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Journal of Catalysis 225 (2004) 466–478
JOURNAL OF CATALYSIS
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Low-temperature ammonia oxidation on platinum sponge studied with positron emission profiling

D.P. Sobczyk,[a] J. van Grondelle,[a] P.C. Thüne,[a] I.E. Kieft,[b] A.M. de Jong,[b,*] and R.A. van Santen[a]

[a] *Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Department of Applied Physics, Centre of Plasma and Radiation Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Received 12 November 2003; revised 26 April 2004; accepted 26 April 2004

Abstract

The low-temperature deactivation of a platinum sponge catalyst used for ammonia oxidation was studied with the positron emission profiling technique (PEP). Evidence that irreversibly adsorbed nitrogen species deactivate the catalyst is presented. Two reactivity regimes are distinguished. Initial fast N_2 production at low surface coverage and a relatively slow N_2 and N_2O production at steady state when the surface is fully covered. The fast deactivation of the platinum sponge is mainly caused by adsorbed nitrogen species. The formation of PtO is relatively slow compared to surface nitride. The fast initial deactivation of platinum sponge by nitrogen and oxygen species is greatly retarded at temperatures above 388 K. Temperature-programmed reaction together with temperature-programmed desorption experiments show reactivation of the catalyst above this temperature.

Keywords: $^{13}NH_3$; $^{15}O_2$; Positron emission profiling; Ammonia oxidation; Deactivation; Platinum; Platinum sponge; Low temperature

1. Introduction

The study of low-temperature ammonia oxidation to nitrogen and water has become of increasing interest due to the need to clean agricultural and industrial waste streams. The need for purification of ammonia slip streams from industrial processes, like the SCR [1] and soda process, was an impulse to start efforts to convert ammonia into harmless products. Platinum-based catalysts are promising in the conversion of gaseous ammonia to harmless N_2 and H_2O at relatively low temperatures. They have a high activity and selectivity for N_2 formation [2–4]. However, the most important drawback of platinum-based catalysts is their fast deactivation.

Gas-phase ammonia oxidation over platinum catalysts at low temperatures has been extensively studied before. Experiments done at ultralow pressure on platinum crystals with different techniques, like SIMS, AES, LEED, EELS, TPD, and TPR, showed the formation of NO, N_2, and H_2O [5–8]. The selectivity toward nitrogen products depends mainly on the temperature and ammonia/oxygen ratio. $NO_{(a)}$ plays a key role in the product formation. However, as Bradley et al. stated [8], at temperatures below 400 K a route for the N_2 formation is opened, which does not involve an $NO_{(a)}$ intermediate. Other reported species present on the surface are $NH_{(a)}$, $O_{(a)}$, and $OH_{(a)}$. The reaction pathways change greatly with the pressure. At atmospheric pressure and low temperature the main products are N_2 and H_2O with N_2O as a by-product. NO is formed at a temperatures of 573 K and higher [2]. IR experiments done by Matyshak et al. suggested that the platinum surface is mainly covered with nitrogen species [9]. TPD, TPR, and XPS studies showed that after a steady-state condition was reached NH and OH species were the main intermediates present at the catalyst's surface [3]. At atmospheric pressure, the role of $NO_{(a)}$ is only attributed to the production of the by-product, N_2O. The mechanism of fast initial deactivation of the platinum catalysts has not been studied extensively. In the 1970s Ostermaier et al. proposed that the initial deactivation of

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[*] Corresponding author.
E-mail address: a.m.de.jong@tue.nl (A.M. de Jong).

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doi:10.1016/j.jcat.2004.04.035

platinum supported on alumina is caused mainly by PtO formation [10,11].

In this paper new insights into the ammonia oxidation mechanism are presented. A previous paper reported on the ammonia adsorption step in the ammonia oxidation [12]. This study is also focused on the deactivation of platinum. First, the conversion and product formation in the ammonia oxidation over the platinum sponge catalyst are presented as a function of temperature. Here, we will demonstrate with positron emission profiling (PEP) experiments that below 413 K the catalyst deactivates due to poisoning of the catalyst surface, mainly by nitrogen species. In addition, the nature of the deactivating species is further investigated with X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and oxidation (TPO). Experiments with NO and N_2O pulses, and with preoxidized platinum sponge provide complementary information on the mechanism of the ammonia oxidation. Finally, we discuss a reaction mechanism of the ammonia oxidation over platinum at low temperatures.

2. Experimental

2.1. Catalytic reactor

The platinum sponge was acquired from Johnson Matthey. The sponge sample was of $> 99.9\%$ purity. The particle size of the sponge was between 250 and 350 µm and the size of the small nonporous particles about 1.0–5.0 µm. The amount of platinum sites calculated from BET measurements is 3.0×10^{18} sites/g and via hydrogen chemisorption 1.3×10^{18} sites/g. The metal surface area is determined with BET to be 0.099 m^2/g. Catalytic tests were performed in a fixed-bed reactor setup equipped with a quadrupole mass spectrometer (Balzers Instruments Omnistar GSD 3000), which was calibrated for on-line analysis of reactants and products. A quartz tube with an internal diameter of 4 mm was used as the reactor. For the experiments a sample of 1.8 g of pure platinum sponge was used in a catalytic bed with a length of 4.0 cm. The experiments were done at temperatures between 323 and 673 K.

Before each experiment the platinum sponge was in situ reduced by heating the sample in a 10 vol% H_2/He flow (40 cm^3/min) from 298 to 673 K. Subsequently the sample was kept at this temperature for 2 h. Then the catalyst was flushed with He for 20 min before the reaction temperature was set.

A preoxidized platinum sponge is obtained in the following way. The reduced catalyst was pretreated with a 1 vol% O_2/He flow (46.5 cm^3/min) for 1 h at 373 K. Oxygen adsorbs dissociatively at this temperature [13–17]. Then the catalyst was flushed with He (46.5 cm^3/min) for 1 h before the reaction temperature was set.

2.2. Steady-state experiments

A reaction mixture was used consisting of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 46.5 cm^3/min. Conversion rates were calculated from the measured concentrations, $(C_{in} - C_{out})/C_{in}$. The steady-state experiments were performed in the temperature range of 413–573 K.

2.3. Positron emission profiling

The Eindhoven 30 MeV cyclotron was used to produce ^{13}N and ^{15}O nuclei. ^{13}N was produced via irradiation of a water target with highly energetic protons of 16 MeV. The irradiation time was 10 min and a typical beam current of 500 nA was used. The target was a flowthrough water target, with a total volume of 7 ml containing a dual foil (Duratherm 600, thickness 15 µm). In this way formed [^{13}N]nitrate and [^{13}N]nitrite were subsequently reduced to $^{13}NH_3$, using DeVarda's alloy method [18,19]. The production method of gaseous pulses of [^{13}N]NH_3 is described elsewhere [20].

To produce labeled oxygen ($^{15}O^{16}O$ written as [^{15}O]O_2), a nitrogen gas target (75 ml/min) at a pressure of 4 bar was continuously irradiated with 9.2 MeV deuterons (500 nA) [21,22]. The irradiated effluent was remotely transported from the target vault into the PEP laboratory. The labeled effluent was transported to a GC passing first sodalime and activated charcoal absorbers to remove by-products of the irradiation. A pulse time of 3–10 s was used to inject [^{13}N]NH_3 or [^{15}O]O_2 into the reactant stream. The concentration of radiolabeled molecules varies in each pulse and thus the absolute concentration of radiolabeled molecules in the various experiments cannot be directly compared. However, the labeled species are either introduced in a large flow of nonlabeled ammonia or as trace amounts in ammonia-free flows. As such, these variations will not affect the results between the various experiments.

The ^{13}N or ^{15}O nuclei emit a positron upon decay. Positron emission profiling is based on the detection of the two 511 keV gamma photons which originate from the annihilation of this positron with an electron. These two 511 keV gamma photons are simultaneously emitted in opposite directions and they travel typically a few centimeters in solid matters. Coincidental detection of the two photons by scintillation detectors (BGO) provides the position of the annihilation. In practice, the tubular reactor is horizontally placed between two arrays (upper and lower) of nine scintillation detectors. In both arrays the detectors were tightly placed, which results in the spatial resolution of 2.9 mm. The average concentration of all radiolabeled molecules within a certain volume (length 2.9 mm) is measured at time intervals of 0.5 s. The measurement of radiolabeled molecules is simultaneous over the total detection length (5 cm), thus within the 17 volume segments. In this way the concentration distribution of radiolabeled molecules can be measured as a function of position and time [23,24].

2.4. PEP pulse experiments

The reduced platinum catalyst was kept under a flow of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 46.5 cm^3/min at 273–573 K (gas hourly space velocity (GHSV) $= 5600\ h^{-1}$). Subsequently, a pulse of $[^{13}N]NH_3$ or $[^{15}O]O_2$ was injected in this reaction flow. The radiolabeled pulse experiments over the platinum and preoxidized platinum sponge were performed in a similar manner.

2.5. XPS

XPS data are obtained with a VG Escalab 200 spectrometer, equipped with an Al-K_α source and a hemispherical analyzer connected to a five-channel detector. Measurements are done at 20 eV pass energy. XP spectra were taken of freshly reduced platinum, and two samples that were used in the ammonia oxidation experiment performed at 323 K, one for 20 s and one for 2 h. All samples were transported to the XP spectrometer in an oxygen-free environment. It was not possible to get a clear O(1s) signal for oxygen on platinum due to the interference with the oxygen signal of the indium foil, which was used to fix the platinum particles to the sample holder.

2.6. Temperature-programmed experiments

Temperature-programmed experiments were performed after the catalyst was deactivated at 323 K. First the catalyst was flushed with He (20 cm^3/min) for 1 h. Next, the temperature was raised with 10 K/min (20 cm^3/min) under He (TPD) or 1.0 vol% O_2/He (TPO) flow or 0.5 vol% NO/He (TP-NO) flow.

3. Results and discussion

3.1. Ammonia oxidation at 323–473 K

Fig. 1 shows the concentration of the formed products (N_2, N_2O, and H_2O) in the ammonia oxidation at 323 and 373 K. The formation of NO was not observed. The detection of the water signal by the mass spectrometer is delayed due to readsorption of water on platinum. Figs. 1A and 1B show two regions, in which the selectivity changes with time. The start of the ammonia oxidation shows a selective formation of nitrogen and water. The second region in the N-product selectivity begins when N_2O evolves. In Fig. 1A this is after 40 s, subsequently N_2 production decreases and N_2O selectivity sharply increases to 16% and decreases in time to 7%. At 373 K the catalyst is highly active longer and the N_2O formation is observed after about 10 min. Concentration profiles for N_2 and N_2O are similar in the temperature range between 323 and 473 K. Initially, only N_2 is formed in this temperature range. At higher temperatures the duration of N_2 formation at a high stable conversion level is greatly extended. It is thought that as the catalyst becomes covered with the reaction intermediates, N_2O evolves (low quantities) and the production of N_2 is strongly reduced. Table 1 presents the initial deactivation time, i.e., the time till the N_2 concentration sharply decreases, in the temperature range 323–473 K. The platinum catalyst possesses a similar high initial activity level at all these temperatures. The initial deactivation time strongly depends on temperature, from 0.6 min at 323 K till 13 min at 373 K. At higher temperatures, however, the deactivation of the catalyst is further retarded. At 398 K the catalyst is deactivated after 16.5 h and at 423 K not even after 24 h time on stream.

To investigate more closely the influence of temperature on the initial deactivation a temperature-programmed reaction experiment is performed (Fig. 2). After the catalyst is deactivated at 373 K, the activity of the catalyst increases at approximately 383 K. The N_2O formation shows an inter-

Table 1
Initial deactivation times for the platinum sponge catalyst

Temperature	Initial deactivation time
323 K	0.6 min
348 K	2.1 min
373 K	13 min
388 K	20 min
423 K	> 20 h

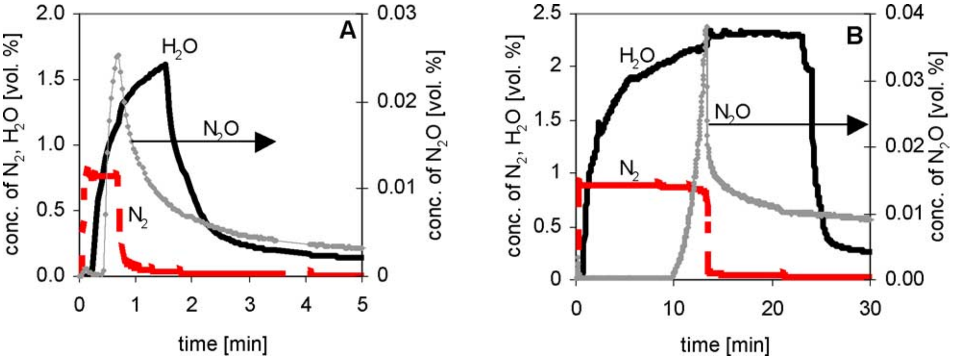

Fig. 1. Concentration of N_2, N_2O, and H_2O versus time for the ammonia oxidation reaction at (A) 323 K, (B) 373 K (GHSV $= 5600\ h^{-1}$, $NH_3/O_2 = 2/1.5$, flow $= 46.5\ cm^3/min$).

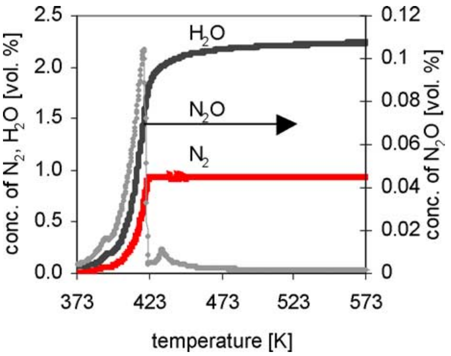

Fig. 2. Ammonia oxidation at 373 K till the catalyst is deactivated followed by a temperature-programmed reaction. TP-reaction part only is shown (10 K/min, GHSV = 5000 h^{-1}, $NH_3/O_2 = 2/1.5$, flow = 46.5 cm^3/min).

esting development. First the concentration of N_2O increases together with N_2 till 413 K and then decreases very fast to a very low concentration. The reactivation behavior of the catalyst is the reverse of the deactivation. Above 413 K production of N_2 is favored above N_2O. Finally, the catalytic activity of the platinum sponge catalyst is restored to its initial value and with similar high selectivity for N_2. Thus, the stable activity of the platinum catalyst above 413 K for a relatively long time suggests that adsorbed species, which deactivate the catalyst at lower temperatures, are not present at the surface.

With respect to initial deactivation of the platinum sponge the conversion of ammonia and oxygen shows an interesting feature. Fig. 3 presents the conversion of both reactants as a function of time at 323 and 373 K. Clearly, as the catalyst is very active in the beginning of the reaction (region 1) both conversions are about 100%. However, as the initial activity of the catalyst rapidly drops, the N_2 concentration decreases (Fig. 1), the conversion of oxygen does not decrease as fast as that of ammonia. In time the conversions of ammonia and oxygen reach the same low conversion level. From the literature it is known that oxygen and ammonia preferentially adsorb on platinum at different sites. Oxygen molecules occupy hollow sites [25–28] whereas ammonia molecules occupy on-top sites [29,30]. NH and NH_2 adsorbates (2-fold); H, O, and N atoms (3-fold) [29]. NO preferentially adsorbs at the fcc hollow site at low coverage, at higher coverage NO additionally adsorbs on the atop site in a tilted geometry [31,32]. Thus, the adsorption of oxygen on platinum should not be completely blocked by ammonia or other surface species. The additional production of water cannot explain this conversion of oxygen, because during the deposition of oxygen the water production is already decreased. We speculate that the formation of subsurface oxygen might be the cause of the slower decrease of the conversion of oxygen or that oxygen adsorbs on the platinum surface without subsequent formation of N_2O and N_2.

3.2. *Positron emission profiling*

The injection of [^{13}N]NH_3 in the reactant flow at the very beginning of the reaction shows in Fig. 4A that ^{13}N-labeled species are formed and adsorbed in front of the catalyst bed (catalyst bed starts at position 1.5 cm). A part of ^{13}N activity went through the total catalyst bed, observed as a thin line of activity during the 10 s of injection time, also at the last positions of the catalyst bed. Since ammonia is initially converted to N_2, the measured activity is gaseous [^{13}N]N_2 (Fig. 1A). Fig. 4A shows that part of the radiolabeled nitrogen species desorb much slower from the catalyst surface, as the slow intensity decrease indicates. A substantial part of the labeled nitrogen species remains adsorbed at the catalyst surface and does not move through the catalyst bed during the measurement time of 30 min. Fig. 4B shows that a labeled oxygen pulse does not remain, in contrast to Fig. 4A, at the catalyst surface. The initial deposition of the O species at the surface is negligible. Oxygen is mainly converted into the gaseous products (water), as conversion of oxygen is very high at that moment. The retention time of water is short, which means that the desorption–readsorption equilibrium of water is fast. This means that water does not compete with ammonia for adsorption sites and thus water does not poison the catalyst surface. This is in line with the results of Van de Broek [33], which showed that the addition of water to the reaction flow does not influence the performance of the catalyst.

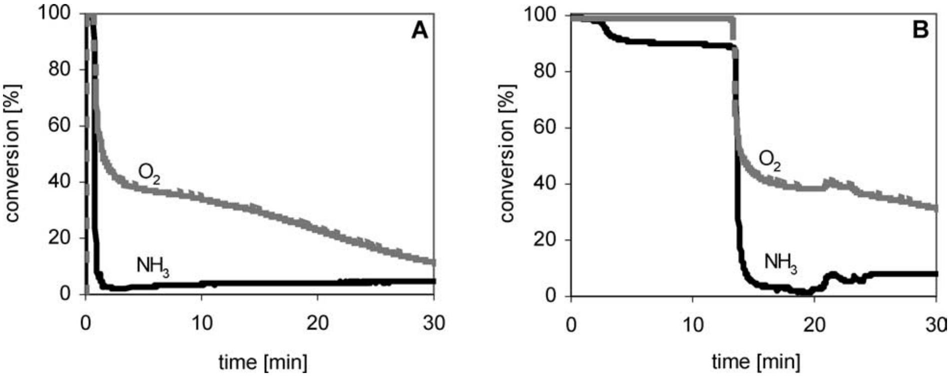

Fig. 3. Conversion of NH_3 and O_2 versus time for the ammonia oxidation reaction at (A) 323 K, (B) 373 K (GHSV = 5600 h^{-1}, $NH_3/O_2 = 2/1.5$, flow = 46.5 cm^3/min).

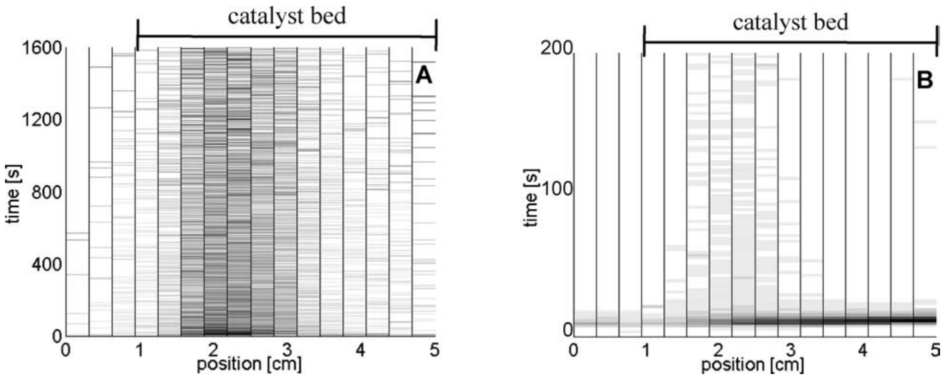

Fig. 4. PEP image of $[^{13}N]NH_3$ and $[^{15}O]O_2$ pulse injection into the reaction stream of NH_3/O_2/He in the first 2 s of the ammonia oxidation. (A) $[^{13}N]NH_3$ PEP image, (B) $[^{15}O]O_2$ PEP image ($T = 323$ K, GHSV $= 5600\ h^{-1}$, $NH_3/O_2 = 2/1.5$, flow $= 46.5\ cm^3/min$). Color intensity represents the concentration of $[^{13}N]NH_3$ or $[^{15}O]O_2$ (dark, high concentration).

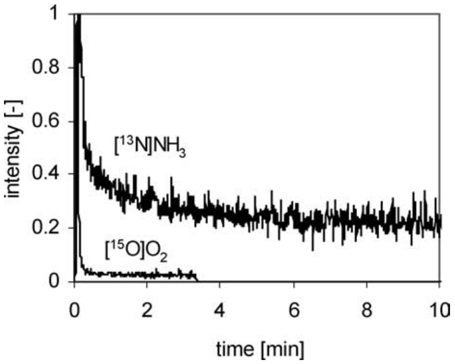

Fig. 5. Normalized sum of radioactivity versus time for $[^{13}N]NH_3$ and $[^{15}O]O_2$ pulse injection into the reaction stream of NH_3/O_2/He in the first 2 s of the ammonia oxidation ($T = 323$ K, GHSV $= 5600\ h^{-1}$, $NH_3/O_2 = 2/1.5$, flow $= 46.5\ cm^3/min$).

Fig. 5 shows the total radioactivity of the nitrogen- and oxygen-containing species adsorbed at the catalyst surface at 323 K. The oxygen containing species do not stay adsorbed at the catalyst, in contrast to the nitrogen species. The ^{13}N profile shows a very fast decrease of the radioactivity in the first 20 s, which is assigned to N_2 formation. A relatively slow decrease of the ^{13}N profile is observed during the 20 to 400 s that reaction is on stream. Fig. 5 clearly shows the injection moment of $^{13}NH_3$ and that after 400 s on stream, a stable amount of ^{13}N activity is left.

To calculate the amount of irreversibly adsorbed N and O species the sum of radioactivity at 5 positions is used. Table 2 shows the amount of the irreversibly adsorbed radiolabeled nitrogen and oxygen species at 323–423 K. With increasing temperatures less nitrogen is deposited on the platinum catalyst and the amount of oxygen deposition is rather stable up to 373 K. The PEP images do not differ too much up to 373 K. As already shown in Fig. 2 the catalyst is very active above 413 K and all ammonia and oxygen are converted to nitrogen and water.

As already stated discussed Fig. 4A, the ammonia oxidation reaction proceeds at the first positions of the catalyst bed. These positions are mainly deactivated with nitrogen species. The high activity of the catalyst is maintained due to the movement of the reaction front to the next positions in the catalyst bed. This is observed, for example, at 323 K when $[^{13}N]NH_3$ is injected at the moment that the reaction was already 20 s on stream (not shown). Thus, in time this deactivation front moves to the end of the catalyst bed, the catalyst is covered with reaction species and the deactivation of the catalyst is observed. An experiment with a half amount of the catalyst also supports this reaction front movement. This experiment showed in the same way the formation and concentration of the products; however, the catalyst remained active for half the time of the normally applied catalyst bed. Thus, below 413 K the catalyst remains initially active because the reaction zone moves to the subsequent bed positions, after the previous positions became fully covered with the adsorbed reaction species.

Injection of a $[^{13}N]NH_3$ or $[^{15}O]O_2$ pulse after the initial deactivation of the catalyst confirmed that the platinum surface is fully covered and that conversion of ammonia and oxygen is low (not shown). Certainly, no significant amount of the nitrogen or oxygen species remains adsorbed at the catalyst surface. A similar behavior was seen after 2 h on stream. This result for $[^{15}O]O_2$ pulses contrasts Fig. 3, as we expected to observe a significant deposition of $[^{15}O]O_2$ on the surface. We cannot explain this obvious difference, especially because both measurements are reliable and reproducible.

Table 2
Percentage of the labeled species remaining at the catalyst after a radiolabeled pulse was injected in the reaction flow at the start of the ammonia oxidation

Temperature (K)	^{13}N remained adsorbed (%)	^{15}O remained adsorbed (%)
323	27 ± 3	3 ± 1
348	16 ± 2	2 ± 1
373	17 ± 2	4 ± 1
423	< 1	< 1

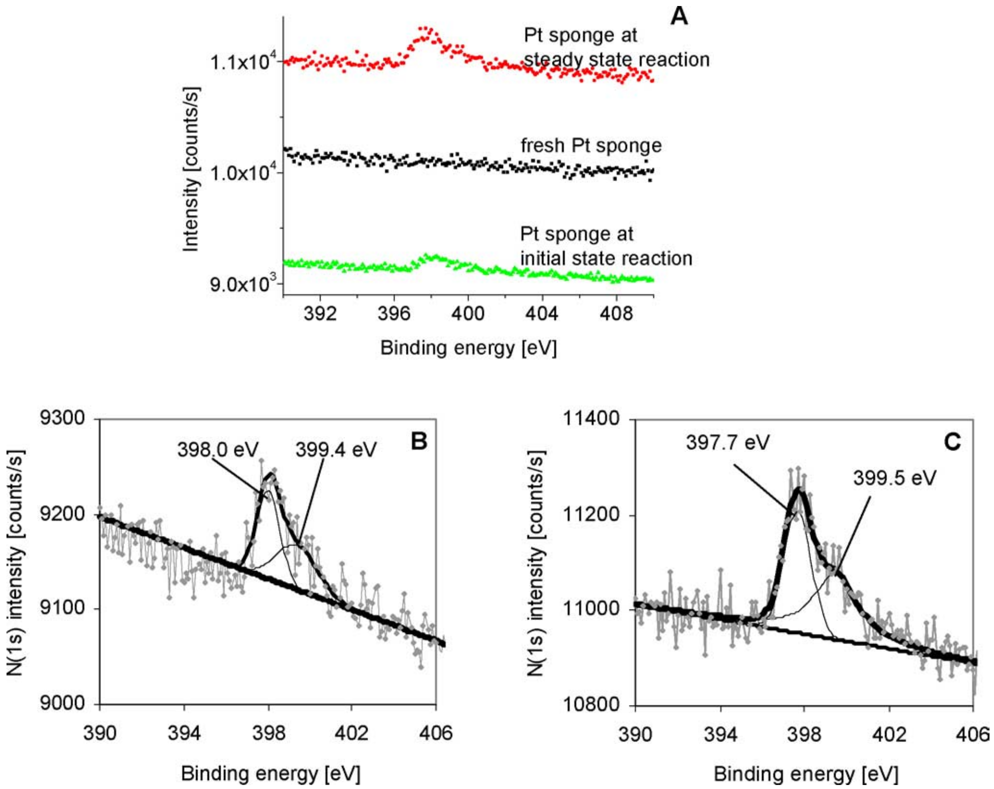

Fig. 6. XP N(1s) spectra of a platinum sponge catalyst. (A) fresh; after 20 s ammonia oxidation on stream (Pt sponge at initial state); and after 2 h on stream (Pt sponge at steady state); (B) enlargement of N(1s) spectrum of Pt sponge at initial state; (C) enlargement of N(1s) spectrum of Pt sponge at steady state.

3.3. Characterization of the adsorbed nitrogen/oxygen species

3.3.1. X-ray photoelectron spectroscopy (XPS)

In this X-ray photoelectron spectroscopy experiment the ammonia oxidation reaction was stopped after respectively 20 s and 2 h on stream and then the reactor was flushed with He. Therefore the gaseous products of the ammonia oxidation are expected to be desorbed from the catalyst surface and should not be present in the XP spectra. The first sample was taken the moment the catalyst started to deactivate showing N_2 and N_2O as the products at a still relatively high conversions. The second sample was taken when the catalyst is totally deactivated showing N_2 and N_2O as the products at very low conversions. Fig. 6A shows the XP-spectra of these samples and a clean background for N(1s) for a reduced platinum sponge.

At the beginning of the N_2 and N_2O formation a broad asymmetric peak is observed, which is centered around 398 eV. The intensity of the N(1s) signal of the deactivated catalyst is higher. The relative number of N(1s) species per platinum area, normalized to indium, is about 35% lower in the initial state of the oxidation than after the total deactivation of the catalyst. The shape of the peak at a binding energy of 398 eV does not change significantly for both experiments as presented in Figs. 6B and 6C. For the N(1s) spectrum at low coverage a symmetric peak was found at a binding energy of 398.0 eV with a small shoulder around 399.4 eV. With higher coverage the symmetric peak was observed at 397.7 eV and the shoulder at 399.5 eV. This result shows similar features to earlier XPS experiments on deactivated platinum sponge performed by Van den Broek et al. [3].

According to Sun et al. [34], the peak at lower binding energy of 398.0 eV is assigned to NH and the peak at higher binding energy to NH_2 species. The BE peaks representing $NO_{(a)}$ [35,36], NH_3 [34,37], N_2 [38], N_2O [39], and atomic nitrogen [40] were not observed in our XP spectra. With respect to the $NO_{(a)}$ this indicates that $NO_{(a)}$ can be only present at very low quantities at the catalyst surface.

3.3.2. Temperature-programmed desorption (TPD)

In the TPD spectrum three products are observed. N_2, N_2O, and H_2O. Fig. 7 shows that N_2O desorbs first, already at 388 K. We assume that N_2 and N_2O are not molecularly bound on the surface at the start of the TPD experiment because it is thermodynamically favorable for N_2 and N_2O to desorb from platinum [41,42]. Then the desorption of N_2O indicates that the reaction of $NO_{(a)}$ with $N_{(a)}$ took place. The amount of produced N_2O is relatively low. This explains the XPS results in which NO was not detected on the platinum surface. Further, Fig. 7 shows that the peak of N_2 has two shoulders with peak maxima at 433 K and at 483 K. Again, water desorption is concomitant with nitrogen desorption. The mass spectrometer signal of water is somewhat delayed due to the longer residence time of water on platinum caused by the readsorption of water as will be shown

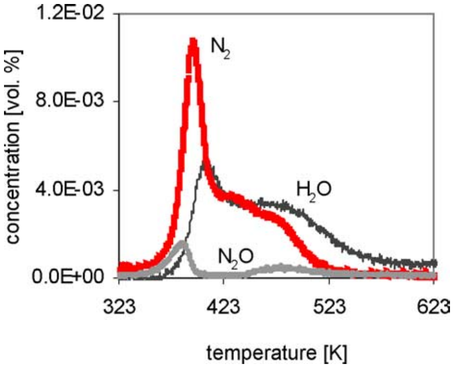

Fig. 7. Formation of N_2, N_2O, and H_2O measured by online mass spectrometry in a temperature-programmed desorption experiment after ammonia oxidation at 323 K (10 K/min, He flow of 40 cm^3/min).

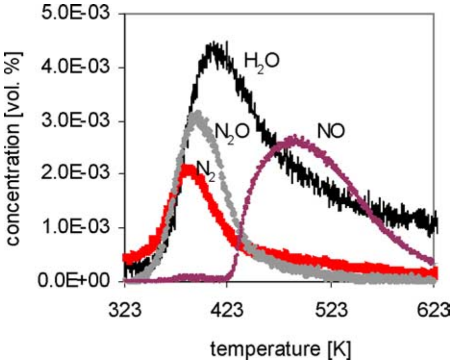

Fig. 8. Formation of N_2, N_2O, and H_2O measured by online mass spectrometry in a temperature-programmed oxidation experiment after ammonia oxidation at 323 K (10 K/min, 1.0 vol% O_2/He flow of 40 cm^3/min).

in Section 3.6. This simultaneous desorption of nitrogen and water indicates that surface reactions of both oxygen- and nitrogen-containing species occur. The presence of atomic nitrogen on the surface is not likely, because recombination of atomic nitrogen would lead directly to N_2 without water formation. Absence of atomic nitrogen on the surface is also in agreement with the XPS measurements. At this relatively high surface coverage some $O_{(a)}$ and OH is left on the surface, trapped in between NH_x species. For that reason the production of water through the reaction of two hydroxyls is only partly responsible for the water formation,

$$2OH_{(a)} \leftrightarrow H_2O + O_{(a)} + {}^*.$$

The atomic oxygen reacts further with NH_x species abstracting hydrogen. Two possible routes for the OH involvement in the formation of N_2 can be proposed, either from NH or NH_2. At low temperature the reaction of NH with OH to form water is favored with reaction energy of −11 kcal/mol [29]. The twostep reaction of NH_2 (via NH) with OH has a reaction energy of −26 kcal/mol:

$$NH_{(a)} + OH_{(a)} \rightarrow N_{(a)} + H_2O_{(a)},$$
$$2N_{(a)} \rightarrow N_2 + 2^*.$$

At higher temperatures NH_2 reacts to form N_2:

$$NH_{2(a)} + OH_{(a)} \rightarrow NH_{(a)} + H_2O_{(a)},$$
$$NH_{(a)} + OH_{(a)} \rightarrow N_{(a)} + H_2O_{(a)},$$
$$2N_{(a)} \rightarrow N_2 + 2^*.$$

The third nitrogen peak with a maximum at 483 K is most probably formed via an $NO_{(a)}$ intermediate, already formed at much lower temperatures. A relatively high surface coverage promotes the NO formation, but desorption of NO is slow at these relatively low temperatures [8,43,44].

3.3.3. Temperature-programmed oxidation

The most important results from the TPO experiment are the evolution of one N_2 peak, together with one H_2O peak and additional NO evolution at higher temperatures (Fig. 8).

Nitrogen is formed at 383 K followed by the water production with a peak maximum at 403 K. The production of N_2O is clearly much higher than in the TPD experiment. This can be explained by the reaction of NH with $O_{(a)}$ or $OH_{(a)}$, which gives atomic nitrogen and water as in the TPD experiment:

$$NH_{(a)} + OH_{(a)} \rightarrow N_{(a)} + H_2O_{(a)},$$
$$NH_{(a)} + O_{(a)} \rightarrow N_{(a)} + OH_{(a)}.$$

$O_{2(g)}$ will adsorb and dissociate on every vacant site which becomes available. This will lead to a production of $NO_{(a)}$:

$$NH_{(a)} + 2O_{(a)} \rightarrow NO_{(a)} + OH_{(a)} + {}^*,$$
$$N_{(a)} + O_{(a)}NO_{(a)} + {}^*.$$

Thus, at the surface there will be a competition between reactions toward N_2 or N_2O:

$$2N_{(a)} \rightarrow N_2 + 2^*,$$
$$NO_{(a)} + N_{(a)} \rightarrow N_2O + 2^*,$$
$$NO_{(a)} + NH_{(a)} \rightarrow N_2 + OH_{(a)} + {}^*,$$
$$NO_{(a)} + NH_{(a)} \rightarrow N_2O + H_{(a)} + {}^*.$$

The TPO spectrum shows that the maximum of the N_2 peak appears at lower temperatures than the maximum of the N_2O peak. This indicates that the production of N_2O is dependent on the formation of $NO_{(a)}$ from $NH_{(a)}$ species or on the availability of free sites for oxygen adsorption and dissociation.

At higher temperatures, one additional peak evolves with a maximum at 493 K, which is assigned to NO. This suggests that at a certain moment the sole species originating from NH_x on the platinum surface is $NO_{(a)}$. Apparently, oxygen strongly promotes the NO formation and blocks the N_2 and N_2O production.

3.3.4. Temperature-programmed reaction with NO (TP-NO)

Fig. 9 shows the products of the reaction between the surface species left after the ammonia oxidation and NO from

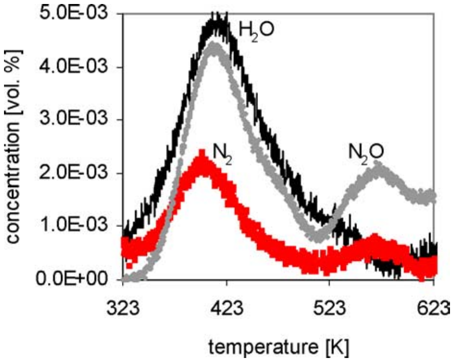

Fig. 9. Formation of N_2, N_2O, and H_2O measured by online mass spectrometry in temperature-programmed NO experiment after ammonia oxidation at 323 K (10 K/min, 0.5 vol% NO/He flow of 40 cm^3/min).

the gas phase. Nitrogen evolves at 398 K followed by the water production with a peak maximum at 413 K. The N_2O production is much higher than in the TPD and TPO experiments. The maximum of the N_2O peak appears at 413 K, higher than the maximum of the N_2 peak. This was already observed in the TPO spectrum and indicates that the N_2O production is dependent on the formation of $N_{(a)}$ from $NH_{(a)}$ species and the availability of free sites for NO adsorption. The increased N_2O production can be explained by the reaction of NH with $O_{(a)}$ or $OH_{(a)}$, which gave nitrogen and water in the TPD experiment. First, atomic nitrogen is produced:

$$NH_{(a)} + OH_{(a)} \rightarrow N_{(a)} + H_2O_{(a)},$$

$$NH_{(a)} + O_{(a)} \rightarrow N_{(a)} + OH_{(a)}.$$

N_2 starts to desorb and some vacant sites are created. $NO_{(g)}$ will adsorb on the available sites which leads to the production of N_2O,

$$N_{(a)} + NO_{(a)} \rightarrow N_2O_{(g)} + 2^*.$$

Thus, as already stated there is a competition between reactions toward N_2 or N_2O. The excess of $NO_{(a)}$ leads to a higher production of N_2O. The production of N_2O and N_2 reaches a certain maximum; at 473 K both gases are no longer produced. This indicates that the NO dissociation does not take place, because no N_2O or N_2 are formed. At 573 K some $N_2O_{(g)}$ and $N_{2(g)}$ are formed again, which probably originate from the NH_2 species. The dissociation of the $NO_{(g)}$ starts above 623 K (not shown).

3.4. *Experiments on preoxidized platinum*

Before ammonia oxidation was started, the platinum sponge catalyst was first preoxidized as described in the experimental part. Fig. 10 shows the conversion and selectivity of the preoxidized catalyst at 373 K. The same selectivity characteristics as on the reduced platinum sponge catalyst are observed (Fig. 1). Thus, the high oxygen surface coverage does not favor initial nitrous oxide formation. The conversion of ammonia and oxygen proceeds now at the same level; as expected no additional oxygen deposition is measured. The main difference with the reduced platinum sponge is the faster deactivation of the preoxidized catalyst at temperatures below 413 K (Table 3). However, above 413 K also the preoxidized catalyst keeps a high activity and selectivity toward nitrogen. Thus, the presence of oxygen at the platinum surface does not cause a permanent deactivation of the catalyst. Above 413 K the catalyst is reduced by ammonia.

The deactivating effect of unreacted oxygen was confirmed by the $[^{15}O]O_2$-labeled PEP experiments. In these experiments $[^{15}O]O_2$ was first injected on reduced platinum sponge before the ammonia oxidation was started. In contrast to the $[^{15}O]O_2$ pulse in the reaction flow stream

Table 3
Initial deactivation times for the preoxidized platinum sponge catalyst and the percentage of the ^{15}O-labeled species remaining at the catalyst when pulse was injected before the start of the ammonia oxidation reaction

Temperature (K)	Initial deactivation time (min)	^{15}O preadsorbed and not removed (%)
323	0.2	11 ± 1
348	0.8	10 ± 1
373	5	12 ± 1
423	–	< 1

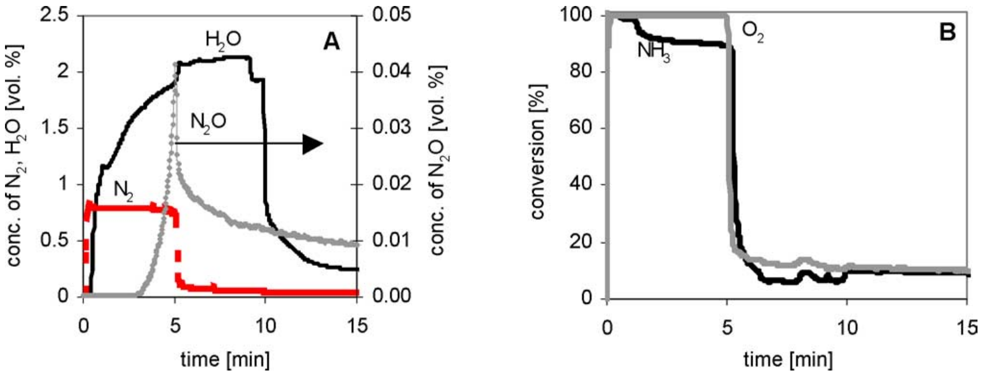

Fig. 10. Ammonia oxidation reaction performed at 373 K on a preoxidized platinum sponge catalyst. (A) concentration of N_2, N_2O and H_2O versus time, (B) conversion of NH_3 and O_2 versus time (GHSV = 5600 h^{-1}, $NH_3/O_2 = 2/1.5$, flow = 46.5 cm^3/min).

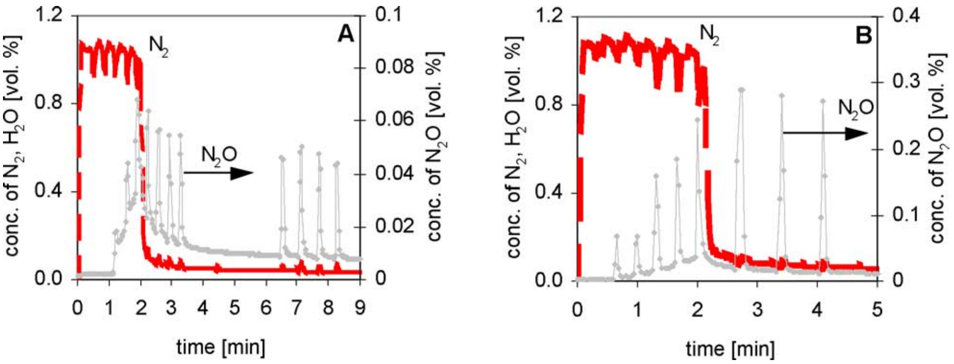

Fig. 11. Concentration of N_2 and N_2O versus time for ammonia oxidation reaction at 348 K; during the reaction (A) NO pulses were injected, (B) N_2O pulses were injected ($GHSV = 5600\ h^{-1}$, $NH_3/O_2 = 2/1.5$, flow $= 46.5\ cm^3/min$).

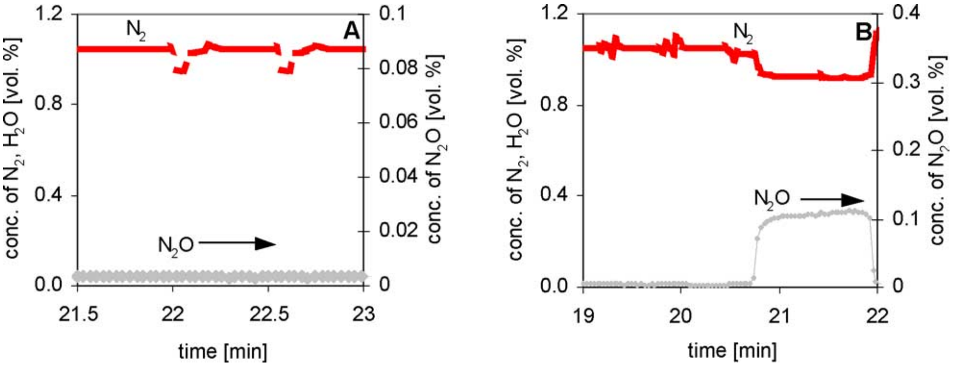

Fig. 12. Concentration of N_2 and N_2O versus time for ammonia oxidation reaction at 423 K; during the reaction (A) NO pulses were injected, (B) N_2O pulses were injected ($GHSV = 5600\ h^{-1}$, $NH_3/O_2 = 2/1.5$, flow $= 46.5\ cm^3/min$).

(Table 2) now 10% of pulsed oxygen remains at the catalyst surface (Table 3). Thus, some oxygen species are formed at the surface, which are unreactive with respect to water or nitrous oxide. In a similar experiment the adsorbed $[^{15}O]O_2$ was placed under hydrogen flow (not shown), which resulted in the formation of water, but also a significant amount of (unreactive) oxygen remained adsorbed at the surface. The formation of oxygen islands on platinum provides a possible explanation for this unreactive adsorbed oxygen phase.

3.5. NO and N_2O pulse experiments

In this set of experiments the ammonia oxidation reaction was carried out, wherein diluted NO (Fig. 11A) or N_2O pulses (Fig. 11B) were injected into the reaction stream. These pulse experiments are compared with He pulses for correct interpretation of the data, since the injection of a pulse into the reaction stream causes a visible short decrease in the product formation as the reaction flow is substantially diluted at that moment. Thus, the comparison to what extent, for example, nitrogen is diluted with NO and the He pulses indicate if nitrogen is formed due to the NO pulse. Fig. 11A shows NO pulses at 348 K. In the beginning of the reaction NO adsorbs at the catalyst because the NO pulses are not detected with MS. First, some N_2 is formed (first two pulses), however, also a part of NO remains adsorbed at the surface. As the catalyst becomes deactivated with increasing surface coverage, the consecutive NO pulses are converted into N_2 and N_2O. At high surface coverage, when the catalyst is deactivated, NO selectively forms N_2O, which is in line with our earlier findings [12]:

$$NH_{x(a)} + NO_{(a)} \rightarrow N_2O_{(a)} + H_{x(a)},$$

$$H_{x(a)} + O_{(a)} \rightarrow OH_{x(a)}.$$

This indirectly supports the interpretation of the XPS measurement, showing that the NO species are not present at the catalyst surface otherwise they would react toward N_2O. It should be noted that the water signal does not show any concentration changes in all of the performed pulse experiments. Fig. 11B shows that the N_2O pulses are converted at the beginning of the reaction selectively into nitrogen. With the increasing surface coverage less nitrogen is formed and N_2O leaves unconverted the catalyst bed. Thus, at 348 K N_2O decomposes into nitrogen and probably atomic oxygen with the restriction that the surface coverage is relatively low. This decomposition of N_2O is in line with the literature [45,46]; moreover, it is also reported that the rate of the N_2O decomposition is retarded by oxygen. In Fig. 12 similar NO and N_2O pulse experiments are shown, however, at a higher temperature (423 K) where the catalyst is still very active and the surface coverage is low.

Fig. 12A shows production of nitrogen as a consequence of the NO pulses. At this temperature and low surface cov-

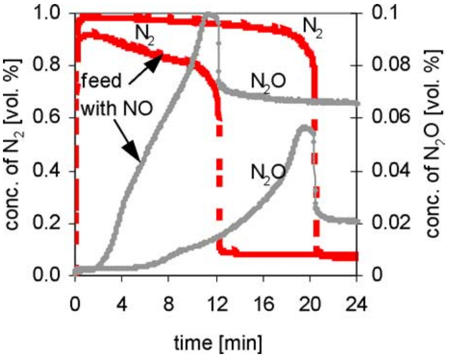

Fig. 13. Ammonia oxidation experiment with NO traces in the flow (NO/He flow of 0.5 vol% of 10 cm^3/min) compared to the standard ammonia oxidation experiment without NO traces at 388 K (GHSV = 5600 h^{-1}, $NH_3/O_2 = 2/1.5$ flow = 46.5 cm^3/min).

erage the formation of nitrogen from NO is plausible, since NO can dissociate or directly react with the NH_x species. Fig. 12B illustrates that N_2O decomposes to nitrogen. However, if N_2O is added continuously to the reaction stream then the decomposition of N_2O ends. This means that the platinum catalyst is able to decompose only relatively low amounts of N_2O. The oxygen signal does not show any additional formation of oxygen, which suggests that formed atomic oxygen is consumed in a reaction with ammonia.

In order to investigate whether NO dissociates at platinum below 413 K, a steady-state ammonia oxidation experiment is performed with some of NO in the reactant stream (Fig. 13). Clearly, NO has a deactivating effect, as the initial deactivation of the catalyst is much faster. This faster deactivation is also observed at lower reaction temperatures. This indicates that the decomposition of NO and/or reaction of NO with the NH_x species is much slower than the deposition of the NH_x species at the surface. With increasing surface coverage more N_2O is formed and even after the catalyst is deactivated NO is fully converted into N_2O (also observed in the NO pulse experiments).

3.6. Desorption of water

The PEP, XPS, and TPD experiments have indicated that mainly nitrogen-containing species (NH_2, NH) cause the deactivation of the catalyst. The oxygen species, especially formed hydroxyls, are not causing the profound deactivation of the catalyst. This suggests that the production of water through the reaction of two hydroxyls is much faster than the endothermic reaction between NH and OH:

$$2OH_{(a)} \leftrightarrow H_2O_{(g)} + O_{(a)} + {}^* \quad \text{(fast)},$$

$$2NH_{(a)} + OH_{(a)} \rightarrow N_{2(g)} + H_2O_{(g)} + 3^* \quad \text{(slow)}.$$

The formation of water via hydroxyls and the desorption of water at low temperatures is investigated with PEP in $[^{15}O]O_2$ pulse experiments injected in a hydrogen or ammonia flow. Figs. 14A and 14B show that a $[^{15}O]O_2$ pulse (very low concentration) at 323 K in ammonia or hydrogen flow on the platinum sponge shows a distinct desorption profile, which is assigned to desorbing water. In this experiment before oxygen dissociation took place there were no adsorbed nitrogen species at the surface, which is different compared to the ammonia oxidation reaction.

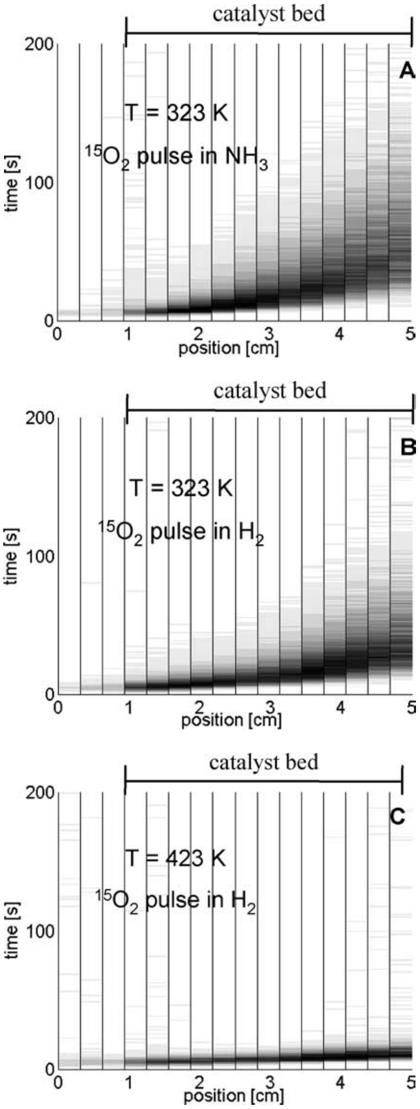

Fig. 14. PEP image of a pulse injection of $[^{15}O]O_2$ on Pt sponge (flow = 46.5 cm^3/min) (A) in 1 vol% NH_3/He flow at 323 K; (B) in 4 vol% H_2/He flow at 323 K; (C) in 4 vol% H_2/He flow at 423 K.

As already noted, oxygen adsorbs dissociatively on platinum. The oxygen atoms react with ammonia or hydrogen toward water, the only oxygen-containing product. In both experiments the water formation proceeds most probably via the reaction of hydroxyls. This indicates for the ammonia oxidation at low temperatures that the water formation via hydroxyls is not the rate-determining step. The desorbing water (low quantities) readsorbs on platinum and obviously with increasing temperature water leaves the catalyst bed faster (Fig. 14C). The recombination of OH also results in the formation of very reactive $O_{(a)}$.

4. Reaction mechanism

The dissociation of ammonia is greatly enhanced by the presence of atomic oxygen on the surface, which has been reported earlier [12]:

$$O_{2(g)} + 2^* \rightarrow 2O_{(a)},$$
$$NH_{3(g)} + {}^* \leftrightarrow NH_{3(a)}.$$

At the very beginning of the reaction hydrogen is stripped from ammonia by dissociatively adsorbed oxygen forming the NH_x and OH species. These reactions are exothermic, relatively fast, and proceed under all used conditions:

$$NH_{3(a)} + O_{(a)} \rightarrow NH_{2(a)} + OH_{(a)},$$
$$NH_{2(a)} + O_{(a)} \rightarrow NH_{(a)} + OH_{(a)},$$
$$NH_{(a)} + O_{(a)} \rightarrow N_{(a)} + OH_{(a)}.$$

Moreover as shown in Section 3.6 the recombination of $OH_{(a)}$ toward water and active $O_{(a)}$ takes place at all studied temperatures.

4.1. Temperatures below 398 K

4.1.1. Active regime

XPS measurements and temperature-programmed experiments have shown that after the deactivation of the catalyst the surface of platinum is fully covered with NH and NH_2 species. The PEP experiments also indicated that mainly nitrogen-containing species cause the deactivation of the catalyst. This means that the endothermic reactions between NH_x and OH are not proceeding very fast. The production of water through the reaction of two hydroxyls is much faster:

$$2OH_{(a)} \leftrightarrow H_2O + O_{(a)} + {}^*.$$

In this way formed active oxygen reacts instantly with NH_x species. Atomic nitrogen is not observed in XPS measurements, probably because of the recombination of two $N_{(a)}$ forms N_2:

$$2N_{(a)} \rightarrow N_2 + 2^*.$$

The formation of atomic nitrogen could proceed via either $NH_{x(a)}$ or $NO_{(a)}$. The reaction of NH with atomic oxygen is exothermic and very fast. The reaction of NH_x with OH is less probable since for these reactions a higher energy barrier needs to be overcome. The reaction of NH with OH is also proposed by Van den Broek et al. [3] to be the rate-determining step in the ammonia oxidation:

$$NH_{(a)} + O_{(a)} \rightarrow N_{(a)} + OH_{(a)},$$
$$NH_{(a)} + OH_{(a)} \rightarrow N_{(a)} + H_2O_{(a)}.$$

The formation of nitrogen via an $NO_{(a)}$ intermediate is not favorable at low temperatures. At temperatures below 380 K it has been reported on Pt(100) that the dissociation of NO is prohibited [8,47–49]. Both proposed reactions for the formation of $N_{(a)}$ via $NO_{(a)}$ require the dissociation of nitric oxide and therefore the recombination of N adatoms is a more feasible option. Moreover, the formation of NO under these conditions is apparently not favorable, because the deactivated catalyst is mainly covered with NH_x species (NH and NH_2), instead with NO. Thus, at low surface coverage NO seems not to be the dominant species, probably due to the low oxygen surface coverage, which disfavors the formation of NO. It should be noted that the NO dissociation temperature might be lower for our platinum catalyst due to possible dislocation preferences and the resulting presence of steps. The formation of some nitrogen from the NO pulses in the ammonia/oxygen flow at 348 K demonstrates this.

The formation of N_2O is not observed when the catalyst is active and at low temperatures. The N_2O pulse experiments showed that small amounts of N_2O decompose on platinum to form nitrogen and atomic oxygen, and for that reason the selectivity toward nitrogen is high.

4.1.2. Inactive regime

As the catalyst deactivates, the NH_x species are formed faster via ammonia adsorption than removed via nitrogen formation, the selectivity of the catalyst changes, and N_2O starts to be formed. First, $NO_{(a)}$ needs to be formed or it was already formed in the active stage:

$$NH_{(a)} + 2O_{(a)} \rightarrow NO_{(a)} + OH_{(a)} + {}^*,$$
$$N_{(a)} + O_{(a)} \rightarrow NO_{(a)} + {}^*.$$

$NO_{(a)}$ cannot desorb at these temperatures [7,8,50] and therefore reacts toward N_2O. The NO pulse experiments show that N_2O can also be formed via the reaction of NO with NH_x species:

$$N_{(a)} + NO_{(a)} \rightarrow N_2O_{(g)} + 2^*,$$
$$NH_{x(a)} + NO_{(a)} \rightarrow N_2O_{(a)} + H_{x(a)}.$$

Our TPO experiment (Fig. 8) showed that NO desorbs from platinum from about 423 K, but only at high oxygen surface coverage. In Fig. 1 a drastic decrease of nitrogen and N_2O formation is observed, which can be explained in terms of the moving reaction front through the catalyst bed. As the reaction zone arrives at the last positions, N_2O cannot decompose any more since there is no fresh platinum surface left. As the last positions are deactivated, the catalyst's activity sharply decreases and the surface remains covered mainly with NH and NH_2. This is supported in the XPS N(1s) measurement, but also indirectly by the NO pulse experiments.

A preoxidized catalyst deactivates much faster than the reduced platinum sponge. Ammonia adsorption and dissociation are accelerated by the presence of oxygen. Thus, the NH_x species cover the platinum surface much faster. The concentration profiles for nitrogen and nitrous oxide do not change, which indicates that the reaction mechanism is not changed for the preoxidized catalyst.

4.2. Temperatures above 398 K

Deactivation of the catalyst is not observed at these temperatures and only N_2 and H_2O are formed. The change in the reaction mechanism is indicated by the reactivation experiment (Fig. 2), in which N_2O formation rapidly decreases, suggesting a change in the reaction mechanism depending on the surface coverage. The N_2O decrease cannot only be explained by the decomposition of N_2O at platinum, as described in the N_2O pulse experiments. Certainly, only low amounts of N_2O can be decomposed:

$$N_2O_{(a)} \rightarrow N_2 + O_{(a)}.$$

Above 398 K the deposition of the NH_x species on platinum does not take place, as shown in the PEP experiments. Thus, the NH_x species are now much more reactive. However, also the NO pulse experiments showed that NO can be selectively converted into nitrogen. The TPD, TPO, and TP-NO experiments showed that above 423 K NO is present at the surface leading to N_2, N_2O, or NO depending on the surface coverage. To conclude, three reaction pathways are responsible for the nitrogen formation, via the exothermic reaction of NH_x species with $O_{(a)}$, endothermic reactions of NH_x with OH, or via the NO and NH_x reaction.

5. Conclusion

Below 388 K, two different product distributions in the ammonia oxidation are observed, depending on the surface coverage. At low coverage (catalyst is active) N_2 and H_2O are selectively produced via stripping of hydrogen from ammonia by oxygen atoms. Moreover as shown in Section 3.6 the recombination of $OH_{(a)}$ toward water and active $O_{(a)}$ takes place at all studied temperatures. With PEP, it was observed that already when the catalyst is still active, adsorbed nitrogen species are formed which stay irreversibly adsorbed at the catalyst surface and do not form any gaseous products. These nitrogen species mainly cause the poisoning of the platinum catalyst, thus retarding the adsorption of reactants. XPS and temperature-programmed experiments identified those as $NH_{2(a)}$ and $NH_{(a)}$. The oxygen species do not poison the catalyst, unless oxygen is preadsorbed on the platinum. The main reason for the deactivation of the platinum catalyst is the fact that the $NH_{x(a)} + OH_{(a)}$ reaction is much slower than formation of water via hydroxyls. In this way the NH and NH_2 remain unreactive at the surface and they block the active sites. The nitrogen formation proceeds via the recombination of atomic nitrogen and not via an $NO_{(a)}$ intermediate. Low surface coverage does not favor $NO_{(a)}$ formation and below 400 K the dissociation of NO is prohibited. Moreover, the addition of NO to the reaction flow causes faster deactivation of the platinum sponge. The preoxidized platinum sponge deactivates faster than the platinum sponge due to surface poisoning caused partly by the nitrogen species and partly by unreactive oxygen.

At high surface coverage, when the catalyst deactivates, the selectivity of the catalyst changes. Next to N_2 also N_2O is formed. The intermediate $NO_{(a)}$ seems to be mainly involved in the formation of a very low amount of N_2O. The higher consumption of O_2 than of NH_3 suggests that oxygen is involved in a relatively slow PtO formation. The initial deactivation of the platinum catalyst is obviously a case of self-poisoning. The fact that the catalyst is regenerated after a reduction step with hydrogen to its initial activity supports this.

Above 388 K nitrogen and water are formed and the catalyst maintains its high initial activity. The NO pulse experiments indicate that small quantities of NO can be selectively converted to nitrogen. Also N_2O decomposes to nitrogen, which explains the high selectivity toward nitrogen. However, the reaction route for the nitrogen formation at higher temperatures is still unclear.

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