

## Article

# Mechanistic Investigation of the Reduction of NO<sub>x</sub> over Pt- and Rh-Based LNT Catalysts

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**Abstract:** The influence of the noble metals (Pt *vs.* Rh) on the NO<sub>x</sub> storage reduction performances of lean NO<sub>x</sub> trap catalysts is here investigated by transient micro-reactor flow experiments. The study indicates a different behavior during the storage in that the Rh-based catalyst showed higher storage capacity at high temperature as compared to the Pt-containing sample, while the opposite is seen at low temperatures. It is suggested that the higher storage capacity of the Rh-containing sample at high temperature is related to the higher dispersion of Rh as compared to Pt, while the lower storage capacity of Rh-Ba/Al<sub>2</sub>O<sub>3</sub> at low temperature is related to its poor oxidizing properties. The noble metals also affect the catalyst behavior upon reduction of the stored NO<sub>x</sub>, by decreasing the threshold temperature for the reduction of the stored NO<sub>x</sub>. The Pt-based catalyst promotes the reduction of the adsorbed NO<sub>x</sub> at lower temperatures if compared to the Rh-containing sample, due to its superior reducibility. However, Rh-based material shows higher reactivity in the NH<sub>3</sub> decomposition significantly enhancing N<sub>2</sub> selectivity. Moreover, formation of small amounts of N<sub>2</sub>O is observed on both Pt- and Rh-based catalyst samples only during the reduction of highly reactive NO<sub>x</sub> stored at 150 °C, where NO<sub>x</sub> is likely in the form of nitrites.

**Keywords:** NO<sub>x</sub> release; RhBa/Al<sub>2</sub>O<sub>3</sub>; PtBa/Al<sub>2</sub>O<sub>3</sub>; NO<sub>x</sub> storage reduction

## 1. Introduction

The control of air pollutants from mobile sources is currently a noteworthy dispute in the environmental protection field. The environmental regulations (EURO VI and US Tier 2) mandate strict emission limits, which drive the ongoing improvement of abatement technologies. Among the different approaches able to control NO<sub>x</sub> emissions under a rich oxygen environment, the ammonia-Selective Catalytic Reduction (SCR) and the NO<sub>x</sub> Storage Reduction (NSR) methods are feasible solutions [1–5]. In the SCR technique, urea is injected into the exhausts as a precursor of the reducing agent (NH<sub>3</sub>), and reacts with NO<sub>x</sub> over metal-exchanged zeolites (Cu-CHA, Fe-ZSM-5). Due to issues related to the presence of injection systems and urea storage units, this technology is preferable for heavy duty trucks and large diesel cars [4], whereas the NSR approach is preferable for light duty vehicles [3].

Catalytic systems used in the NSR technology consist of a high-surface area carrier (like Al<sub>2</sub>O<sub>3</sub>) supporting alkaline or alkaline-earth metal oxides (typically Ba, K) and platinum group metals (PGM), such as Pt, Rh, or Pd [6]. The abatement of nitrogen oxides is accomplished by a cycling operation based on alternate long fuel-lean (60–90 s) and short fuel-rich (3–5 s) conditions. Under lean conditions, NO<sub>x</sub> are adsorbed on the catalyst in form of nitrites/nitrates [7–13]; then, a rich excursion of the engine

creates a net reducing atmosphere that leads to the reduction of the stored  $\text{NO}_x$ . The regeneration leads mainly to  $\text{N}_2$ ; however, by-products such as  $\text{NH}_3$  or  $\text{N}_2\text{O}$  may also be produced [14].

In spite of the fact that several investigations shed lights on fundamental aspects of the chemistry and mechanism during  $\text{NO}_x$  storage and reduction [7–9,15], still many challenges are open for dispute; in particular, the effect of the nature of the noble metal on both the adsorption and reduction of  $\text{NO}_x$ . Typical catalyst formulations include different platinum group metals (PGM) such as Pt, Pd, or Rh, but the debate concerning the precise role of each constituent is still open. In particular, it has been reported that Pd or Rh are more reactive than Pt in the reduction of adsorbed  $\text{NO}_x$ , more selective to  $\text{N}_2$ , and with higher sulfur resistance [16–19].

In a previous work by some of us [20], Pt- and Rh-based catalysts have been prepared, characterized, and tested under lean/rich conditions at different temperatures. It has been found that the Rh-based samples exhibit a superior ability to release  $\text{O}_2$  from the surface at lower temperatures with respect to Pt, suggesting the presence of a promoting effect on the spillover process of  $\text{NO}_x$  to the precious metal, controlling the subsequent release and reduction of  $\text{NO}_x$ . Aiming to a better understanding of the different catalytic behavior of Rh- and Pt-based catalysts, specifically in the reduction of the adsorbed  $\text{NO}_x$  species, in this study we have considered the same Rh-Ba/ $\text{Al}_2\text{O}_3$  and Pt-Ba/ $\text{Al}_2\text{O}_3$  catalysts used in the previous work [20] and we have analyzed their reactivity in the reduction of the stored  $\text{NO}_x$ . For this purpose different techniques have been used, including Temperature Programmed Desorption (TPD), Temperature Programmed Surface Reaction (TPSR), and Temperature Programmed Isotopic Exchange (TPIE) experiments by using  $\text{H}_2$  as a reducing agent, along with  $\text{NH}_3$  (an intermediate species in the reduction of  $\text{NO}_x$  with  $\text{H}_2$ ). Considering that nitrates and nitrites are involved as stored species in the  $\text{NO}_x$  storage and reduction processes [21], the thermal stability and reactivity of both species have been analyzed, and results are reported in the following.

## 2. Results and Discussion

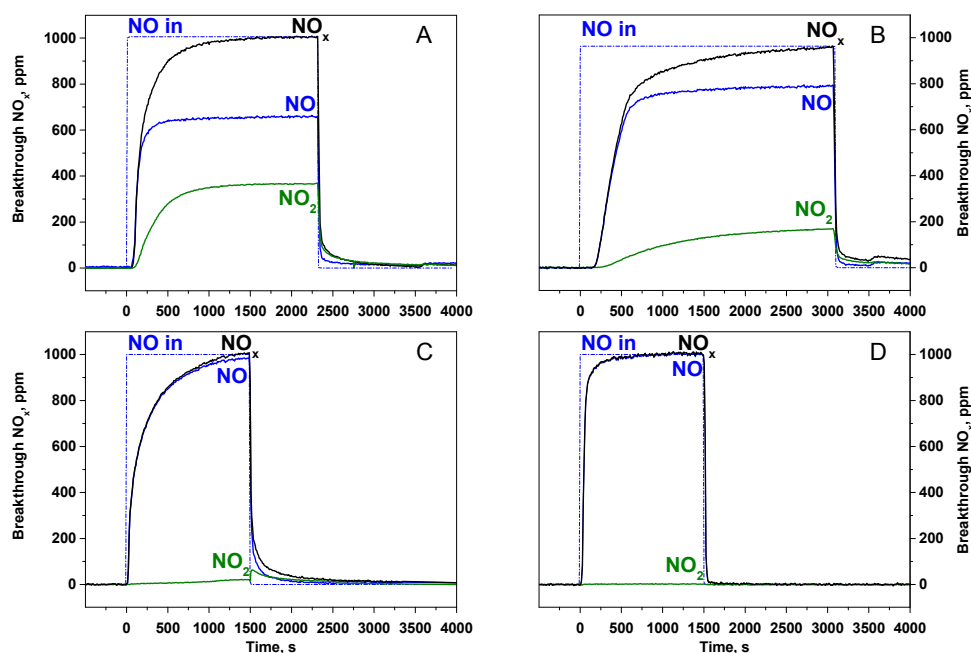
### 2.1. Reactivity of $\text{NO}_x$ Species Stored at 350 °C (Nitrates)

#### 2.1.1. Adsorption of $\text{NO}_x$ at 350 °C

Figure 1A,B show the results obtained during the  $\text{NO}_x$  storage phase performed at 350 °C over Pt-Ba and Rh-Ba catalyst samples, respectively. In the case of the Pt-Ba sample, the breakthrough of NO was detected after 50 s. Then, the nitrogen oxide concentration increases with time, until a steady state is reached (near 660 ppm). The  $\text{NO}_x$  storage is accompanied by evolution of  $\text{NO}_2$  due to oxidation of NO over Pt sites. When the concentration of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) reached the inlet value, the NO concentration is decreased to zero in a stepwise manner. A tailing in the  $\text{NO}_x$  concentration is observed due to desorption of weakly adsorbed species from the catalytic surface; this desorption is further enhanced (although in minor amount) by the removal of oxygen at  $t = 3500$  s. The total amount of  $\text{NO}_x$  stored at steady state is 0.254 mmol/g<sub>cat</sub>; roughly 40% desorb from the surface after NO and  $\text{O}_2$  shutoff.

A similar picture is obtained in case of the Rh-containing sample, although with some differences (Figure 1B). Upon NO admission at  $t = 0$  s, a longer dead time is observed in the  $\text{NO}_x$  concentration (211 s) which then slowly approaches the inlet concentration.  $\text{NO}_2$  formation is also detected, although in lower amounts with respect to the Pt-Ba catalyst. At the end of adsorption phase, roughly 0.683 mmol/g<sub>cat</sub> of  $\text{NO}_x$  are adsorbed on the surface.

The data shows that the Rh-Ba catalyst has a higher storage capacity, but lower NO oxidation activity than Pt-Ba. As a matter of fact, the Ba utilization at steady-state (*i.e.*, the amount of Ba involved in the storage assuming formation of  $\text{Ba}(\text{NO}_3)_2$  species) is 14% and 34% for Pt-Ba and Rh-Ba, respectively. The higher storage capacity of the Rh-containing catalyst, in spite of its lower NO oxidizing capabilities, might be related to the higher noble metal dispersion of this system compared to the Pt-based catalyst sample. Indeed, it has been reported for the Pt-containing systems that the storage ability of the catalyst increases with increased noble metal dispersion [22].

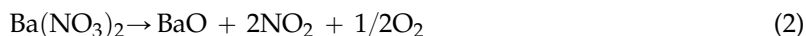
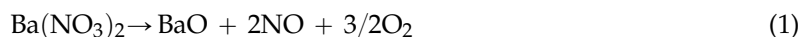


**Figure 1.** Adsorption of NO (1000 ppm) + O<sub>2</sub> (3%) in He, carried out at 350 °C and 150 °C over Pt–Ba/Al<sub>2</sub>O<sub>3</sub> (panel A and C, respectively) and Rh–Ba/Al<sub>2</sub>O<sub>3</sub> (panel B and D, respectively).

### 2.1.2. TPD Experiments

The thermal stability of the NO<sub>x</sub> species stored at 350 °C (nitrates) has been investigated by Temperature Programmed Desorption (TPD) experiments. The results are depicted in Figures 2A and 3A for Pt–Ba and Rh–Ba, respectively. In both cases, the onset temperature of thermal desorption is slightly lower than the adsorption temperature (330 °C *vs.* 350 °C). The most abundant decomposition products are NO and O<sub>2</sub>. NO<sub>2</sub> is also observed at the reactor outlet, although in minor amounts. Almost all nitrates initially present on the surface have been decomposed during TPD, as pointed out by negligible evolution of N-containing products obtained in subsequent cleaning procedure with H<sub>2</sub> (not shown).

The release of NO, NO<sub>2</sub>, and O<sub>2</sub> follows the overall stoichiometry of reactions (Equations (1) and (2)):

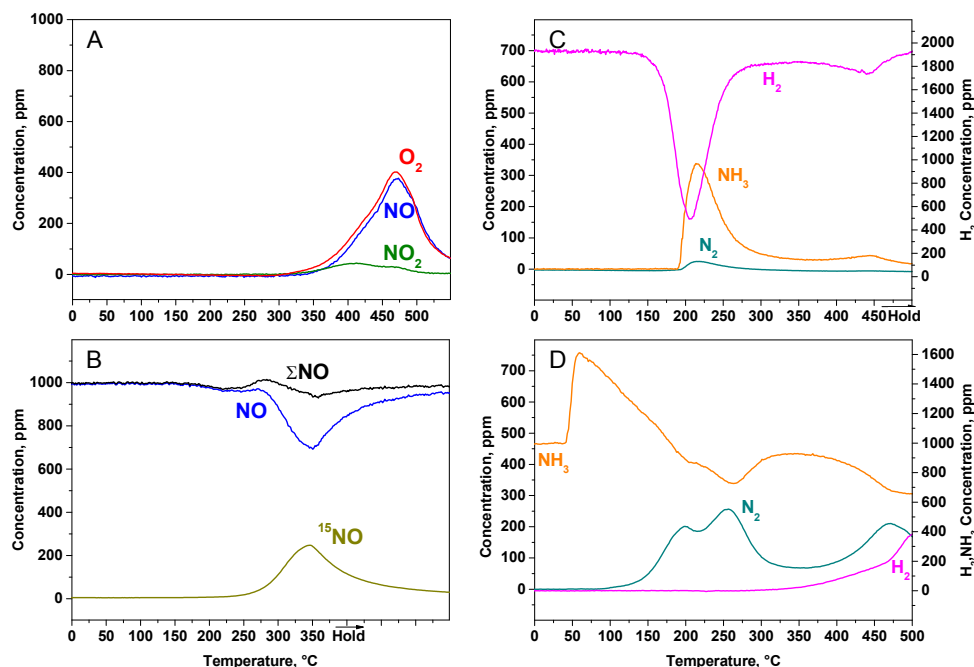


From the experimental data, it is possible to estimate the N/O atomic ratio of the gaseous products released during the TPD run. The calculated integral N/O ratio results 0.37 and 0.39 for Pt–Ba and Rh–Ba catalyst, respectively. The values are in agreement with the expected N/O ratio for nitrate decomposition, *i.e.*, 0.4.

It has been reported that the decomposition of surface NO<sub>x</sub> is driven by the presence of reduced noble metal, and it may occur at the interface between Ba and the noble metal sites [23,24]. Upon decomposition of the stored species, it is suggested that oxygen ad-atoms are formed at the metal sites; when the temperature is high enough, O<sub>2</sub> desorption occurs and metallic sites are restored, which serve as centers for the decomposition of the stored NO<sub>x</sub>. Accordingly, the presence of the noble metal is expected to enhance the decomposition of surface nitrates [10].

No significant differences are observed in terms of nitrate decomposition threshold between the Pt- and Rh-based catalysts. Notably, in a previous work by some of us [20], it has been shown that nitrate decomposition is favored over Rh–Ba than over the Pt-containing sample when NO<sub>x</sub> are stored at low temperature (150 °C) starting from NO<sub>2</sub>. It has been suggested that Rh promotes NO<sub>x</sub>

desorption due to easier release of O<sub>2</sub> from the surface; this creates vacant sites on Rh, accessible for the decomposition of surface NO<sub>x</sub>. The observation that after NO/O<sub>2</sub> adsorption at 350 °C the two catalyst exhibit a similar behavior upon decomposition of the stored nitrates (see Figures 2A and 3A), might be explained considering that the nitrate decomposition occurs, in this case, at high temperatures (above 300 °C), where the rate determining step of the process is not the O-release from the noble metal.



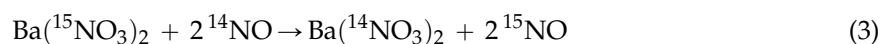
**Figure 2.** Temperature Programmed Desorption, TPD (A); Temperature Programmed Isotopic Exchange, TPIE (B); Temperature Programmed Surface Reaction, TPSR: H<sub>2</sub>-TPSR (C); and NH<sub>3</sub>-TPSR (D) experiments following adsorption of NO (1000 ppm) + O<sub>2</sub> (3%) at 350 °C over Pt–Ba/Al<sub>2</sub>O<sub>3</sub>.

### 2.1.3. TPIE Experiments

The isotopic exchange experiments have been used by some of us [25,26] to characterize the NO<sub>x</sub> release step, and is herein employed the check whether the nature of the noble metal (Pt and Rh) has an impact on this process. Accordingly, the NO<sub>x</sub> adsorption is carried out at 350 °C using labeled NO molecules (*i.e.*, <sup>15</sup>NO/O<sub>2</sub> in He) and the catalyst has been heated under gaseous <sup>14</sup>NO up to 350 °C. The obtained results are shown in Figures 2B and 3B for Pt–Ba and Rh–Ba catalysts, respectively.

In the case of the Pt–Ba sample (see Figure 2B) the exchange is monitored above 225 °C, as pointed out by the evolution of <sup>15</sup>NO and corresponding consumption of <sup>14</sup>NO. The overall NO<sub>x</sub> concentration remains constant, if one excludes the small <sup>14</sup>NO uptake above 200 °C, followed by a marginal release. This indicates that there is no significant net NO uptake/release during the experiment. After prolonged treatment at 350 °C, the <sup>15</sup>NO profile reaches the background level; upon cleaning with H<sub>2</sub> at the end of the experiment, no labeled N-containing products have been observed, indicating that the isotopic exchange is complete.

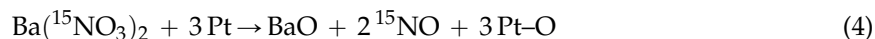
The evolution of <sup>15</sup>NO and the corresponding consumption of <sup>14</sup>NO are in agreement with the occurrence of reaction (Equation (3)):



describing the exchange of the stored <sup>15</sup>NO<sub>x</sub> with gaseous <sup>14</sup>NO.

The isotopic exchange occurs at lower temperatures if compared to thermal decomposition of surface nitrates (225 °C *vs.* 330 °C, compare Figure 2A,B). As discussed elsewhere [25], it is likely

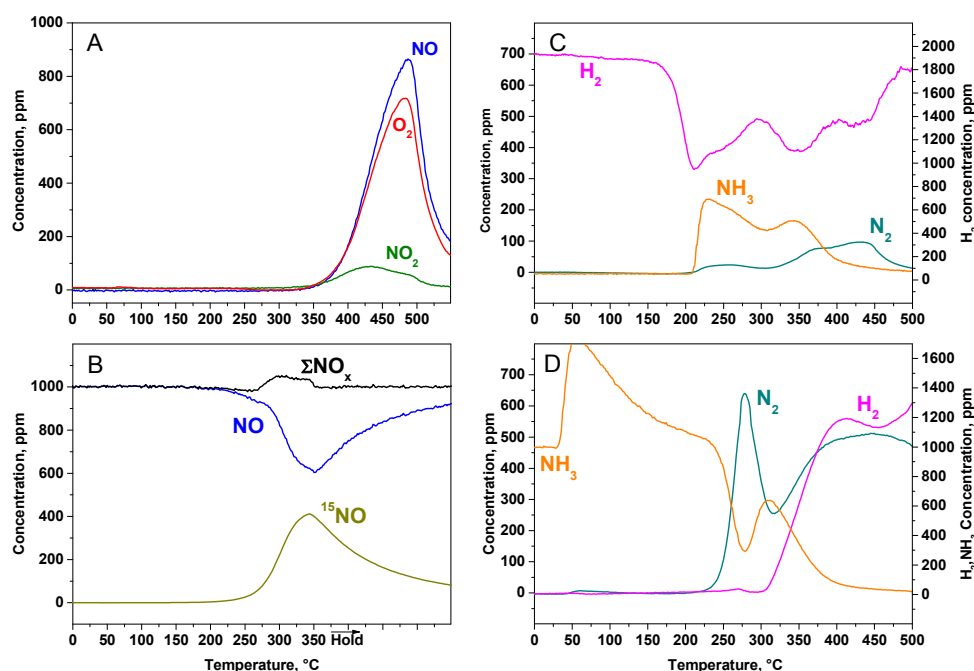
that the isotopic exchange is a redox process involving Pt sites, occurring according to the following overall stoichiometries:



possibly involving the intermediacy of nitrites [26]. It is likely that labeled nitrates are reduced at metallic Pt sites leading to  $^{15}\text{NO}$  evolution and formation of Pt–O species (Equation (4)). Pt–O species then oxidize  $^{14}\text{NO}$  present in the gas phase to give adsorbed unlabeled nitrate species and restoring the metallic Pt sites (Equation (5)). The  $\text{NO}_x$  release is catalyzed by metallic centers; in fact, no exchange is observed in the absence of the noble metal [25].

The results shown in Figure 2B closely resembles these obtained in a previous work [25], although the catalytic material used in the study had a different Pt dispersion ( $D_{\text{Pt}} = 52\%$  *vs.* 11%). This apparently indicates that in the investigated range of operating conditions the metal dispersion does not affect the onset of isotopic exchange, being this process likely influenced by the presence of reduced metal sites.

In the case of the Rh-containing sample (Figure 3B), similar results have been obtained. The threshold of isotopic exchange is observed in the same temperature range; also, in this case, the isotopic exchange is almost complete (>95%) at the end of experiment. Accordingly, it appears that the  $\text{NO}_x$  release is not markedly affected by both the nature of the noble metal and its dispersion.



**Figure 3.** TPD (A); TPIE (B); H<sub>2</sub>-TPSR (C); and NH<sub>3</sub>-TPSR (D) experiments following adsorption of NO (1000 ppm) + O<sub>2</sub> (3%) at 350 °C over Rh–Ba/Al<sub>2</sub>O<sub>3</sub>.

#### 2.1.4. TPSR Experiments

The reactivity of surface nitrates stored on Pt–Ba and Rh–Ba catalysts has been investigated with H<sub>2</sub> and NH<sub>3</sub> under temperature programming (TPSR experiments). The results of H<sub>2</sub>-TPSR runs are shown in Figures 2C and 3C for Pt–Ba and Rh–Ba samples, respectively. Over the Pt–Ba system, the onset temperature of hydrogen consumption is observed near 150 °C (Figure 2C). The initial H<sub>2</sub> uptake is not accompanied by the evolution of reaction products; only above 180 °C ammonia evolution is observed, with a maximum near 220 °C. The delay in the NH<sub>3</sub> evolution with respect to

H<sub>2</sub> consumption is likely related to the initial involvement of H<sub>2</sub> in the reduction of Pt sites. Above 200 °C a small N<sub>2</sub> production is also observed. Above 220 °C the H<sub>2</sub> concentration starts to increase due to depletion of adsorbed nitrates and this increase is accompanied by the decrease in the evolution of NH<sub>3</sub> (and of N<sub>2</sub>). Neither NO nor N<sub>2</sub>O are observed among the reaction products.

H<sub>2</sub> consumption and NH<sub>3</sub> evolution are in line with the stoichiometry of the following reaction (Equation (6)):



Notably, the onset temperature for the nitrate reduction (150 °C) is lower than that of thermal decomposition (TPD, 330 °C) and isotopic exchange (250 °C). As discussed elsewhere [25], the reduction of the stored NO<sub>x</sub> involves the spillover of the stored NO<sub>x</sub> species towards reduced metallic sites, followed by the release of NO<sub>x</sub> and the reduction of the released NO<sub>x</sub>. The driving force for the onset of reduction is the presence of metallic sites; accordingly, the reduction of the noble metal by H<sub>2</sub> initiates the process. Once NO is released, it is readily dissociated into N- and O-ad-atoms on Pt sites; these species then react with H-ad-species leading to NH<sub>3</sub> and H<sub>2</sub>O, respectively. In fact, it has been shown that the reaction between gaseous NO and H<sub>2</sub> occurs at temperatures well below those monitored in the case of NO<sub>x</sub> adsorbed species (data herein not reported), near 50 °C, indicating that the NO<sub>x</sub> release is the rate-determining step in the reduction process of the stored NO<sub>x</sub>.

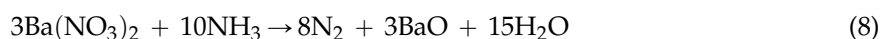
The results obtained over the Rh–Ba sample (Figure 3C) present similar features with respect to the Pt–Ba catalyst, although the onset for H<sub>2</sub> consumption (and NH<sub>3</sub> evolution) is shifted to slightly higher temperatures. The hydrogen consumption shows a complex behavior with minima near 200 °C and 350 °C with corresponding to ammonia formation, and a minimum near 420 °C associated with N<sub>2</sub> evolution. The complex dynamics of H<sub>2</sub> consumption are likely due to the presence of a population of adsorbed nitrates having different reactivity e.g., surface *vs.* bulk-like NO<sub>x</sub> ad-species. In particular, the high-temperature N<sub>2</sub> peak is likely related to the occurrence of the NH<sub>3</sub> decomposition (Equation (7)):



that, in fact, is well catalyzed by Rh sites (see below).

The data show that over Rh–Ba the onset temperature for the reduction is shifted towards slightly higher temperature with respect to the Pt–Ba sample, pointing out the higher reactivity of the Pt- *vs.* Rh-containing catalyst in the reduction of the stored nitrates by H<sub>2</sub> in spite of the lower dispersion of Pt in Pt–Ba/Al<sub>2</sub>O<sub>3</sub>. As a matter of fact, Harold and co-workers [22] showed that over model Pt–Ba catalysts, the reduction of the stored NO<sub>x</sub> is favored upon increasing the Pt dispersion. In our case, the Pt-based has a lower dispersion than the Rh-containing catalyst but a higher reactivity; this is likely related to the higher reducibility of Pt with respect to Rh.

The reactivity of stored nitrates has also been investigated using NH<sub>3</sub> as reductant (NH<sub>3</sub>-TPSR), due to the role of this species as intermediate in N<sub>2</sub> formation [27]. The results are shown in Figures 2D and 3D in the case of Pt–Ba and Rh–Ba catalysts, respectively. In the case of the Pt–Ba catalyst, evolution of ammonia is seen upon heating the sample due to its desorption from the catalyst surface. For this reason, the threshold of NH<sub>3</sub> consumption is difficult to detect; however, based on N<sub>2</sub> formation, the reaction with stored NO<sub>x</sub> is seen starting near 120 °C. The consumption of NH<sub>3</sub> and the corresponding N<sub>2</sub> evolution are in line with the stoichiometry of reaction (Equation (8)):



The N<sub>2</sub> profile shows complex dynamics, possibly due to the reduction of NO<sub>x</sub> species with different reactivity. Above 350 °C N<sub>2</sub> formation occurs together with H<sub>2</sub> due to occurrence of the NH<sub>3</sub> decomposition reaction (Equation (7)). These results confirm that ammonia is an effective reducing agent for the stored nitrates, its reactivity being similar to that of H<sub>2</sub> over this catalyst. Worth noting is that neither NO nor N<sub>2</sub>O are detected at the reactor outlet, *i.e.*, the reaction is very selective to nitrogen.



The results of  $\text{NH}_3$ -TPSR of nitrates stored over Rh–Ba-based catalyst are presented in the Figure 3D. The onset of nitrate reduction (based on products evolution) is observed near 230 °C, a higher value than over Pt–Ba. Additionally, comparison of Figure 3C, D also shows that ammonia is, by far, less reactive than  $\text{H}_2$  in the reduction of the stored nitrates over Rh–Ba.  $\text{N}_2$  evolution shows a sharp maximum near 280 °C and then its concentration increases with temperature, along with  $\text{H}_2$ . The primary  $\text{N}_2$  production is related to the reduction of the stored  $\text{NO}_x$ , while secondary  $\text{N}_2$  formation is associated to the  $\text{NH}_3$  decomposition, effective over the Rh-based catalyst sample above 300 °C. Furthermore, in the case of the Rh–Ba catalyst neither NO nor  $\text{N}_2\text{O}$  are observed at the reactor outlet, *i.e.*, the reaction is fully selective to  $\text{N}_2$ .

The results obtained over both catalysts pointed out that  $\text{NH}_3$  is an effective reductant for nitrates, which are selectively reduced to  $\text{N}_2$ . The Rh–Ba catalyst showed a much lower reactivity than the Pt–Ba sample in the reduction of stored nitrates by  $\text{NH}_3$ , in line with lower reducibility of this sample, which however exhibits a much higher activity in the decomposition of ammonia to nitrogen and hydrogen (Equation (7)).

## 2.2. Reactivity of $\text{NO}_x$ Species Stored at 150 °C (Nitrites)

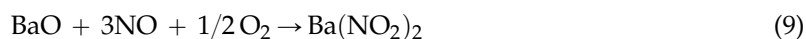
### 2.2.1. Adsorption of $\text{NO}_x$ at 150 °C

Figure 1C, D shows the results of  $\text{NO}_x$  adsorbed at 150 °C over Pt–Ba and Rh–Ba catalysts, respectively. On the basis of FT-IR spectroscopic analysis carried out over catalysts having similar composition, adsorption of  $\text{NO}_x$  at this temperature leads to the formation of nitrite ad-species [10,15].

In the case of the Pt-containing catalyst (Figure 1C), the total uptake of NO is negligible and the amounts of  $\text{NO}_x$  stored at steady state is small, 0.280 mmol/g<sub>cat</sub>. At this temperature, Pt exhibits only a minor activity in the NO oxidation and only 25 ppm of  $\text{NO}_2$  are detected at steady-state conditions.

Additionally, in the case of the Rh–Ba catalyst (Figure 1D), the  $\text{NO}_x$  breakthrough is observed immediately after NO admission to the reactor, but no  $\text{NO}_2$  is formed in this case. This confirms the lower oxidizing properties of Rh, as compared to Pt. The amount of  $\text{NO}_x$  adsorbed on the surface is lower than on Pt–Ba being, in this case, 0.106 mmol/g<sub>cat</sub>.

The results show that both catalysts are active in the storage of  $\text{NO}_x$  at low temperatures, but the Pt–Ba operates more efficiently than Rh–Ba, at variance with what observed at 350 °C. At 150 °C adsorption proceeds via the nitrite route [21], which involves the activation of  $\text{O}_2$  over the noble metal subsequently transferred to adjacent Ba sites. This would favor a stepwise oxidative adsorption of NO in the form of nitrite-like ad-species on Ba sites, according to the stoichiometry of the reaction (Equation (9)). Accordingly, a cooperative effect between Pt–Ba neighboring couples appears to be relevant for this route.



Notably, at variance with that observed at 350 °C, the Rh–Ba sample shows a lower storage capacity than Pt–Ba, in spite of the higher dispersion of Rh *vs.* Pt. This is likely related to the negligible oxidizing capabilities of Rh–Ba, if compared to Pt–Ba at such low temperatures. In fact, no  $\text{NO}_2$  formation has been observed from NO at 150 °C in the case of the Rh–Ba sample (see Figure 1D). If one considers that formation of nitrites requires an oxidizing step, the low storage capacity observed at this temperature over the Rh–Ba sample is likely related to its poor oxidation capability.

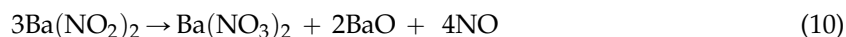
### 2.2.2. TPD Experiments

The thermal stability of the  $\text{NO}_x$  species adsorbed at 150 °C has been analyzed by TPD experiments, and results are shown in Figures 4A and 5A for Pt–Ba and Rh–Ba catalysts, respectively. The desorption of the decomposition products has been observed starting from 150 °C in both catalyst samples, and occurs in two distinct temperature regions. Below 300–350 °C only NO is detected,

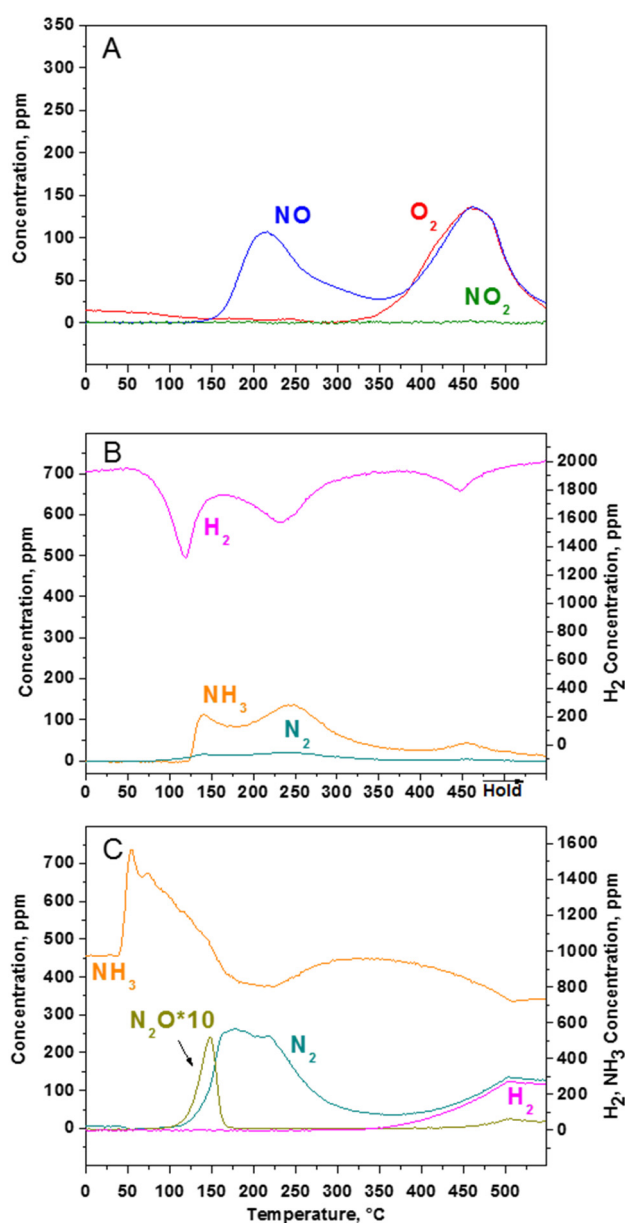
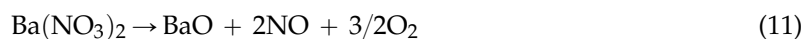
whereas above 350 °C the release of NO is accompanied by the evolution of oxygen. In both cases, no NO<sub>2</sub> is detected at the reactor outlet.

Almost all stored NO<sub>x</sub> initially present on the catalysts have been removed from the surface, as demonstrated by limited amount of N-containing species detected in a subsequent reduction with H<sub>2</sub>.

In line with other works [28], in the low temperature region the disproportion of nitrites to nitrates and NO is likely to occur according to the stoichiometry of the reaction (Equation (10)).

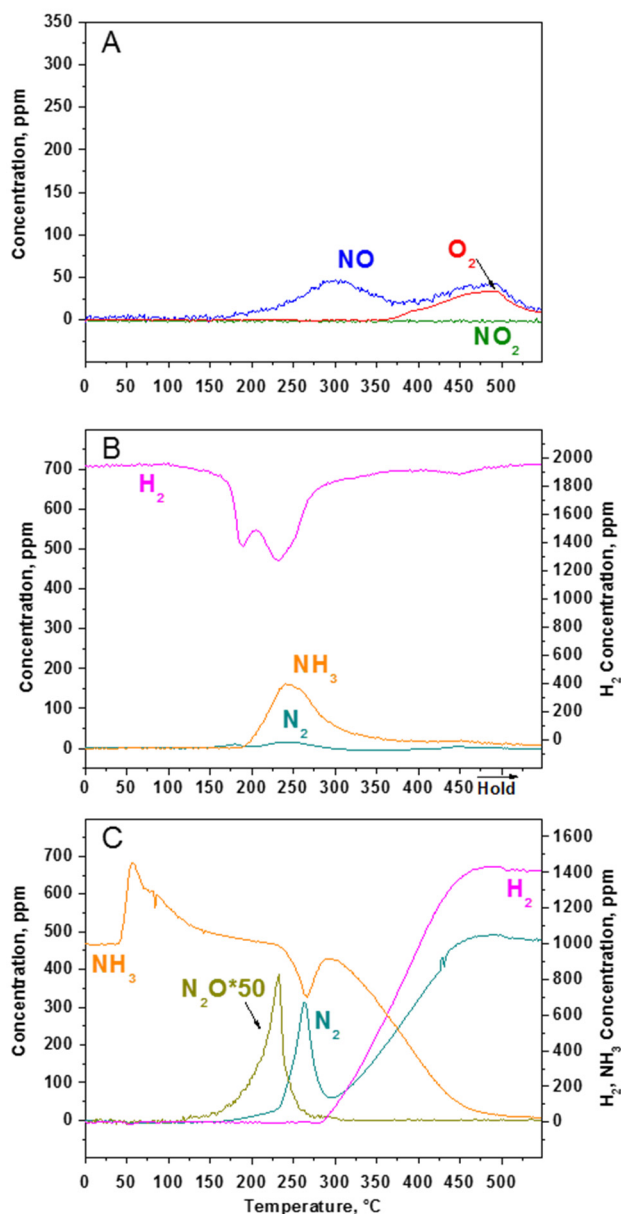


This would explain the evolution of NO alone. Then, the high temperature NO/O<sub>2</sub> peak is associated with the decomposition of the nitrates (formed according to reaction (Equation (10))), *i.e.*, reaction (Equation (11)):



**Figure 4.** TPD (A); H<sub>2</sub>-TPSR (B); and NH<sub>3</sub>-TPSR (C) experiments following adsorption of NO (1000 ppm) + O<sub>2</sub> (3%) at 150 °C over Pt-Ba/Al<sub>2</sub>O<sub>3</sub>.





**Figure 5.** TPD (A); H<sub>2</sub>-TPSR (B); and NH<sub>3</sub>-TPSR (C) experiments following adsorption of NO (1000 ppm) + O<sub>2</sub> (3%) at 150 °C over Rh–Ba/Al<sub>2</sub>O<sub>3</sub>.

In fact, the integral N/O ratios estimated over the whole TPD run are near 0.57 for Pt–Ba and 0.62 for Rh–Ba, values that are in reasonable agreement with theoretical value (0.67) expected from nitrite decomposition. On the other hand, the integral N/O molar ratio evaluated for the high temperature desorption peaks are near 0.28 for Pt–Ba and 0.32 for Rh–Ba, in line with the decomposition of nitrate species following the stoichiometry of the reaction (Equation (11)).

In any case, the decomposition of the stored nitrites presents similar features over both the Pt–Ba and Rh–Ba catalyst samples; however, over the Rh-based catalyst less intense TPD peaks are observed due to lower amounts of initially stored NO<sub>x</sub> species.

### 2.2.3. TPSR Experiments

The reactivity of NO<sub>x</sub> species adsorbed at 150 °C has also been analyzed in the presence of H<sub>2</sub> and NH<sub>3</sub> under temperature programming, and results are shown in the Figures 4B and 5B, respectively.

In the case of the Pt–Ba catalyst (Figure 4B), H<sub>2</sub> consumption is observed slightly above 85 °C, and this is likely related to the reduction of Pt sites. The product formation is observed close to 125 °C, as pointed out by ammonia evolution. NH<sub>3</sub> profile shows two maxima in correspondence with H<sub>2</sub> consumption; the first at low temperature near 150 °C, while a second peak is observed at higher temperature, close to 250 °C. Then, H<sub>2</sub> concentration starts to increase due to depletion of adsorbed NO<sub>x</sub> species; near 450 °C a further small consumption is seen accompanied by the evolution of NH<sub>3</sub>. The reaction is very selective towards ammonia, only traces of N<sub>2</sub> are detected; no appreciable amounts of NO or N<sub>2</sub>O are seen at the reactor outlet.

Over the Rh–Ba catalyst (Figure 5B), after H<sub>2</sub> admission an initial consumption is seen with a minimum near 190 °C, without formation of reaction products. Like the case of Pt, this is possibly related to the reduction of Rh sites. Above 200 °C, evolution of NH<sub>3</sub> is observed, with a corresponding H<sub>2</sub> consumption. Additionally, in this case almost complete selectivity to ammonia is recorded without NO or N<sub>2</sub>O among reaction products.

Comparing Figures 5B and 4B it clearly appears that the onset temperature for nitrites reduction with H<sub>2</sub> is lower over Pt–Ba catalyst than over Rh–Ba, as observed in the case of nitrate reduction. The initial step of the reaction is likely the reduction of the noble metal sites, as pointed out by the initial H<sub>2</sub> consumption. Then the reaction involves the release of NO<sub>x</sub> in the gas phase followed by the reduction of the released NO<sub>x</sub>. It can be argued that the reactivity of the noble metal in the reduction of the stored NO<sub>x</sub> species is related to the capability of the reductant to keep the noble metal in a reduced state. Accordingly, the data show that Rh is less reducible than Pt.

Finally, the reactivity of NO<sub>x</sub> species stored at 150 °C has also been investigated using NH<sub>3</sub> as a reducing agent and results are shown in the Figures 4C and 5C for Pt–Ba and Rh–Ba catalysts, respectively.

In the case of Pt–Ba, an initial small formation of N<sub>2</sub>O (note that the signal has been multiplied by a factor of 10) is observed starting from 110 °C, *i.e.*, at temperatures very similar to those observed in the case of H<sub>2</sub> (see Figure 4B). Then, upon increasing the temperature, N<sub>2</sub>O is no longer detected and N<sub>2</sub> formation is observed whose concentration increases, showing a broad maximum in the 150–250 °C temperature range. Above 350 °C the formation of H<sub>2</sub> along with N<sub>2</sub> is also observed, due to the occurrence of the NH<sub>3</sub> decomposition (Equation (7)).

Notably, no N<sub>2</sub>O formation has been observed upon the reduction of surface nitrates (see Figure 2C). Considering that significant amounts of N<sub>2</sub>O can be formed in the presence of gaseous NO only [29], this likely reflects the easier NO release (and hence the presence of undissociated NO molecules) from the surface nitrites, as compared to nitrates.

Similar results have been obtained over Rh–Ba (Figure 5C). In fact, in this case nitrites are reduced by NH<sub>3</sub> with an initial N<sub>2</sub>O evolution starting from 150 °C, *i.e.*, at higher temperatures with respect to the Pt–Ba sample (see Figure 4C). Then the formation of N<sub>2</sub> is observed; its evolution shows a complex profile with a maxima near 265 °C and 450 °C and then keeps constant until the end of the run. Above 300 °C, the occurrence of the NH<sub>3</sub> decomposition reaction is well evident, at variance with that observed in the case of Pt–Ba. Accordingly, the N<sub>2</sub> peak with maximum near 265 °C is attributable to the reduction of the stored NO<sub>x</sub> ad-species, while the subsequent N<sub>2</sub> evolution is related to the NH<sub>3</sub> decomposition reaction.

Accordingly, also over the Rh-based system N<sub>2</sub>O formation is observed upon the reduction of nitrites but not of nitrates. In fact, nitrates release NO at high temperature than nitrites, and this favors N<sub>2</sub> formation instead of N<sub>2</sub>O since at such temperatures Pt and Rh sites are in a reduced state.

### 3. Experimental Section

The catalytic tests have been carried out over homemade Pt–Ba/Al<sub>2</sub>O<sub>3</sub> (1/16/100 *w/w*) and Rh–Ba/Al<sub>2</sub>O<sub>3</sub> (0.5/16/100 *w/w*) catalysts. Briefly, the catalysts have been prepared by sequential impregnation of the support with an aqueous solution of noble metal precursor and then of barium precursor, according to the standard incipient wetness method. Pt–Ba/Al<sub>2</sub>O<sub>3</sub>, hereafter denoted as

Pt–Ba, showed specific surface area of  $131 \text{ m}^2 \cdot \text{g}^{-1}$  with final Pt dispersion of 11.1% [20]. In case of Rh–Ba/ $\text{Al}_2\text{O}_3$ , indicated as Rh–Ba, the catalyst specific surface area is  $135 \text{ m}^2 \cdot \text{g}^{-1}$  with Rh dispersion is 42.3%. Further details on catalyst preparation and characterization can be found elsewhere [20].

The reactivity tests have been performed in an homemade quartz micro-reactor (7 mm internal diameter) loaded with 60 mg of catalyst sample (sieved at 70–125  $\mu\text{m}$ ). A total flow rate of  $100 \text{ N} \cdot \text{cm}^3 \cdot \text{min}^{-1}$  has been used. The temperature of the catalyst is measured and controlled by a K-type thermocouple (Tersid, Milano, Italy) placed in the catalytic bed. Due to the low catalyst loading and the diluted reductant concentration, significant thermal effects can be neglected and, hence, the catalytic layer can be safely assumed to be isothermal. The reaction products exiting the reactor are monitored by a mass spectrometer (Omnistar 200, Pfeiffer Vacuum, Asslar, Germany), a UV- $\text{NO}_x$  analyzer (Limas 11HW, ABB, Zurich, Switzerland) and a micro gas chromatograph (Agilent 3000A, Santa Clara, CA, USA) directly connected to the reactor outlet, and providing complementary qualitative and quantitative analysis. Further details on the analytical equipment and procedure can be found elsewhere [27].

Prior the catalytic runs, the samples were subjected to a conditioning procedure in order to obtain a reproducible catalyst behavior; this procedure involves few  $\text{NO}_x$  adsorption ( $\text{NO}$  1000 ppm +  $\text{O}_2$  3% *v/v* in He) and reduction ( $\text{H}_2$  2000 ppm in He) cycles until steady state behavior is obtained. Afterwards, the catalysts are treated with  $\text{H}_2$  at 400 °C for 30 min in order to remove residual N-containing species.

The thermal stability and reactivity of  $\text{NO}_x$  species stored on the catalysts at 150 °C and 350 °C have been analyzed by TPD (Temperature Programmed Desorption) and TPSR (Temperature Programmed Surface Reaction), with  $\text{H}_2$  and  $\text{NH}_3$  as reducing agents, and by isotopic exchange (TPIE, Temperature Programmed Isotopic Exchange) experiments. These adsorption temperatures have been chosen since storage at such conditions lead to the formation of nitrite and nitrate adspecies, respectively, as shown by FTIR (Fourier Transform InfraRed) experiments carried out over similar catalysts [21]. Adsorption has been carried out at the selected temperature starting from  $\text{NO}$  (1000 ppm) +  $\text{O}_2$  (3% *v/v*) in flowing He up to steady state conditions, followed by a He purge at the same temperature and cooling to room temperature (RT) under He.

In a typical TPD experiment, after  $\text{NO}_x$  adsorption as described above, the sample has been heated under temperature programming from 50 °C to 500 °C (10 °C/min). In the case of TPSR experiments, after  $\text{NO}_x$  adsorption at 150 °C and 350 °C and He purge,  $\text{H}_2$  (2000 ppm) or  $\text{NH}_3$  (1000 ppm) have been admitted to the reactor at 40 °C and the temperature has been increased up to 450 °C (or 500 °C) at a rate of 10 °C/min.

Finally, in the Temperature Programmed Isotopic Exchange (TPIE) experiments, labelled  $^{15}\text{NO}_x$  have been adsorbed starting from a  $^{15}\text{NO}/\text{O}_2$  mixture. After purge with He at the same temperature of adsorption and cooling down to 50 °C,  $^{14}\text{NO}$  was admitted to the reactor and the temperature was eventually increased up to 350 °C at 10 °C/min. Then, a rich phase has been performed with  $\text{H}_2$  (2000 ppm) to reduce adsorbed  $\text{NO}_x$  species.

In all runs, nitrogen mass balance calculations have been carried out by the difference between the amounts of stored  $\text{NO}_x$  and those of N-containing products evolved during the rich phase. Nitrogen mass balance typically closes within  $\pm 5\%$ .

#### 4. Concluding Remarks

In this work, the thermal stability/reactivity of  $\text{NO}_x$  stored over alumina supported Pt–Ba and Rh–Ba catalysts has been investigated, aiming at a better understanding of the behavior of Pt *vs.* Rh in the adsorption/reduction of  $\text{NO}_x$  under lean conditions. For this purpose, the behavior of alumina-supported Pt and Rh samples promoted with Ba have been compared in the adsorption of  $\text{NO}_x$  at different temperatures. The reactivity of the adsorbed species with various reductants has then been analyzed.

The results obtained upon storage of  $\text{NO}_x$  at 350 °C and at 150 °C (leading to the formation of nitrates and nitrites, respectively) pointed out that both catalyst samples effectively store  $\text{NO}_x$ . However, whereas the Rh-based catalyst showed a higher storage capacity at 350 °C, the Pt-containing sample exhibits higher performances at low temperatures (150 °C). On the other hand, the Pt-based catalyst showed a higher NO oxidation capability at all the investigated temperatures. It has been suggested that the higher storage capacity of the Rh-containing sample at high temperature is related to the higher dispersion of Rh if compared to Pt, which ensures a better noble metal-Ba interaction. On the other hand the lower storage capacity of Rh-Ba/ $\text{Al}_2\text{O}_3$  at 150 °C is related to its lower oxidizing properties, the limiting factor of the Rh-based catalyst at low temperature.

Nitrates and nitrites stored over Pt-Ba/ $\text{Al}_2\text{O}_3$  and Rh-Ba/ $\text{Al}_2\text{O}_3$  showed similar thermal stability, as pointed out by TPD experiments. Nitrates also showed a similar reactivity during isotopic exchange experiments, to probe the NO release properties of these species. Under a mechanistic point of view, isotopic exchange experiments revealed that the process of  $\text{NO}_x$  release does not involve thermal decomposition as a preliminary step. Instead, the  $\text{NO}_x$  release is a redox process not significantly affected by the type of noble metal but controlled over the investigated samples by the reactivity of NO. In fact, when more active reductants are used, *i.e.*,  $\text{H}_2$  and  $\text{NH}_3$ , a clean distinction could be evidenced between Pt and Rh. The primary effect of the noble metal is the decrease of the threshold temperature for the reduction of the stored  $\text{NO}_x$ . In particular the Pt based catalyst promotes the reduction of both nitrites and nitrates at lower temperatures if compared to the Rh-containing sample. Since the regeneration mechanism is driven by reduction of the noble metal sites (Pt or Rh), this points out the superior reducibility of Pt-Ba/ $\text{Al}_2\text{O}_3$ . When  $\text{H}_2$  is used as a reductant, the reduction of the stored  $\text{NO}_x$  is very selective to  $\text{NH}_3$  over both catalysts. On the other hand,  $\text{N}_2$  is selectively produced upon reduction of the stored  $\text{NO}_x$  with  $\text{NH}_3$ . This is in line with the intermediacy of ammonia in nitrogen formation during regeneration of NSR catalysts. Notably, the Rh-based catalyst also showed a significant reactivity in the  $\text{NH}_3$  decomposition reaction, as opposed to Pt. Under practical applications, this may affect the  $\text{NH}_3$  slip occurring during lean/rich operations.

Finally, a small  $\text{N}_2\text{O}$  production is seen over both catalysts at the early stage of reduction of stored  $\text{NO}_x$  species (nitrites and nitrates) when ammonia is used as reductant, and in the case of nitrites only. In fact, nitrites release NO at lower temperatures than nitrates and this would favor  $\text{N}_2\text{O}$  formation. In this respect, no significant differences have been observed between the Pt- and the Rh-based catalyst samples.

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