It must be pointed that in some of these publications (15, 18) the possibility of a LH mechanism was rejected simply by the fact that hardly any NO adsorption was observed in the *absence of O$_2$*. The present study on MnO$_x$/Al$_2$O$_3$ proves that this is a very dangerous criterion to use.

It is very remarkable that in all these studies the possibility of parallel LH and ER pathways has not been addressed. Recently, competition of both reaction mechanisms was proposed for CuO/Al_2O_3 catalysts (26). The similarities between the reported conclusions and the observations in the present study are striking: the SCR reaction proceeds for a considerable part *via* an ER mechanism, but the LH pathway contributes to a certain extent to the total N_2 production. The latter reaction is believed to proceed between nitrite species and amides. The exact nature of the active nitrite has not been singled out by the authors in (26), whereas this study suggests bridged nitrites to be the main nitrite source in a LH pathway.

Role of Oxygen in the SCR Reaction Cycle

In the introduction three possible contributions of O_2 with respect to the SCR reaction are mentioned. The relevance of these possible roles can be discussed according to the results presented.

In many studies, both on chromia (28) and V_2O_5 based catalysts (4, 5, 7, 18, 28, 34, 35), the role of O_2 is proposed to be the reoxidation of the surface. On both systems, kinetic studies (36–38) show the reaction to be zero order in O_2 at concentrations above 0.5–1 vol%. Moreover, the reaction to N_2 continues, be it at a much lower rate, after removing O_2 from the reaction mixture. These phenomena are explained by the fact that lattice oxygen can participate in the reaction in the absence of O_2. The reaction rate is lowered due to the increasing amount of oxygen vacancies, but continues to some extent because NO can, be it at a lower rate than O_2, reoxidise the surface as well. As the reaction is studied on these systems at 523–673 K, this participation of lattice oxygen is in agreement with the reports on Mars and Van Krevelen mechanisms (39, 40), operative in the 500–800 K temperature window.

The results on MnO_x/Al_2O_3 differ at several points from the above-mentioned catalysts. First, this catalyst is active for the SCR reaction at temperatures below 473 K, thus making Mars and Van Krevelen type mechanisms very unlikely. Second, in kinetic studies (11) a reaction order in O_2 of about 0.5 has been determined in the concentration range 0–10 vol% O_2. Third, the N_2 production quickly decreases to almost zero upon removal of O_2 from the gas stream (Fig. 8); the N_2/Mn ratio is not higher than 0.03 after this switch. As we know that the surface coverage of NH_3 on the verge of switching is high enough to establish N_2/Mn ratios close to one (Fig. 6, Table 3), the role of O_2 must be the activation of one of the reactants at the surface (or both). If the function of O_2 would simply be the reoxidation of the surface the N_2 production would proceed until every adsorbed NH_3 molecule had reacted. Then, a lack of oxidised sites to begin a new catalytic cycle (starting with NH_3 adsorption) would stop the reaction. In part I of this study (1) it was shown that O_2 has a strong positive influ-

ence on the adsorption of NO as nitrites and nitrates. In this paper we demonstrated that the SCR reaction partly proceeds *via* a LH mechanism and that bridged and monodentate nitrites are reactive intermediates at temperatures below 473 K. Besides, it has been shown that under reaction conditions at 423 K few reactive nitrites are present at the surface, indicating that these nitrites quickly react once formed. As a result, for the N_2 produced *via* a LH mechanism the response to withdrawal of O_2 can be explained by an instantaneous deficiency of reactive nitrites. An important role of O_2 to assist in the formation of reactive NO complexes was proposed on other SCR catalysts like Ce-HMOR catalysts (29) and CuO/Al_2O_3 catalysts (26, 41).

The results in this study show that the larger part of the produced N_2 is formed *via* the parallel ER pathway. Hence, formation of reactive nitrites cannot be the only role of O_2 as the ER reaction pathway is also immediately blocked (Fig. 8). By consequence, activation of the other reactant (NH_3) appears to be dependent on reactive oxygen species at the surface. In the previous paper (1) it was shown that O_2 hardly changes the relative distribution of adsorbed NH_3 species at 323 K, whereas the present results show a considerable H-abstraction rate at 423 K in the presence of both NO and O_2. Hence, an indirect role of NO in the H-abstraction reaction cannot be excluded. Possibly, H-abstraction is an equilibrium which is drawn to the side of NH_2 species due to the reaction of NO with these NH_2 species. According to this equilibrium, it can be explained that IR results at 323 K show only a small amount of NH_2 species, whereas a high initial reaction rate is observed at this temperature when NO and O_2 are added to a surface with preadsorbed NH_3 (Fig. 3).

For $Cu_3V_2O_8$ SCR catalysts (42), it has been proposed that O_2 facilitates both H-abstraction from adsorbed NH_3 and formation of reactive NO-complexes. Probably, oxygen plays a comparable role in the transformation of coordinated NH_3 to NH_2 species at the start of the catalytic cycle (see the discussion above). Upon removal of O_2 from the gas stream the NH_3 activation step is blocked, resulting in instantaneous termination of the N_2 production *via* the ER pathway.

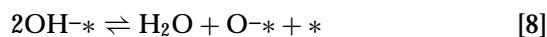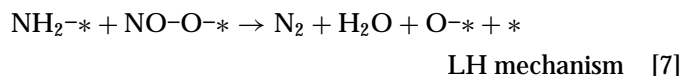### Deactivating Effect of Bidentate and Bridged Nitrates

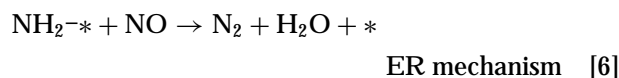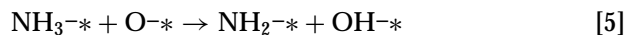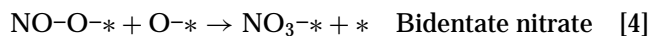The results presented here show a deactivation of the 2 wt% Mn/Al_2O_3 catalyst under reaction conditions at 423 K, until a constant reaction rate is established after approximately 150 h (Fig. 1). Moreover, a comparable deactivation of the catalyst proceeds during a treatment of 9 h in NO and O_2 at this temperature (Fig. 6). TPD of the deactivated catalysts (Fig. 7) shows that stable NO complexes are responsible for this deactivation. In the previous paper (1) these NO complexes, with high thermal stability, were already identified as bridged nitrates and (mainly) bidentate nitrates. These species are readily formed at 423 K

in a NO + O$_2$ mixture, but only at a very slow rate in a NO + NH$_3$ + O$_2$ mixture, due to the strong adsorption properties of NH$_3$. Moreover, not all catalytic sites are blocked by nitrate formation, as the residual NO conversion remains significant.

The TPRD results of Fig. 3 show that at temperatures above 500 K these nitrates are able to react with adsorbed NH$_3$ to N$_2$ and H$_2$O. The reactivity is confirmed by the additional step-response experiment in which NH$_3$ is removed from the reaction mixture at 523 K and reintroduced after 9 h: the deactivation observed at 423 K is absent at 523 K. By consequence, bidentate nitrates, which are thermally stable up to 650 K, are able to deactivate the surface at temperatures below 500 K, whereas they act as active SCR intermediates at temperatures above 500 K. This discrepancy in the role of bidentate nitrates with respect to the SCR reaction has rarely been reported previously. On CuO/Al$_2$O$_3$ (26), Centi *et al.* demonstrated that formation of bidentate and bridged nitrates on the surface lowered the activity for NH$_3$ oxidation. In a subsequent paper (41), they demonstrated how bidentate nitrates, formed from the surface oxidation of nitrites, cause a self-deactivation of the catalyst for the SCR reaction. However, they did not investigate the effect of the temperature on the role of nitrates; therefore, they did not report on possible reactivity of these nitrates at higher temperatures.

Catalytic Cycle of the SCR Reaction

According to the preceding discussion on the SCR reaction mechanism on MnO$_x$/Al$_2$O$_3$ catalysts the following reaction scheme can be formulated for temperatures below 500 K:

$$O_2 + 2* \rightleftharpoons 2O\text{-}* \tag{1}$$

$$NH_3 + * \rightleftharpoons NH_3\text{-}* \quad \text{Lewis acid Mn}^{3+} \text{ site} \tag{2}$$

$$NO + O\text{-}* \rightleftharpoons NO\text{-}O\text{-}*$$
$$\text{Bridged and monodentate nitrites} \tag{3}$$

$$NO\text{-}O\text{-}* + O\text{-}* \rightarrow NO_3\text{-}* + * \quad \text{Bidentate nitrate} \tag{4}$$

$$NH_3\text{-}* + O\text{-}* \rightarrow NH_2\text{-}* + OH\text{-}* \tag{5}$$

$$NH_2\text{-}* + NO \rightarrow N_2 + H_2O + *$$
$$\text{ER mechanism} \tag{6}$$

$$NH_2\text{-}* + NO\text{-}O\text{-}* \rightarrow N_2 + H_2O + O\text{-}* + *$$
$$\text{LH mechanism} \tag{7}$$

$$2OH\text{-}* \rightleftharpoons H_2O + O\text{-}* + * \tag{8}$$
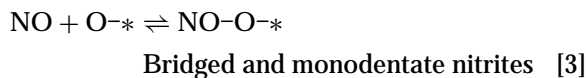
At temperatures above 500 K bidentate nitrates are also able to react to N$_2$. The reaction steps [6] and [7] run parallel, but the major part of the N$_2$ is produced *via* step [6]. Possibly, step [5] can be written as an equilibrium. Further

modelling of steady state kinetic data on the basis of this scheme will be performed in the near future.

CONCLUSIONS

In the preceding paper (1) the nature of the surface compounds, formed upon separate low temperature adsorption of NO and NH$_3$ in the presence of O$_2$ on MnO$_x$/Al$_2$O$_3$ catalysts, has been identified. In this paper, the reactivity of these complexes with respect to the selective catalytic reduction of NO at temperatures below 473 K has been evaluated. The following conclusions can be drawn.

The SCR reaction starts with the transformation of coordinated NH$_3$ on Mn^{3+} ions to NH$_2$ species. Ammonium ions formed on Brønsted acid sites do not react at the reaction temperature in the presence of NO and O$_2$.

At temperatures below 473 K, the N$_2$ production exclusively results from a 1:1 reaction between NO and NH$_3$. The SCR reaction can proceed between adsorbed NH$_2$ species with both NO from the gas phase (Eley–Rideal mechanism) and adsorbed nitrite species (Langmuir–Hinshelwood mechanism). Labelling studies showed that N$_2$ is simultaneously produced by both parallel pathways. Bridged nitrites and, to a lesser extent, monodentate nitrites are able to react with NH$_2$ at temperatures below 473 K. These nitrites react very quickly once formed, resulting in a low nitrite coverage of the surface under reaction conditions.

Lattice oxygen cannot participate in the SCR reaction in the absence of gas phase O$_2$ over MnO$_x$/Al$_2$O$_3$ catalysts. Therefore, the role of O$_2$ in the catalytic scheme cannot exclusively be explained by reoxidation of the surface. As far as an ER mechanism is operative, the main role of O$_2$ is H-abstraction from adsorbed NH$_3$, resulting in NH$_2$ species. In the parallel LH pathway O$_2$ assists in both H-abstraction of NH$_3$ and the formation of reactive nitrite intermediates.

In a NH$_3$/NO/O$_2$ mixture bidentate nitrates are formed on the surface at a slow rate at temperatures below 500 K, thus partly deactivating the catalyst. In contrast, at higher temperatures these species serve as active SCR intermediates.

REFERENCES

1. Kijlstra, W. S., Brands, D. S., Poels, E. K., and Bliek, A., *J. Catal.* **170**, No. 2 (1997).
2. Kapteijn, F., Singoredjo, L., Van Driel, M., Andreini, A., Moulijn, J. A., Ramis, G., and Busca, G., *J. Catal.* **150**, 105 (1994).
3. Kijlstra, W. S., Poels, E. K., Bliek, A., Weckhuysen, B. M., and Schoonheydt, R. A., *J. Phys. Chem. B* **101**, 309 (1997).

4. Topsøe, N.-Y., *Science* **265**, 1217 (1994).

5. Topsøe, N.-Y., Dumesic, J. A., and Topsøe, H., *J. Catal.* **151**, 241 (1995).

6. Wachs, I. E., Deo, G., Weckhuysen, B. M., Andreini, A., Vuurman, M. A., De Boer, M., and Amaridis, M., *J. Catal.* **161**, 211 (1996).

7. Ramis, G., Busca, G., Bregani, F., and Forzatti, P., *Appl. Catal.* **64**, 259 (1990).

8. Ramis, G., Li, Y., and Busca, G., *Catal. Today* **28**, 373 (1996).

9. Centi, G., Perathoner, S., Biglino, D., and Giamello, E., *J. Catal.* **151**, 75 (1995).

10. Ramis, G., Li, Y., Busca, G., Turco, M., Kotur, E., and Willey, R. J., *J. Catal.* **157**, 523 (1995).

11. Kijlstra, W. S., Daamen, J. C. M. L., Van de Graaf, J. M., Van der Linden, B., Poels, E. K., and Bliek, A., *Appl. Catal. B: Environ.* **7**, 337 (1996).

12. Rajadhyaksha, R. A., and Knözinger, H., *Appl. Catal.* **51**, 81 (1989).

13. Gasior, M., Haber, J., Machej, T., and Czeppe, T., *J. Mol. Catal.* **43**, 359 (1988).

14. Schneider, H., Tschudin, S., Schneider, M., Wokaun, A., and Baiker, A., *J. Catal.* **147**, 5 (1994).

15. Ozkan, U. S., Kunthekar, M. W., and Cai, Y. P., *Ind. Eng. Chem. Res.* **33**, 2924 (1994).

16. Efstathiou, A. M., and Fliatoura, K., *Appl. Catal. B: Environ.* **6**, 35 (1995).

17. Miyamoto, A., Kobayashi, K., Inomata, M., and Murakami, Y., *J. Phys. Chem.* **86**, 2945 (1982).

18. Inomata, M., Miyamoto, A., and Murakami, Y., *J. Catal.* **62**, 140 (1980).

19. Arakawa, T., Mizumoto, M., Takita, Y., Yamazoe, N., and Seiyama, T., *Bull. Chem. Soc. Jpn.* **50**, 1431 (1977).

20. Tagaki-Kawai, M., Soma, M., Onishi, T., and Tamaru, K., *Can. J. Chem.* **58**, 2132 (1980).

21. Takagi-Kawai, M., Soma, M., Onishi, T., and Tamaru, K., *J. Catal.* **50**, 441 (1977).

22. Kantcheva, M., Bushev, V., and Klissurski, D., *J. Catal.* **145**, 96 (1994).

23. Duffy, B. L., Curry-Hyde, H. E., Cant, N. W., and Nelson, P. F., *J. Phys. Chem.* **98**, 7153 (1994).

24. Dines, T. J., Rochester, C. H., and Ward, A. M., *J. Chem. Soc. Faraday Trans.* **87**, 1473 (1991).

25. Komatsu, T., Ogawa, T., and Yashima, T., *J. Phys. Chem.* **99**, 13053 (1995).

26. Centi, G., and Perathoner, S., *J. Catal.* **152**, 93 (1995).

27. Schneider, H., Scharf, U., Wokaun, A., and Baiker, A., *J. Catal.* **147**, 545 (1994).

28. Niiyama, H., Murata, K., Can, H. V., and Echigoya, E., *J. Catal.* **62**, 1 (1980).

29. Ito, E., Lugt, P. M., Burgers, M. H. W., Rigutto, M. S., Van Bekkum, H., and Van den Bleek, C. M., *Appl. Catal. B: Environ.* **4**, 95 (1994).

30. Kapteijn, F., Van Langeveld, A. D., Moulijn, J. A., Andreini, A., Vuurman, M. A., Turek, A. M., Jehng, J.-M., and Wachs, I. E., *J. Catal.* **150**, 94 (1994).

31. Singoredjo, L., Slagt, M., Van Wees, J., Kapteijn, F., and Moulijn, J. A., *Catal. Today* **7**, 157 (1990).

32. Bijsterbosch, J. W., Van Langeveld, A. D., Kapteijn, F., and Moulijn, J. A., *Vibr. Spectr.* **4**, 245 (1993).

33. Pinaeva, L. G., Suknev, A. P., Budneva, A. A., Paukshtis, E. A., and Bal'zhinimaev, B. S., *J. Mol. Catal. A: Chem.* **112**, 115 (1996).

34. Ozkan, U. S., Cai, Y., and Kunthekar, M. W., *J. Catal.* **149**, 390 (1994).

35. Lietti, L., Forzatti, P., and Berti, F., *Catal. Lett.* **41**, 35 (1996).

36. Inomata, M., Miyamoto, A., Ui, T., Kobayashi, K., and Murakami, Y., *Ind. Eng. Chem. Prod. Res. Dev.* **21**, 424 (1982).

37. Duffy, B. L., Curry-Hyde, H. E., Cant, N. W., and Nelson, P. F., *Appl. Catal. B: Environ.* **5**, 133 (1994).

38. Tuenter, G., Van Leeuwen, W. F., and Snepvangers, L. J. M., *Ind. Eng. Chem. Prod. Res. Dev.* **25**, 633 (1986).

39. Nováková, J., *in* "Catalysis Reviews" (H. Heinemann, Ed.), Vol. 4, p. 77. Dekker, New York, 1971.

40. Boreskov, G. K., *Disc. Faraday Soc.* **41**, 263 (1966).

41. Centi, G., and Perathoner, S., *Catal. Today* **29**, 117 (1996).

42. Yoshida, S., Ueda, A., and Tarama, K., *Ind. Eng. Chem. Prod. Res. Dev.* **18**, 283 (1979).