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Low-temperature ammonia oxidation over Pt/γ-alumina: the influence of the alumina support

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Deactivation of a Pt/γ-alumina catalyst used for low-temperature ammonia oxidation was studied using positron-emission profiling (PEP). Evidence is presented that irreversibly adsorbed nitrogen and oxygen species deactivate the catalyst. This deactivation is further accelerated by preadsorption of oxygen on the catalyst. Ammonia strongly interacts with the alumina support. A steady state of the ammonia oxidation reaction is reached after the alumina sites are saturated with ammonia. PEP experiments show that spillover of oxygen to the support is not significant during the ammonia oxidation.

KEY WORDS: $^{13}NH_3$; $[^{13}N]NH_3$, $^{15}O_2$, $[^{15}O]O_2$; ammonia oxidation; deactivation; platinum; Pt/γ-alumina; positron-emission profiling.

1. Introduction

The literature on low-temperature ammonia oxidation over alumina-supported Pt catalysts is relatively scarce [1–6]. Nitrogen and nitrous oxide (up to 25%) are the only nitrogen-containing product molecules. Several groups found [1–3] that the Pt crystallite size significantly affects the catalytic activity, smaller crystallites having a lower activity than larger ones. It was also concluded that deactivation is related to oxygen poisoning of the surface, resulting in bulk oxidation of Pt. In a more recent study, Van den Broek *et al.* [5] observed a similar particle size effect, although deactivation was explained by inhibition of the reaction intermediates. This was derived from the fact that the deactivation process is reversible by removing these intermediates upon heating to 473 K under reaction conditions. The study of reaction mechanisms over metal surfaces is more difficult for supported catalysts than for single crystals [7] because of the coexistence of particles of different sizes, various orientations of the metal crystals, ill-defined chemical and structural states of the surface during the catalytic reaction, possible influence of the support and heat or mass transfer limitations. The oxidation of ammonia by oxygen over a pure Pt sponge exhibits a deactivation, which is strongly dependent on temperature [8]. We identified that deactivation of these catalytic materials is mainly caused by poisoning of the surface by nitrogen-containing species (NH and NH_2), in line with earlier work [9]. The main question to be addressed in the current contribution is if the reaction mechanism of ammonia oxidation over Pt/γ-Al_2O_3 is similar to that on the platinum sponge catalyst. Moreover, this will give insight into the influence of the presence of the alumina support and into deactivation phenomena. Positron-emission profiling (PEP) is applied to provide *in situ* information on the reaction species.

A suitable technique to study *in situ* transient and steady-state phenomena at atmospheric pressure is positron-emission profiling (PEP) [10–12]. This technique offers a unique possibility to study the various processes at the catalyst surface over a wide temperature range. PEP is a technique in which minute ($\sim 10^{-15}$ moles) quantities of radiolabeled molecules emitting positrons are injected as pulses into the feed of packed-bed reactors. The concentration distribution of radiolabeled molecules can be measured as a function of time and position within a tubular reactor bed. In this study, we used ^{13}N-labeled ammonia and ^{15}O-labeled oxygen pulses.

In this communication, the conversion and the product formation in the ammonia oxidation over the Pt/γ-alumina and preoxidized Pt/γ-alumina catalysts are presented as a function of temperature. The nature of the deactivating species is further investigated with temperature-programmed desorption (TPD). In addition, we will demonstrate that below 473 K the catalyst deactivates because of poisoning of the catalyst surface by oxygen and nitrogen species. The PEP experiments provide complementary information on the influence of the alumina support on the reaction.

2. Experimental

2.1. Ammonia oxidation

Ammonia oxidation experiments were carried out in a single-pass microflow reactor. Typically, an amount of

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catalyst (1.0 wt% Pt/γ-alumina) was put in a quartz reactor with an internal diameter of 4 mm. Pt/γ-alumina was prepared by pore volume impregnation of a solution of $Pt(NH_3)_4(OH)_2$ into a 250–450 μm sieve fraction of γ-alumina (Ketjen, BET surface area 188 $m^2\,g^{-1}$, average pore diameter 106 Å, iron contamination 0.015 wt%) followed by drying at 373 K and reduction at 723 K in hydrogen. The cluster size of platinum is determined to be 1.4 nm. On-line gas-phase analysis was carried out by a quadrupole mass spectrometer (Balzers Instruments Omnistar GSD 3000). The experiments were done at temperatures between 323 and 673 K. For the oxygen spillover experiments, a γ-alumina (Ketjen E-000) sample of the same sieve fraction was employed.

Prior to a typical experiment, the catalyst was reduced *in situ* by heating from 298 to 673 K in a 10 vol% H_2/He flow (40 mL min^{-1}). Subsequently, the sample was kept at this temperature for 2 h followed by an He flushing period for 0.33 h. The temperature was then decreased to the desired reaction temperature. A preoxidized Pt/γ-alumina is obtained in the following way: the reduced catalyst was pretreated with a 1 vol% O_2/He flow (48 mL min^{-1}) for 1 h at 373 K followed by He flushing for 1 h. Oxygen adsorbs dissociatively at this temperature as follows by several reports [13–17].

The reaction mixture for ammonia oxidation consisted of 2.0 vol% NH_3 and 1.5 vol% O_2 in He at a total flow of 48 mL min^{-1}. Turnover frequencies (TOF) are calculated on the basis of the MS analyses of nitrogen products and are expressed per unit of metal surface area. Steady-state experiments were performed in the temperature range of 423 to 573 K.

Temperature-programmed experiments were performed after the catalyst was deactivated at either 348 or 473 K. First, the catalyst was flushed with He for 1 h. Then, the temperature was raised with 10 K/min (20 mL min^{-1}) under He flow.

2.2. Positron-emission profiling

The Eindhoven 30 MeV cyclotron was used to irradiate 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 flow-through 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 was described elsewhere [20].

To produce labeled oxygen ($^{15}O^{16}O$ written as [^{15}O]O_2), a nitrogen gas target nitrogen (75 mL min^{-1}) at a pressure of 4 bar was continuously irradiated with 9.2 MeV deuterons (500 nA) [21–23]. The irradiated effluent was remotely transported from the target vault into the PEP laboratory. The labeled effluent was transported to a GC by first passing soda lime and then 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 ^{13}N and ^{15}O nuclei emit a positron upon decay. PEP is based on the detection of the two 511 keV γ-photons that 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 matter. Coincidental detection of two photons by scintillation detectors (BGO) provides the position of the annihilation. In practice, the tubular reactor is placed in between 18 scintillation detectors. In this way, the concentration distribution of radiolabeled molecules can be measured as a function of position and time [11,24].

In a typical PEP experiment, the reduced Pt/γ-alumina catalyst was kept under an NH_3/O_2/He flow (GHSV = 5600 h^{-1}, $NH_3/O_2 = 2/1.5$, flow = 46.5 mL min^{-1}) in the temperature range of 273 to 573 K. Subsequently, a pulse of [^{13}N]NH_3 or [^{15}O]O_2 was injected into the reaction feed mixture. In some experiments, radiolabeled pulses were injected over the reduced Pt/γ-alumina or Pt-free γ-alumina support in He or O_2/He flow (GHSV = 5600 h^{-1}, 46.5 mL min^{-1}).

3. Results and discussion

3.1. Ammonia oxidation on Pt/γ-Al_2O_3 and preoxidized Pt/γ-Al_2O_3

3.1.1. Ammonia oxidation at 323 to 473 K

Figure 1 displays the activities of Pt/γ-Al_2O_3 and preoxidized Pt/γ-Al_2O_3 as a function of the reaction temperature. Clearly, a strong deactivation sets in within 4 min for both catalysts. The conversions of ammonia and oxygen decreased to below 5% within 20 min and a steady-state regime is reached. The initial catalytic activity for the experiments carried out at 323 and 373 K is low. Strikingly, the TOFs are lower for the oxidized catalyst indicating that adsorbed oxygen strongly affects catalyst performance at these temperatures and ammonia will not reduce the preoxidized surface. At a temperature of 423 K, a maximum in activity is reached in less than 2 min followed by a slow decrease. At 473 K this decrease is less pronounced. However, in both cases the catalysts deactivate quite strongly after approximately 4 min. The activity of preoxidized Pt/γ-Al_2O_3 at 423 and 473 K is slightly higher than that of Pt/γ-Al_2O_3. This similar catalytic behavior of both catalysts is in agreement with results obtained for a Pt sponge catalyst (not shown). However, the rapid decrease in activity of the supported catalysts

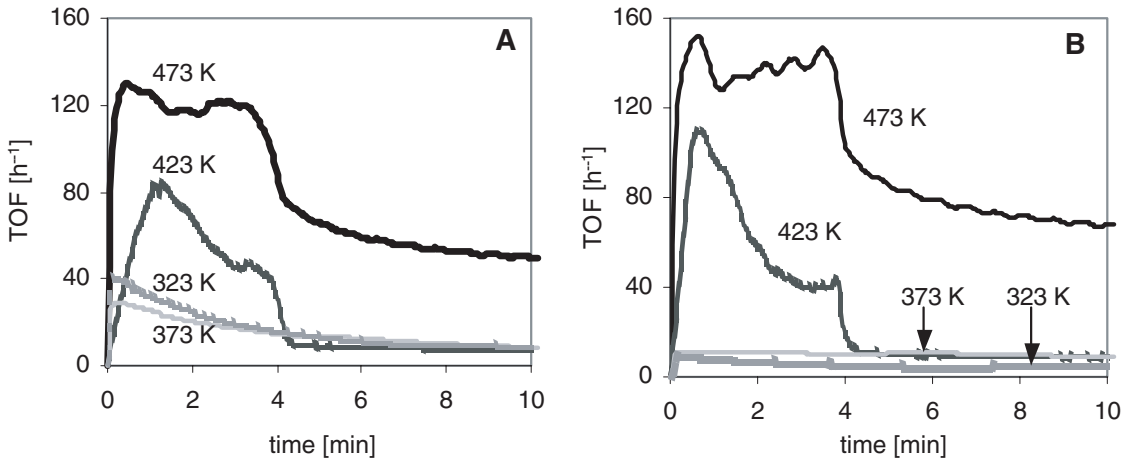

Figure 1. Turnover frequency for the ammonia oxidation reaction at 323–473 K over (a) 1 wt% Pt/γ-Al_2O_3 and (b) preoxidized 1 wt% Pt/γ-Al_2O_3 (GHSV = 5600 h^{-1}, NH_3/O_2 = 2/1.5, flow = 46.5 mL min^{-1}).

contrasts the findings for the sponge. This will be discussed later.

The selectivity to nitrogen and nitrous oxide for both catalysts is very similar in the studied temperature range. Figure 2 exemplifies the selectivity to nitrogen products in ammonia oxidation over Pt/γ-Al_2O_3 at 373 K. The main initial product is dinitrogen. However, almost instantaneously, the selectivity to N_2 drops followed by the production of N_2O. At steady state, the selectivity of N_2O is about 5%. With increasing surface coverage, the formation of adsorbed NO is favorable, and NO decomposition or desorption does not proceed [25–28]. Importantly, NO was not observed under the present reaction conditions. Table 1 lists the N_2O selectivities for both catalysts at various temperatures. It follows that more nitrous oxide is formed with increasing temperatures.

3.2. Temperature-programmed desorption

Figure 3 shows the evolution of reaction products in the TPD experiments, performed after ammonia oxidation over 1 wt% Pt/γ-Al_2O_3 at 348 K (surface A) and 473 K (surface B). It should be noted that before a temperature-programmed desorption (TPD) experiment is started, a significant amount of ammonia is adsorbed during the reaction on the alumina sites. During TPD, further reactions may take place between these ammonia molecules, adsorbed nitrogen-containing species, and oxygen atoms. Desorption of ammonia is much more pronounced in the low-temperature experiment (surface A). Conversely, much more water is formed during TPD of the surface generated upon ammonia oxidation at 473 K (surface B). Moreover, a higher concentration of nitrous oxide is observed. The desorption of a significantly higher amount of oxygen-containing species from surface B suggests that the deactivation is related to the presence of oxygen species. The situation is different for surface A in which desorption of nitrogen-containing species is dominant. Dinitrogen evolves with maxima around 400 and 620 K. The latter peak is accompanied by the evolution of N_2O, which is in line with the reported onset temperature for nitrous oxide formation of 613 K by Li and Armor [29]. The adsorbed NO species involved in N_2O formation must be formed below 400 K, since a very small nitrous oxide evolution was found for surface B. From these data, we infer that the dominant species at low temperature (below 400 K) are nitrogen species, whereas the surface is filled with oxygen species at higher temperatures. We suggest that the deactivation is caused by the dominance of these species at the deactivated surfaces.

A further temperature-programmed reaction experiment was performed to investigate reactivation of the catalyst (figure 4). First, the catalyst is deactivated during ammonia oxidation at 323 K and is subsequently heated in the reaction mixture to temperatures above 520 K. This temperature was chosen since the TPD experiment indicated that desorption of the majority of nitrogen species takes place below 500 K. A significant

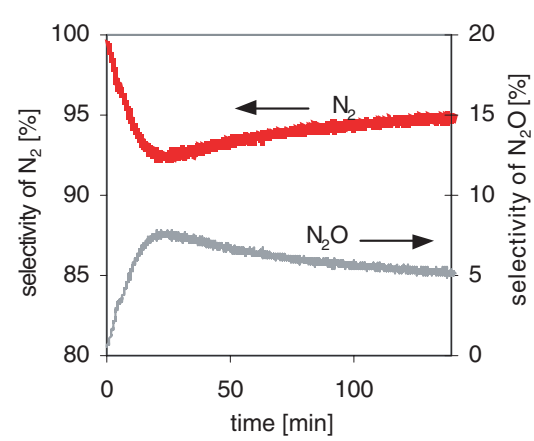

Figure 2. Selectivity to N_2 and N_2O vs. time for ammonia oxidation reaction at 373 K over 1 wt% Pt/γ-Al_2O_3 (GHSV = 5600 h^{-1}, NH_3/O_2 = 2/1.5, flow = 46.5 mL min^{-1}).

Table 1
Selectivity for the stoichiometric ammonia oxidation on 1 wt% Pt/γ-Al_2O_3 and preoxidized 1 wt% Pt/γ-Al_2O_3 at 323 to 473 K

Temperature (K)	Pt/γ-Al_2O_3 N_2O selectivity (%) (initial/at steady state)	Preoxidized Pt/γ-Al_2O_3 N_2O selectivity (%) (initial/at steady state)
323	0.3/3.8	2.5/4.0
373	0.5/5.0	3.3/4.6
423	1.7/6.3	5.6/6.0
473	7.1/5.2	6.8/4.8

amount of N_2O evolves before the catalyst is reactivated. One observes that above the reaction temperature the catalyst is reactivated and mainly produces nitrogen and water.

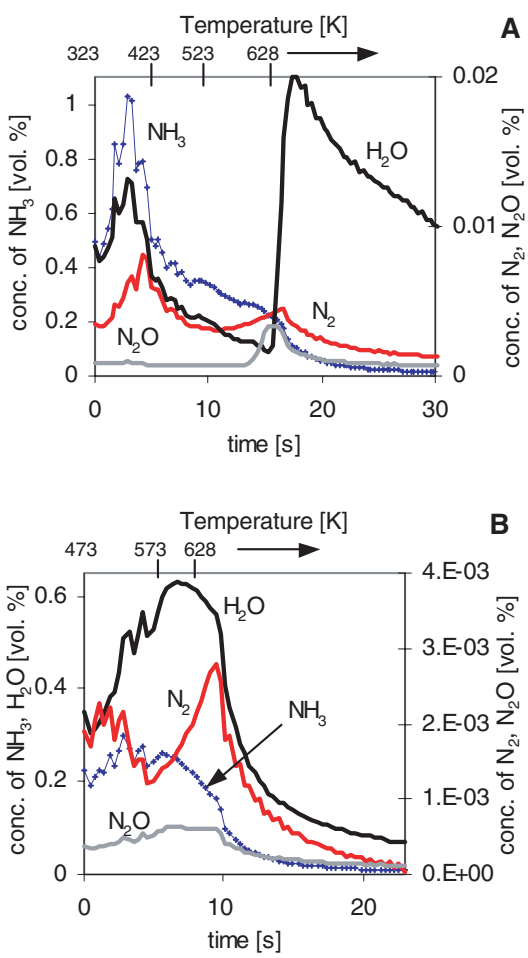

Figure 3. Evolution of N_2, N_2O, NH_3, and H_2O measured by on-line mass spectrometry in a temperature-programmed desorption experiment over 1 wt% Pt/γ-Al_2O_3 after (a) ammonia oxidation performed for 1 h at 348 K and (b) ammonia oxidation performed for 1 h at 473 K (TPD conditions: 10 K min^{-1} up to 628 K, He flow of 40 mL min^{-1}).

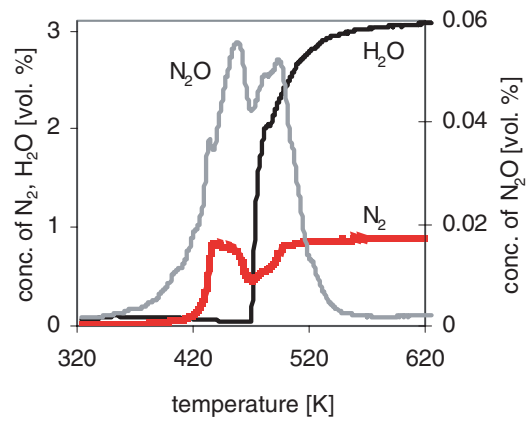

Figure 4. Ammonia oxidation at 323 K for a prolonged time followed by a temperature-programmed reaction. Only the temperature-programmed reaction is shown (20 K min^{-1}, GHSV = 5600 h^{-1}, NH_3/O_2 = 2/1.5).

3.3. [^{13}N]NH_3 and [^{15}O]O_2 PEP experiments

Figure 5 shows the PEP images of a [^{13}N]NH_3 pulse in the reaction mixture at the start of the reaction at 348 and 473 K. The radiolabeled ammonia pulse travels through the catalyst bed as a single pulse for the experiment carried out at 348 K. The retention time of these ^{13}N species is relatively long (figure 5(c)), which excludes the possibility that the ^{13}N concentration is related to the $^{13}N_2$ or $^{13}N_2O$ species because their retention times are in the order of seconds. Moreover, the observed retention time is in accordance with the breakthrough time of ammonia in the reaction. Therefore, most of the observed radiolabeled ammonia was only adsorbed/desorbed on the γ-alumina sites. Figure 5(c) shows that a small part of the activity remained on the catalyst bed at 348 K. As only [^{13}N]NH_3 reversibly adsorbs on the alumina sites, we infer that these ^{13}N species are adsorbed on the platinum sites. This small amount of remaining radiolabeled species originates from the conversion of a small amount of radiolabeled ammonia to adsorbed nitrogen species. This result is in agreement with the TPD experiment (figure 3), which indicated that nitrogen species poison the catalyst. At 473 K, the PEP results point toward a totally different situation. First, the catalyst shows a much higher activity at the beginning of the catalyst bed. Moreover, most of the radiolabeled ammonia is converted to nitrogen and nitrous oxide, as derived from the relatively small residence time of ^{13}N species in the catalyst bed (figure 5(b) and (c)). A small part of the injected [^{13}N]NH_3 slowly leaves the catalyst bed because of readsorption on the alumina sites. The fact that no detectable activity remained on the catalyst bed, despite the high conversion, indicates that the oxygen species mainly deactivate the catalyst. This agrees with the results of the earlier TPD experiments.

[^{15}O]O_2 pulse experiments show very different PEP images compared to those of [^{13}N]NH_3 pulse experi-

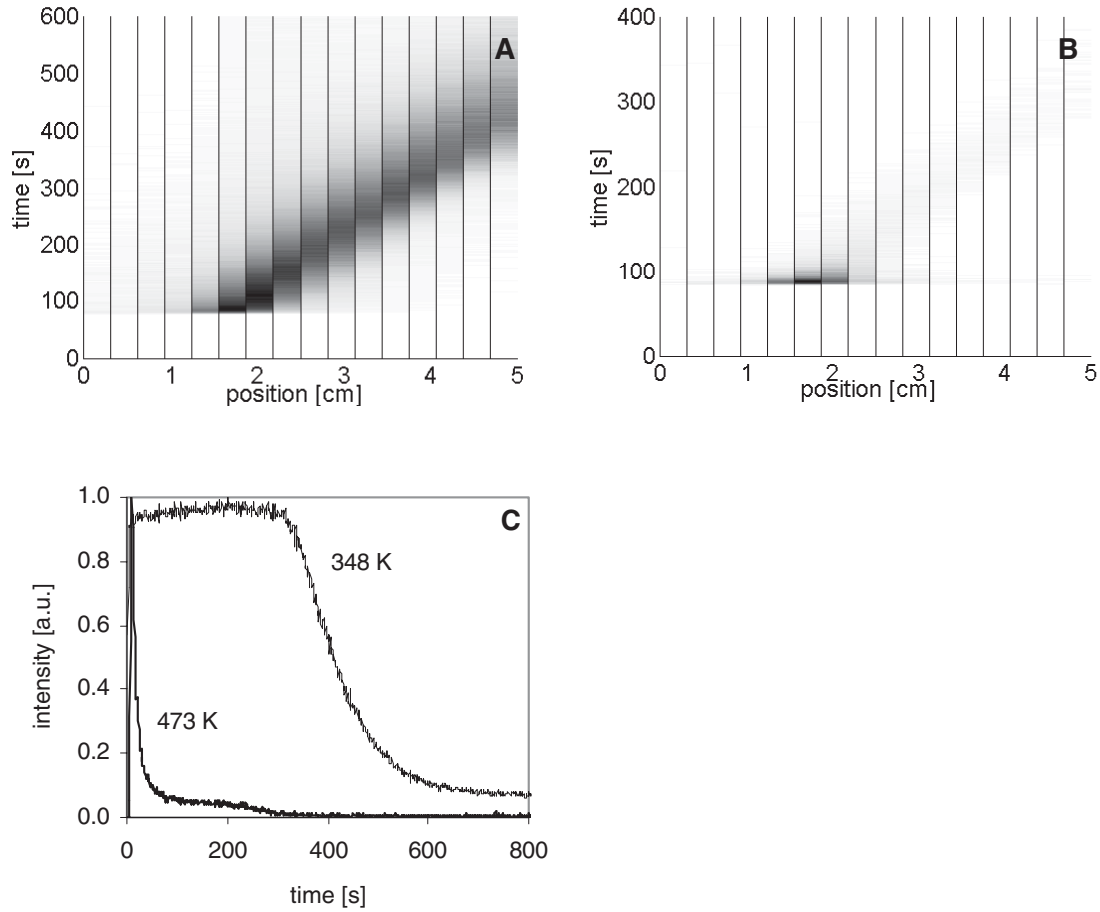

Figure 5. PEP images of a pulse injection of $[^{13}N]NH_3$ on 1 wt% $Pt/\gamma\text{-}Al_2O_3$ at (a) 348 K and (b) 473 K, and (c) integrated ^{13}N concentration as a function of time for the presented temperatures. Color intensity represents the concentration of $[^{13}N]NH_3$ (GHSV = 5600 h^{-1}, NH_3/O_2 = 2/1.5, flow = 46.5 mL min^{-1}).

ments. Figure 6 shows a typical PEP image when $[^{15}O]O_2$ is injected in the reaction mixture at 323 to 473 K during the first minute of the reaction. Generally, it is observed that the major part of the ^{15}O concentration leaves the catalyst bed very fast, and about 10% of the labeled oxygen remains adsorbed at the catalyst surface. This means that oxygen partly adsorbs irreversibly and poisons the catalyst. The ^{15}O profile shows that oxygen interacts with the catalyst over the whole length of the catalyst bed.

3.4. Oxygen adsorption on $Pt/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$

Figure 7 shows that preadsorbed $[^{15}O]O_2$ on 1 wt% $Pt/\gamma\text{-}Al_2O_3$ is not removed or consumed by the ammonia/oxygen flow. This is somewhat surprising, since on a platinum sponge catalyst 90% of $[^{15}O]O_2$ is removed by the ammonia/oxygen flow (not shown). In a similar experiment, preadsorbed $[^{15}O]O_2$ on 1 wt% $Pt/\gamma\text{-}Al_2O_3$ is also not removed by hydrogen. This result suggests that adsorbed $[^{15}O]O_2$ is not present on the platinum sites but rather on the alumina sites. However, this leaves the question whether oxygen adsorbs on the support or if it derives from spillover from Pt sites. To further elucidate this, $[^{15}O]O_2$ experiments are performed on pure $\gamma\text{-}Al_2O_3$. Figure 8 shows the adsorption of $[^{15}O]O_2$ on pure $\gamma\text{-}Al_2O_3$ at different temperatures. The PEP results show that a part (up to 25%) of the injected $[^{15}O]O_2$ remains adsorbed on alumina. The adsorbed $[^{15}O]O_2$ on the alumina sites cannot be exchanged with an oxygen flow, which points to a very slow exchange or an irreversible character of the adsorption. It should be noted that the amount of oxygen that can be adsorbed on the alumina sites is relatively low, as the oxygen concentration in the $[^{15}O]O_2$ pulse is about 10^{-15} moles. Still, the fact that the minor part of the injected $[^{15}O]O_2$ remains adsorbed on $\gamma\text{-}Al_2O_3$ contrasts the adsorption of labeled oxygen on $Pt/\gamma\text{-}Al_2O_3$ (figure 7) where all of the adsorbed oxygen (10^{-15} moles) remained adsorbed. A possible explanation is provided by spillover of adsorbed oxygen atoms from platinum sites to the catalyst support, which is also reported for the $Pt/\gamma\text{-}Al_2O_3$ system [30–33].

Although there are some indications that spillover occurs, the fact that only a small part of the total

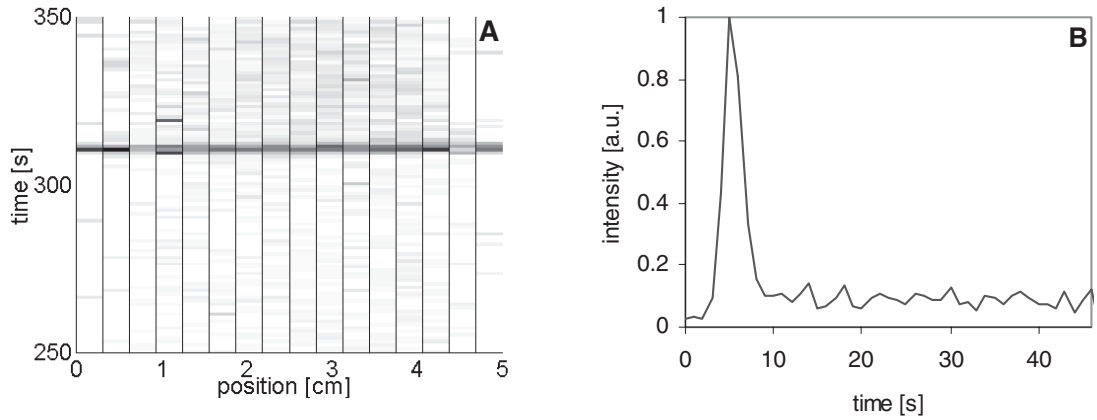

Figure 6. PEP image of a pulse injection of $[^{15}O]O_2$ on 1 wt% $Pt/\gamma\text{-}Al_2O_3$ at 423 K. PEP images are very similar from 323 to 473 K: (a) PEP image and (b) normalized concentration as a function of time. Color intensity represents the concentration of $[^{15}O]O_2$ (GHSV = 5600 h^{-1}, $NH_3/O_2 = 2/1.5$, flow = 46.5 mL min^{-1}).

radiolabeled oxygen pulse remains on the surface and that the water adsorption from Pt sites during a typical TPD experiment is substantial results in the notion that the major part of the deactivation is caused by oxygen adsorption on Pt sites.

4. Deactivation of the catalyst—general discussion

4.1. Start of the reaction

A closer look at the influence of the alumina support on the deactivation process, especially in the first minutes of the reaction, shows a sudden deactivation after 4 min at 323 and 373 K (figure 1). This coincides with the detection of ammonia in the reactor effluent. This breakthrough of ammonia is further investigated by comparing the breakthrough time of ammonia using a reaction mixture ($O_2/NH_3/He$), and using ammonia (NH_3/He) with identical partial pressure as the reaction mixture (table 2).

At all temperatures, oxygen is detected almost immediately after the start of the reaction. The retention time of oxygen in the catalyst bed is around 1 s, while the retention time of the ammonia in the catalyst bed is much longer. The radiolabeled ammonia experiment (figure 5) showed that the adsorption/desorption equilibrium of ammonia on alumina determines the movement of ammonia through the catalyst bed. This is caused by the adsorption of ammonia on the acid sites of γ-alumina. To presaturate the large amount of the alumina sites with ammonia, a relatively long adsorption time is needed, delaying the breakthrough of ammonia. This results in the following picture of the ammonia oxidation reaction on $Pt/\gamma\text{-}Al_2O_3$. In the first seconds, ammonia oxidation takes place at the beginning of the catalyst bed. A major part of ammonia saturates the alumina acidic site, while a small part

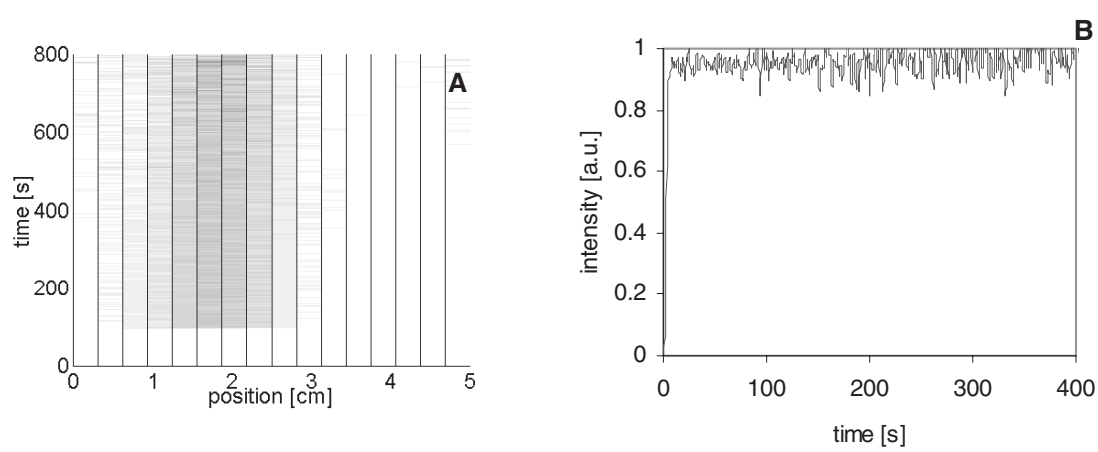

Figure 7. PEP image of a pulse injection of $[^{15}O]O_2$ in He flow on 1 wt% $Pt/\gamma\text{-}Al_2O_3$ at 423 K followed by the start of ammonia oxidation exactly 30 s later: (a) PEP image and (b) normalized concentration a as function of time. Color intensity represents the concentration of $[^{15}O]O_2$ (GHSV = 5600 h^{-1}, He flow = 46.5 mL min^{-1}).

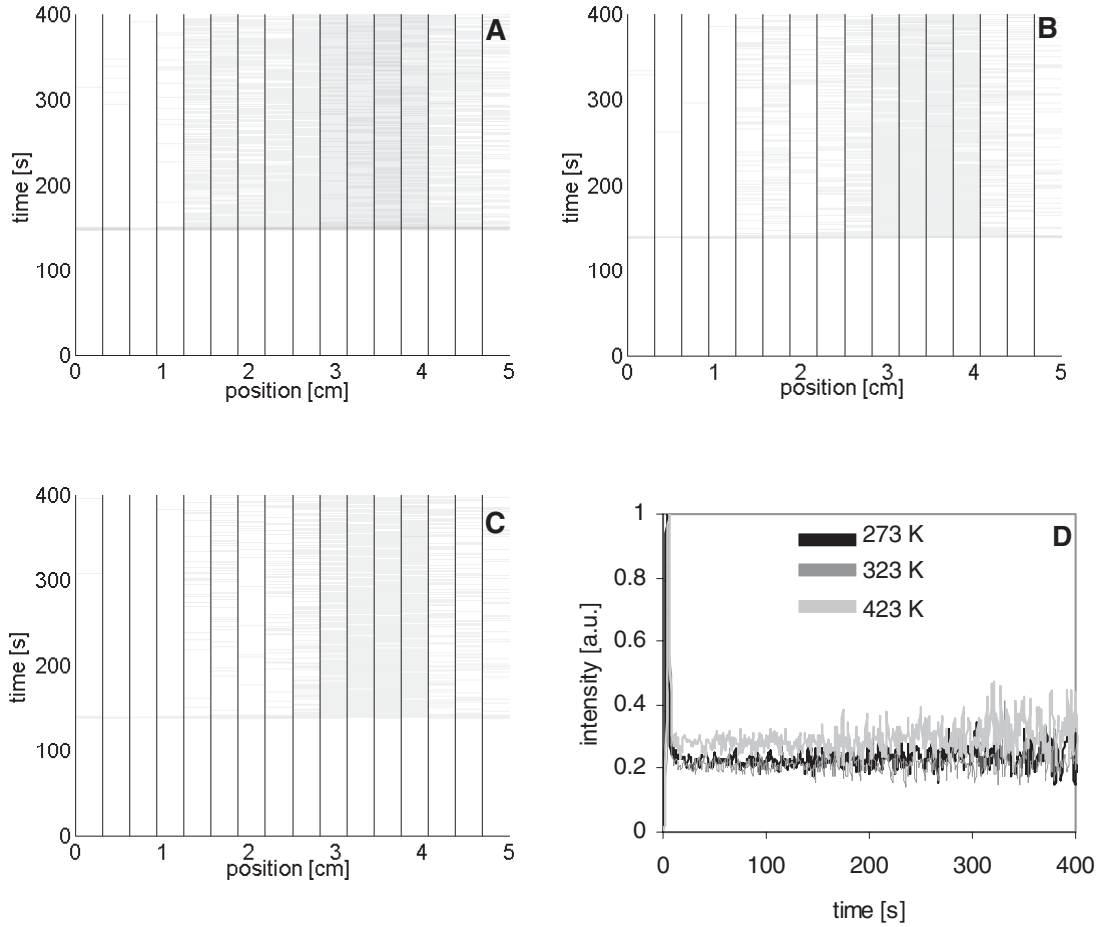

Figure 8. PEP image of a pulse injection of $[^{15}O]O_2$ in He flow on γ-Al_2O_3 at (a) 323 K, (b) 373 K, (c) 423 K, and (d) normalized concentration as a function of time. Color intensity represents the concentration of $[^{15}O]O_2$ (GHSV = 5600 h^{-1}, NH_3/O_2 = 2/1.5, flow = 46.5 mL min^{-1}).

reacts with oxygen atoms adsorbed on Pt sites. Oxygen is mainly adsorbed on these latter sites. Owing to the adsorption of ammonia on alumina, the reaction does not proceed under stoichiometric conditions. The reaction zone moves to the end of the catalyst bed as ammonia saturates the alumina sites. However, since oxygen travels much faster through the catalyst bed, dissociatively adsorbed oxygen atoms are present in the remainder of the catalyst bed (figure 6). The spillover experiments indicated that only a small part of adsorbed oxygen migrates to the alumina support. Thus, in the first minutes of the reaction, the platinum sites are preoxidized before the ammonia (reaction) front reaches them.

In conclusion, the experiments with Pt/γ-Al_2O_3 can therefore be interpreted as experiments on a preoxidized Pt/γ-Al_2O_3 surface.

4.2. Temperature dependence

4.2.1. Below 400 K

Below 400 K it is observed that the Pt/γ-Al_2O_3 catalyst quickly deactivates. Pt/γ-Al_2O_3 and preoxi-

Table 2
Comparison of the deactivation and breakthrough time for ammonia and oxygen measured with MS

Temperature (K)	Deactivation time (min)	Breakthrough time of NH_3 (min)	Breakthrough time of O_2 (min)
323	Immediate, slow decrease	7.0	+/−0.02
373	Immediate, slow decrease	4.7	+/−0.02
423	4	3.9	+/−0.02
473	4	3.8	+/−0.02

dized Pt/γ-Al_2O_3 show a deactivation similar to the Pt sponge catalyst [8]. Moreover, the [^{13}N]NH_3 pulse experiments showed that deactivation is caused by dominant adsorption of nitrogen species. This is in line with TPD experiments, which showed that when the catalyst is heated a significant amount of nitrogen desorbs. The preadsorption of oxygen accelerates the deactivation process. The first steps in the ammonia oxidation, stripping hydrogen from ammonia by oxygen atoms to the NH_x species, are accelerated. The [^{15}O]O_2 pulse experiments showed that the oxygen species also remain adsorbed at the catalyst surface during the reaction. This is in contrast with the Pt sponge catalyst, in which mainly the nitrogen species caused the deactivation. Several explanations are possible for this different behavior. Foremost, in the alumina-supported catalyst, the reaction proceeds in an excess of oxygen due to the preferential adsorption of ammonia on the alumina support (figure 5(a)). Moreover, the small particle size of the Pt clusters may be relevant, since the preoxidation treatment has a more profound effect on smaller particles. The product selectivity on Pt/γ-Al_2O_3 shows similar features as for the Pt sponge catalyst. Nitrogen is the main product. From the beginning of the reaction, the platinum surface of Pt/γ-Al_2O_3 is covered with the oxygen species, which in turn favors the formation of N_2O. NO is not detected in the gas phase. We assume that the formation of water via the hydroxyls is faster than the formation of nitrogen via the hydroxyls' reaction with the NH_x species. In this way, the platinum surface is covered with the NH_x species.

4.2.2. Above 400 K

According to the reaction mechanism on the Pt sponge catalyst [8], above 400 K the Pt/γ-Al_2O_3 catalyst should not deactivate. The reaction of hydroxyls with NH_x is relatively fast at this temperature, and the NH_x species could react with adsorbed NO to form nitrogen selectively. The TPD experiment (figure 3(b)) showed that water was the main product of this experiment. The conclusion that above 400 K the oxygen species mainly deactivate the catalyst is confirmed by the [^{13}N]NH_3 and [^{15}O]O_2 PEP experiments. A reasonable explanation for the deactivation of Pt/γ-Al_2O_3 at 473 K, in contrast to the Pt sponge, is the formation of Pt oxide. Owing to the strong adsorption of ammonia on the alumina sites, the reaction takes place in excess of oxygen. Most of the platinum sites of Pt/γ-Al_2O_3 are preoxidized before the reaction takes place. However, the preoxidized catalyst is not deactivated, and thus the catalyst deactivates during the ammonia oxidation reaction. High local temperatures are generated on the catalyst surface during the reaction event, which probably enhance the oxide formation. Oxygen-rich reaction conditions in combination with the small platinum clusters cause the deactivation. The deactivation of smaller platinum crystallites is known to be more pronounced than that for larger ones [2,5]. Above 520 K the catalyst is not deactivated, probably because of the increased ability of ammonia to reduce the metal surface.

5. Conclusions

Alumina-supported Pt particles exhibit a lower activity in low-temperature ammonia oxidation than Pt sponge materials. Moreover, deactivation is more severe in the supported case indicating that supported Pt is not an adequate catalyst for the title reaction. Below 400 K, Pt/γ-alumina was found to be almost inactive. Pre-exposure of the reduced catalyst to oxygen lowers the initial TOF, suggesting that adsorbed oxygen atoms accelerate the deactivation. An important drawback of the application of the γ-alumina support was identified as it preferentially adsorbs ammonia, resulting in a fast covering of the Pt surface by oxygen species. This deactivation occurs concomitantly by the deactivation of strongly adsorbed NH_x species. Oxygen spillover to the alumina support appears to be rather small. Moreover, the alumina support itself is inactive for the oxidation of ammonia. At reaction temperatures in excess of 400 K, Pt/γ-alumina shows a much higher initial activity, although typically, below 520 K deactivation is still observed. In this temperature range, deactivation is mainly caused by inhibition by oxygen atoms. Due to the adsorption of ammonia on alumina, the initial reaction proceeds in an oxygen-rich environment. It is found that the catalyst exhibits a stable activity at reaction temperatures in excess of 520 K, presumably because of the removal of adsorbed oxygen and NH_x species.

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