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NO_x removal catalysis under lean conditions

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Abstract

The storage-reduction of NO_x over Pt–Ba/Al_2O_3 samples is analyzed in this work. It is pointed out that the storage of NO in the presence of excess oxygen proceeds through two parallel routes: (i) the "nitrate route" where NO is oxidized to NO_2 on Pt sites followed by NO_2 disproportionation on Ba sites to form nitrates with evolution of gaseous NO; (ii) the "nitrite route", where NO is oxidized on Pt sites and directly stored on Ba neighbouring sites in the form of nitrites that are then oxidized to nitrates. The latter route possibly dominates at high Ba loadings.

Concerning the reduction of the stored NO_x, the bulk of data indicates that the process under isothermal conditions is not initiated by the release of NO_x in the gas phase but occurs through a Pt-catalysed reduction of adsorbed NO_x species. This route requires the co-presence of Pt and Ba on the same support. It is speculated that H_2 is activated on Pt sites and spills on the alumina support towards nitrate ad-species where it operates the reduction, although alternative explanations are possible.

Keywords: Lean deNO_x; NO_x storage mechanism; NO_x reduction mechanism; LNT systems; Pt–Ba/Al_2O_3 catalyst; Transient Response Method; Hydrogen

1. Introduction

Lean NO_x Traps (LNT) have been developed and put into the market by Toyota to remove NO_x in vehicles equipped with lean burn engines [1]. The use of these engines is wide spreading nowadays due to their capability to ensure lower CO_2 emissions and improved fuel economics as compared to traditional stoichiometric engines [2,3]. 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_x, CO and of hydrocarbons and the reduction of stored NO_x as well.

In spite of the fact that a number of papers have been published on the catalytic behavior of Pt–Ba/Al_2O_3 catalysts, the mechanism of the NO_x adsorption and of their subsequent reduction has not been completely clarified so far [4]. In our labs, an extensive investigation has been undertaken aiming at elucidating the NO_x-storage characteristics of Pt–Ba/Al_2O_3 catalyst samples and of the adsorbed NO_x species [5–12]. In particular, NO and NO_2 adsorption experiments have been carried out in the presence and in the absence of oxygen; FT-IR spectroscopy and the transient response method (TRM) have been used as complementary techniques. The collected data are herein presented and discussed, and a novel pathway for the NO_x storage that implies the direct uptake of NO in the presence of oxygen to form nitrites [11] at Ba sites nearby Pt is also addressed.

Then, the reduction of the stored NO_x species has been investigated, aiming at a better understanding of the reduction process. For this purpose the thermal stability/reactivity in the presence of H_2 of the adsorbed NO_x species has been analyzed under different conditions, and results are shown in the following. H_2 has been used as a reductant in view of the potential applications of on-board reforming units for the production of reducing agent [13].

2. Experimental

The Pt–Ba/γ-Al_2O_3 (1/20/100 w/w) sample was prepared by incipient wetness impregnation of commercial alumina with aqueous solution of platinum dinitro-diammine and of barium acetate, followed by drying and calcination at 500 °C for 5 h [5,9,11]. The Pt–Ba/γ-Al_2O_3 sample is characterized by a large surface area (140 m^2/g) and a large pore volume (0.80 cm^3/g). The Pt dispersion, measured by H_2 chemisorption of the

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reduced catalyst, is 64%. Pt–Ba/γ-Al_2O_3 catalysts with different Ba loadings have also been prepared, as well as binary Pt/γ-Al_2O_3 and Ba/γ-Al_2O_3 samples, and a physical mixture Pt/Al_2O_3 + Ba/Al_2O_3 obtained by mixing specific amounts of the binary Pt/γ-Al_2O_3 and Ba/γ-Al_2O_3 samples.

The study of the adsorption of NO_x has been performed under transient conditions at 350 °C by imposing step changes in the inlet NO_x concentration, while continuously analyzing the gases exiting the reactor with a mass spectrometer. FT-IR spectroscopy has also been used as a complementary technique to analyze the catalyst surface species formed during the adsorption of NO_x. The thermal stability/reactivity of the adsorbed NO_x has been analyzed by thermal decomposition in He (thermal programmed desorption run, TPD), by heating in flowing H_2 (temperature programmed surface reaction, TPSR) and at constant temperature by imposing a stepwise changes in the H_2 inlet concentration (TRM). In the case of TPD and TPSR experiments, after NO_x adsorption and He purge at the adsorption temperature, the samples were cooled down to RT under flowing He. Then the samples were heated at 15 °C/min up to 600 °C in He (He-TPD) or in He + H_2 (2000 ppm) (H_2-TPSR). Reduction of NO_x adsorbed species was also performed at the same temperature of the storage phase after the He purge by imposing a stepwise change in H_2 inlet concentration ($0 \rightarrow 2000$ and $2000 \rightarrow 0$ ppm in pure He).

In each run 60 mg of catalyst in the powder form (75–100 μm) were used with a total flow rate of 100 cm^3/min STP. The flow rate of the feed gases was measured and controlled by mass-flow controllers (brooks 5850 TR), and the gases were mixed in a single stream before entering the reactor.

Further details about the experimental apparatus and procedures can be found in [9,11].

3. Results and discussion

3.1. NO_x adsorption

As a preliminary run, the adsorption of NO in the presence of oxygen over the Pt–Ba/γ-Al_2O_3 sample has been investigated. As shown in Fig. 1A upon admission of NO (at $t = 0$ s) both the NO and NO_2 outlet concentrations show a significant delay, indicating that large amounts of NO_x are stored on the catalyst surface. FT-IR spectra showed that the adsorption of NO initially occurs primarily in the form of nitrites, which are readily transformed into nitrates so that at the end of the NO pulse, at catalyst saturation, nitrates are the prevalent species [11].

FT-IR spectra collected under operando conditions [9] during NO adsorption in the presence of excess oxygen over Pt–Ba/alumina confirmed that: (i) nitrites represent the major NO_x adsorbed species at the initial stage of adsorption before NO_x breakthrough (observed after 4 min); (ii) nitrites are progressively transformed into nitrates during storage; (iii) a parallel route involving the direct formation of nitrates, although of minor importance, cannot be excluded.

The adsorption of NO/O_2 on the Ba(16)/γ-Al_2O_3 sample has also been investigated. The results, not shown for brevity, indicate that the binary sample adsorbs small quantity of NO_x species; also in this case NO_x adsorbs initially in the form of nitrites, which are then transformed into nitrates. Both the rate of nitrite formation and that of their oxidation to nitrates are higher on Pt–Ba/γ-Al_2O_3 than on Ba/γ-Al_2O_3, pointing out a catalytic role of Pt at 350 °C. The adsorption of NO_2 has also been considered over both the Pt–Ba/γ-Al_2O_3 and Ba/γ-Al_2O_3 samples (Fig. 2). The data collected over both catalyst samples showed a significant adsorption of NO_2, occurring with a simultaneous release of NO. In particular over the Ba/γ-Al_2O_3 sample the NO_2 adsorption occurs according to the stoichiometry of the following disproportionation reaction:

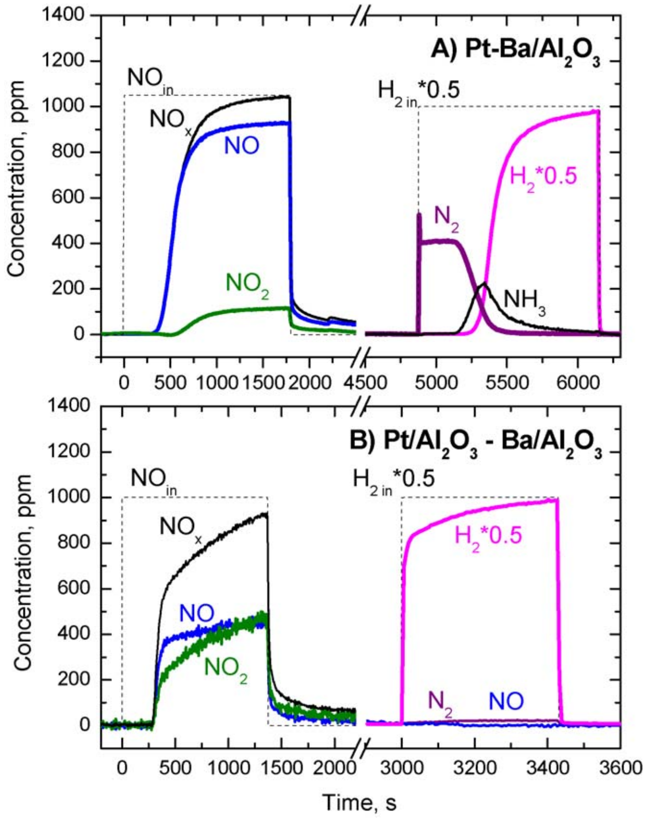

Fig. 1. Storage f NO_x upon NO/O_2 admission and reduction by H_2 over Pt–Ba/γ-Al_2O_3 (1/20/100 w/w) catalyst (A) and over Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture (B); NO, NO_2, N_2, NH_3, H_2O, H_2 outlet concentration and NO, H_2 inlet concentration with time.

$$O^{2-} + 3NO_2 \rightarrow 2NO_3^{-} + NO \uparrow \qquad (1)$$

which implies the release of one NO molecule for $3NO_2$ adsorbed molecules. Accordingly, NO outlet concentration is detected before NO_2 in line with the NO_2 disproportionation reaction. Similar results have been obtained over Pt–Ba/γ-Al_2O_3, but in this case the NO outlet concentration is related to both NO_2 disproportionation and NO_2 decomposition reactions.

Notably, IR spectra showed in this case on both samples the formation of nitrates species only, already from the very beginning of the experiments.

The bulk of data suggested that over Pt–Ba/γ-Al_2O_3 catalysts the adsorption of NO in the presence of excess

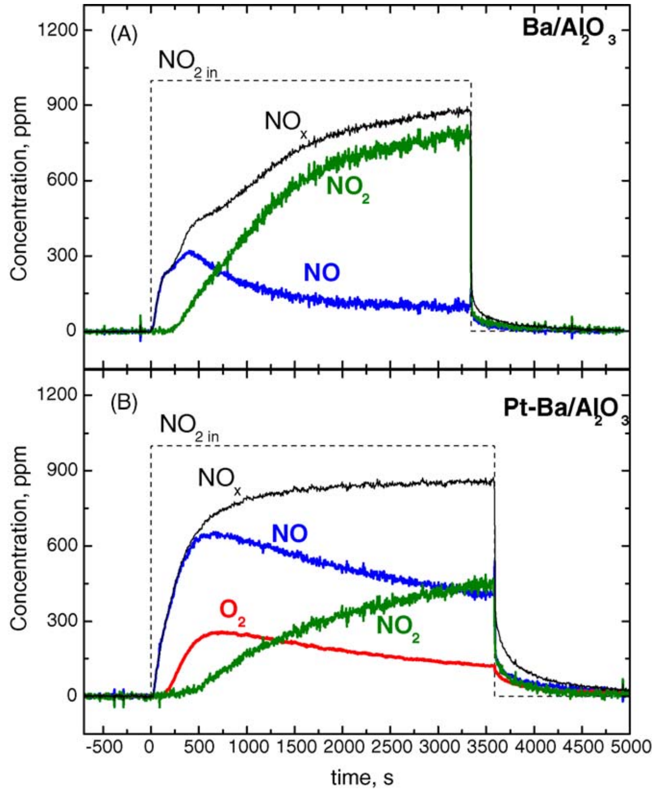

Fig. 2. Storage of NO_x upon NO_2 admission at 350 °C over (A) Ba/γ-Al_2O_3 and (B) Pt–Ba/γ-Al_2O_3 (1/20/100 w/w) catalysts NO, NO_2, NO_x, O_2 outlet concentration and NO_2 inlet concentration with time.

oxygen proceeds through two parallel routes: (i) the so-called ‘‘nitrate route’’ which implies the oxidation of NO to NO_2 on Pt sites, followed by NO_2 disproportionation on Ba sites to form nitrates with evolution of NO in the gas phase; (ii) the ‘‘nitrite route’’, where NO is oxidized at Pt sites and directly stored onto Ba neighbouring sites in the form of nitrite ad-species, which are then progressively transformed into nitrates. The proposed reaction pathway for NO_x adsorption over supported Pt–Ba catalysts is depicted in Fig. 3.

It has also been suggested that the presence of Pt–Ba couples (i.e. the existence of a Pt–Ba interaction) is relevant for the ‘‘nitrite route’’ [7,10,11,14]. In this respect, it is of interest to investigate the effect of the catalyst Ba loading since it is expected that this would affect the number of Pt–Ba neighbouring couples. Accordingly, catalysts with different Ba loadings, up to 30% by weight, have been prepared and tested in the NO_x adsorption. The results obtained by applying a rectangular step feed of NO in the presence of excess oxygen show that both the NO_x breakthrough and the storage capacity of the catalysts increase with the Ba content up to a maximum which is observed for the catalyst with Ba loading of 23% w/w. Moreover the increase in the Ba loading resulted in a strong increase of the percentages of Ba involved in the storage (from 4% for the sample with 5% Ba up to 25% ca. for the Pt–Ba(23)/γ-Al_2O_3 catalyst). Accordingly it is speculated that upon increasing the Ba loading (up to a maximum value) the number of Pt–Ba neighbouring couples increases, thus favouring the storage of NO_x via the ‘‘nitrite’’ route. This also results in a better utilization of the Ba component.

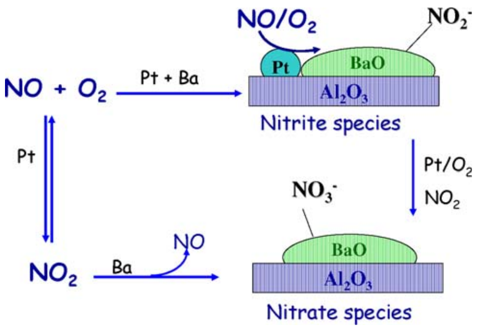

Fig. 3. Reaction pathway for NO_x adsorption over supported Pt–Ba catalysts.

3.2. Reduction–decomposition of the stored NO_x

As previously reported, the thermal stability/reactivity of the adsorbed NO_x has been analyzed at constant temperature by imposing a stepwise changes in the H_2 inlet concentration (TRM), by thermal decomposition in He (TPD) and by heating in flowing H_2 (TPSR).

Fig. 1A shows the results obtained upon stepwise addition of H_2 (at $t = 4800$ s) in He at 350 °C over Pt–Ba/alumina after NO_x storage at the same temperature. From Fig. 1 it appears that H_2 is immediately and completely consumed and only N_2 is observed among the products. The reaction is very fast and is limited by the concentration of H_2. After prolonged reduction time (more than 500 s with 2000 ppm H_2) the concentration of nitrogen decreases to zero, that of H_2 progressively increases, and NH_3 is observed at the reactor exit. Accordingly, initially the reduction process is very selective (almost quantitative) to N_2; then NH_3 formation is well evident. Notably, upon H_2 admission a temperature increases of about 3–5 °C has been observed, so that the reduction was performed under nearly isothermal conditions. Although N_2O is not observed as reduction product (as also indicated by GC analyses), its production in small amounts cannot be excluded.

The presence of different reduction products suggest that different reactions are involved in the process. Accordingly, the following stoichiometries could be invoked to explain the formation of N_2 and NH_3, respectively:

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O \tag{2}$$

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

In order to analyze the reactivity/stability of adsorbed species and to obtain information on the reduction mechanism, the removal of NO_x species adsorbed during the storage phase of a TRM experiment at 350 °C has also been carried out in different ways, i.e. TPD (thermal decomposition in He) and TPSR (heating in flowing 2000 ppm H_2 in He). In this case the storage phase was followed by flowing in pure He at the same temperature for prolonged time and cooling the catalyst (in pure He) down to room temperature. Such conditions allow the desorption of weakly adsorbed NO_x species. In the TPD run (Fig. 4A) the onset of the desorption of stored NO_x is observed

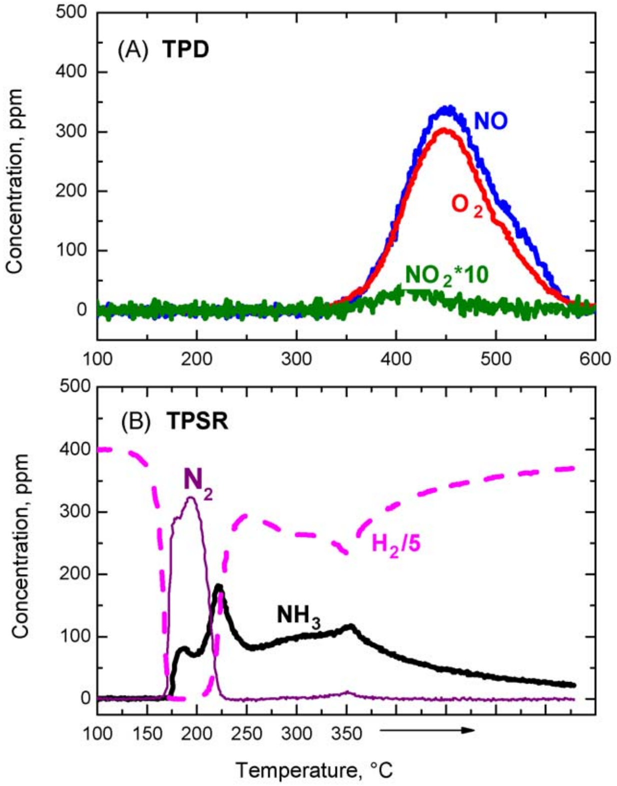

Fig. 4. (A) TPD in He and (B) TPSR in H_2 (2000 ppm) after NO/O_2 adsorption at 350 °C over Pt–Ba/γ-Al_2O_3 catalyst.

above 350 °C, i.e. the NO_x adsorption temperature. Similar results were obtained after NO_x adsorption at different temperatures (300 and 400 °C); no desorption peaks were observed in the TPD runs at temperatures below that used for adsorption. The data clearly indicate that adsorbed NO_x species does not decompose at temperature below that of adsorption.

A completely different picture is observed when heating the stored NO_x in the presence of H_2 (TPSR run, Fig. 4B). Indeed in this case H_2 is consumed starting from 140 °C; the formation of N_2 (which represents the major reaction product) and of NH_3 is also observed in correspondence with H_2 consumption. This points out the reduction of the stored NO_x; notably the reduction is very fast showing complete consumption of H_2 at 170 °C.

As it clearly appears from the figure, N_2 and NH_3 outlet concentrations are initially overlapped. However, most of the ammonia formation follows that of nitrogen and is observed when unconverted hydrogen is detected at the reactor outlet, as in the case of the reduction of stored NO_x accomplished at 350 °C (see Fig. 1). Therefore the chemical features of the reduction of stored NO_x are similar at high and low *T*.

The results clearly prove that the reduction of stored NO_x under almost isothermal conditions (i.e., in the absence of significant thermal effects) is not initiated through the thermal release of NO_x in the gas phase but occurs through a truly catalytic chemical route that leads to reduction of NO_x adsorbed species.

To better clarify the role of the active elements, i.e. Pt and Ba, the same experiments have been also performed over a physical mixture of Pt/γ-Al_2O_3–Ba/γ-Al_2O_3. The results of a complete NO_x storage–reduction cycle performed at 350 °C are shown in Fig. 1B. Comparing the results reported in Fig. 1 it clearly appears that the system presents an adsorption capability similar to that of the ternary catalyst. However in this case it is likely that the storage capacity is associated only to the nitrate route (NO oxidation to NO_2 over Pt and formation of nitrate species by NO_2 disproportionation over Ba), due to the lack of any Pt–Ba couples. However it appears from Fig. 1 that the NO_x species stored onto the physical mixture cannot be reduced by hydrogen under isothermal conditions at constant temperature; NO_x adsorbed during the lean phase do not react with H_2 since no products were detected during the rich phase.

To remove the stored NO_x species from the physical mixture a TPD run was accomplished after the adsorption–reduction cycle at 350 °C (results here not shown). The evolution of NO and O_2 originating from the decomposition of nitrates, and of small amounts of NO_2 as well, is observed with a temperature threshold near 350 °C. As in the case of the ternary Pt–Ba/γ-Al_2O_3 sample, the adsorption temperature rules the decomposition temperature during the TPD run.

A TPSR experiment was also performed over the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture following adsorption of NO in flowing He + 3% oxygen at 350 °C. The consumption of H_2 is observed starting at around 350 °C with production of ammonia, together with minor amounts of nitrogen. The temperature thresholds of the TPSR run is very similar to that of TPD, indicating that the process is initiated through the thermal release of stored NO_x. Accordingly, NO_x are desorbed from Ba/alumina and are then reduced over Pt/alumina; the rate determining step of the reaction is indeed the desorption of stored NO_x. Notably, formation of huge amounts of ammonia is observed in this case, suggesting that the Pt-catalysed reduction of NO with H_2 over Pt/γ-Al_2O_3 is highly unselective to nitrogen. As a matter of facts, a dedicated temperature programmed reaction (TPR) experiment carried out with NO/H_2 mixtures over Pt/γ-Al_2O_3 showed that the reaction between gaseous NO and hydrogen starts at 70 °C and leads mainly to ammonia.

Accordingly, the data collected over both the ternary catalyst and on the physical mixture showed that the co-presence of Pt and Ba on the same support is required to reduce under quasi-isothermal conditions the adsorbed NO_x species; besides, it also affects the selectivity of the reduction process. Indeed on the ternary catalyst where Pt and Ba sites are dispersed on the same alumina particles the reduction of adsorbed NO_x species could be easily achieved either under quasi isothermal conditions or at low temperature during TPSR experiments, leading in any case to N_2 at first and as major reaction product. The collected data indicate that on the ternary catalyst the reduction process is not initiated by the NO_x thermal release to the gas phase; accordingly, a specific catalytic function is operative at low T to reduce NO_x ad-species. It is speculated that H_2, activated on Pt sites, spills on the alumina support towards nitrate ad-species where it operates the reduction either promoting the decomposition of nitrates to gaseous NO and/or NO_2 [4], which are subsequently reduced on Pt, or directly reacting with the

NO_x ad-species. A specific route involving NO_x ad-species present on Ba sites neighbouring Pt might also be suggested. In this respect a possible interaction between Pt and Ba, already pointed out in [12] as a key factor for NO_x adsorption, would play an important role also in determining activity and selectivity of their subsequent reduction. However, in this case still a question remains concerning the involvement (under near isothermal conditions) of nitrate species adsorbed on Ba sites remote from Pt, if any. In this respect, a role of the surface diffusion of NO_x ad-species towards Pt sites has also been proposed [4]; in this case NO_x are decomposed at reduced Pt sites, and the role of the reductant is to keep Pt in a reduced state.

The problem of the selectivity during the reduction of the stored NO_x is also of great importance. As a matter of fact N_2 and NH_3 can be obtained during the regeneration of catalyst with H_2. Preliminary activity tests have shown that the gas phase reductant concentration and/or the concentration of the stored NO_x, along with the proximity with Pt sites, may affects the selectivity to nitrogen of the reduction process. These aspects, which dominate the reactivity and selectivity of the reduction process, are presently under investigations in our laboratories.

Notably, all the suggested mechanisms are consistent with the results obtained over the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture where Pt and Ba sites are dispersed on different support particles: this rules out any hydrogen/NO_x spillover contribution and the presence of Pt–Ba neighbouring species. Accordingly in this case the reduction of NO_x ad-species (i.e. catalyst regeneration) can only be accomplished by thermal decomposition of nitrates adsorbed on Ba, followed by diffusion of NO_x in the gas phase towards Pt sites where they are reduced.

4. Conclusions

It is suggested that the storage of NO in the presence of excess oxygen proceeds through two parallel routes: (i) the ‘‘nitrate route’’ where NO is oxidized to NO_2 on Pt sites followed by NO_2 disproportionation on Ba sites to form nitrates with evolution of gaseous NO; (ii) the ‘‘nitrite route’’, where NO is oxidized at Pt sites and directly stored on Ba neighbouring sites in the form of nitrites that are then oxidized to nitrates. The latter route possibly dominates at high Ba loadings.

Concerning the reduction of the stored NO_x, the bulk of data indicates that the reduction of stored NO_x on the Pt–Ba/alumina: (i) is not initiated by the thermal release of NO_x in the gas phase; (ii) occurs through a Pt-catalysed reduction of adsorbed NO_x species. It is speculated that H_2 is activated on Pt sites and spills on the alumina support towards nitrate ad-species where it operates the reduction either promoting the decomposition of nitrates to gaseous NO and/or NO_2 (which are subsequently reduced on Pt), or directly reacting with the NO_x ad-species. A specific route involving NO_x ad-species present on Ba sites neighbouring Pt might also be suggested, as well as a role of the surface diffusion of NO_x ad-species towards Pt sites. These aspects are presently under investigations in our laboratories.

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