Figure01a

Figure01a

Figure04

Figure02

Figure03

Figure05a

Figure05b

Figure05c

Figure06a

Figure06b

Figure07a

Figure07b

Figure08a

Figure08b

Figure09a

Figure09b

Figure10a

Figure10b

Figure11

Ammonia reactions with the stored oxygen in a commercial lean NO_x trap catalyst

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Abstract

Ammonia is an important intermediate of the NO_x reduction in a NO_x storage and reduction catalyst (aka lean NO_x trap). NH₃ formed under rich conditions in the reduced front part of the catalyst is transported by convection downstream to the unregenerated (still oxidized) zone of the catalyst, where it further reacts with the stored oxygen and NO_x. In this paper, the kinetics and selectivity of NH₃ reactions with the stored oxygen are studied in detail with a commercial Ba-based NO_x storage catalyst containing platinum group metals (PGM), Ba and Ce oxides. Furthermore, steady-state NH₃ decomposition, NH₃ oxidation by O₂ and NO, and N₂O decomposition are examined in light-off experiments. Periodic lean/rich cycling is measured first with O₂ and NH₃, and then with NO_x+O₂ and NH₃ to discriminate between the NH₃ reactions with the stored oxygen and the stored NO_x. The reaction of NH₃ with the stored O₂ is highly selective towards N₂, however a certain amount of NO_x and N₂O is also formed. The formed NO_x by-product is efficiently adsorbed on the NO_x storage sites such that the NO_x is not detected at the reactor outlet except at high temperatures. The stored NO_x reacts with NH₃ feed in the next rich phase, contributing to the N₂O formation. Water inhibits the reactions of NH₃ with the stored oxygen. On the contrary, the presence of CO₂ increases the NH₃ consumption. CO₂ is able to provide additional oxygen for NH₃ oxidation, forming -CO in analogy to the reverse water gas shift reaction.

Key words: NH₃ oxidation, oxygen storage, catalyst, selectivity, exhaust gas aftertreatment

Preprint submitted to Elsevier

September 26, 2014

1 Introduction

The NO_x storage and reduction catalyst (NSRC, aka lean NO_x trap, LNT) is a device designed for exhaust gas aftertreatment from Diesel and gasoline lean-burn engines in passenger cars. It works under alternating lean and rich conditions. When nitrogen oxides NO_x are adsorbed on the catalyst surface during the longer lean period (low CO and hydrocarbon (HC) concentration, excess of O_2) and then reduced within the short rich period (high CO, H_2 and HC concentrations, low O_2 concentration). During the rich period, a moving reduction front divides the catalyst into two parts – the region close to the monolith inlet is already reduced, while the downstream part is still oxidized [1]. Depending on the local reaction conditions, several N-products (N_2 , NO, NH_3 and N_2O) can be formed during the NO_x reduction.

Ammonia is an important intermediate of the LNT regeneration. NH_3 is a major local product of the NO_x reduction in the front, fully reduced part of the catalyst. The formed NH_3 is transported by convection downstream into the oxidized zone, where it can react with the oxygen and NO_x stored on the catalyst surface [1,2,3,4,5,6,7,8,9,10]. The selectivity of ammonia re-oxidation during the LNT regeneration is a major concern in the practical application, as the N_2O or NO by-products are undesired.

While the steady state NH_3 reaction with the oxygen introduced in the feed leads to a significant formation of N_2O and NO_x [11], the reaction of NH_3 with the pre-stored oxygen was reported to be highly selective towards N_2 [9]. The selectivity of $\text{NO}_x + \text{NH}_3$ reactions over PGM sites depends mainly on temperature, PGM redox state, and NO/ NH_3 ratio. At low temperatures (around the light-off), N_2O is a major by-product of NH_3 reaction with NO. Selectivity towards N_2O decreases with temperature as NO dissociates more readily and PGM sites are kept in a reduced state by NH_3 , which is favorable for N_2 formation [12,13]. Furthermore, at high temperatures N_2O can be reduced to N_2 [12]. Over the entire temperature range, the NO/ NH_3 ratio is a key parameter determining the selectivity: High NO/ NH_3 ratio favors N_2O formation, while at low NO/ NH_3 ratio almost complete selectivity to N_2 can be achieved [9]. This effects drives also the selectivity of NH_3 reaction with stored NO_x . If local NO_x release from adsorption sites is slow compared to PGM reduction rate, then the reaction is highly selective towards N_2 [12,14]. However, when local NO_x release is faster than the corresponding PGM reduction, the selectivity towards N_2O increases [15,16]. Even if N_2O can be formed in NO_x storage catalyst directly also with the other reducing agents available in the exhaust

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gas mixture (e.g., CO, hydrocarbons) under local excess of NO and oxygen on PGM sites [15,16], it is important to understand the role of NH₃ in driving the selectivity of the LNT regeneration process.

Practically all commercial NO_x storage catalysts contain Ce oxides which are known for their oxygen storage properties and water gas shift activity, as well as low-temperature NO_x storage. The presence of CO₂ and H₂O in the automotive exhaust stream influences the redox state of ceria and thus the overall operation of the catalyst. Both CO₂ and H₂O can act as oxidizing agents and oxidize the reduced ceria as described by the following reactions [17]:

Furthermore, CO₂ can adsorb directly on ceria sites to form carbonate species. At low temperatures, CO₂ is adsorbed on both ceria forms (oxidized Ce⁴⁺ as well as reduced Ce³⁺). At high temperatures, thermally unstable carbonates related to the oxidized Ce⁴⁺ form desorb, therefore the total amount of the adsorbed CO₂ decreases as temperature increases. When oxygen is introduced, the re-oxidation of Ce³⁺ to Ce⁴⁺ takes place and CO₂ is simultaneously desorbed [18,19]. The carbonates tend to decompose more easily in presence of H₂O [20]. Altogether, it is obvious that the presence of H₂O and CO₂ in the exhaust gas plays a key role in the reactions involving stored oxygen on cerium oxides.

In this paper, we investigate activity and selectivity of NH₃ reactions over range of operating conditions in a commercial LNT catalyst containing platinum group metals (PGM), Ba and Ce oxides. Steady-state NH₃ self-decomposition as well as oxidation by O₂ and NO are examined in light-off experiments. Periodic lean/rich cycling is measured first with O₂ and NH₃, and then with NO_x+O₂ and NH₃ to discriminate between the NH₃ reactions with the stored oxygen and the stored NO_x. The attention is focused mainly on the reactions of NH₃ with the stored oxygen, on the reaction selectivity towards N₂O and NO, and on the effects of CO₂ and H₂O in the feed mixture.

2 Experimental

The experiments were carried out in a nearly isothermal laboratory bench flow reactor [21]. The inlet mixture was prepared from individual synthetic

gases (CO, C₃H₆, O₂, NO, NH₃, CO₂) and evaporated H₂O admixed into the carrier gas (N₂) using online mass flow controllers. The multiway valve was used for rapid switching ($\Delta t \approx 0.1$ s) between the lean and the rich inlet gas mixtures that were prepared independently in two lines. The evolution of the outlet concentrations was sampled on-line by high speed, high resolution FT-IR analyzer (MultiGas 2030 HS, MKS Instruments). For the measurements of H₂ and O₂ (cannot be detected in IR), the quadrupole mass spectrometer (Omnistar GSD, Pfeiffer Vacuum) was used.

A commercial Ba-based NO_x storage catalyst containing platinum group metals, Ba and Ce oxides was used during the measurements. The catalyst was coated on a 400 cpsi cordierite substrate. Two identical rectangular bricks in series (each 31.0 mm long, 31.0 mm wide and 5.5 mm high) were fitted to the steel lab reactor. Prior to the measurement series, the catalysts were degreened for 2 hours at 550 °C by lean/rich cycling with NO_x in the feed (lean: 7 % O₂, rich: 1.3 % H₂, both: 300 ppm NO, 7 % CO₂, 7 % H₂O, N₂ balance). Before each experiment, the catalyst was reduced by 1% H₂ for 15 minutes at 400°C to remove the stored NO_x from the catalyst surface. Total gas flow rate during the experiments (GHSV) was 50 000 h⁻¹.

The light-off experiments were performed in order to study NH₃ decomposition in the absence and presence of CO₂ and H₂O, and NH₃ oxidation with O₂ and with NO at different NH₃/NO ratios. Temperature range during the light-off experiments was 50–550 °C with the heating rate of 1.5 °C/min. The isothermal lean/rich cycling was performed in a temperature range 100–550 °C with the step of 50 °C. This involved the cycling between O₂ and NH₃, and then also NO_x+O₂ and NH₃ to discriminate between the NH₃ reactions with the stored oxygen and the stored NO_x. [The influence of CO₂ and/or H₂O in the feed on the conversions and selectivities during the cycling was also tested.](#)

3 Results and discussion

3.1 NH₃ and N₂O reactions at steady state

The following reactions were examined at steady state: (i) NH₃ decomposition in the absence and in the presence of H₂O and CO₂, (ii) NH₃ oxidation by O₂, (iii) NH₃ oxidation by NO at different NH₃/NO ratios, and (iv) N₂O decomposition.

Comparison of NH₃ decomposition in the absence and in the presence of CO₂ and H₂O is depicted in Figure 1. NH₃ starts to decompose above 350 °C both in the presence and in the absence of CO₂ and H₂O. As it can be seen in Figure 1a,

NH₃ is decomposed to molecular N₂ and H₂. At higher temperatures (above 450 °C) the presence of CO₂ and H₂O slightly inhibits the NH₃ decomposition reaction, which results in higher concentration of NH₃ passing through the reactor without being consumed. In the case when only CO₂ (no H₂O) was present in the reaction mixture, the NH₃ decomposition rate was the same as in the case when no CO₂ and H₂O were introduced into the reactor, thus revealing that it is the presence of H₂O that is responsible for the inhibition of NH₃ decomposition reaction.

It can be seen in Figure 1b that the highest concentration of H₂ appears at the reactor outlet in the absence of CO₂ and H₂O. The reason is that H₂ formed by NH₃ decomposition can further react with CO₂ via reverse water gas shift (RWGS) reaction, producing CO. The presence of H₂O (one of the RWGS reaction products) in the feed mixtures shifts the reaction equilibrium back towards reactants. Therefore, less H₂ is consumed and less CO is produced in the presence of both CO₂ and H₂O than in the case when only CO₂ is present in the feed mixture.

Figure 1. The evolution of the outlet a) NH₃ and N₂ and b) CO and H₂ concentrations during the NH₃ decomposition performed in the absence and in the presence of CO₂ and H₂O. The inlet gas composition: 3000 ppm NH₃, 0/7 % CO₂, 0/7 % H₂O, N₂ balance.

The results of NH₃ oxidation by oxygen are shown in Figure 2. The light-off of NH₃ oxidation is observed at about 210 °C. The main products of the reaction are N₂ and N₂O at lower temperatures, and NO and NO₂ at higher temperatures. The N₂O curve follows a bell shape, with the maximum at about 320 °C.

The comparison of NH₃ conversions and NO_x, NO₂, N₂O and N₂ outlet concentrations during the NH₃ oxidation by NO with different α =NH₃/NO ratios is depicted in Figure 3. In the case when NH₃/NO=0.67, the light-off of NH₃+NO reaction is at about 180 °C and both N₂ and N₂O are formed around this temperature. At higher temperatures, both NH₃ and NO are totally consumed and no N₂O is observed at the reactor outlet, which means only N₂ is formed (cf. N₂ concentration calculated from the balance). The reaction thus follows equation (3) when both NH₃ and NO are fully consumed.

Figure 2. The evolution of the outlet concentrations during the NH_3 oxidation by oxygen. The inlet gas composition: 1000 ppm NH_3 , 8 % O_2 , 7 % CO_2 , 7 % H_2O , N_2 balance.

In the case when $\alpha = \text{NH}_3/\text{NO} = 0.25$ (Figure 3), the composition of the inlet mixture corresponds to the stoichiometry of reaction 4, and thus N_2O formation should be favorable.

However, both N_2 and N_2O can be observed at the reactor outlet. This means that $\text{NH}_3 + \text{NO}$ reaction follows both equations 3 and 4. This leads to a lower NO consumption than expected according to the stoichiometry of equation (4) and unreacted NO can be observed at the reactor outlet. Up to 350 °C, practically the same amount of N_2 and N_2O is formed, which means that the extent of both reactions is similar. As the temperature increases, the N_2O concentration decreases and the N_2 concentration increases, which indicates that reaction 3 becomes prevailing. This is also demonstrated by the higher concentration of unreacted NO at the reactor outlet.

A product distribution of steady-state ammonia oxidation reactions, both with O_2 and NO , over the tested LNT catalyst containing Ba and Ce oxides is similar to the results reported for $\text{Pt}/\text{Al}_2\text{O}_3$ ammonia oxidation catalysts [22,23,24,25,26,27]. This means that the presence of Ba and Ce storage sites does not influence significantly the selectivity of steady-state NH_3 oxidation.

N_2O decomposition experiment in the presence of O_2 , CO_2 and H_2O was performed at steady state in the temperature range 250–550 °C with the temperature step of 50 °C. The results are depicted in Figure 4. The N_2O decomposition starts at about 400 °C and its extent increases with temperature. This decomposition may also contribute to generally lower N_2O yields observed during LNT operation at high temperatures [15].

Figure 3. The evolution of the NH_3 conversions and the outlet concentrations during the NH_3 oxidation by NO performed at different $\alpha = \text{NH}_3/\text{NO}$ ratios. The inlet gas composition: 160/430 ppm NH_3 , 640 ppm NO , 7 % CO_2 , 7 % H_2O , N_2 balance.

Figure 4. The evolution of the N_2O outlet concentration during the N_2O decomposition reaction. The inlet gas composition: 90 ppm N_2O , 2 % O_2 , 5 % CO_2 , 5 % H_2O , N_2 balance. The experiments performed at steady state at each temperature point.

3.2 Reactions of NH_3 with the stored oxygen

As it is known in the literature, the lean and rich gases can come into contact with each other at lean/rich and rich/lean transitions due to axial backmixing [28]. Thus, the inflow NH_3 , used as the reductant during the NH_3 experiments done in the present study, could have been mixed with the inflow O_2 of the lean mixture and reacted over PGM sites giving rise to N_2O and/or NO_x in analogy to the steady state NH_3 oxidation over PGM sites (cf. Figure 2). To minimize this effect and to reveal only the reactions with the stored oxygen, O_2 in the lean mixture was shut down 2 s prior to the switch to the rich phase and introduced again 2 s after the rich phase end (cf. the dashed vertical lines in Figure 5 and the following Figures).

To elucidate the reaction pathways of NH_3 with the stored oxygen, lean/rich cycling experiments were performed in the absence of NO_x in the feed. The results at several different temperatures are shown in Figure 5. After switching to the rich period, NH_3 readily reacts with the O_2 stored on the catalyst surface.

When the stored oxygen is depleted, NH_3 appears at the reactor outlet. The delay of NH_3 breakthrough increases with the increasing temperature, which is in line with the temperature dependence of the effective oxygen storage capacity. Furthermore, at temperatures above $350\text{ }^\circ\text{C}$, NH_3 is partly decomposed to N_2 and H_2 (Figure 1), which leads to a lower NH_3 limit concentration at the reactor outlet at the end of the rich period.

The reaction of NH_3 with the stored oxygen is highly selective towards molecular N_2 , but also a certain amount of NO_x and N_2O can be formed (Figure 5b,c).

The formed NO_x peak does not break through to the reactor outlet at lower-intermediate temperatures, because the formed NO_x are efficiently adsorbed on the NO_x storage sites along the monolith sample. The effective NO_x storage capacity decreases with temperature, so that the NO_x peak can be observed at the reactor outlet only at $T > 400\text{ }^\circ\text{C}$ (Figure 5c). In steady-state $\text{NH}_3 + \text{O}_2$ reaction, the NO_x product is prevailing at high temperatures (Figure 2) but in the case of stored oxygen, the selectivity to NO is still rather low even at high temperatures (Figure 5c).

By contrast, minor N_2O peaks appear at the lean/rich transient at lower-intermediate temperatures ($150\text{--}300\text{ }^\circ\text{C}$). Two factors were identified to contribute to the highest N_2O peak (ca. 7 ppm) observed at $300\text{ }^\circ\text{C}$: (i) higher oxygen storage capacity and thus higher overall NH_3 conversion than at low temperatures, and (ii) the high effective NO_x storage capacity of the catalyst enabling the storage of the NO_x by-products over the lean phase and subsequent $\text{NO}_x + \text{NH}_3$ reaction leading to the N_2O formation in the next rich phase.

The secondary N_2O peak at the rich/lean transient is observed only at low temperatures (cf. Figure 5b) where the NH_3 adsorption is significant and the slowly desorbing NH_3 could react with the oxygen feed (cf. Figure 5a). By this mechanism, traces of N_2O are formed throughout the entire lean phase at $150\text{ }^\circ\text{C}$.

The effects of CO_2 and/or H_2O present in the feed mixture on the NH_3 kinetics during the oxygen storage and reduction experiments are depicted in Figures 6–9. The presence of water in the feed mixture results in a shorter delay of the ammonia breakthrough, which indicates that H_2O may decrease the effective oxygen storage capacity of the catalyst by inhibiting NH_3 reaction with oxygen storage sites. As H_2O is the reduction product, H_2O desorption would be considerably inhibited under the high partial pressure of water (both in the case of H_2O -only and $\text{CO}_2 + \text{H}_2\text{O}$ present in the inlet mixture). In contrast, the NH_3 consumption increases when CO_2 is present in the dry inlet gas mixture. We suggest that CO_2 can provide additional oxygen for the NH_3 oxidation during the rich period according to equation (1). The summary reaction

Figure 5. The evolution of the outlet a) NH₃, b) N₂O and c) NO_x concentrations during the oxygen storage and reduction experiments (40 s lean, 30 s rich) at different temperatures. The inlet gas composition: 7 % O₂ (lean), 3000 ppm NH₃ (rich), 7 % CO₂, 7 % H₂O, N₂ balance (common). Dashed lines denote 2-s short O₂-free phases applied between the lean and the rich periods to avoid the inlet NH₃ and O₂ mixing.

for the second part of the redox cycle is then

and the entire process represents an analogy to the reverse water gas shift reaction. The presence of CO was detected in the outlet gas at higher temperatures (cf. Figure 9b), confirming this mechanism. At lower temperatures, the formed -CO can stay adsorbed on the catalytic sites without desorption to the gas phase. The accumulated -CO is then oxidized back to CO₂ after the switch to the next lean phase. This -CO accumulation effect was already confirmed by DRIFTS for a similar situation [16].

In the case when both CO₂ and H₂O are present in the inlet gas mixture, excess water slows down the whole redox cycle as it is one of the NH₃ oxidation products. Water also limits the accumulation of adsorbed -CO species on the catalyst surface. Finally, it shifts the equilibrium of the reverse water gas shift reaction towards the reactants so that a lower amount of CO and a higher amount of H₂ product can be observed at higher temperatures (Figure 9b).

The effect of CO₂ on the secondary N₂O peak is significant (cf. Figures 6b–8b).

As discussed above, the highest CO amount is accumulated on the catalyst surface in the case when CO₂ is present in a dry inlet gas mixture, and these are also the conditions where the secondary N₂O peak is the highest. This indicates that the adsorbed CO may contribute to the secondary N₂O formation. Similarly, increased secondary N₂O formation in the presence of CO₂ was already reported for the reduction of the stored NO_x with H₂ [16]. Therefore, a possible reaction pathway for the secondary N₂O peak formation during the lean/rich cycling with O₂ and NH₃ in the presence of CO₂ may involve formation of NO_x by the reaction of NH₃ with the stored oxygen followed by the NO_x adsorption, and the subsequent reaction of the adsorbed NO_x with the CO accumulated on the surface when the gas mixture switches back to lean.

Figure 6. The evolution of the outlet a) NH₃ and b) N₂O concentrations during the oxygen storage and reduction experiments (60 s lean, 60 s rich) at 200 °C. The inlet gas composition: 7 % O₂ (lean), 3000 ppm NH₃ (rich), 0/7 % CO₂, 0/7 % H₂O, N₂ balance (common). Dashed lines denote 2 s short O₂-free phases applied between the lean and the rich periods to avoid the inlet NH₃ and O₂ mixing.

Figure 7. The evolution of the outlet a) NH₃ and b) N₂O concentrations during the oxygen storage and reduction experiments (60 s lean, 60 s rich) at 300 °C. The inlet gas composition: 7 % O₂ (lean), 3000 ppm NH₃ (rich), 0/7 % CO₂, 0/7 % H₂O, N₂ balance (common). Dashed lines denote 2 s short O₂-free phases applied between the lean and the rich periods to avoid the inlet NH₃ and O₂ mixing.

Figure 8. The evolution of the outlet a) NH_3 and b) N_2O concentrations during the oxygen storage and reduction experiments (60 s lean, 60 s rich) at 425 °C. The inlet gas composition: 7 % O_2 (lean), 3000 ppm NH_3 (rich), 0/7 % CO_2 , 0/7 % H_2O , N_2 balance (common). Dashed lines denote 2 s short O_2 -free phases applied between the lean and the rich periods to avoid the inlet NH_3 and O_2 mixing.

Figure 9. The evolution of the outlet a) H_2 and b) CO concentrations during the oxygen storage and reduction experiments (60 s lean, 60 s rich) at 425 °C. The inlet gas composition: 7 % O_2 (lean), 3000 ppm NH_3 (rich), 0/7 % CO_2 , 0/7 % H_2O , N_2 balance (common). Dashed lines denote 2 s short O_2 -free phases applied between the lean and the rich period to avoid the inlet NH_3 and O_2 mixing.

3.3 NO_x storage and reduction with NH_3

To complete the picture of NH_3 reactions in the LNT by the interaction with the stored NO_x , the lean/rich cycling with $\text{NO}_x + \text{O}_2$ and NH_3 was performed at different temperatures. The evolution of the outlet NO_x , NH_3 and N_2O concentrations measured during the lean/rich cycling at 200 °C and 425 °C are depicted in Figure 10. When compared with Figure 5, it is obvious that the main source of N_2O here is the reaction of NH_3 with the stored NO_x and not with the stored O_2 .

In order to avoid mixing of O_2 in the lean mixture with NH_3 in the rich mixture, the oxygen in the lean mixture was again turned off 2 s before the switch to the rich period and turned on 2 s after the switch to the lean period. As it can be seen, the O_2 switch-off before the rich period leads to a partial desorption of the stored NO_x . After the introduction of the rich mixture,

more NO is desorbed and the NO peak is accompanied by the primary N₂O peak appearing at the reactor outlet. When the catalyst surface is reduced, NH₃ also appears at the reactor outlet. The delay of the NH₃ breakthrough depends on temperature and is determined by the rate of ammonia reactions with the stored NO_x and O₂ [2,3]. As it can be seen, the N₂O is produced by the NH₃ reactions with the stored NO_x mainly at lower temperatures °C (Figure 10a), while at higher temperatures, the selectivity is shifted almost completely towards N₂ (Figure 10b). After the O₂ is switched on in the lean mixture, the secondary N₂O can be observed at the reactor outlet at lower temperatures (cf. Figure 10a). This behavior is analogous to the other reducing agents (H₂, CO, C₃H₆) [15].

Figure 10. Detail of the outlet NO_x, NH₃ and N₂O concentrations during the lean/rich cycling experiments (120 s lean, 40 s rich) at a) 200 °C and b) 425 °C. The inlet gas composition: 7 % O₂ (lean), 3000 ppm NH₃ (rich), 300 ppm NO, 0/7 % CO₂, 0/7 % H₂O, N₂ balance (common). Dashed lines denote 2 s short O₂-free phases applied between the lean and the rich periods to avoid the inlet NH₃ and O₂ mixing.

The overall (cycle-averaged) NO_x and NH₃ conversions and N₂O yields during the lean/rich cycling are summarized in Figure 11. The NO_x conversion achieves its maximum at 300 °C. At low temperatures, the NH₃ is not yet fully active in the NO_x reduction, and at high temperatures, the effective NO_x adsorption capacity decreases. The longer rich period gives the higher NO_x conversion, however the NH₃ conversion is then less than 100 %, which can be confirmed by NH₃ slip. The length of the rich period does not have any significant effect on the N₂O formation, because the N₂O is formed mainly in the first part of the rich phase as a product of the NO_x reduction over incompletely reduced PGM sites with local excess of NO over the reducing agent [15,16]. This behavior is again qualitatively in line with the other reductants (H₂, CO, C₃H₆) reported in [15].

4 Conclusions

The activity and selectivity of the NH₃ reactions with the stored oxygen were

Figure 11. Temperature dependence of the integral NO_x and NH_3 conversions and the N_2O yield calculated from the lean/rich cycling experiments (120 s, 20/40 s rich). The inlet gas composition: 7 % O_2 (lean), 3000 ppm NH_3 (rich), 300 ppm NO , 0/7 % CO_2 , 0/7 % H_2O , N_2 balance (common).

studied in detail over range of operating conditions with a commercial Ba-based NO_x storage catalyst containing Ce oxides. Periodic lean/rich cycling was measured first with O_2 and NH_3 , and then with $\text{NO}_x + \text{O}_2$ and NH_3 to discriminate between the NH_3 reactions with the stored oxygen and the stored NO_x . The reaction of NH_3 with the stored O_2 was highly selective towards N_2 , however a certain amount of NO_x and N_2O was also formed. The formed NO_x by-product was efficiently adsorbed on the NO_x storage sites so that the NO_x product was not detected at the reactor outlet except at higher temperatures, where a minor NO_x slip peak was measured during the first part of the regeneration. The stored NO_x reacted with NH_3 in the next rich phase, contributing to the N_2O formation. N_2O was emitted in two peaks — at the transition from the lean to rich period (primary peak) as well at the transition back from the rich to lean period (secondary peak).

The effects of CO_2 and H_2O in the feed mixture were also studied. The presence of CO_2 in the dry feed increased the NH_3 consumption in the reactions of NH_3 with the stored oxygen. CO_2 was able to provide additional oxygen for NH_3 oxidation, forming CO in analogy to the reverse water gas shift reaction. At lower temperatures, the formed $-\text{CO}$ remained on the catalyst surface and increased the selectivity towards N_2O at the transition back to the lean conditions. On the contrary, water inhibited the NH_3 oxidation reactions and suppressed the "promoting" effect of CO_2 when both water and CO_2 were present together.

Steady-state experiments showed that $\text{NH}_3 + \text{NO}$ reaction over PGM sites can be highly selective towards N_2 , however, this holds only for a balanced or NH_3 -rich composition of the reaction mixture. As soon as NO_x is in excess, the selectivity towards N_2O increases substantially. With this respect, NH_3 exhibits similar behavior in the NO_x reduction as any other reducing agent present in the exhaust (e.g., CO or hydrocarbons). N_2O starts to decompose spontaneously at temperatures above 400°C even under oxygen excess.

5 Acknowledgements

This work was supported by the Czech Ministry of Education (Project LH 12086) and U.S. Department of Energy (DOE) Vehicle Technologies Office. The authors gratefully acknowledge the support and guidance of program managers Gurpreet Singh, Ken Howden, and Leo Breton at DOE.”

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