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Mechanistic aspects of the reduction of stored NOx over Pt–Ba/Al_2O_3 lean NO_x trap systems

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Abstract

In this paper the mechanisms that rule the reduction by hydrogen of NO_x species adsorbed at different temperatures were investigated over a model LNT Pt–Ba/Al_2O_3 catalyst and over the corresponding Ba/Al_2O_3 system to address the role of the noble metal component in such mechanisms.

It was found that the reduction proceeds according to a dual-step mechanism in which hydrogen reacts fast and at low temperature with nitrates producing ammonia, which however is not a terminal product as it can further react with other nitrate species leading selectively to N_2.

The results collected in the analysis of each of the dual-step reactions showed that they both occur through a Pt-catalyzed pathway active at very low temperatures, which does not involve the thermal decomposition of the adsorbed NO_x species as a preliminary step.

Keywords: Lean deNO_x; NO_x reduction mechanism; LNT systems; Pt–Ba/Al_2O_3 catalyst; Transient response method; NO_x storage reduction; NSR

1. Introduction

The so-called lean NO_x trap (LNT) or NO_x storage–reduction (NSR) catalytic systems are nowadays considered one of the most promising technological solutions for the NO_x removal in the exhausts of lean-burn (e.g. diesel) engines [1,2]. The use of these engines is significantly increasing in Europe also on light-duty vehicles due to their capability to ensure lower CO_2 emissions and improved fuel economics as compared to traditional stoichiometric engines [3].

LNT materials typically consist of a NO_x storage component, such as an alkaline earth metal oxide (e.g. Ba), and of a noble metal (e.g. Pt) that catalyzes the oxidation of NO, CO and of hydrocarbons and the reduction of stored NO_x as well [1–3]. The earth metal oxide and the noble metal are dispersed over a high surface area carrier, such as Al_2O_3. These catalysts work under periodic changes between lean (NO_x storage) and rich conditions (NO_x reduction).

The chemistry and mechanisms occurring during the lean and the rich phases of LNT systems are still a matter of debate in the literature. Several studies have been published in the past on the mechanisms of the NO_x storage [2,4,5], whereas more recently most papers are focusing on the reduction step [6–18]. Most authors agree that the first step in the reduction process is the decomposition of the nitrate surface species to gas phase NO_x, followed by their reduction to N_2 but also to NH_3 and N_2O. The nitrate decomposition can be driven by either the decrease in the oxygen concentration level that lowers the equilibrium stability of nitrates [2,16], or by temperature increase caused by the heat produced during the reducing reactions [12,14]. A low temperature Pt-catalyzed route which operates the nitrate reduction under nearly isothermal conditions has also been proposed [8,16,17].

In this paper the mechanisms that rule the reduction of adsorbed NO_x species by hydrogen are analysed and the role of the Pt component in such mechanisms is addressed. For this purpose, the reactivity of a model ternary Pt–Ba/Al_2O_3 catalyst and of the corresponding Pt free sample has been considered. The reactivity of hydrogen with NO_x stored at different temperatures (200 and 350 °C) is studied under both temperature programming and isothermal conditions. The

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reactivity of ammonia as a reducing agent is addressed as well, in view of its possible involvement in the regeneration of LNTs, and results are reported below.

2. Experimental

Homemade Pt–Ba/γ-Al_2O_3 (1/20/100, w/w), Pt/γ-Al_2O_3 (1/100, w/w) and Ba/γ-Al_2O_3 (20/100, w/w) model catalyst samples have been considered in this study. The Pt/γ-Al_2O_3 sample was prepared by impregnation of a γ-Al_2O_3 calcined at 700 °C (Versal 250 from UOP) with a solution of $Pt(NH_3)_2(NO_2)_2$ (Strem Chemicals, 5% Pt in ammonium hydroxide) followed by drying at 80 °C and calcination at 500 °C for 5 h. The obtained sample (S_a = 190 m^2/g; Pt dispersion = 82%) was impregnated with an aqueous solution of $Ba(CH_3COO)_2$ (Strem Chemical, 99%) and further calcined at 500 °C for 5 h to prepare the ternary Pt–Ba/γ-Al_2O_3 catalyst (S_a = 137 m^2/g; Pt dispersion = 70%). The Ba/γ-Al_2O_3 sample was prepared by impregnation of the bare γ-alumina support with barium acetate (S_a = 140 m^2/g). Further details on the characterisation of the samples are reported elsewhere [4–6].

Mechanistic aspects of the reduction of NO_x adsorbed species were investigated by the temperature-programmed surface reaction (TPSR) and transient response method (TRM) techniques. Before each test the adsorption of NO_x was carried out by imposing a rectangular step feed of NO (1000 ppm in He + 3%, v/v O_2) of appropriate length, in order to have similar amounts of NO_x ad-species prior to each reduction test. NO_x adsorption was carried out at 200 and 350 °C and was followed by a He purge at the same temperature to provoke the desorption of weakly adsorbed species.

In the case of the temperature-programmed surface reaction (TPSR) experiments, after NO_x adsorption at 200 or 350 °C the catalyst was cooled down to RT in flowing He and eventually heated at 10 °C/min under flow of H_2 (2000 ppm in He + 1%, v/v H_2O) or ammonia (1000 ppm in He) up to 400–500 °C. On the other hand, during transient response method (TRM) experiments, after NO_x adsorption at 200 or 350 °C the reduction of the stored nitrates was carried out at constant temperature, in the range 100–200 °C (and at 350 °C in the case of NO_x adsorption at 350 °C) by feeding rectangular step feeds of H_2 (2000 ppm in He + 1%, v/v H_2O). At the end of the reduction procedure, when the concentration of the reaction products at the reactor outlet was negligible, the catalyst was again heated up to 350 °C and hydrogen was added to the reactor to complete the reduction of the stored NO_x. This procedure allowed the quantification of the extent of nitrate removal at each temperature (efficiency of NO_x removal).

The reactivity of NH_3 with NO was also investigated by temperature-programmed reaction (TPR) experiments: in this case a flow of NO (1000 ppm) and NH_3 (1000 ppm) in He was admitted to the reactor at room temperature and then the catalysts were linearly heated up to 500 °C at 10 °C/min.

Before the catalyst testing, the samples were conditioned by performing a few adsorption/regeneration cycles with NO/O_2 (1000 ppm NO and 3%, v/v O_2 in He) and H_2 (2000 ppm in He) at 350 °C, respectively, with an inert purge (He) in between. Conditioning lasted until a reproducible behaviour was obtained; typically this required three to four cycles. All the experiments have been performed with 60 mg of catalyst (100–150 μm) loaded in a microreactor and using a total flow rate of 100 cm^3/min STP. The reactor outlet was connected to a mass spectrometer for the complete analysis of reactants and products. Further details on the experimental apparatus and procedures can be found elsewhere [4,6,8].

3. Results and discussion

3.1. NO_x storage at 200 and 350 °C

Typical results obtained following a rectangular step feed of NO in O_2 (NO_x storage phase) at T = 200 and 350 °C are shown in Fig. 1A and B, respectively. The outlet concentration of NO, NO_2 and NO_x (=NO + NO_2) are displayed, along with that of the NO inlet concentration (NO_{in}).

In the case of the data obtained at 200 °C, upon NO addition at t = 0 s, the NO outlet concentration showed a dead time, thus indicating that NO_x were stored on the catalyst surface. After ~80 s the NO reactor outlet concentration increased with time, eventually reaching a value of 900 ppm before NO was removed from the feed flow at 600 s. A correspondent evolution

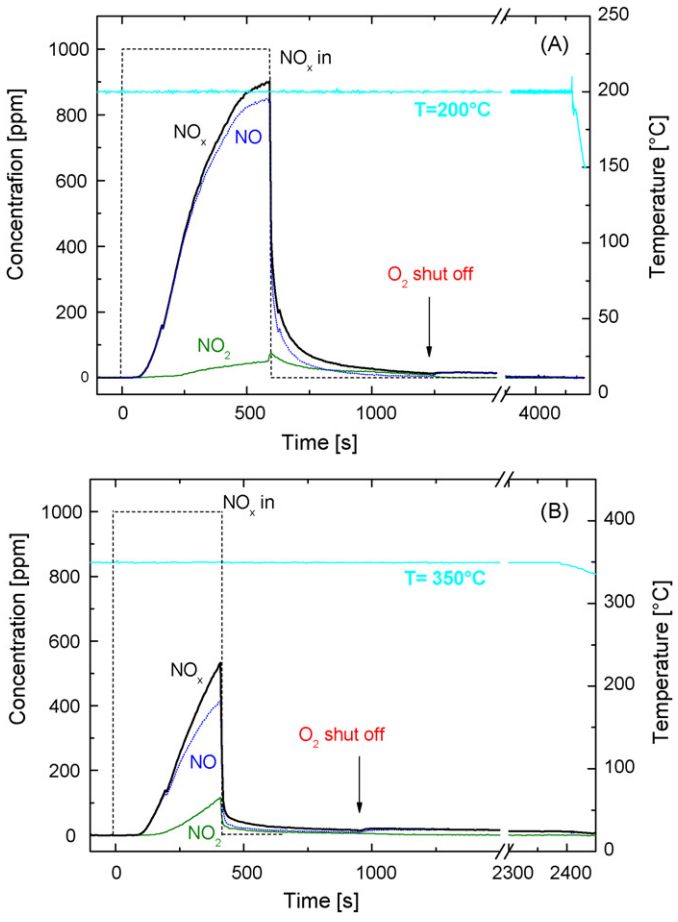

Fig. 1. Temporal evolution of NO, NO_2 and NO_x (=NO + NO_2) outlet concentrations during adsorption of NO (1000 ppm) in He + O_2 (3% v/v) at 200 (A) and 350 °C (B) over the Pt–Ba/γ-Al_2O_3 catalyst.

of NO_2 was also observed, pointing out that NO was partially oxidized to NO_2. The area included between the NO inlet and the outlet NO_x concentration traces is proportional to the amounts of NO_x stored on the catalyst surface. After adsorption at 200 °C values of stored NO_x near 3×10^{-4} mol/g_{cat} were estimated.

Data collected at 350 °C were qualitatively very similar to those obtained at 200 °C; NO and NO_2 were both detected at the reactor outlet, with NO breakthrough appearing before NO_2. However, inspection of the figure points out that the NO_x storage capacity at 350 °C was significantly enhanced, in line with the effect of temperature on the NO_x adsorption [2,4,6]. Amounts of adsorbed NO_x near 4×10^{-4} mol/g_{cat} were estimated after 400 s in this case. Besides, a significantly higher NO_2 concentration was observed, indicating a higher NO oxidation to NO_2.

In both cases, upon restoring the NO inlet concentration back to zero, the outlet NO and NO_2 concentrations decreased showing a pronounced tail which was related to a slow desorption/decomposition of weakly adsorbed NO_x species. An additional small NO desorption was observed upon switching off the oxygen flow (He purge), in line with the effect of oxygen partial pressure on the stability of nitrate species formed onto the catalyst surface [7,16].

It is worth mentioning that previous studies concerning the NO_x adsorption process indicated that nitrites and nitrates are formed on the catalyst surface upon NO/O_2 adsorption [4,5]. Nitrates were found to be most abundant species over the catalyst surface after adsorption at 350 °C, whereas non-negligible amounts of nitrite species may also be present at lower temperatures [4,5].

3.2. Reactivity of stored NO_x with H_2: TPSR experiments

Following NO_x storage at 200 and 350 °C H_2-TPSR experiments were carried out to address the reactivity of hydrogen in the presence of water in the reduction of the stored NO_x species. Fig. 2 shows the results of the TPSR run in terms of H_2, NH_3 and N_2 concentration profiles with temperature. No other species were detected, if one excludes water (not shown in the figure).

In the case of the TPSR experiment carried out after NO_x adsorption at 200 °C (Fig. 2A), the temperature threshold for hydrogen consumption was observed near 40–50 °C. A correspondent evolution of ammonia was observed while negligible amounts of nitrogen were formed. The H_2 consumption peak shows a minimum near 90 °C and then its concentration increases up to the inlet value due to the depletion of NO_x adsorbed species. Complete removal of the adsorbed NO_x species was achieved at temperatures slightly above 150 °C.

Very similar results were obtained after NO_x adsorption at 350 °C; however in this case the temperature onset for NH_3 detection is shifted at slightly higher temperatures and the reduction process lasted up to 250 °C. This may suggest that the species stored at 200 °C are more easily reducible. Besides, the higher amounts of NH_3 which were detected in this case are in line with the larger amounts of NO_x stored at 350 °C.

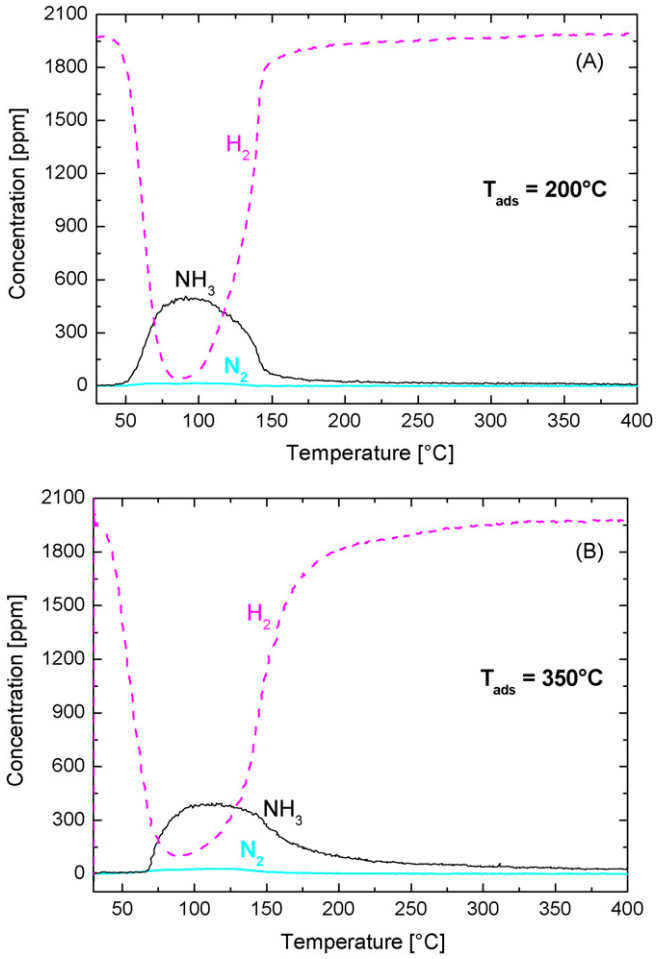

Fig. 2. TPSR in H_2 (2000 ppm) + H_2O (1% v/v) in He after NO/O_2 adsorption at 200 (A) and 350 °C (B) over the Pt–Ba/γ-Al_2O_3 catalyst.

In any case, the higher reactivity of hydrogen towards NO_x adsorbed species is worth noting, H_2 being able to reduce quantitatively NO_x adsorbed species already at very low temperature. Besides, it is worth noticing that almost complete selectivity to ammonia was observed in these conditions. The obtained data are in line with the occurrence of the following overall reaction:

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O \quad (1)$$

The minor amounts of nitrogen which were detected correspond to the occurrence of the following overall reaction:

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O \quad (2)$$

which however accounts for less than 5% of the overall H_2 consumption.

3.3. Reactivity of stored NO_x with H_2: TRM experiments

The results obtained in the case of TRM experiments carried out at 100, 150 and 200 °C after adsorption of NO_x at 200 °C and at 100, 150 and 350 °C after NO_x adsorption at 350 °C are displayed in Fig. 3. The concentration profiles of hydrogen, nitrogen and ammonia are displayed as a function of time.

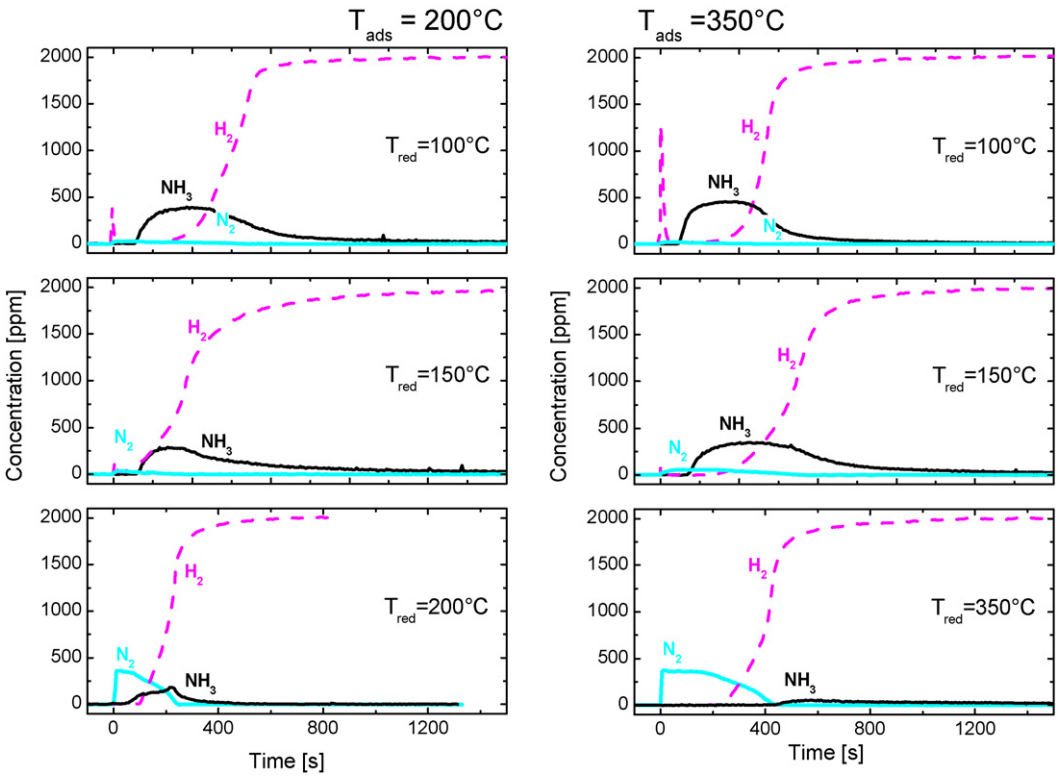

Fig. 3. Temporal evolution of H_2, N_2 and NH_3 outlet concentrations during reduction with H_2 (2000 ppm) + H_2O (1% v/v) in He over the Pt–Ba/γ-Al_2O_3 catalyst at 100, 150 and 200 °C (TRM runs): the left column shows the TRM runs after NO/O_2 adsorption at 200 °C and the right column shows the corresponding experiments after NO/O_2 adsorption at 350 °C.

The analysis of the data collected after NO_x storage at 200 °C shows that at 100 °C, upon hydrogen admission to the reactor at $t = 0$ s, a small hydrogen peak is initially observed. Then H_2 is completely consumed for about 250 s, and eventually its concentration slowly increased with time restoring the inlet value in about 800 s. Ammonia formation was observed with a delay of about 80 s, while nitrogen production was seen in negligible amounts, its concentrations being always below 30 ppm.

Accordingly, in line with data collected during the TPSR run, at 100 °C the reduction was fast and efficient leading mainly to ammonia. Notably, almost all the stored NO_x have been removed by the H_2 treatment at 100 °C (roughly 97%), as pointed out by the nitrogen balance between adsorption and regeneration, and an overall selectivity to ammonia close to 95% was measured.

The picture was not significantly modified when the reduction was performed at 150 °C: again the process was very fast and efficient, the main reaction product being ammonia. The measured selectivity to ammonia was close to 95%. However, in this case the initial, small H_2 peak is hardly visible. Conversely, significant differences were observed during the regeneration process at 200 °C. In this case, upon step addition of H_2 at $t = 0$ s, the NO_x stored at the same T were readily reduced to N_2: initially H_2 was completely consumed and the N_2 outlet concentration immediately increases to the level of 370 ppm. After roughly 60 s, ammonia was also detected even if in smaller amounts if compared to nitrogen.

It is worth noticing that the N_2 concentration of 370 ppm well corresponds to the stoichiometry of reaction between nitrates and H_2 [2,6,8], reaction:

$$Ba(NO_3)_2 + 5H_2 \rightarrow BaO + N_2 + 5H_2O \quad (2)$$

Hence the set of TRM data obtained after NO_x storage at 200 °C point out that the increase in the reduction temperature did not affect significantly the NO_x reduction capability (which always approached 100%), but decreased the selectivity to ammonia from 95% measured at 100 and 150 °C down to 22% at 200 °C.

Fig. 3 also shows the results of TRM experiments carried out at different temperatures (100, 150, 350 °C) after adsorption of NO_x at 350 °C.

At 100 and 150 °C the reduction of stored nitrates with hydrogen occurred rapidly and efficiently, leading almost quantitatively to formation of ammonia. At 350 °C, i.e. the temperature at which the adsorption process was carried out, the reduction reaction led immediately to the formation of nitrogen, followed by a small production of ammonia. A nitrogen selectivity value near 90% was estimated in this case.

Experiments were also run at temperatures between 200 and 350 °C (data not reported herein): it was found that the N_2 formation increases with temperature, so that the highest N_2 formation is seen at 350 °C.

Accordingly TRM data collected after NO_x adsorption at 200 or 350 °C pointed out that the increase in the reduction temperature led to a modification of the selectivity of the

reduction process. In fact selective reduction of the stored NO_x to ammonia is seen at low temperatures, whereas nitrogen is progressively formed upon increasing the reduction temperatures above 150 °C.

The higher reactivity of the stored NO_x towards H_2 is worth noting, along with the observed selective formation of NH_3 at low temperatures. There is no common agreement in the open literature on the pathways that lead to the reduction of the stored NO_x, and particularly on the formation of ammonia. As already reported elsewhere [8], a Pt-catalyzed route must be invoked in the reduction of the stored NO_x under isothermal conditions, which does not involve, as a preliminary step, the thermal decomposition of the adsorbed NO_x. It is likely that initially H_2 is adsorbed and activated over the Pt sites, and then it spreads on the catalyst surface. The adsorbed hydride species provoke the decomposition of the stored nitrates to gaseous NO_x, which are reduced to N_2 and/or NH_3 over the Pt sites by H_2. As a matter of fact it was shown that the NO reduction by H_2 can be accomplished at temperatures as low as 60 °C over the same Pt–Ba/Al_2O_3 catalyst sample used in this study [9]. Besides, studies on the reduction of NO by H_2 over Pt showed that the selectivity of the process basically depends on the relative surface concentration of the –N, –H and –O adsorbed entities, which in turn is governed by the operating conditions (and specifically by the H_2/NO ratio) [2,8,18]. In our case, the very high selectivity to ammonia which is observed at low temperatures suggests that high H/N and H/O ratios are locally attained on the catalyst surface where the reaction takes place, thus driving the selectivity to ammonia and water.

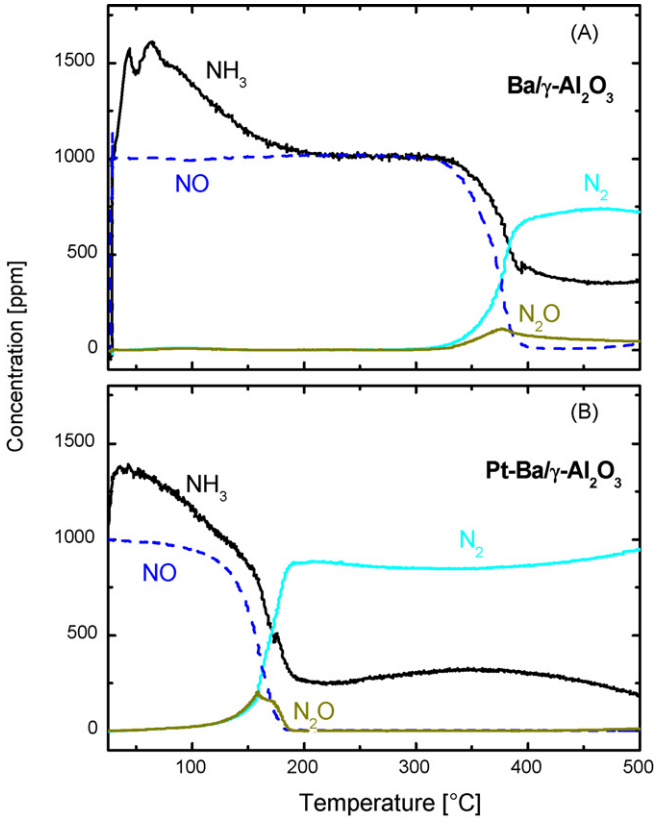

Fig. 4. TPR in NH_3 (1000 ppm) + NO (1000 ppm) over the Ba/γ-Al_2O_3 (A) and Pt–Ba/γ-Al_2O_3 (B) catalysts.

The initial H_2 peak which is seen at the lowest temperatures (see Fig. 3) is possibly related to the presence of an induction step for the reaction, e.g. to the activation of the surface nitrates. Accordingly at low temperature the H_2 uptake is fast but the nitrate decomposition is slow, thus leading a build-up of adsorbed H species on the catalyst surface which inhibits further H_2 uptake. This provokes the spike in the H_2 concentration which is initially seen at low temperatures. Once the surface nitrates start to decompose, H_2 is consumed in the reduction of the evolved NO_x and the H_2 concentration drops to zero.

The selective formation of NH_3 observed at low temperatures and its significant decrease upon increasing the temperature (with formation of N_2) is worth noting and suggests that NH_3 plays as intermediate species in the formation of N_2, occurring only at higher temperatures. Accordingly it may be suggested that the formation of N_2 during the regeneration of LNTs by H_2 likely occurs via a two-step pathway involving at first the fast formation of ammonia upon reaction of nitrates with H_2, followed by the slower reaction of the so-formed ammonia with the stored nitrates or gas-phase NO_x leading to the selective formation of N_2. To better analyse these aspects, the reactivity of NH_3 with gaseous NO and with stored NO_x was also addressed.

3.4. Reactivity of NH_3 with NO: TPR experiments

To analyse the reactivity of ammonia as reducing agent and to understand the role of the Pt in the reactions, a series of temperature-programmed reaction (TPR) experiments were performed by flowing gaseous NO (1000 ppm) and NH_3 (1000 ppm) over the Pt–Ba/Al_2O_3 ternary sample and over the corresponding binary Ba/Al_2O_3 catalyst.

Fig. 4 shows the collected results in terms of ammonia, NO, N_2, N_2O concentration profiles versus temperature.

In the case of the Ba/Al_2O_3 system (Fig. 4A), after an initial desorption of ammonia from the catalyst surface, a reaction occurred starting from 320 °C with consumption of NO and ammonia and simultaneous formation of nitrogen, along with minor amounts of N_2O.

At 500 °C, NO concentration was almost zero, ammonia was present in 350 ppm, nitrogen was roughly 730 ppm and a few tens of ppm of N_2O were also detected: these values are in line with the occurrence of the following reactions:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (3)$$

$$8NO + 2NH_3 \rightarrow 5N_2O + 3H_2O \quad (4)$$

It is worth noting that reaction (3) corresponds to the well-known slow SCR reaction [19].

The NO + NH_3 TPR run was also performed over the ternary Pt–Ba/Al_2O_3 catalyst and the results are shown in Fig. 4B. In this case NO and ammonia react at lower temperatures, close to 100 °C, with simultaneous formation of nitrogen and N_2O: the production of N_2O shows a maximum near 200 ppm at 160 °C and then decreases to zero. NO conversion reached 100% at

200 °C and then the concentration values of ammonia, NO and nitrogen were constant up to 350 °C and in line with the occurrence of the Slow SCR reactions (3) and (4).

At temperature above 350 °C the ammonia concentration further decreases due to the occurrence of the NH_3 decomposition reaction to nitrogen and hydrogen:

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (5)$$

Indeed, a dedicated TPR run in which only ammonia was fed to the reactor during a heating ramp confirmed that on the ternary catalyst ammonia decomposed to nitrogen and hydrogen according to the expected 1/3 ratio at temperatures higher than 350 °C.

The NO + NH_3 TPR runs presented in Fig. 4 pointed out that the investigated LNT systems are active in the SCR reactions of NO with NH_3. The comparison among the temperature thresholds measured over the two catalysts indicates the catalytic action played by Pt, whose addition resulted in the decrease in the onset of the reactions from 320 °C (observed over the Ba/Al_2O_3 system) down to 100 °C (for the Pt–Ba/Al_2O_3 catalyst).

A similar TPR run was also performed over the Pt/Al_2O_3 binary sample (results herein not shown): the results showed that the reaction over the Ba free sample started around 200 °C, pointing out that the co-presence of Pt and Ba seems also to affect significantly the activity of the system. Furthermore, the product distribution is also positively affected by the co-presence of Pt and Ba: in fact on the ternary catalyst the N_2O production was limited and is negligible above 200 °C, as opposite to the Pt/Al_2O_3 sample for which N_2O formation is observed in a wide temperature range.

3.5. Reactivity of NH_3 with nitrates: TSPR experiments

Finally, the reactivity of NH_3 with stored NO_x was addressed over both the Pt–Ba/Al_2O_3 and Ba/Al_2O_3 catalysts. In the case of the Pt–Ba/Al_2O_3 sample the NO_x adsorption was carried out by saturating the systems in a flow consisting of 1000 ppm NO + 3% v/v O_2 + He at 350 °C; then after purging and cooling in He down to RT, 1000 ppm of ammonia were admitted to the reactor and the catalyst was heated up to 500 °C (NH_3-TPSR). A similar procedure was used in the case of the binary Ba/γ-Al_2O_3 sample but NO_2 (1000 ppm in He) was used instead of NO + 3% v/v O_2 + He.

The results of the NH_3-TPSR experiments collected over the Ba/γ-Al_2O_3 and the Pt–Ba/γ-Al_2O_3 catalysts are shown in Fig. 5A and B, in terms of ammonia, NO, N_2 and N_2O concentration profiles versus temperature.

In the case of the Pt free sample (Fig. 5A), the ammonia profile shows a desorption peak at low temperature associated with physisorbed species, and the remains near the inlet value up to 350 °C where a small decrease was observed. At the same time, nitrogen was produced with a peak close to 60 ppm around 440 °C. Accordingly the data point out that over the Ba/γ-Al_2O_3 ammonia is able to reduce nitrates species only above 350 °C, i.e. above the onset for thermal decomposition of the stored NO_x [8,17]. This indicates that the stored NO_x are thermally decomposed to gaseous NO_x which then react with NH_3. As a matter of fact, the previous TPR experiments showed in Fig. 4A indicated the occurrence of the ammonia and NO reaction at these temperatures.

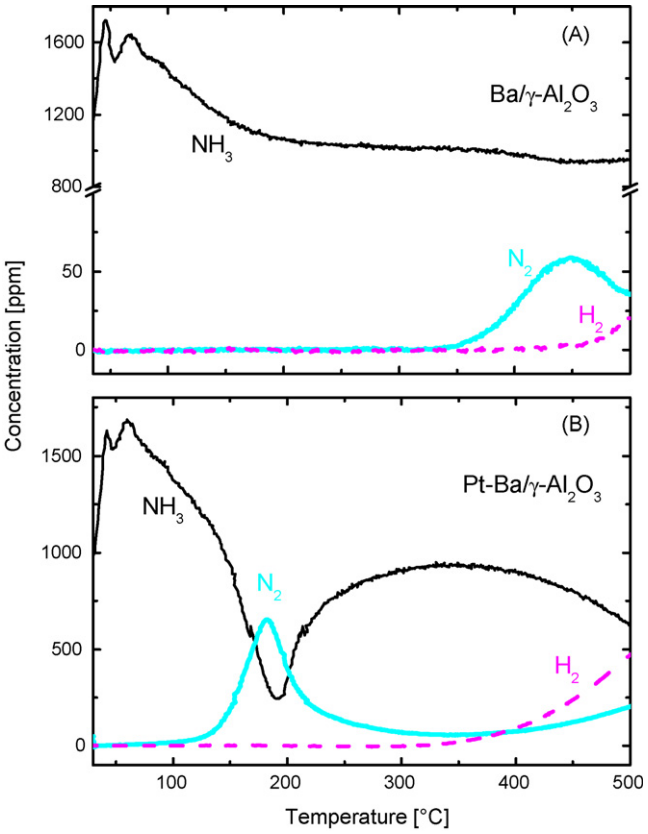

Fig. 5. TPSR in NH_3 (1000 ppm) after NO/O_2 adsorption at 350 °C over the Ba/γ-Al_2O_3 (A) and Pt–Ba/γ-Al_2O_3 (B) catalysts.

Finally, above 470 °C, the hydrogen concentration started increasing due to ammonia decomposition reaction (5). N_2O was not detected in significant amounts.

A different picture is evident in the case of the ternary system: inspection of Fig. 5B shows that ammonia is able to reduce NO_x adsorbed species at temperatures as low as 130 °C. Indeed, after an initial desorption peak with maximum near 70 °C, ammonia consumption was well evident above 130 °C accompanied by a symmetrical evolution of nitrogen. Around 180 °C the nitrogen production reached a maximum value of 650 ppm and then started decreasing due to the depletion of nitrates stored over the catalyst surface. The N_2 concentration and NH_3 consumption are in line with the stoichiometry of the reaction between nitrates and ammonia, reaction (6):

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

As expected, at temperatures higher than 350 °C, the ammonia concentration decreased again, and nitrogen and hydrogen evolution was observed due to the ammonia decomposition reaction (5).

Neither NO nor N_2O have been detected in appreciable amounts during the experiment.

The comparison of the data shown in Fig. 5A and B clearly points out that Pt plays a major role in the reduction of the stored nitrates in that these species are readily reduced to N_2 by NH_3 at temperatures well below that of their thermal decomposition, as opposite to the Pt-free sample (Fig. 5A). This indicates that the reaction between ammonia and stored nitrates is a Pt-catalyzed reaction that does not involve the thermal release of NO in the gas phase as a first step.

The mechanisms involved in this step are not yet completely understood; however it is worth noting that the nitrate + NH_3 reaction has a different selectivity if compared to the NO + NH_3 reaction (Fig. 4) in that significant amounts of N_2O are formed in the NO + NH_3 case. This possibly suggests that adsorbed nitrates directly participate in nitrogen formation during the regeneration of LNT catalysts.

These aspects are currently under investigation in our labs.

3.6. Mechanistic aspects in the regeneration of LNTs by H_2

The results previously discussed clearly indicate that NO_x stored either at 200 or 350 °C can be very efficiently reduced by H_2 already at low temperatures, above 60 °C, with almost exclusively formation of ammonia. As the reduction temperature is increased, significant amounts of nitrogen are also detected, so that at high temperatures N_2 formation is prevalent (see Fig. 3). Besides, during TRM experiments, N_2 formation is always observed before that of ammonia.

Ammonia itself exhibits a significant activity in the reduction of gaseous NO and of adsorbed nitrate species, but the temperature threshold of this reaction is higher (130–140 °C) than that measured for hydrogen (60–70 °C). In the case of the NH_3 + nitrates reaction the selective formation of nitrogen was observed, whereas in the NH_3 + NO reaction small amounts of N_2O were also observed.

Accordingly these data suggest that the formation of N_2 during the regeneration of LNTs by H_2 under nearly isothermal conditions (i.e. in the absence of significant temperature increases) likely occurs via a two-step pathway involving at first the fast formation of ammonia upon reaction of nitrates with H_2 (reaction (1)), followed by the slower reaction of the so-formed ammonia with the stored nitrates leading to the selective formation of N_2 (reaction (6)):

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O \quad (1)$$

$$3/5Ba(NO_3)_2 + 2NH_3 \rightarrow 8/5N_2 + 3/5BaO + 3H_2O \quad (6)$$

The sum of reactions (1) and (6) leads to the overall stoichiometry for the reduction of nitrates by H_2, reaction (2):

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O \quad (2)$$

According to this mechanistic scheme, N_2 formation occurs upon reaction of ammonia with the stored nitrates, this step being rate determining in the formation of nitrogen. In fact ammonia formation upon reduction of the stored nitrates with hydrogen (reaction (1)) is very fast.

Once ammonia is formed, it may further react with adsorbed nitrates or with gaseous NO_x. In the first case the reaction is very selective towards nitrogen, whereas small amounts of N_2O were detected in the NH_3 + NO reaction. This may suggest that adsorbed nitrates, instead of NO, participate in nitrogen formation during the regeneration of LNT catalysts. The details of this reaction are still unknown, but it is clear that this step is catalyzed by the Pt component. These aspects are currently under investigation in our labs.

The two-step pathway described above for nitrogen formation from adsorbed nitrates is able to account for the temporal evolution of the product selectivity which is observed during TRM experiments carried out at high temperatures, with nearly complete N_2 selectivity at the beginning of the reduction process and significant ammonia formation near the end of the regeneration step (see Fig. 3). In a recent paper from Purdue University and Cummins [14] the authors provide a simplified scheme able to explain both the very high N_2 selectivity and the temporal sequence of the products. Shortly, the authors refer to the presence of a localized reaction front which travels through the trap during regeneration: nitrogen and ammonia are formed upon reaction of H_2 with nitrates, but high efficiency of the NSR catalyst in converting NO_x mostly to N_2 is achieved because ammonia further reacts with nitrates to produce N_2. Accordingly only N_2 is observed at the reactor outlet during the initial period of the regeneration; NH_3 breakthrough is then observed due to the depletion of NO_x left in the bed to consume the NH_3 formed as the front reaches breakthrough. Similar conclusions have been derived in [18].

Our data provide further indications on the mechanisms involved in the regeneration of LNTs and on the role of ammonia in the process; it also explains the change in the selectivity which is observed upon changing the temperature in TRM experiments (Fig. 3), as also pointed out in [18]. In fact the high reactivity of H_2 towards nitrates (leading to ammonia) and the ''plug-flow'' type of the process lead to the complete consumption of the reductant H_2 in the reactor and to the formation of an H_2 front traveling inside the reactor. At low temperature, namely below 150 °C, the H_2 front is not very steep (indeed the H_2 breakthrough trace is not steep, see Fig. 3) due to the decrease of the rate of reaction (1); accordingly NH_3 formation occurs in a wider zone of the trap. Besides, due to the low temperature, ammonia can hardly react with the stored nitrates to form N_2 according to reaction (6). As a result poor nitrogen formation is observed and NH_3 breakthrough precedes that of H_2. On the other hand at higher temperatures the H_2 front is steep due to the high rate of reaction (1) and NH_3 formation is localized in a small zone of the trap. Besides ammonia readily reacts with nitrates left upstream of the H_2 front (reaction (6)) and this drives the selectivity to N_2. Accordingly in this case N_2 is immediately observed at the reactor outlet and the NH_3 breakthrough is seen at or after the H_2 breakthrough, i.e. when the H_2 front reaches the end of the trap and nitrates stored behind the H_2 front are depleted.

According to this mechanistic proposal, the reduction of the stored NO_x leads initially to NH_3 formation at the H_2 front; the formed NH_3 then reacts (if the temperature is high enough) with nitrates stored downstream the H_2 front. Hence NH_3 and N_2

formation occurs in different zones of the LNT trap, although partially overlapped.

4. Conclusions

In this paper we have investigated the reduction by hydrogen of nitrates stored at different temperatures over LNT Ba/Al_2O_3 and $Pt–Ba/Al_2O_3$ model catalysts.

It is proposed that the regeneration of LNTs under nearly isothermal conditions proceeds according to a two-step mechanism in which the first step is the fast reaction of hydrogen with nitrates producing ammonia, followed by a slower reaction of the latter with nitrate species leading selectively to N_2.

The bulk of data collected studying the reactions of the two-step mechanism indicated that both proceed through a Pt-catalyzed pathway which does not involve, as a preliminary step, the thermal decomposition of the adsorbed NO_x species.

Possible mechanisms include the activation of H_2 on Pt sites, followed by hydrogen spillover on the alumina support towards nitrate ad-species which are decomposed to NO_x and released in the gas phase. These species are readily reduced to ammonia due to high H/N ratio which is locally attained; ammonia then reacts with the stored nitrates leading to the formation of nitrogen. This two-step pathway along with the development of an H_2 front traveling in the reactor during the regeneration is able to explain the typical sequence of products obtained during the regeneration of LNTs, with nitrogen anticipating ammonia; the different reactivity of steps 1 and 2 also accounts for the observed changes in selectivity with temperature, with N_2 formation increasing with temperature.

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