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New insights in the NO_x reduction mechanism with H_2 over Pt–Ba/ γ-Al_2O_3 lean NO_x trap catalysts under near-isothermal conditions

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Abstract

Mechanistic aspects of the reduction of stored NO_x with hydrogen were analyzed over model Ba/γ-Al_2O_3 and Pt–Ba/γ-Al_2O_3 LNT trap catalysts and over a Ba/γ-Al_2O_3–Pt/γ-Al_2O_3 physical mixture. NO_x species were stored and stabilized at 350 °C under controlled conditions, and their stability/reactivity was then analyzed under different atmospheres (He and hydrogen) either at constant temperature or with temperature programming under nearly isothermal conditions, that is, in the absence of significant thermal effects. The collected data indicate that over the Pt–Ba/Al_2O_3 catalyst, the reduction of stored NO_x occurs at temperatures below those corresponding to their thermal stability. This indicates that the reduction of stored nitrates occurs in typical NSR catalysts according to a Pt-catalyzed surface reaction, which does not involve the thermal decomposition of the adsorbed NO_x species as a preliminary step. The occurrence of such a pathway also requires the co-presence of the storage element and of the noble metal on the same support, because this route does not operate when they are dispersed on different support particles.

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

1. Introduction

Lean-burn engines produce lower CO_2 emissions and provide better fuel economy compared with traditional stoichiometric engines. However, the three-way catalyst (TWC) technology that is currently used worldwide in vehicles with engines working under stoichiometric conditions has not yet resulted in acceptable emission reductions when used in lean-burn after-treatment devices. In addition, upcoming regulations in Europe, the U.S., and Japan also require significant reductions in NO_x emissions from diesel engines specifically [1]. To reduce NO_x to N_2 under oxygen-rich environment with acceptable fuel penalties, in the 1990s Toyota researchers proposed the so-called "NO_x storage-reduction" (NSR) catalysts [2]. Basically, an NSR catalyst consists of an alumina support on which an alkali or alkali-earth metal compound (e.g., Ba) and a noble metal (Pt) are deposited. These catalysts operate under cyclic conditions; during the lean period, NO_x are stored on Ba, whereas during the subsequent short rich phase, the adsorbed NO_x species are reduced to nitrogen on Pt.

Although these catalysts are currently used on a commercial scale in Japan, a common agreement on the mechanistic aspects of the storage of NO_x species and of their reduction is still lacking [3]. Whereas several papers have analyzed the storage phase [4–9], few studies have been devoted to the analysis and understanding of the chemistry of the reduction process. In this respect, the common idea is that the regeneration of NSR catalysts includes the initial release of NO_x from the catalyst surface (i.e., from the alkali or alkali-earth metal compound), followed by its further reduction to N_2 or other products [3]. In particular, it is believed that the reduction of NO_x in a rich environment occurs according to the well-established TWC chemistry and mechanisms, although the presence of alkali or alkaline-earth components may affect the process. Proposed mechanisms include (i) NO decomposition on reduced Pt sites (where the role of the reductant is to reduce Pt–O to Pt, which is the active species effecting the NO decomposition to N_2) [10] or (ii) the direct reaction between released NO_x species and the hydrocarbon reductant molecules on the precious metal sites [11].

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On the other hand, the debate on the possible mechanisms governing NO_x release remains open. It has been suggested that the NO_x release is driven by (i) heat generated on the reducing switch (thermal release) [12]; (ii) the decrease in the gas-phase oxygen concentration, which destabilizes the stored nitrates according to the following reaction [13]:

$$(NO_3{}^-)_2 \leftrightarrow O^{2-} + (1/2)O_2 + 2NO_2, \quad (1)$$

(iii) spillover and reduction of NO_2 onto Pt sites, thus shifting from left to right equilibrium (1); or (iv) establishment of a net reducing environment that decreases the equilibrium stability of nitrates [13–16]. Poulston and Rajaram [16] investigated the regeneration of nitrated Pt–Ba/γ-Al_2O_3 catalysts by heating the catalyst samples under various atmospheres (He, CO, hydrogen) and concluded that in the presence of the reductant species, the decomposition temperature of the nitrate is significantly reduced. A different mechanism has been proposed by Liu and Anderson [13], who reported that the reductant molecule (or an activated reductant molecule spilled over from Pt) may interact directly with NO_x stored on the storage component where nitrates are reduced to nitrites which then release NO and gaseous oxygen,

$$(NO_3{}^-)_2 \rightarrow (NO_2{}^-)_2 \rightarrow O^{2-} + (1/2)O_2 + 2NO. \quad (2)$$

It is noteworthy that many of the proposed mechanisms have been derived from experiments that were carried out under not fully controlled conditions or that did not analyse the full spectrum of reaction products. For instance, in several cases the adsorption of NO_x was accomplished by contacting the catalyst sample with NO_x while changing the temperature. This obviously complicates the picture, hindering an accurate analysis both of the stability of stored nitrates under inert and/or reducing environments and of the onset of the reduction reactions.

Accordingly, to gain further insight into the mechanism governing the reduction of adsorbed NO_x species and to better elucidate the role of the different catalyst components (noble metal and storage component) in the process, we analysed the stability/reactivity of NO_x adsorbed over model Ba/γ-Al_2O_3 and Pt–Ba/γ-Al_2O_3 catalysts. In these experiments, NO_x was stored on the catalyst surface under controlled conditions at selected temperatures representative of real operating conditions; care was taken to control the conditions at which adsorption was carried out. Also, in all cases the samples were kept under inert flow at the same temperature used for adsorption, to provoke desorption of weakly adsorbed species. The stability/reactivity of the stored NO_x was then analyzed under different atmospheres (inert and reducing) and at fixed temperature/temperature programming, including thermal decomposition in He (temperature-programmed desorption [TPD]), heating in flowing H_2 (temperature-programmed surface reaction [TPSR]), and at constant temperature by imposing stepwise changes in the H_2 inlet concentration (transient response method [TRM]). In particular, He-TPD experiments allowed us to analyse the thermal stability of nitrate species adsorbed at high T onto the catalyst surface, H_2-TPSR experiments provided information on the stability of nitrate species under a reducing environment, and isothermal reduction runs were carried out at the same temperature of the adsorption runs, to analyze the stability of nitrate species in the presence of H_2 at constant temperature. Note that all of these experiments were performed under near-isothermal conditions in the catalyst bed, that is, in the absence of any significant thermal effects on the lean/rich switches and/or temperature programming due to the dilute conditions used in the experiments.

Similar experiments have also been previously carried out over a Ba/γ-Al_2O_3–Pt/γ-Al_2O_3 physical mixture [17]. Results have been compared with those obtained over the Pt–Ba/γ-Al_2O_3 sample to assess the role of the co-presence of Pt and Ba on the alumina support in the stability/reactivity of adsorbed nitrates and to gain further insight into the mechanisms of the reduction of stored NO_x.

2. Methods

2.1. Materials

The Pt/γ-Al_2O_3 (1/100 w/w) sample was prepared by impregnating a γ-Al_2O_3 carrier calcined at 700 °C (Versal 250, La Roche Chemicals; surface area, 200 m^2/g; pore volume, 1.2 cm^3/g) with a solution of $Pt(NH_3)_2(NO_2)_2$ (Strem Chemicals, 5% Pt in ammonium hydroxide), followed by exsiccation at 80 °C overnight and calcination at 500 °C for 5 h. A portion of the prepared Pt/γ-Al_2O_3 sample was impregnated with aqueous solutions 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 (1/20/100 w/w) catalyst. A Ba/γ-Al_2O_3 (20/100 w/w) sample was also prepared by impregnating the bare γ-alumina support with barium acetate. The physical mixture Pt/Al_2O_3 + Ba/Al_2O_3 was obtained by mixing specific amounts of the binary Pt/γ-Al_2O_3 and Ba/γ-Al_2O_3 samples.

2.2. Apparatus and catalyst conditioning

The catalytic tests were performed in a flow microreactor system equipped with a mass spectrometer for complete analysis of reactants and products [4,5]. Before testing, all of the catalyst samples were conditioned to obtain a reproducible behaviour. This conditioning involved several adsorption/regeneration cycles. Because the experiments were performed in the absence of CO_2 and regeneration was carried out with H_2 or by heating, this led to the transformation of $BaCO_3$ which was originally present on the calcined samples into BaO/$Ba(OH)_2$.

2.3. NO_x adsorption

The NO_x adsorption on the samples was run at constant temperature (usually 350 °C) by imposing a rectangular step feed of NO (1000 ppm) in flowing He + 3% v/v O_2. For the Ba/γ-Al_2O_3 binary catalyst, which does not adsorb significant amounts of NO_x in these conditions [4,5], adsorption was carried out with NO_2 (1000 ppm) in flowing He. The NO (or NO_2)

flow was maintained up to catalyst saturation, after which the inlet NO (or NO_2) concentration was decreased to zero. In the case of NO adsorption, in which O_2 was also present, the oxygen concentration was also decreased to zero after NO. The samples were then kept under inert flow for about 1 h at the same temperature used for adsorption, to provoke the desorption of weakly adsorbed species (He purge).

2.4. Catalyst regeneration

NO_x species adsorbed during the storage phase were removed by thermal decomposition in He (TPD run), by heating in flowing H_2 (TPSR run), and at constant temperature by imposing a stepwise change in the H_2 inlet concentration (TRM). In the TPD and TPSR experiments, after NO_x adsorption and He purge at the adsorption temperature (see above), the samples were cooled to room temperature under flowing He. Then the samples were heated at a rate of 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 ($0 \to 2000$ ppm and $2000 \to 0$ ppm in pure He). Further details about the experimental apparatus and procedures have been reported elsewhere [4,5,17].

3. Results and discussion

3.1. Ba/γ-Al_2O_3 catalyst

3.1.1. NO_x adsorption

The sample was saturated by feeding NO_2 at 350 °C; the results are illustrated in Fig. 1. At $t = 0$ s, 1000 ppm of NO_2 was added to the He flow while monitoring the concentration of the species exiting the reactor. Fig. 1 shows that the NO_2 storage was slow and accompanied by evolution of NO. As reported elsewhere [3–9], the NO_2 storage occurred in this case according to the stoichiometry of the following global disproportion reaction:

$$BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO\uparrow, \qquad (3)$$

which led to the formation of nitrates onto the catalyst surface and to the evolution of gaseous NO.

At the end of the catalyst saturation, at 5750 s, the NO_2 feed was switched off and the catalyst was purged under He flow at 350 °C for 1 h. The drop in NO_2 gas-phase concentration led to a very limited desorption of previously adsorbed NO_x species, as indicated by the absence of any significant tail in both the NO and NO_2 concentration traces in correspondence of the NO_2 switch. This desorption process may be related to the decomposition of weakly bonded Ba-nitrate species or to nitrates formed onto the alumina support, which are not stable at this temperature. However, this latter contribution would be expected to be of minor relevance, because the alumina support is almost completely covered by Ba, as demonstrated by FTIR data reported previously [18].

3.1.2. He-TPD

At the end of the adsorption procedure, the catalyst was cooled to room temperature, and a linear temperature ramp was imposed while feeding He to provoke the thermal decomposition of nitrates present on the catalyst surface. Fig. 2 shows the corresponding results in terms of NO, NO_2, and O_2 concentration traces versus T. As expected, no desorption peaks were observed below 350 °C (i.e., below the adsorption temperature). The decomposition of nitrates species present on the catalyst surfaces was apparent only above 350 °C; in line with previous reports [3,4,9,15,16,18–20], decomposition of nitrates resulted in the initial evolution of NO_2, followed by NO and O_2. The process was not complete at temperatures as high as 600 °C; the catalyst was then kept at 600 °C until desorption of nitrates was complete.

The data indicate that nitrates formed on NO_2 adsorption at 350 °C followed by He purge at the same temperature do not decompose appreciably below the adsorption temperature during

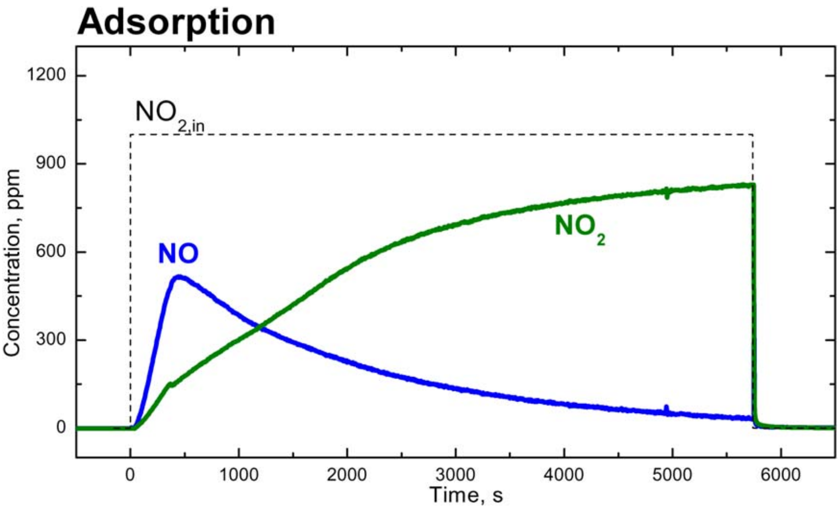

Fig. 1. Temporal evolution of NO and NO_2 outlet concentrations during adsorption of NO_2 (1000 ppm in He) at 350 °C on the Ba/γ-Al_2O_3 catalyst.

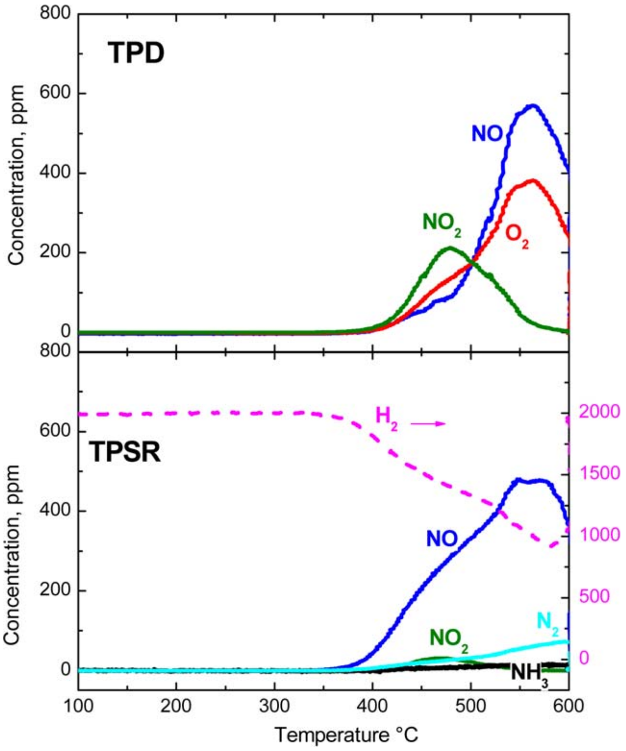

Fig. 2. TPD in He and TPSR in H_2 (2000 ppm in He) after NO_2 adsorption at 350 °C over Ba/γ-Al_2O_3 catalyst.

the TPD run under inert atmosphere. Hence the adsorption temperature rules the thermal stability of the adsorbed NO_x species.

3.1.3. *H_2-TPSR*

The effect of a reducing agent (H_2) on the stability of nitrates was then analysed. The binary Ba/γ-Al_2O_3 catalyst was saturated with NO_2 at 350 °C as described above (see Fig. 1), and, after cooling to room temperature, the sample was heated to 600 °C at 15 °C/min while feeding He in the presence of 2000 ppm of hydrogen. The results are shown in Fig. 2. In this case NO desorption was observed above 350 °C, along with minor amounts of NO_2 and N_2 and traces of NH_3. The consumption of H_2 was also observed in the same temperature range associated with nitrate decomposition.

A comparison with the TPD data discussed above shows that the decomposition of nitrates was not affected or was only slightly favoured by the presence of hydrogen (the decomposition temperature threshold was decreased by roughly 20 °C). In contrast, decomposition under a reducing atmosphere led to a different product distribution, with a significant decrease in NO_2 concentration accompanied by a corresponding increase in NO concentration. In addition, oxygen evolution could not be detected, whereas the formation of nitrogen and, to a lesser extent, of ammonia was observed.

These results parallel those reported by Cant and Patterson [15], who analyzed the thermal stability of nitrate species formed over a BaO/Al_2O_3 sample on uptake of NO_2 at 300 °C under both inert and reducing atmospheres. In particular, these authors explained the decrease in NO_2 concentration and the formation of N_2 in the presence of hydrogen according to the following stoichiometries:

$$NO_2 + H_2 \rightarrow NO + H_2O \tag{4}$$

and

$$NO + H_2 \rightarrow (1/2)N_2 + H_2O, \tag{5}$$

which also account for H_2 consumption. According to specific experiments carried out in our labs, these reactions are catalyzed or involve a specific reactivity of adsorbed NO_x, because no reaction between NO_2 and H_2 was observed up to 500 °C in an empty reactor. Notably, Cant and Patterson [15] reported no changes in the threshold temperature for nitrate decomposition on switching from inert to reducing atmosphere, due to the experimental procedure used in the study (with the TPD run launched at 300 °C, i.e., the same temperature used for NO_2 adsorption).

3.1.4. *TRM*

Finally, we studied the stability of nitrates in the presence of hydrogen at constant temperature. After the storage phase at 350 °C (see Fig. 1), 2000 ppm of H_2 was admitted to the reactor kept at the adsorption temperature; the results are reported in Fig. 3. Neglecting the initial H_2 spike, the outlet H_2 concentration quickly approached the feed value, indicating that hydrogen was not involved in reactions with stored nitrates. In fact, no formation of any reaction product was observed. This indicates that adsorbed nitrates are stable under these conditions, as was also indicated out by the foregoing TPD and TPSR data.

3.2. *Pt–Ba/γ-Al_2O_3 catalyst*

To analyse the effect of Pt on the stability/reactivity of the stored NO_x, we performed the same experiments as described for the Ba/γ-Al_2O_3 sample over the ternary Pt–Ba/γ-Al_2O_3 catalyst.

3.2.1. *NO_x adsorption*

Fig. 4 shows the results collected at 350 °C over the ternary Pt–Ba/γ-Al_2O_3 catalyst on adsorption of NO_x starting from NO in He + O_2. As opposed to Ba/γ-Al_2O_3, due to the presence of Pt, efficient NO_x storage can be obtained from NO/O_2 [4]. As shown in Fig. 4, at $t = 0$ s, NO was admitted to the reactor under a flow of He + 3% v/v of oxygen. Evolution of both NO and NO_2 was observed at the reactor outlet with a significant dead time; the concentration of these species slowly increased with time, approaching the asymptotic values corresponding to the NO_x feed concentration (NO + NO_2) after about 1000 s. Accordingly, large amounts of NO_x were stored. Moreover, formation of NO_2 in the gas phase indicates that Pt is active in the NO oxidation reaction. Notably, as indicated in a dedicated FTIR analysis, nitrates are the major adsorbed species present at catalyst saturation [4]. These species are spectroscopically indistinguishable from those formed from NO_2 in the Ba/γ-Al_2O_3 catalyst.

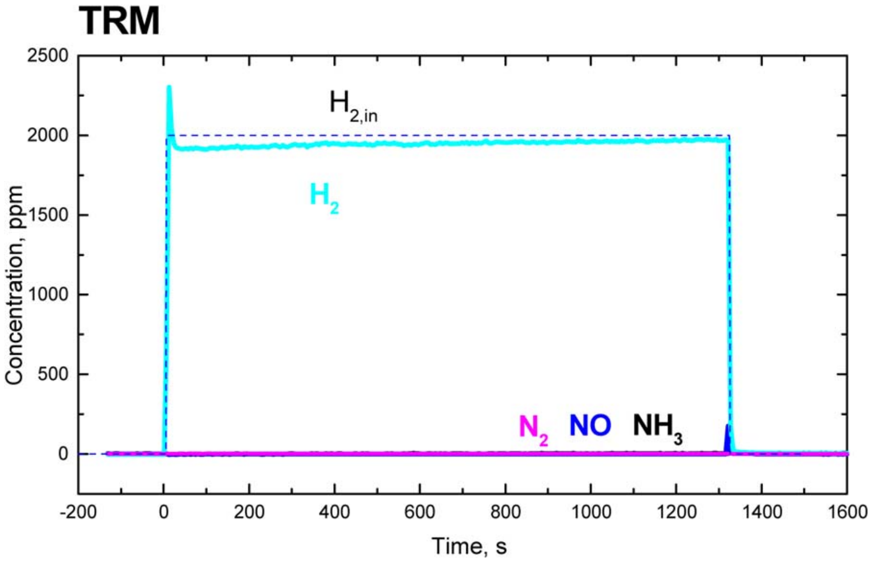

Fig. 3. Temporal evolution of H_2, N_2, NO and NH_3 outlet concentrations upon reduction with H_2 (2000 ppm in He) at 350 °C (TRM run) after NO_2 adsorption at 350 °C on the Ba/γ-Al_2O_3 catalyst.

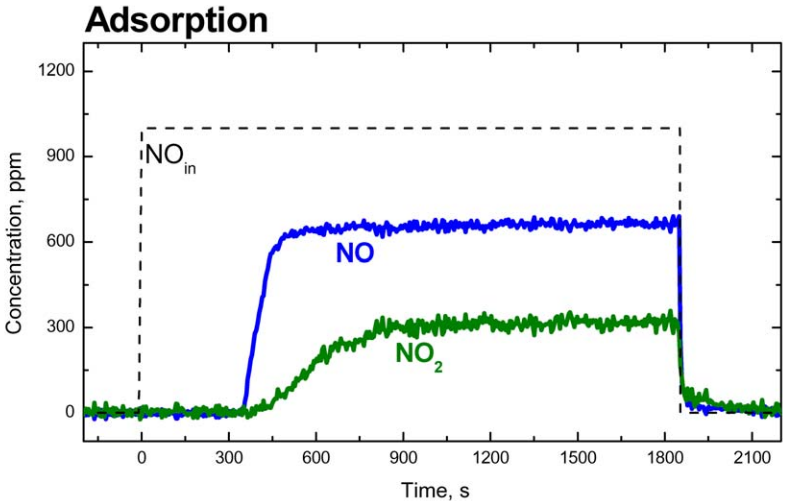

Fig. 4. Temporal evolution of NO and NO_2 outlet concentrations during adsorption of NO (1000 ppm) in He + O_2 3% v/v at 350 °C on the Pt–Ba/γ-Al_2O_3 catalyst.

At the end of the NO pulse, near 1900 s, a small desorption of NO_x was observed. The oxygen concentration was then also decreased to zero, while maintaining the catalyst at 350 °C under He flow (He purge). This led to an additional small release of NO_x (not shown in the figure). As already discussed for the Ba/γ-Al_2O_3 catalyst, this NO_x desorption process is related to the decomposition of weakly bonded Ba-nitrate species or to minor amounts of nitrates formed on the alumina support.

3.2.2. He-TPD

After NO/O_2 adsorption at 350 °C and the subsequent He purge at the same temperature, the catalyst was cooled to room temperature under a He flow. Then a TPD run in He was performed; the results are reported in Fig. 5. No desorption peaks were observed in the low-temperature range; as expected, decomposition of stored NO_x species was apparent only above 350 °C (i.e., the NO_x adsorption temperature).

In this case, NO and O_2 represented the major decomposition products, along with minor quantities of NO_2. Compared with the binary Ba/γ-Al_2O_3 sample, the complete decomposition of previously stored NO_x was achieved at lower temperatures, indicating that Pt affects the decomposition of adsorbed nitrates.

The effect of Pt in the decomposition of stored nitrates is well established in the literature [3,4,13,15,18,21,22]. As a matter of fact, a decrease of 50 °C in the peak temperature for nitrate decomposition after adsorption of NO_x at room temperature on a change from the Ba/γ-Al_2O_3 to the Pt–Ba/γ-Al_2O_3 catalyst has been reported [18]. Coronado and Anderson [21] reported a similar effect and suggested that the decomposition of nitrates occurs at the interface between the Ba component and the noble metal, which thus promotes nitrate decomposition. Along similar lines, Olsson et al. [22] invoked the presence of a spillover mechanism of NO_2 from Ba to Pt to explain the

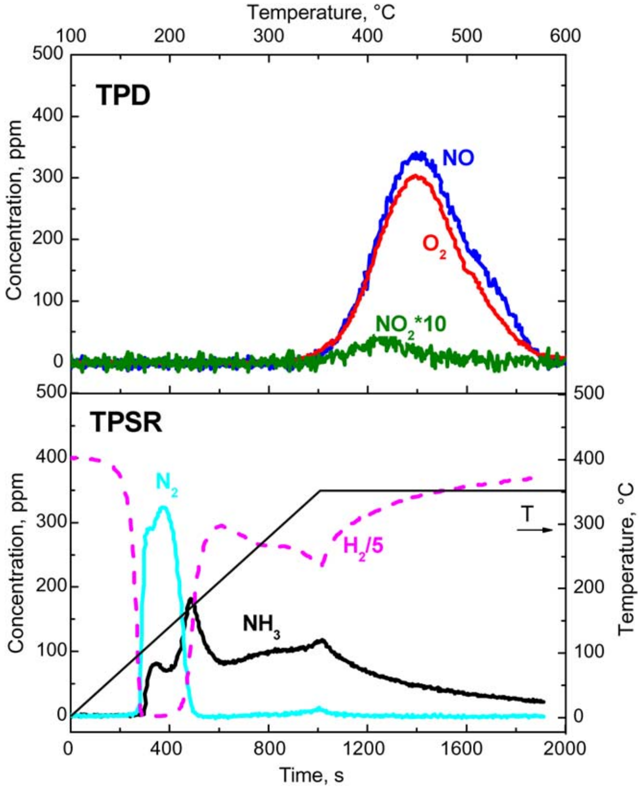

Fig. 5. TPD in He and TPSR in H_2 (2000 ppm in He) after NO/O_2 adsorption at 350 °C on the Pt–Ba/γ-Al_2O_3 catalyst.

decreased desorption temperature of nitrates in Pt–Ba/γ-Al_2O_3 compared with that in Ba/γ-Al_2O_3.

It may be argued that the differences in nitrate decomposition observed between the Pt–Ba/γ-Al_2O_3 and the Ba/γ-Al_2O_3 samples are not entirely related to the presence of Pt, but are also associated with the differing extent of nitration of the Ba phase, due to the differing exposure times of the two experiments (5700 s with NO_2 for Ba/γ-Al_2O_3 vs. 1800 s with NO/O_2 for Pt–Ba/γ-Al_2O_3). Nonetheless, as reported previously [4,18], Pt always favours the decomposition of the stored nitrates regardless of the extent of nitration of the Ba phase and the gas-phase composition used for NO_x adsorption (NO_2 and NO/O_2).

In addition, the presence of Pt also affects the product distribution observed during the TPD run. Indeed, over the Ba/γ-Al_2O_3 sample, significant NO_2 desorption was observed, in contrast to the ternary Pt–Ba/γ-Al_2O_3 catalyst, for which only minor amounts of NO_2 were detected. These differences can be ascribed to the Pt-catalyzed NO_2 decomposition to NO and O_2.

We performed further TPD experiments over the ternary catalyst after NO_x adsorption at different temperatures, 300 and 400 °C (results not shown). Again, in line with the experiment performed at 350 °C, no desorption peaks were observed at temperatures below that used for adsorption. These data further confirm that the NO_x adsorption temperature rules the temperature threshold for the decomposition of the adsorbed nitrates under inert atmosphere.

3.2.3. H_2-TPSR

We performed a TPSR run with H_2 over the ternary catalyst after the NO_x storage phase at 350 °C (see Fig. 4), followed by He purge at the same temperature and cooling at room temperature under He flow. The results of the TPSR run are shown in Fig. 5. Hydrogen was converted starting at 140 °C; the H_2 concentration decreased very rapidly, and corresponding N_2 and NH_3 formation was apparent. Accordingly, these data show that surface nitrates reacted with H_2 already at low temperatures, near 150 °C. Nitrate reactivity was very high, so that at 170 °C, hydrogen was completely consumed, and the formation of the reaction products was limited by the H_2 concentration. Notably, the nitrate surface species, which were formed at 350 °C and did not appreciably decompose under inert atmosphere at this temperature, quickly reacted with H_2 at temperatures well below the adsorption temperature (140 vs. 350 °C).

TPSR experiments were also performed after NO_x adsorption at 300 and 400 °C (results here not shown). The temperature threshold for H_2 consumption is not significantly affected by the temperature at which saturation was carried out; indeed, in all cases H_2 consumption was always observed from 140 °C, with formation of N_2 and NH_3. Accordingly, also in these cases the stored nitrates react with H_2 at temperatures well below those of adsorption. Notably, most of the NH_3 was formed after N_2 on the depletion of surface nitrates.

The data clearly indicate that in the case of the Pt–Ba/γ-Al_2O_3 catalyst the reduction of NO_x adspecies occurs at temperatures below those corresponding to their thermal decomposition and is not affected by the temperature at which NO_x adsorption is carried out. This indicates that during TPSR experiments the reduction of stored NO_x is not initiated by their thermal decomposition after NO_x release in the gas phase, but instead a Pt-catalyzed chemical route must be invoked. We address this point later.

3.2.4. TRM

The reactivity/stability of adsorbed NO_x species was also analyzed at constant temperature. Again, after NO_x saturation carried out at 350 °C (see Fig. 4), followed by a He purge, 2000 ppm of H_2 were admitted to the reactor at the same temperature (Fig. 6; $t = 0$ s). As shown in Fig. 6, nitrogen was immediately produced, its concentration being limited by the amount of H_2 fed to the reactor. Then the N_2 concentration decreased, due to depletion of the adsorbed NO_x species, and evolution of ammonia was observed. At the same time, the H_2 concentration increased reaching the inlet value. As was observed during TPSR experiments, NH_3 formation was detected on depletion of the adsorbed nitrate species.

The step addition of hydrogen to the reactor was accompanied by a small increment of the catalyst temperature (3–5 °C), due to the occurrence of the exothermic reduction reaction, so that the run was actually performed under nearly isothermal conditions. This rules out a possible thermal release of NO_x species on the H_2 switch. Accordingly, in line with the results of the TPSR experiments, the NO_x adspecies, which do not decompose on the ternary system under inert atmosphere at 350 °C, could be easily reduced by adding hydrogen at the

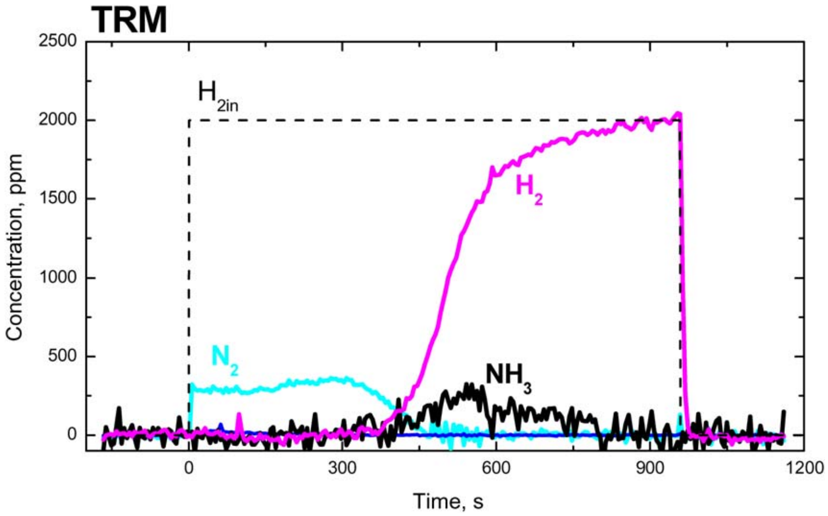

Fig. 6. Temporal evolution of H_2, N_2, NO and NH_3 outlet concentrations during reduction with H_2 (2000 ppm in He) at 350 °C (TRM run) after NO/O_2 adsorption at 350 °C on the Pt–Ba/γ-Al_2O_3 catalyst.

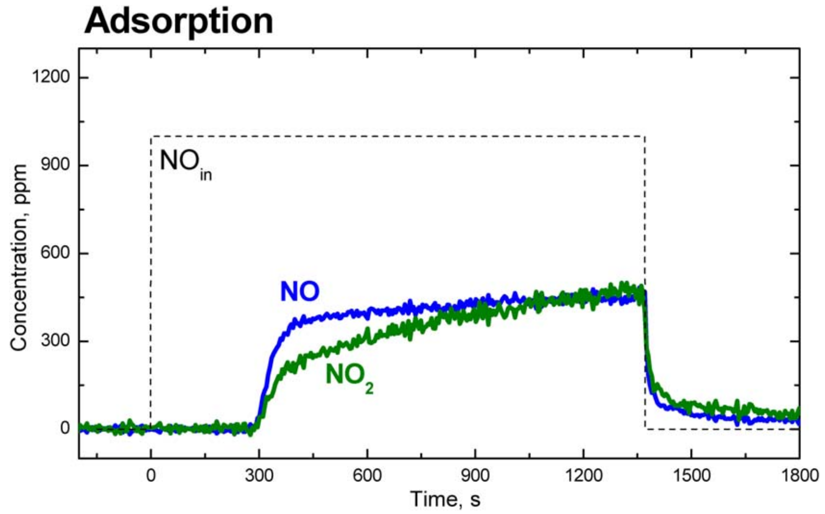

Fig. 7. Temporal evolution of NO and NO_2 outlet concentrations upon adsorption of NO (1000 ppm) in He + O_2 3% v/v at 350 °C on the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture.

same temperature. This further confirms the occurrence of a Pt-catalyzed pathway for nitrate reduction under near-isothermal conditions which not involves the thermal decomposition of the stored NO_x.

3.3. *Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture*

We ran the same series of experiments over a physical mixture of the binary Pt/γ-Al_2O_3 and Ba/γ-Al_2O_3 samples. The mixture was prepared with dosed amounts of the two starting binary catalysts to load in the reactor the same amounts of Pt and Ba than in the case of the ternary catalyst. Notably, the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture includes both components of the reference ternary system, Ba (responsible for the NO_x storage) and Pt (which effects the oxidation/reduction functions [4,17]); however, in the physical mixture Pt and Ba are deposited on different alumina particles.

3.3.1. *NO_x adsorption*

The experimental procedure for the NO_x adsorption process parallels that already discussed in the case of the ternary Pt–Ba/γ-Al_2O_3 sample; related results are presented in Fig. 7. Both the NO and NO_2 outlet concentrations exhibit dead times of about 250 s, and then slowly grow with time up to their steady-state values of 500 ppm. The presence of NO_2 in the gas phase indicates that NO was readily and efficiently oxidized over Pt, as expected. It clearly appears that the physical mixture is able to adsorb significant amounts of NO_x species, comparable to those found in the case of the ternary catalyst (see Fig. 4); indeed, the two catalytic systems were characterized by similar breakthrough times, but the physical mixture also showed a higher oxidizing capacity, as pointed out by the higher NO_2/NO ratio at steady state. As already discussed elsewhere [17], it is speculated that in this case the NO_x storage occurs via NO oxidation to NO_2 on Pt, followed by nitrate formation on Ba via

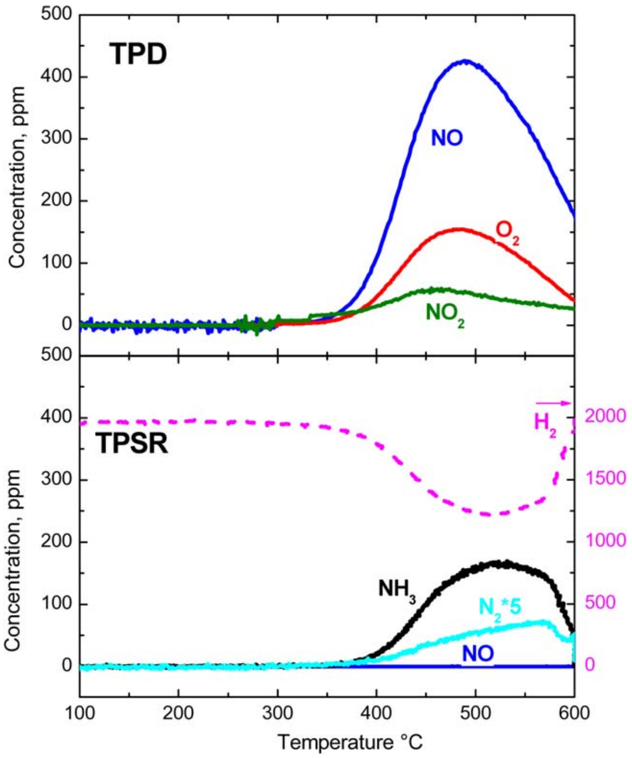

Fig. 8. TPD in He and TPSR in H_2 (2000 ppm) after NO/O_2 adsorption at 350 °C on the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture.

NO_2 disproportion (3). A parallel FTIR study indicated that nitrate species were formed at catalyst saturation [23].

On decreasing the NO inlet concentration, near 1350 s, a tail is observed in the NO_x concentration, due to the decomposition of weakly adsorbed Ba nitrates and/or nitrate species formed over the alumina support; an additional release of NO_x (not shown in the figure) was noted on switching (keeping the temperature at 350 °C) to pure He.

3.3.2. He-TPD

After NO/O_2 adsorption at 350 °C (Fig. 7) and the subsequent He purge at the same temperature, the catalyst was cooled to room temperature. A TPD experiment was then performed, whose results are shown in Fig. 8 in terms of NO, NO_2, and O_2 concentration versus T. The thermal decomposition of nitrate species present onto the catalyst surface is responsible for the evolution of NO, NO_2, and O_2; the temperature threshold for the decomposition was near 350 °C, and the process was not yet complete at temperatures as high as 600 °C. Accordingly, a high thermal stability of nitrate species is evident for this catalyst despite the presence of Pt, which was claimed to favour nitrate decomposition in the case of the ternary Pt–Ba/γ-Al_2O_3 sample. This is in line with the absence in the physical mixture of any Pt–Ba interface and/or of the possibility of NO_x spillover from Ba to Pt; according to the literature indications discussed above, in fact, both such features have been claimed to promote the nitrate decomposition process.

3.3.3. H_2-TPSR

Fig. 8 shows the results obtained in the TPSR experiment performed on the physical mixture after NO_x adsorption at 350 °C (Fig. 7). Like in the case of the TPD run previously discussed, nitrates do not decompose appreciably up to 350 °C also in the presence of a reducing agent; only above 350 °C consumption of H_2 was observed, along with evolution of ammonia and of minor amounts of nitrogen. At the end of the TPSR run at 600 °C, the reduction of the stored nitrates was not yet complete.

Accordingly, the data indicate that on the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture, the reduction of stored NO_x is a slow process governed by the rate of the thermal decomposition of the surface nitrate species. Indeed, the features of the TPSR run (i.e., temperature threshold, peak temperature, etc.) closely resemble those seen in the TPD run performed over the same sample; however, NH_3 and N_2 were detected at the reactor outlet instead of NO/NO_2. It has been suggested that in the case of the physical mixture surface nitrates (stored at Ba sites) are thermally decomposed to NO_x on heating at the same temperature threshold of the TPD experiment; once released in the gas phase, NO_x are reduced by H_2 on Pt sites.

Comparing these results with those obtained over the Pt–Ba/γ-Al_2O_3 ternary sample, it clearly appears that the presence of Pt in the physical mixture does not decrease the temperature threshold for the reduction of the stored nitrates, as indeed was observed in the ternary sample, in which nitrate reduction was monitored at temperatures as low as 140 °C. This clearly indicates that the previously invoked Pt-catalyzed reduction mechanism of the stored nitrates involves the presence of Pt and Ba dispersed over the same particle support.

Finally, it is also worth emphasizing that on the physical mixture, the reduction of the adsorbed NO_x is highly selective toward ammonia. As a matter of fact, in a dedicated NO + H_2 TPR experiment over the binary Pt/γ-Al_2O_3 sample (results not reported), it was found that the reaction between gaseous NO and hydrogen started already at very low temperature (near 70 °C) and formed primarily ammonia. This indicates that the gas-phase reduction of NO by H_2 over Pt/γ-Al_2O_3 leads primarily to NH_3, as indeed was observed in this case.

3.3.4. TRM

Finally, the reactivity/stability of NO_x species adsorbed onto the physical mixture was analyzed under isothermal conditions after NO_x adsorption at 350 °C (see Fig. 7), with results shown in Fig. 9. This figure shows that nitrates stored on the physical mixture cannot be regenerated by H_2 under isothermal conditions at constant temperature; the NO_x adsorbed during the lean phase did not react with H_2, because no reaction products were detected on admission of hydrogen to the reactor. The low H_2 consumption seen in Fig. 9 is likely associated with reduction/uptake on Pt sites. The stored nitrates were thus removed by heating the catalyst at high temperatures under He flow (TPD), obtaining results very similar to those shown in Fig. 8.

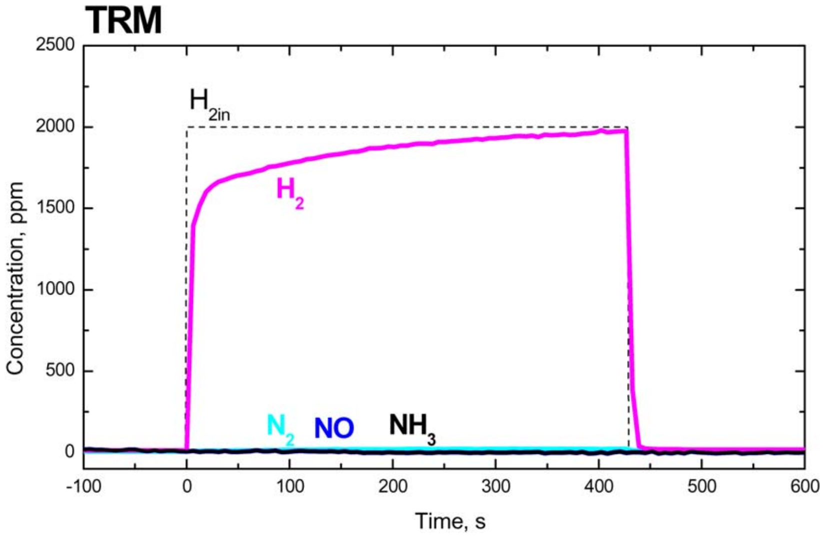

Fig. 9. Temporal evolution of H_2, N_2, NO and NH_3 outlet concentrations upon reduction with H_2 (2000 ppm in He) at 350 °C (TRM run) after NO/O_2 adsorption at 350 °C on the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture.

4. Mechanistic implications

The results reported herein provide relevant information concerning mechanistic aspects involved in the regeneration of NO_x trap catalysts under near-isothermal conditions. In particular, our data point to a mechanism for the reduction of stored NO_x involving a Pt-catalysed pathway operating at low temperatures and under isothermal conditions and implying the copresence of Pt and Ba on the same particle support. This route implies a different pathway than the proposed mechanism for the regeneration of NO_x trap catalysts, which involves an initial thermal decomposition of the stored nitrates, followed by reduction of the released NO_x over Pt. In principle, both pathways may effect the reduction of stored NO_x; however, because the thermal decomposition/reduction route requires the initial thermal decomposition of adsorbed nitrates, it is likely to be effective only on lean/rich cycling with significant thermal effects, as indeed occurs in applications in which significant oxygen concentrations are present in the flue gases during the rich phase and where high reductant concentrations are used for catalyst regeneration [24]. In contrast, under near-isothermal conditions (such as those investigated in this work), the Pt-catalysed pathway discussed above is effective, whereas the thermal decomposition/reduction route cannot be operational. In fact, the foregoing data demonstrate that nitrate species formed at high temperatures either from NO/O_2 or NO_2 do not readily decompose under inert atmosphere at the temperatures at which adsorption was carried out. Indeed, on switching from NO/O_2 to O_2 and then to pure He, only a small release of NO_x was observed, due to the decomposition of the less-stable nitrate adspecies. Consequently, the outlet NO_x concentration was very low and approached zero very slowly. It has been reported that NO_x adsorption is partially driven by equilibrium [13]; in our experiments, nitrates are formed under flowing conditions, which possibly results, when steady-state conditions are established, in a close approach to the thermodynamic equilibrium of reaction (1) for the specific experimental condition adopted herein. The decrease in NO_x and/or O_2 concentration creates a driving force for nitrate decomposition; our data indicate that this process readily involves a very small amount of adsorbed nitrates, because most of the stored NO_x decomposes at a negligible rate. This is also confirmed by TPD data showing that whatever the temperature at which the adsorption process was carried out, no NO_x desorption peaks were observed at temperatures below those adopted during adsorption, if a He purge was carried out after saturation to remove the weaker adsorbed species and cooling under flow of He (to avoid NO_x readsorption). Accordingly, the adsorption temperature rules the thermal stability of the stored nitrates in all of the catalytic systems considered in this study.

These data are apparently at variance with a few results reported in the literature [13,16]. For instance, during a TPD experiment performed over a Pt–Ba/Al_2O_3 catalyst, Poulston and Rajaram [16] observed the evolution of NO at low temperature after storage from NO/O_2 at 300 °C. However, in this case the NO_x adsorption procedure was not fully described and could have implied the contact of the sample with NO/O_2 also at low temperatures. Along similar lines, Liu and Anderson [13] analyzed the stability in air of nitrates stored over Ba/Al_2O_3 and Pt–Ba/Al_2O_3 catalysts exposed to NO_2 at 400 °C. Also in this case the authors pointed out the desorption of NO_x at low temperatures; however, the samples were cooled to room temperature in flowing NO_2 before the TPD run, thus allowing low-temperature adsorption of NO_x.

Notably, in line with other studies [3,4,13,15,18,21,22], our data show that Pt promotes the rate of nitrate decomposition. Indeed, comparing Figs. 2 and 5 demonstrates that on the ternary catalyst, the complete desorption of NO_x is achieved before the end of the TPD run (at 600 °C), as opposed to the Pt-free sample, for which complete removal of the stored nitrates was not yet achieved even at the end of the TPD run and could be obtained only after prolonged heating at 600 °C. Pt does not affect the thermodynamics of nitrate decomposition (i.e., the driving force for the decomposition), but does modify the kinetics of this reaction, promoting the rate of nitrate decomposition. Furthermore, the comparison between the ternary Pt–Ba/Al_2O_3 sample and the Pt/Al_2O_3–Ba/Al_2O_3 physical mixture (i.e., between samples with the same nominal composition but prepared differently) shows that Pt affects the rate of nitrate decomposition only if Pt and Ba are dispersed over the same particle support, in line with previous reports suggesting either the role of a Pt–Ba interface in nitrate decomposition [21] or the possibility of NO_x spillover between Pt and Ba [22].

We also analysed the stability/reactivity of the stored nitrates in a reducing environment. In the Ba/Al_2O_3 sample, H_2 had only a minor effect on the decomposition of nitrates. Apparently, the nitrate decomposition closely resembles that observed in He, if one neglects a slight decrease (by roughly 20 °C or less) in the temperature threshold. Moreover, a partial reduction of NO_2 to NO and N_2 can also be observed, in line with the results reported by Cant and Patterson [15], due to the reaction of H_2 with the released NO_x. These findings suggest that also in this case the nitrate decomposition is driven by a thermal effect, and that the presence of a net reducing environment does not play a significant role in the decomposition of nitrates stored over Ba. These conclusions were also confirmed by the run performed under isothermal conditions at constant temperature (see Fig. 3), showing no effect of hydrogen on the stored nitrates.

Similar results were also observed in the case of the Pt/Al_2O_3–Ba/Al_2O_3 physical mixture, that is, decomposition of the stored nitrates could be attained only by heating the catalyst up to temperatures above those adopted for catalyst saturation, even in the presence of hydrogen. However, in this case ammonia formation was observed (along with minor amounts of nitrogen) on nitrate decomposition and NO_x release in the gas phase. This is due to the reaction between released NO_x and H_2 on Pt sites, which, as shown by dedicated experiments, is highly unselective toward ammonia.

In contrast, a very different picture was apparent in the case of the ternary Pt–Ba/Al_2O_3 catalyst. In this case the stored nitrates, which do not appreciably decompose up to the adsorption temperature (350 °C in the case of Fig. 4), were readily reduced to N_2 and NH_3 at temperatures as low as 140 °C (i.e., more than 200 °C below the adsorption temperature). On the basis of the data discussed above, having observed that stored nitrates do not decompose up to the adsorption temperature, the reduction process cannot be initiated by the decomposition of stored nitrates induced by thermal effects, followed by the reduction of the NO_x released in the gas phase. Accordingly, a specific catalytic role of Pt must be invoked to explain the occurrence of the low-temperature reduction of stored NO_x. Moreover, considering that the low-temperature reduction of stored nitrates is not active in the Pt/Al_2O_3–Ba/Al_2O_3 physical mixture (in which Pt is present), it is clear that the co-presence of the storage element (Ba) and of the noble metal (Pt) on the same support particle is a prerequisite for the low-temperature reduction of the stored nitrates by H_2.

The picture derived from the TPSR results is further confirmed considering the reduction experiments performed at constant temperature (Fig. 6). The data collected on the ternary catalyst clearly indicate that the reduction of the stored NO_x can be attained under near-isothermal conditions as well, as opposed to both the binary Ba/γ-Al_2O_3 sample and the physical mixture.

A similar effect was also reported by Poulston and Rajaram [16], who studied the regeneration of nitrated Pt–Ba/γ-Al_2O_3 catalysts by heating the catalyst sample under either inert or reducing flow. These authors were unable to detect any N_2 formation, but did deduce the occurrence of a reduction reaction of the stored nitrates from the decreased amount of NO_x evolved on heating in H_2 versus He. Furthermore, having observed an increase of the low-temperature NO desorption peak when the heating was done in H_2 flow, they concluded that the decomposition temperature of the nitrates was significantly reduced in the presence of the reductant. As pointed out above, this is instead related to the Pt-catalyzed reduction of the stored NO_x. It is also noted that the low-temperature NO desorption peaks observed by Poulston and Rajaram [16] are likely due to the specific catalyst saturation procedure used in their study, having observed in our runs that nitrates do not readily decompose under inert atmosphere at temperatures below those used during adsorption.

In conclusion, our work indicates that reduction of stored nitrates under near-isothermal conditions (i.e., in the absence of any significant thermal effect) occurs in typical NSR catalysts according to a Pt-catalyzed surface reaction that does not involve, as a preliminary step, thermal decomposition of the adsorbed NO_x species. The occurrence of such a pathway also requires the co-presence of the storage element and of the noble metal on the same support, because this route does not operate when they are dispersed on different support particles.

A possible mechanism that is consistent with our findings involves the activation of H_2 on Pt sites, followed by its spillover onto the alumina support toward nitrate adspecies. The reduction of stored nitrates is then effected, either promoting the decomposition of nitrates to gaseous NO and/or NO_2, which are then reduced on Pt (by, e.g., reduction of nitrates to nitrites, followed by nitrite decomposition [13]), or directly reacting with the NO_x adspecies. An alternative mechanism involving the surface diffusion of NO_x adspecies toward Pt sites has also been proposed [3]; in this case, NO_x is decomposed at reduced Pt sites, and the role of the reductant is to keep Pt in a reduced state. This mechanism is in line with the observed effect of Pt on the thermal decomposition of stored nitrates; however, it implies a high mobility of NO_x species adsorbed onto Ba.

Finally, a specific route involving NO_x adspecies present on Ba sites neighbouring Pt can also be suggested. In this respect, the interaction between Pt and Ba, described previously as a key factor in NO_x adsorption [17], would also play an important role in determining the activity and selectivity of nitrate reduction. The role of Pt–Ba interaction was also pointed out by Coronado and Anderson [21], who suggested that the decomposition of nitrates occurs at the interface between the barium component and the noble metal. If this is the actual mechanism operating in the reduction of stored NO_x, then a question still remains concerning the involvement (under near-isothermal conditions) of nitrate species adsorbed on Ba sites remote from Pt. In fact, it has been previously shown that only a negligible fraction of the adsorbed nitrates is not involved in the subsequent reduction step [25].

The aforementioned mechanisms can explain the differences observed between the ternary Pt–Ba/γ-Al_2O_3 sample and the Pt/γ-Al_2O_3–Ba/γ-Al_2O_3 physical mixture where Pt and Ba sites are dispersed on different support particles. In this case, the reduction of NO_x adspecies (i.e., catalyst regeneration) can be accomplished by the thermal decomposition/reduction pathway discussed above and induced by thermal effects associated with lean–rich cycling in oxygen-containing exhausts. These aspects are currently under investigation in our labs.

5. Conclusion

The bulk of our data show that nitrate species formed at high temperatures from either NO/O_2 or NO_2 (in the case of the Pt-free sample) were stable under inert atmosphere at the temperatures at which adsorption was carried out. Indeed, in all of the TPD runs, the NO_x desorption peaks were observed at temperatures below those adopted for NO_x adsorption. Accordingly, the adsorption temperature rules the thermal stability of the stored nitrates.

The presence of Pt promotes the rate of nitrate decomposition. On the Pt–Ba/Al_2O_3 ternary catalyst, the complete desorption of NO_x was achieved before the end of the TPD run (600 °C), in contrast to the Ba/Al_2O_3 sample, for which complete removal of the stored nitrates was not attained at the end of the TPD run and was reached only after prolonged heating at 600 °C. Furthermore, comparing the ternary Pt–Ba/Al_2O_3 sample and the Pt/Al_2O_3–Ba/Al_2O_3 physical mixture shows that Pt affected the stability of nitrates only if Pt and Ba were dispersed onto the same particle support, in line with the role of a Pt–Ba interface in nitrate decomposition and/or the possibility of NO_x spillover from Ba to Pt.

The stability/reactivity of the stored nitrates in a reducing environment was also analyzed. In the case of the Ba/Al_2O_3 sample, H_2 had a minor effect on the stability of nitrates. Apparently, the nitrate decomposition closely resembled that observed in He, overlooking a slight decrease (roughly 20 °C or less) in the temperature threshold. Moreover, a partial reduction of NO_2 to NO and N_2 was also observed, due to the reaction of H_2 with the released NO_x. Similar results were also found for the Pt/Al_2O_3–Ba/Al_2O_3 physical mixture; however, in this case ammonia formation was also observed, along with minor amounts of nitrogen, due to the reaction between released NO_x and H_2 on Pt sites. In any case, the stored nitrates could not be reduced at constant temperature on either the Ba/Al_2O_3 or the Pt/Al_2O_3–Ba/Al_2O_3 physical mixture.

A completely different picture was observed in the case of the ternary Pt–Ba/Al_2O_3 catalyst. In this case, the stored nitrates were readily reduced to N_2 and NH_3 at temperatures as low as 140 °C (i.e., at temperatures more than 200 °C below that of adsorption), and the reduction was effective under near-isothermal conditions as well. This clearly indicates that the reduction of stored nitrates occurs in typical NSR catalysts according to a Pt-catalyzed surface reaction, which does not involve, as a preliminary step, thermal decomposition of the adsorbed NO_x species. Such a pathway also requires the copresence of the storage element and of the noble metal on the same support, because this route does not operate when they are dispersed on different support particles.

Mechanisms that are consistent with our data may involve the activation of H_2 on Pt sites, followed by spillover on the alumina support toward nitrate adspecies that are decomposed to NO_x (and then reduced on Pt) or directly reduced by spilled hydrogen. A mechanism involving the surface diffusion of NO_x adspecies toward reduced Pt sites can also be proposed. Finally, a specific route involving NO_x adspecies present on Ba sites neighbouring Pt might also be suggested. Note that this latter mechanism can provide a unifying explanation both of the lower stability of nitrates observed over Pt–Ba/Al_2O_3 samples and of the Pt-catalyzed nitrate reduction route evidenced in this work.

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