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The reduction of NO_x stored on LNT and combined LNT–SCR systems

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ABSTRACT

The adsorption–reduction by H_2 of NO_x stored on a model LNT Pt–Ba/Al_2O_3 catalyst sample and on a combined LNT + Fe-ZSM5 SCR catalyst is investigated in this work. The storage of NO_x over the LNT Pt–Ba/Al_2O_3 catalyst leads to nitrite formation at low temperatures, and to nitrate at high temperatures (above 300 °C). The stored NO_x are reduced mainly to NH_3 at low temperatures, and to N_2 at high temperatures. In line with previous data and according to experiments carried out with H_2 and NH_3, a two-step in-series pathway for nitrogen formation is proposed involving at first the fast formation of ammonia upon reaction of NO_x with H_2, followed by the slower reaction of the so-formed ammonia with the stored NO_x leading to N_2. This two-step in-series pathway together with the integral behaviour of the reactor accounts for the temporal evolution of the products which is observed during regeneration of LNT catalysts.

A Fe-ZSM5 SCR placed downstream the LNT catalyst stores NH_3 released during the rich phase from the LNT sample. The stored ammonia is effectively converted to N_2 during the subsequent lean phase, due to the occurrence of the SCR reaction over the Fe-ZSM5 catalyst bed. Hence the presence of a SCR catalyst layer placed downstream a LNT sample leads to the twofold benefit of reducing the NH_3 slip and to increase the NO_x removal efficiency. These advantages are most important at low temperatures, and tend to vanish at high temperatures where the NH_3 slip is less important.

1. Introduction

The transportation sector and in particular diesel-equipped vehicles are blamed as one of the primary sources of NO_x emission. For this reason regulations to control NO_x emission in industrial countries are becoming very severe: in Europe, the next Euro 5 regulations (2009) and the subsequent Euro 6 rules (2014) will require a threefold decrease of NO_x emission for diesel passenger cars, from the current 0.25 g/km set by Euro 4 down to 0.08 g/km (Euro 6).

Three way catalysts (TWC), which are used in the case of stoichiometric gasoline engines, are not effective in the reduction of NO_x under lean conditions, i.e. in the case of diesel engines. Viable solutions for the control of NO_x in this case are the urea-SCR technique, which accomplishes the NO_x reduction by injecting urea (a precursor of NH_3) in the exhaust gases, or the NO_x storage reduction (NSR) or lean NO_x trap (LNT) system [1–3]. In such a technique the removal of NO_x is realized under cyclic conditions, by alternating long lean periods during which NO_x are adsorbed in the form of nitrites and nitrates with short excursions under rich conditions during which the stored NO_x are reduced to N_2. A typical NSR catalyst consists of a NO_x storage component, such as an alkaline or alkaline earth metal oxide (e.g. K and Ba), and of a noble metal (Pt) that catalyses the oxidation of NO, CO and unburned hydrocarbons (UHC) during the lean phase, and the reduction of the stored NO_x during the rich phase. These active elements are dispersed on a high surface area support, such as γ-alumina. Commercial catalyst formulations may include other components such as ZrO_2 or CeO_2–ZrO_2, Pd and Rh, TiO_2 [2,4].

Although urea-SCR is preferred for heavy trucks and mini-van, LNTs are cheaper for small engines [1]. In fact an advantage of this technology with respect to the SCR technique is that LNTs do not make use of an ammonia precursor as a reductant, so that no relevant layout modifications are needed. Still the resistance to thermal ageing and sulphur poisoning of NSR catalysts need to be improved.

Accordingly in the last few years the potential of the LNT technology motivated extensive investigations by the academic and the industrial communities: efforts have been devoted to the analysis of both the storage of NO_x and of the subsequent regeneration of the trap, during which adsorbed NO_x are reduced to N_2 although the formation of other by-products (in particular NH_3) is also observed. As a matter of fact, the chemistry and mechanisms involved in the reduction of stored NO_x are still a matter of debate:

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it has been suggested that the reduction of stored NO_x over NSR catalysts implies at first the release of NO_x from the catalyst surface in the gas phase, followed by the reduction of the released NO_x to N_2 or other products. Based on this scheme, different proposals have been advanced to explain the nitrate decomposition and the reduction of the released NO_x as well. In particular, the reduction of NO_x in a rich environment is thought to occur according to the mechanism of three-way catalysis. However, these routes can hardly explain the very high N_2 selectivity and the temporal sequence of products which is typically observed upon regeneration of LNT systems under nearly isothermal conditions when hydrogen is used as a reductant (with the evolution of ammonia following that of nitrogen). Recently, the involvement of ammonia in the reduction of the stored nitrates by H_2 has been considered [5–9], and a mechanism which is able to account for the high selectivity of the reaction and the temporal sequence of the products during the rich operation has also been proposed [5,7,9]. According to Cumaranatunge et al. [5] and to Mulla et al. [9] a regeneration front develops in the trap during the rich phase, which travels along the trap. Ammonia and N_2 can be simultaneously formed in the H_2-rich zone of the front, according to previously suggested mechanisms for three-way catalysts. However, NH_3 may further react with the nitrates stored downstream the front, leading to the formation of N_2. This would explain the temporal sequence of the products formation with NH_3 breakthrough observed after N_2 production when the stored NO_x start to deplete and are insufficient to react with the NH_3 formed upstream. A similar scheme has also been provided by some of us [7,8], with the formation of an H_2 front travelling along the reactor axis. Moreover, clear evidences have been provided on the fact that N_2 formation involves the occurrence of an in-series two-step molecular process involving at first the formation of NH_3 upon reaction of H_2 with the stored nitrates, followed by the reaction of the so-formed ammonia with nitrates located downstream the H_2 front. This reaction leads selectively to N_2. Notably step 1 (i.e. NH_3 formation) has been found to be much faster than the second step (nitrogen formation upon reaction of nitrates with NH_3). Accordingly the regeneration of the trap proceeds both in the part of the reactor in which nitrates are reduced by H_2 to give ammonia and in the zone in which the ammonia formed upstream reacts with nitrates leading to N_2.

In order to gain further insight on the mechanisms governing the reduction of the stored NO_x and on the role of NH_3 in the process, the reactivity of NO_x stored over a model Pt–Ba/Al_2O_3 catalyst towards H_2 has been further analyzed in this work. In particular in previous experiments [7,8] the reactivity with H_2 of NO_x stored at fixed temperatures, i.e. 250 °C and 350 °C, has been analyzed at different temperature levels. In this work we planned to investigate the reactivity of the stored NO_x in a wider temperature range, and during isothermal cycles in which both the NO_x storage and reduction are carried out at the same temperature. For this purpose, lean–rich cycles (i.e. NO_x adsorption–reduction experiments) have been carried out at different temperatures, while carefully analyzing the formation of the various reaction products. The adsorption and the reduction stages have been separated by an inert purge in between, so to obtain more clear indications on the reaction pathways ongoing during both the NO_x adsorption and reduction phases.

Finally, having observed during the rich step and at low temperatures the formation of significant amounts of NH_3, which leaves the catalyst unreacted (NH_3 slip), the reactivity of a combined LNT–SCR systems in which the model Pt–Ba/Al_2O_3 LNT catalyst sample is placed upstream a commercial SCR catalyst has also been investigated. In principle, by adopting this catalysts configuration, NH_3 formed over LNT during the rich phase can be stored on the SCR catalyst, and consumed in the subsequent lean phase [10,11]. This might lead in principle to both a decrease of the NH_3 slip and a simultaneous increase of NO_x removal.

2. Methods

2.1. Materials

The model Pt–Ba/Al_2O_3 (1/20/100, w/w) LNT catalyst has been prepared by impregnating a binary Pt/Al_2O_3 sample with an aqueous solutions of $Ba(CH_3COO)_2$ (Strem Chemical, 99%), followed by drying at 80 °C and calcination at 500 °C for 5 h. The Pt/Al_2O_3 has been obtained by impregnating a γ-Al_2O_3 carrier calcined at 700 °C (Versal 250 from UOP, surface area of 200 m^2/g and pore volume of 1.2 cm^3/g after calcinations at 700 °C), with a solution of $Pt(NH_3)_2(NO_2)_2$ (Strem Chemicals, 5% Pt in ammonium hydroxide) followed by drying at 80 °C overnight and calcination at 500 °C for 5 h. The calcined Pt–Ba/Al_2O_3 sample has a surface area near 160 m^2/g and a pore volume of 0.82 cm^3/g. Further details on the catalyst preparation and characterization are reported elsewhere [12].

The SCR catalyst is a Fe-ZSM5 sample purchased from Zeolyst International (Fe loading near 1%, w/w, surface area of 200 m^2/g and pore volume of 10 cm^3/g).

2.2. Apparatus and procedures

The NO_x adsorption–reduction tests have been performed in a quartz tubular fixed-bed microreactor connected to a mass spectrometer for complete analysis of reactants and products [12].

Reactivity tests with either a single LNT or SCR catalyst layer (Pt–Ba/Al_2O_3 or Fe-ZSM5) or with a double-bed LNT + SCR arrangement (in which the Fe-ZSM5 SCR catalyst is placed downstream the Pt–Ba/Al_2O_3 sample) have been carried out. In the case of the single-bed experiments 60 mg of catalyst (80–100 μm) have been loaded into the reactor, whereas in the case of the double-bed configuration 60 mg of each catalyst have been used (total catalyst loading of 120 mg). The catalyst temperature has been measured by means of a thermocouple directly immersed in the catalyst bed; in the case of the double-bed experiments the thermocouple has been located in the upper bed. Due to the dilute conditions employed in our experiments, thermal effects have also been found to be negligible upon lean–rich cycling (<2 °C). Accordingly the experiments have been performed under nearly isothermal conditions.

Lean–rich cycles have been carried out at different temperatures. During the lean phase, a pulse of NO (1000 ppm) has been admitted to the reactor in flowing He + 3% (v/v) O_2 until catalyst saturation. Then after a He purge at the same temperature, catalyst regeneration (rich phase) has been carried out with H_2 (2000 ppm in He). Before each test, the catalyst samples have been conditioned by performing a few adsorption/regeneration cycles. Conditioning lasted until a reproducible behaviour has been obtained; this typically required 2–3 cycles.

In a different set of experiments, after catalyst conditioning at 350 °C, NO_x have been adsorbed at the same temperature, followed by a He purge to provoke the desorption of weakly adsorbed species. Then the reduction of the adsorbed NO_x species has been performed both with H_2 and with NH_3 at different temperatures, in the range 100–350 °C. This allowed the analysis of the reduction process starting from the same loading and nature of NO_x adsorbed species. Accordingly during the He purge after the NO_x adsorption at 350 °C the catalyst temperature has been set at the desired value; then a rectangular step feed of H_2 (2000 ppm in He) or NH_3 (1000 ppm in He) has been admitted to the reactor. When the reduction process has been completed (i.e. when the concentration of the products exiting the reactor was negligible), the H_2 or NH_3

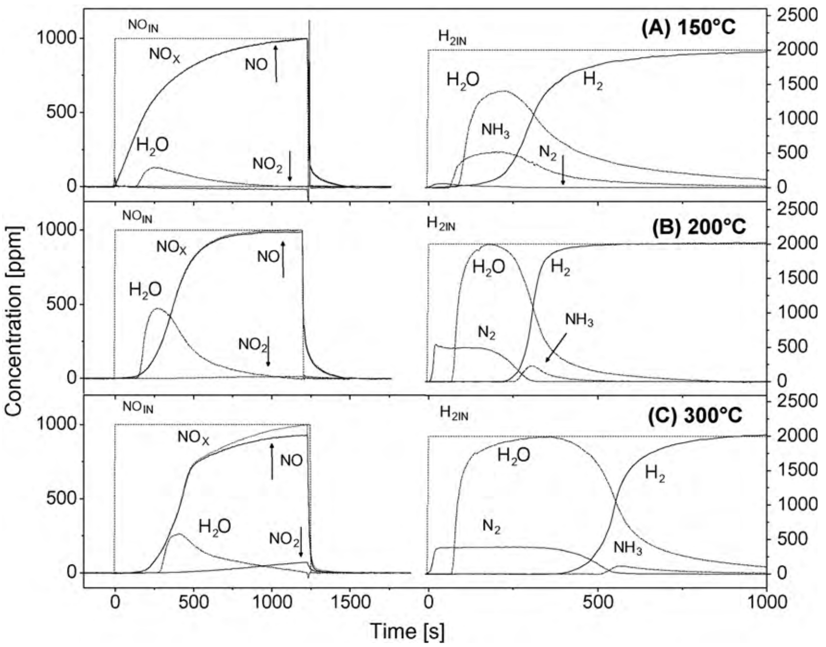

Fig. 1. Lean–rich cycles carried out over the Pt–Ba/Al_2O_3 catalyst sample at 150 °C (A), 200 °C (B) and 300 °C (C). Lean phase: 1000 ppm NO in He + 3% (v/v) O_2; rich phase: 2000 ppm H_2 in He. Catalyst loading 60 mg, flow rate 100 cm^3/min (@ 1 atm and 0 °C).

flow has been stopped and the catalyst has been heated at 350 °C under He flow. Eventually a new H_2 step (2000 ppm in He) has been fed to the reactor at 350 °C to complete the reduction of the residual amounts of stored NO_x left after the previous reducing treatment, if any. In fact dedicated experiments showed that this procedure was able to completely remove the stored NO_x species: accordingly the extent of NO_x reduction during the rich phase at each temperature (efficiency in the reduction of the stored NO_x) could be evaluated.

Notably, due to the dilute conditions employed in the runs, the experiments have been performed under nearly isothermal conditions in the catalyst bed, i.e. in the absence of any significant thermal effects upon the lean/rich switches.

A flow of 100 cm^3/min (@ 1 atm and 0 °C) has always been used during all experiments, both in the case of the single-bed reactor and in the case of the double-bed arrangement.

The selectivity to N_2 of the reduction process has also been estimated. Due to the variations in the product distribution with time, the N_2 selectivity (S_{N_2}) has been estimated as time-weighted average according to the following equation:

$$S_{N_2} = \frac{2n_{N_2}}{2n_{N_2} + n_{NO} + n_{NH_3}} \qquad \text{(a)}$$

In Eq. (a), n_{N_2}, n_{NO} and n_{NH_3} are the total molar amounts of N_2, NO and NH_3, respectively, evolved during the entire reduction phase. N_2O concentration has always been found negligible in the experiments and accordingly this species has not been included in Eq. (a).

The N-balance, estimated by comparing the amounts of NO_x adsorbed during the lean phase with those of the N-containing species formed upon reduction of the stored NO_x, always closed within ±5–10%.

3. Results and discussion

3.1. NO_x storage–reduction over Pt–Ba/Al_2O_3

The NO_x storage–reduction over Pt–Ba/Al_2O_3 has been investigated at different temperatures in the range 150–350 °C, and the results obtained at selected temperatures (150 °C, 200 °C and 300 °C) are shown in Fig. 1. The lean–rich cycles shown in Fig. 1 have been obtained after conditioning of the catalyst at the same temperature with a few adsorption–reduction cycles, until a stable behaviour is obtained.

At the lowest investigated temperature (150 °C, Fig. 1A), upon NO admission to the reactor (t = 0 s) the NO breakthrough is immediately observed. The NO concentration slowly increases with time and eventually reaches the inlet NO concentration value after 1200 s. No significant NO_2 evolution is observed at this temperature. At t = 1250 s the NO inlet concentration is switched off; after the switch a tail is observed in the NO concentration profile, due to the desorption of weakly adsorbed NO_x species.

During NO adsorption the evolution of water is observed. As discussed elsewhere [2,12], this is due to the uptake of NO_x on $Ba(OH)_2$ sites, accompanied by release of H_2O. The amount of NO_x stored at this temperature, estimated by difference from the reactor inlet and the outlet NO_x concentration, is near 3.78×10^{-4} mol/g_{cat} (Fig. 2 and Table 1). This corresponds to an overall Ba utilization (i.e. the fraction of Ba involved in the storage to the overall Ba content of the catalyst, by assuming the formation of either $Ba(NO_2)_2$ or $Ba(NO_3)_2$) close to 15%.

The results obtained upon reduction with H_2 at 150 °C of the NO_x stored at the same temperature are shown in Fig. 1A, right panel. H_2 is completely consumed upon its admission to the reactor; the H_2 breakthrough is observed near 200 s. Minor amounts of N_2 are immediately observed upon H_2 admission, and after roughly 60 s large quantities of ammonia are detected. Water is also formed during reduction, whereas no appreciable amounts of other

Table 1
Amounts of stored NO_x on Pt–Ba/Al_2O_3 catalyst at different temperatures and fraction of surface nitrites.

Temperature (°C)	Stored NO_x (mol/g_{cat})	% Nitrites
150	3.78×10^{-4}	~85
200	5.00×10^{-4}	~20
300	6.04×10^{-4}	~0
350	6.21×10^{-4}	~0

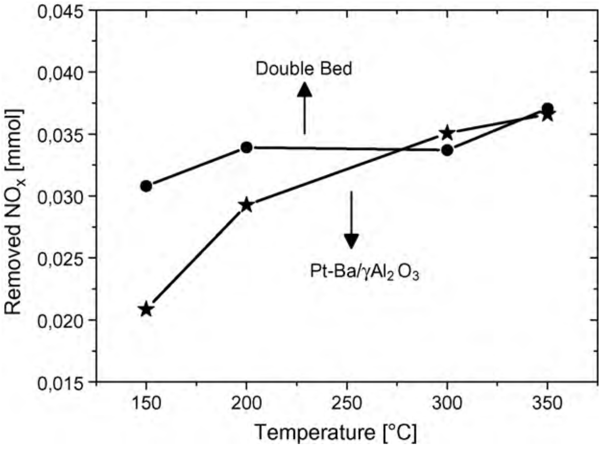

Fig. 2. Amounts of NO_x removed during the lean phase over the Pt–Ba/Al_2O_3 catalyst and the Pt–Ba/Al_2O_3–Fe-ZSM5 double-bed arrangement.

products (e.g. NO and N_2O) are observed at the reactor outlet. Accordingly at this temperature the average N_2 selectivity of the reduction, estimated according to Eq. (a), is very poor (below 10%).

The overall H_2 consumption and the corresponding NH_3 and N_2 formation is due to the reduction of adsorbed NO_x species, according to the stoichiometry of the following global reactions:

$$Ba(NO_2)_2 + 6H_2 \rightarrow 2NH_3 + BaO + 5H_2O \qquad (1)$$

$$Ba(NO_2)_2 + 3H_2 \rightarrow N_2 + BaO + 5H_2O \qquad (2)$$

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O \qquad (3)$$

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O \qquad (4)$$

Reactions (1)–(2) and (3)–(4) accounts for the reduction of nitrites and nitrates, respectively, to NH_3 and N_2. Notably, in reactions (1)–(4) the formation of BaO is envisaged; as pointed out in [12], $Ba(OH)_2$ is also formed by reaction of BaO with H_2O according to the following reaction:

$$BaO + H_2O \rightarrow Ba(OH)_2 \qquad (5)$$

The formation of $Ba(OH)_2$ species during the reduction of stored NO_x is confirmed by the release of water upon NO addition to the catalyst in the adsorption (lean) phase, as previously discussed (Fig. 1).

According to stoichiometries (1)–(4), different amounts of H_2 are consumed when N_2 and NH_3 formation are associated to the reduction of either nitrites (reactions (1) and (2)) or nitrates (reactions (3) and (4)). Thus on the basis of the molar ratio between the amounts of evolved $N_2 + NH_3$ and of consumed H_2, from stoichiometries (1)–(4) the ratio nitrites/nitrates in the stored NO_x can be evaluated, if one neglect any H_2 consumption via other routes (e.g. the reduction of PtO to Pt). Indeed it is estimated that this contribution is at least one order of magnitude lower than that involved in the reduction of the stored NO_x. Calculation showed that nitrites are the most abundant adsorbed species at 150 °C, since they account for near 85% of the overall NO_x (Table 1). This is in line with previous FTIR studies on the adsorption of NO_x over the same catalytic systems showing the presence of a large fraction of nitrites when the adsorption is carried out at low temperatures [13]. Accordingly, due to the poor N_2 formation, it is concluded that reaction (1), and to a minor extent reaction (3), account for more than 90% of the overall H_2 consumption.

Significant changes in the NO_x storage–reduction behaviour are observed upon increasing the temperature. In particular the amounts of stored NO_x increase upon increasing the temperature: at 200 °C and 300 °C (Fig. 1B and C, respectively) the NO_x breakthrough is observed near 150 s and 200 s, respectively; formation of NO_2 is also observed, particularly at 300 °C. A NO_x storage capacity near 5×10^{-4} mol/g_{cat} and 6×10^{-4} mol/g_{cat} is measured at 200 °C and 300 °C, respectively (Fig. 2 and Table 1). The NO_x storage capacity further increases at 350 °C (6.2×10^{-4} mol/g_{cat}). Notably, as it will be discussed below, the increase in the reaction temperature also leads to a decrease of the amount of nitrites stored on the catalyst surface. Indeed nitrites are estimated to be near 20% of the overall NO_x stored at 200 °C, whereas only nitrates are present at 300 °C and 350 °C.

Fig. 1B shows the results obtained upon reduction at 200 °C of NO_x stored at the same temperature. Complete consumption of H_2 is observed and the N_2 outlet concentration immediately increases to a level near 500 ppm upon H_2 admission. The reduction reaction is very fast and minor amounts of NH_3 are observed at the reactor outlet, when the production of N_2 starts to decrease. Accordingly complete selectivity to nitrogen is initially observed, since no appreciable amounts of NO and/or N_2O are observed: the N_2 selectivity decreases at the end of the reduction process, due to NH_3 formation. The time-weighted average N_2 selectivity of the overall reduction process is near 91% in this case.

On the basis of stoichiometries (1)–(4), it is calculated that nitrites represent roughly 20% of the adsorbed NO_x species. Notably, the observed N_2 concentration level near 500 ppm which is observed upon complete H_2 consumption is also consistent with the presence of significant amounts of nitrites. Indeed this concentration value falls between that expected from the reduction by 2000 ppm of H_2 of nitrites (reaction (2), 667 ppm) and of nitrates (reaction (4), 400 ppm).

Further increase of the temperature (300 °C, Fig. 1C) favours the N_2 formation at the expense of ammonia, so that at high temperature the N_2 selectivity of the reduction becomes very high (near 95% at 300 °C). Also in this case, however, the N_2 selectivity changes with time, and ammonia evolution follows that of N_2.

Notably, upon H_2 admission at this temperature the N_2 outlet concentration reaches the level of 390 ppm. This concentration level well corresponds to the stoichiometry of reaction (4), i.e. to the reduction of nitrates by H_2. This indicates that at high temperatures NO_x are stored prevalently in the form of nitrates [14,15].

Similar results have been observed at higher temperatures (350 °C, data not shown).

Accordingly the data discussed above pointed out that at low temperatures (150 °C) NO_x are stored mainly in the form of nitrites, whereas nitrates prevails at high temperatures. Notably, NO_x adsorbed species are reduced selectively to ammonia at low temperature (the N_2 selectivity is near 10% at 150 °C), whereas N_2 formation prevails at high temperatures (300 °C and above). It may be argued that the observed change in selectivity of the reduction process is affected by the nature and the amounts of stored NO_x. However, as discussed below (Fig. 3), very similar results have been obtained upon reduction at various temperatures of NO_x adsorbed at a preset temperature (350 °C, corresponding to the formation of nitrates), and with a similar nitrate loading as well. As a matter of fact even in this case an identical dependence of the N_2 selectivity with temperature is observed, with ammonia and nitrogen formation prevailing at low and high temperatures, respectively.

The observed dependence of the N_2 selectivity with temperature during lean–rich cycles is in line with previous data showing that ammonia is intermediate in the formation of nitrogen upon reduction of nitrates with H_2 [7,8]. This conclusion was mainly derived from the results of temperature programmed surface reaction (TPSR) experiments in which the reactivity of H_2 and of

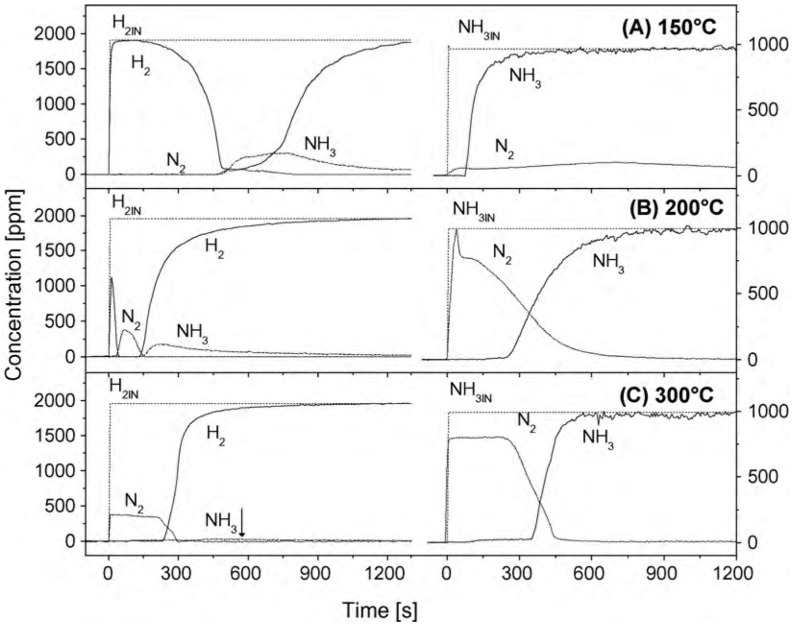

Fig. 3. Rich cycles carried out over the Pt–Ba/Al_2O_3 catalyst sample at 150 °C (A), 200 °C (B) and 300 °C (C) after NO_x adsorption at 350 °C. Reduction with H_2 (2000 ppm in He, left-hand side) and with NH_3 (1000 ppm in He, right-hand side). Catalyst loading 60 mg, flow rate 100 cm^3/min (@ 1 atm and 0 °C).

NH_3 towards nitrates adsorbed over the same Pt–Ba/Al_2O_3 catalyst sample used in this study has been investigated [7,8]. In particular TPSR experiments showed that stored nitrates are easily reduced by H_2 at very low temperatures, leading with almost complete selectivity to the formation of ammonia. NH_3 was also found to be active in the reduction of the stored nitrates, but at higher temperatures if compared to H_2. Notably, complete selectivity to nitrogen is observed during the NH_3 + nitrate reaction, which occurs according to the overall stoichiometry of the following reaction:

$$3Ba(NO_3)_2 + 10NH_3 \rightarrow 8N_2 + 3BaO + 15H_2O \tag{6}$$

Accordingly it is suggested that the reduction of stored NO_x by H_2 occurs via a two-step pathway which involves a first fast step leading to the formation of ammonia (reaction (3)), followed by the slower reaction of ammonia with stored NO_x to form nitrogen (6):

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O \tag{3}$$

$$3Ba(NO_3)_2 + 10NH_3 \rightarrow 8N_2 + 3BaO + 15H_2O \tag{6}$$

Notably, the sum of reactions (3) and (6) leads to the overall stoichiometry for the reduction of nitrates to N_2, i.e. reaction (4):

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O \tag{4}$$

The involvement of nitrates has been suggested in the stoichiometries considered above, but a similar scheme can be envisaged for nitrites as well.

To better analyze these aspects, lean–rich cycles have been performed in which NO_x have been stored at 350 °C (i.e. in the form of nitrates), and the reduction of the stored nitrates has been accomplished with H_2 and NH_3 at different temperatures, in the range 150–350 °C. The results are shown in Fig. 3 which compares the concentration profiles of hydrogen, nitrogen and ammonia measured at the reactor outlet upon reduction of nitrates stored at 350 °C with H_2 (Fig. 3, left panel) and with NH_3 (Fig. 3, right panel) at selected temperatures (150 °C, 200 °C and 300 °C).

In the case of the experiment carried out with H_2, at 150 °C (Fig. 3A) the reaction shows a significant induction period. Indeed initially H_2 is detected unconverted at the reactor outlet; then, after 200 s, the H_2 concentration starts to decrease showing a minimum near 450–750 s. The decrease of the H_2 concentration is accompanied by the evolution of NH_3 and of minor amounts of N_2; however, a delay is observed between NH_3 (and N_2) evolution (near 450 s) and the H_2 uptake (200 s).

The observed induction period possibly indicates that H_2 is initially adsorbed and activated on the catalyst surface. One may speculate that at this low temperature nitrates are initially reduced to nitrites; once nitrites have been formed they are reduced to NH_3 and, to a minor extent, to N_2. Indeed the overall N_2 selectivity is very poor, being below 20%. At this temperature near 80% of the initially adsorbed NO_x could be reduced by H_2 (Fig. 4A).

Upon increasing the reaction temperature at 200 °C (Fig. 3B), the induction period almost disappeared, possibly indicating a faster reduction of nitrates to nitrites, and only a small and sharp H_2 peak is observed upon admission of H_2 to the reactor. N_2

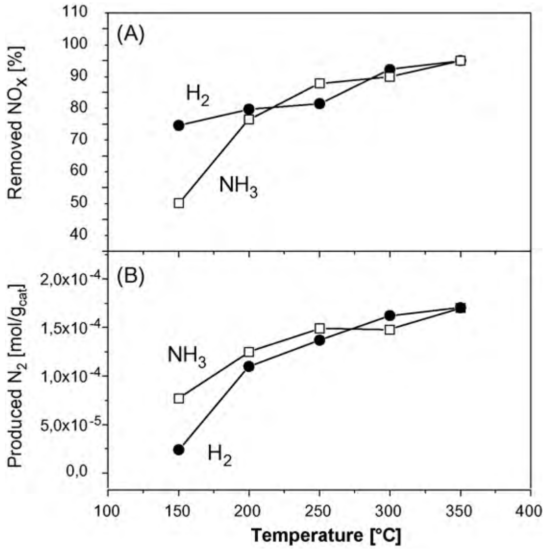

Fig. 4. Efficiency of NO_x removal (A) and amounts of N_2 evolved during the rich phase (B) at various temperatures over the Pt–Ba/Al_2O_3 catalyst upon reduction with H_2 or NH_3.

formation is observed after the H_2 peak, followed by NH_3 evolution which is seen in correspondence of H_2 breakthrough.

For further increase of the reduction temperature the initial H_2 peak is no longer observed: H_2 is fully consumed and N_2 formation is immediately observed upon H_2 admission, with no delay. Ammonia evolution always follows that of N_2 and is accompanied by the detection of unconverted H_2. NH_3 formation significantly decreases with temperature, so that at the maximum investigated temperature (300 °C) negligible amounts of ammonia have been detected.

When the reduction of the stored nitrates is carried out with NH_3 (Fig. 3, right panel), only N_2 has been observed within the products at the reactor outlet. As opposite to H_2, at 150 °C the reactivity of ammonia in the reduction of the stored nitrates is very poor. Only minor amounts of N_2 are detected upon NH_3 addition (near 50–100 ppm) because the reaction is under kinetic control and is limited by the reactivity of ammonia. The reaction proceeds for several minutes (nearly 1 h) and then the N_2 concentration drops to zero (not shown in the figure due to the limited time span). At the end of the reduction process near than 50% of the initially adsorbed nitrates have been reduced (Fig. 4A).

Upon increasing the reduction temperature at 200 °C, the stored NO_x are readily reduced to N_2: in fact upon the step addition of NH_3 at $t = 0$ s ammonia is completely consumed and the N_2 outlet concentration immediately increases to a level near 800 ppm. This concentration value corresponds to that expected from the reduction of nitrates by NH_3 according to the stoichiometry of reaction (6). Roughly 80% of the initially adsorbed nitrates have been removed at this temperature at the end of the reduction (Fig. 4A).

Upon further increase of the reduction temperature (300 °C) the reaction becomes even faster: the NH_3 breakthrough is shifted and becomes very sharp, in line with the effect of temperature on the rate of the reaction.

The results shown in Fig. 4A hence indicate that at low temperatures (150 °C) H_2 is more reactive than NH_3 in the reduction of adsorbed nitrates, at variance with that reported by Mulla et al. [9] who reported that NH_3 is as effective than H_2 in the regeneration of the stored NO_x. However, at higher temperatures the reactivity of H_2 and of NH_3 becomes similar, in line with the results of Mulla et al. [9]. Notably, at low temperatures NH_3, and not N_2, is formed when using H_2 as a reductant. It is worth of note that comparable amounts of nitrogen are obtained upon reduction of stored nitrates with hydrogen and with ammonia at any temperature (Fig. 4B). This confirms that the reaction of ammonia with nitrates is rate determining in the two-step in-series process for nitrogen formation.

The two-step in-series pathway suggested for nitrogen formation from adsorbed nitrates accounts for the temporal evolution of the product selectivity which is observed during the experiments shown in Fig. 1, and for the increase in the selectivity of the reduction process with temperature as well. In fact, the occurrence of a fast reaction of H_2 with the stored NO_x to give ammonia and the integral ‘‘plug-flow'' behaviour of the reactor implies the complete consumption of the reductant H_2 in the catalyst bed leading to the formation of an H_2 front travelling along the reactor axis. As sketched in Fig. 5, at a given instant of the regeneration phase the initial part of the trap, upstream the H_2 front, has already been regenerated and the Ba storage sites have been restored in the form of BaO and/or $Ba(OH)_2$. In the zone corresponding to the development of the H_2 front, the formation of ammonia due to reduction of nitrates by H_2 (fast reaction) is taking place; the formed ammonia may compete with H_2 in the reduction of stored NO_x in this part of the trap or may react with NO_x stored in part of the trap immediately downstream the H_2 front, i.e. in the absence of H_2, if the temperature is high enough. Finally in the last part of the trap the nitrates initially stored have not yet been reduced.

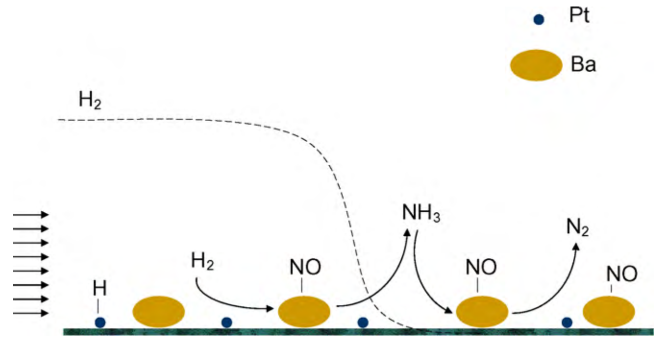

Fig. 5. Sketch of the reduction mechanism of the Pt–Ba/Al_2O_3 LNT catalyst upon regeneration with H_2.

According to this picture, when the regeneration of the trap is carried out at low temperatures (150 °C), H_2 reacts with surface NO_x to give NH_3 according to reactions (1) and/or (3), and an H_2 front develops. Due to the low temperature, ammonia can hardly react with the stored NO_x to form N_2, and this lead to the evolution of ammonia as major reaction product (Fig. 1A). When the H_2 front reaches the end of the trap, the H_2 breakthrough is observed and regeneration of the trap is completed.

Upon increasing the reaction temperature, the reactivity of NH_3 with stored NO_x becomes appreciable and this leads to the formation of N_2 which is indeed immediately detected at the reactor outlet (Fig. 1B). Since H_2 is by far more reactive than NH_3 towards surface nitrates, it is likely that NH_3 reacts preferentially with nitrates located downstream the H_2 front. This leads to a NH_3 consumption and to an increase of the N_2 selectivity. When the H_2 front reaches the end of the trap, the H_2 breakthrough is observed along with NH_3, being the regeneration of the trap completed. According to this mechanism N_2 detection at the reactor outlet precedes that of NH_3.

Due to the occurrence of the suggested two-step in-series pathway for the reduction of stored NO_x by H_2, and because of the different temperature thresholds associated to the reactivity of H_2 and NH_3 with the stored NO_x, the release of NH_3 (i.e. the NH_3 slip) is more relevant at low temperatures in the case of the investigated Pt–Ba/Al_2O_3 LNT catalyst sample. This is indeed apparent from Fig. 6 which shows that the amounts of ammonia released upon

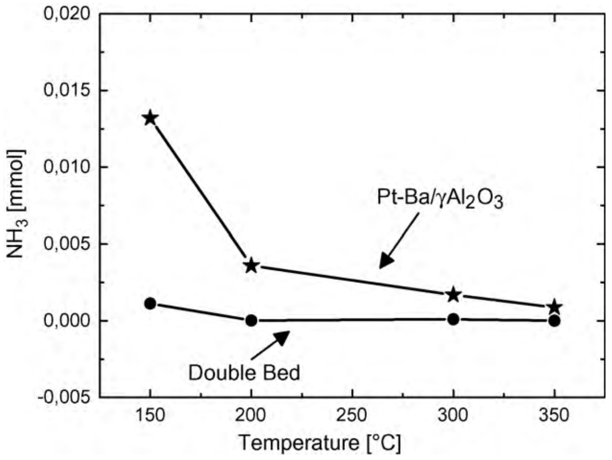

Fig. 6. Amounts of NH_3 evolved during the rich phase upon reduction with H_2 at various temperatures over the Pt–Ba/Al_2O_3 catalyst and over the Pt–Ba/Al_2O_3–Fe-ZSM5 double-bed arrangement.

regeneration of the stored NO_x significantly decreases on increasing the reaction temperature.

3.2. Lean–rich operation over a double-bed LNT + SCR reactor

NH_3 which is released from the LNT catalyst during rich operation (in particular at low temperatures) due to its poor reactivity towards the stored NO, can be stored on a SCR catalyst located downstream the LNT catalyst bed. The stored ammonia can in principle react with NO_x during the subsequent lean phase, with a double benefit of increasing the overall NO_x removal efficiency and decreasing the NH_3 slip. To analyze these aspects, an in-series double-bed arrangement has been tested, in which a SCR sample (Fe-ZSM5) has been placed downstream the Pt–Ba/Al_2O_3 LNT catalyst sample previously investigated. This catalyst configuration has been tested under the same experimental conditions adopted for the single Pt–Ba/Al_2O_3 LNT catalyst layer.

Fig. 7A–C shows the results obtained during the NO_x storage–reduction experiments carried out over double-bed configuration at 150 °C, 200 °C and 300 °C, respectively. As in the case of the data shown in the case of the Pt–Ba/Al_2O_3 LNT catalyst sample, also in this case the data shown in Fig. 7 have been obtained after catalyst conditioning, until a reproducible behaviour is obtained in the lean–rich cycles.

At the lowest investigated temperature (150 °C, Fig. 7A), upon NO admission to the reactor (t = 0 s) the NO breakthrough is immediately observed, as in the case of the single Pt–Ba/Al_2O_3 catalyst layer. However, a slower increase of the NO_x concentration trace with time is observed in this case (compares Figs. 1A and 7A), so that at the end of the lean phase a higher amount of NO_x has been removed from the gas phase (Fig. 2). Notably, besides water, N_2 evolution is also observed during the lean phase, as opposite to what observed in the case of the single Pt–Ba/Al_2O_3 catalyst (Fig. 1A). As will be discussed in the following, N_2 formation is related in this case to the reaction between NH_3 stored on the SCR catalyst bed during the previous rich phase and NO_x not adsorbed on the Pt–Ba/Al_2O_3 catalyst layer (see below).

After adsorption at 150 °C, the stored NO_x have been reduced with H_2 at the same temperature (Fig. 7A). As apparent from the figure, H_2 is completely consumed upon its admission to the reactor, and its breakthrough is observed after 200 s. Upon H_2 admission the evolution of minor amounts of N_2 are observed at the reactor outlet, along with very small amounts of NH_3. Water is also formed during reduction, whereas no appreciable amounts of other products (e.g. NO and N_2O) has been observed.

The overall H_2 consumption is much higher than that expected from the corresponding NH_3 and N_2 formation according to the stoichiometries of reactions (1)–(4). This fact, along with the absence at the reactor outlet of the relevant NH_3 amounts which instead have been observed in the case of the Pt–Ba/Al_2O_3 single-bed arrangement (see Fig. 1), suggests that NH_3 which is released from the LNT catalyst during the rich phase is effectively retained over the Fe-ZSM5 SCR catalyst placed downstream. This makes almost negligible the NH_3 slip at this temperature (Fig. 6). As a matter of fact, the presence of ammonia stored in the reactor after regeneration with H_2 has been proved by dedicated TPD experiment carried out at the end of the rich pulse at selected temperatures (results not shown). These experiments showed the desorption of NH_3 in amounts comparable to those obtained during the rich phase of the Pt–Ba/Al_2O_3 single-bed reactor (Fig. 1). Since NH_3-TPD experiments performed over the Pt–Ba/Al_2O_3 sample pointed out that this catalyst has a negligible capacity to store NH_3, it is concluded that ammonia is stored on the Fe-ZSM5 SCR catalyst, as expected.

Ammonia stored on the Fe-ZSM5 SCR catalyst is involved in the reduction of gaseous NO_x during the subsequent lean phase, as pointed out by the relevant N_2 formation which accompanies the NO_x storage (see Fig. 7A, left panel). The reaction of gaseous NO_x with stored ammonia occurs according to the well-known stoichiometry of the SCR reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{7}$$

The occurrence of the SCR reaction is also pointed out by the detection of significant amounts of water during the lean phase.

Worth to note that in the case of the double-bed configuration, during the lean phase gas phase NO_x are removed both by adsorption on the LNT sample, and by reaction with ammonia over the SCR catalyst. Accordingly this leads to a significant increase in the NO_x removal efficiency as compared to the Pt–Ba/Al_2O_3 single-bed arrangement particularly at low temperatures (Fig. 2). It is also

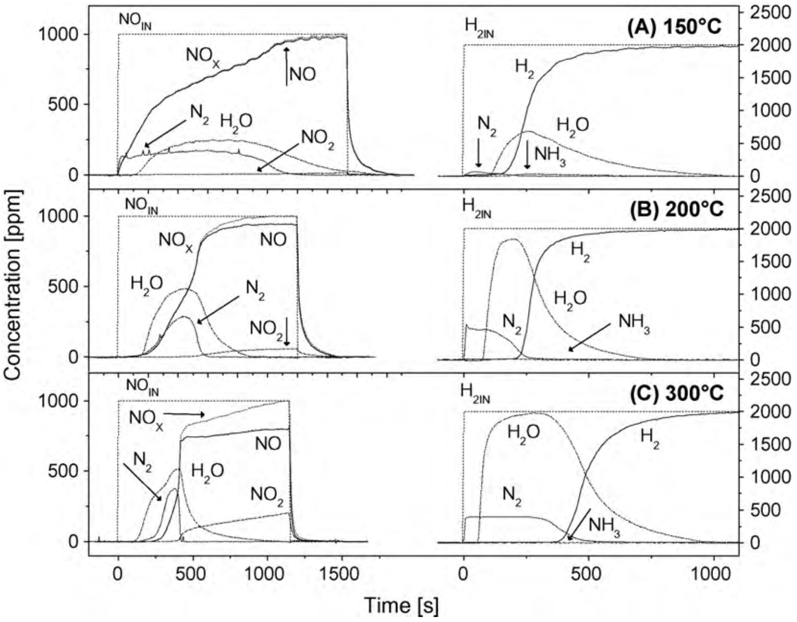

Fig. 7. Lean–rich cycles carried out over the Pt–Ba/Al_2O_3–Fe-ZSM5 double-bed arrangement at 150 °C (A), 200 °C (B) and 300 °C (C). Lean phase: 1000 ppm NO in He + 3% (v/v) O_2; rich phase: 2000 ppm H_2 in He. Catalyst loading 60 mg Pt–Ba/Al_2O_3 + 60 mg Fe-ZSM5; flow rate 100 cm^3/min (@ 1 atm and 0 °C).

worth to stress that at this temperature (150 °C) nitrogen is not formed during the rich phase, but during the lean cycle.

The increase of the reaction temperature (200 °C and 300 °C, Fig. 7B and C) enhances the NO_x removal efficiency during the lean phase (Fig. 2). This is due to the increase of the NO_x uptake with temperature of the Pt–Ba/Al_2O_3 sample, since the amounts of N_2 evolved in the lean phase (pointing out the occurrence of the SCR reaction over the Fe-ZSM5 catalyst) decreases. Notably, at these temperatures the fast-SCR reaction (8) is likely to occur, due to the formation of small amounts of NO_2 formed upon NO oxidation on the Pt–Ba/Al_2O_3 sample:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad (8)$$

As a matter of fact, NO_2 evolution is monitored in the case of the double-bed arrangement (Fig. 7) only after N_2 formation, whereas the NO breakthrough is seen with N_2 evolution (see e.g. Fig. 7C, left panel). This suggests that NO_2 is readily involved in the SCR reaction with the stored NH_3, in line with the grater reactivity of the fast-SCR reaction (8) if compared to the standard SCR pathway (7) [16,17].

Finally, it is worth to note that no ammonia is seen during the rich phase at 200 °C and 300 °C: hence complete N_2 selectivity is attained during the reduction, and the NH_3 slip is negligible at all investigated temperatures.

Accordingly, upon comparing the data obtained in the case of the double-bed arrangement (Fig. 7) and over the Pt–Ba/Al_2O_3 sample (Fig. 1), it clearly appears that the presence of a SCR catalyst layer placed downstream the LNT catalyst significantly increases the NO_x removal efficiency and decreases the NH_3 slip. This is summarized in Figs. 2 and 6, which also point out that the observed differences are well evident at low temperatures, but tend to vanish on increasing the temperature.

The superior catalytic performances of the Pt–Ba/Al_2O_3 + Fe-ZSM5 SCR double-bed arrangement at low temperature are due to the NH_3 trapping capacity and SCR-DeNO$_x$ activity of the SCR catalyst bed placed downstream the LNT catalyst. In fact as shown in Fig. 6, the LNT catalyst shows a significant NH_3 slip at low temperatures. The decrease of the ammonia slip in the case of the LNT + SCR arrangement is due to the trapping of NH_3 on the SCR catalyst bed. Ammonia which is stored on the SCR catalyst bed reacts with gaseous NO_x during the subsequent lean period, due to the high activity of the Fe-ZSM5 catalyst in the SCR reaction. This leads to the consumption of NO_x and to the corresponding formation of N_2. Consequently in the case of the double-bed arrangement the NO_x removal during the lean phase occurs according to two different routes, i.e. NO_x adsorption (in the form of nitrite and nitrates) on the LNT catalyst, and reaction with stored NH_3 according to the SCR reaction over the Fe-ZSM5 sample. Indeed as shown by specific NO_x adsorption experiments, not reported in the present work for the sake of brevity, the contribution of the Fe-ZSM5 sample to the storage of NO_x is negligible.

Since the NH_3 slip from the LNT catalyst decreases on increasing the temperature, the contribution of the NO_x removal according to the SCR pathway decreases with temperature. This leads to a decrease of the amounts of nitrogen produced during the lean phase with temperature, and to a corresponding increase in the production of N_2 during the rich phase.

4. Conclusions

The adsorption–reduction by H_2 of NO_x stored on a model LNT Pt–Ba/Al_2O_3 catalyst sample and on a combined LNT + Fe-ZSM5 SCR catalyst has been investigated in the present study. The storage of NO_x over the LNT Pt–Ba/Al_2O_3 catalyst leads to nitrite formation at low temperatures, and to nitrate at high temperatures (above 300 °C). The stored NO_x are reduced mainly to NH_3 at low temperatures, and to N_2 at high temperatures. In line with previous data, and according to specific experiments with H_2 and NH_3 carried out in the present study, a two-step in-series pathway for nitrogen formation involving at first the formation of ammonia upon reaction of NO_x with H_2, followed by the slower reaction of the so-formed ammonia with the stored NO_x to give N_2 has been proposed. Indeed different temperature thresholds for these two steps have been pointed out, with step 1 (reduction of the stored NO_x to give ammonia) being much faster than step 2 (formation of nitrogen by reaction of ammonia with NO_x). As a consequence, step 2 is rate determining in the formation of nitrogen so that under the experimental conditions adopted in the present study (i.e. nearly isothermal conditions) the reaction of ammonia with stored NO_x does represent the major route for nitrogen formation.

The two-step in-series pathway described above together with the integral behaviour of the reactor is able to account for the temporal evolution of the products which is observed during regeneration of LNT catalysts. Indeed the occurrence of a fast reduction step of the adsorbed NO_x by H_2 to give ammonia and the integral “plug-flow” behaviour of the reactor implies the complete consumption of the reductant H_2 and the formation of an H_2 front travelling along the reactor axis. Ammonia is readily formed upon reaction of H_2 with the stored NO_x; if the temperature is high enough ammonia reacts with NO_x left downstream the H_2 front and this drives the selectivity to N_2, which is immediately observed at the reactor outlet. Accordingly the NH_3 breakthrough is seen together or after the H_2 breakthrough, i.e. when the H_2 front reaches the end of the trap.

When the temperature is low the rate of NO_x reduction by H_2 to give ammonia is slower, the hydrogen front is less steep and the reduction of stored nitrates by ammonia is significantly slower. As a result a small nitrogen selectivity is observed.

The presence of a Fe-ZSM5 SCR placed downstream the LNT catalyst is able to store NH_3 released during the rich phase from the LNT sample. The stored ammonia is effectively converted to N_2 during the subsequent lean phase, due to the occurrence of the SCR reaction over the SCR catalyst bed. Accordingly in the case of the double-bed arrangement the NO_x removal during the lean phase follows two different routes, i.e. NO_x adsorption (in the form of nitrite and nitrates) on the LNT catalyst, and reaction of NO with stored NH_3 according to the SCR reaction over the Fe-ZSM5 sample.

It is concluded that the presence of a SCR catalyst bed placed downstream a LNT sample leads to the double benefit of reducing the NH_3 slip and to increase the NO_x removal efficiency: these advantages are particularly evident al low temperatures, where the NH_3 slip from the LNT layer is significant, and tend to vanish at high temperatures where the NH_3 slip is less important.

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