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## UNIVERSITÀ DEGLI STUDI DI TORINO

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**The influence of CO<sub>2</sub> and H<sub>2</sub>O on the storage properties of  
Pt-Ba/Al<sub>2</sub>O<sub>3</sub> LNT catalyst studied by FT-IR spectroscopy and  
transient microreactor experiments.**

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## **ABSTRACT**

The effect of CO<sub>2</sub> and H<sub>2</sub>O on the NO/O<sub>2</sub> storage over a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> LNT catalyst was investigated in the temperature range 150-350 °C by combining FT-IR spectroscopy and microreactor flow experiments. It is found that the presence of water shows negligible effect on the NO<sub>x</sub> storage at all the temperatures studied. Otherwise, the presence of CO<sub>2</sub> inhibits the “nitrite route” (initial formation of surface nitrites and their subsequent evolution to nitrates), whereas the “nitrate route” (involving NO oxidation to NO<sub>2</sub> over Pt and its subsequent adsorption on Ba in the form of nitrates) proceeds as in the absence of CO<sub>2</sub>. The inhibition effect of CO<sub>2</sub> on nitrite formation increases on increasing the temperature,. This behavior is likely related to the different thermal stability of nitrites and carbonates and, in particular, to the decreasing ability of nitrites to displace carbonates on increasing temperature. Simultaneously, the presence of CO<sub>2</sub> in the feed significantly shortens or eliminates the dead time in the NO<sub>x</sub> breakthrough at the reactor outlet. As a consequence, the presence of dead time in the absence of CO<sub>2</sub> has been correlated to the occurrence of the nitrite route.

*Keywords:* Pt-Ba/Al<sub>2</sub>O<sub>3</sub>, NO<sub>x</sub> storage, CO<sub>2</sub>, operando FT-IR, Transient microreactor experiments

## 1. INTRODUCTION

"Lean NO<sub>x</sub> Traps" (LNTs) represent a viable technology for the reduction of NO<sub>x</sub> under lean conditions [1]. These catalytic systems are made by noble metals (e.g. Pt and/or Rh) and NO<sub>x</sub> storage elements (Ba and K), supported over a high surface area carrier. The NO<sub>x</sub> removal occurs under cyclic conditions by alternating long phases under lean conditions where NO<sub>x</sub> are stored on the catalyst surface, with short rich phases during which the stored NO<sub>x</sub> are reduced to N<sub>2</sub> by a reductant.

Both the NO<sub>x</sub> storage and reduction steps have been extensively investigated by several authors [1-8]. Concerning the storage phase, in previous works of our groups we have used *in situ* and *operando* FT-IR spectroscopy and transient flow reactor experiments to gain complementary information on the gas phase composition and the surface species formed during the adsorption of NO<sub>x</sub> from NO/O<sub>2</sub> mixture on a model Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst [9-11]. In particular the existence of two different pathways has been envisaged for the storage of NO<sub>x</sub>:

*i*) the first route, hereafter denoted as "nitrate route", implies the preliminary oxidation of NO to NO<sub>2</sub> on Pt sites (reaction (1)), followed by NO<sub>2</sub> storage onto storage compounds in the form of nitrates through a disproportionation reaction (reactions (2) + (3)):

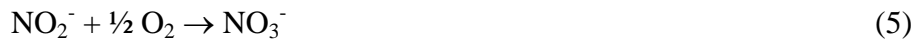


According to this pathway, nitrites and nitrates are expected at the beginning of the storage (reaction (2)). However in previous studies on NO<sub>2</sub> adsorption [9, 10], nitrites are not detected on the surface even at the very beginning of the storage, likely due to their very fast oxidation to nitrate species (reaction (3));

ii) the second route, hereafter denoted as "nitrite route", is based on the oxidative adsorption of NO at Pt-BaO border leading to the formation of nitrite adspecies according to the stoichiometry of the following overall reaction (4):



In this case a cooperative effect operates between the noble metal and the nearby storage component so that NO is oxidized and adsorbed as  $\text{NO}_2^-$  at the Ba site before it is oxidized to  $\text{NO}_2$ . Notably, at variance to the *nitrate* pathway, the *nitrite* route accomplishes the storage of  $\text{NO}_x$  in the form of nitrites only. The stored nitrites might be further oxidized to nitrates by  $\text{O}_2$ , so that the formation of nitrates is expected as consecutive reaction (reaction (5)):



As shown in [11], the nitrite route is the unique pathway involved in the storage of  $\text{NO}_x$  at low temperatures (e.g. at  $150^\circ\text{C}$ ) from  $\text{NO}/\text{O}_2$  since relevant amounts of  $\text{NO}_x$  are stored in the form of nitrites only at such low temperatures and the oxidation of NO to  $\text{NO}_2$  is not observed to a significant extent. However at higher temperatures, i.e. above  $200\text{-}250^\circ\text{C}$ , the formation of  $\text{NO}_2$  and of nitrates is also observed, along with nitrites. Notably, nitrites are the prevalent species at the initial stages of the storage with  $\text{NO}/\text{O}_2$ , while nitrates represent the most abundant adsorbed species after prolonged contact. This suggests that at high temperatures nitrites are intermediates in the formation of nitrates according to reactions (4) + (5). Besides, in the presence of  $\text{NO}_2$  the storage of  $\text{NO}_x$  also occur according to the nitrate pathway.

These conclusions have been reached based on experiments carried out in the absence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the gas stream [11], which however are known to affect the  $\text{NO}_x$  storage behavior of LNT catalysts. Chaugule et al. [12], who investigated the effect of  $\text{CO}_2$  on  $\text{NO}_x$  storage from  $\text{NO}_2/\text{O}_2$  mixtures at  $300^\circ\text{C}$  on catalysts with different Ba loading, pointed out that nitrates could replace the preformed carbonates and carboxylates in absence of  $\text{CO}_2$  in the gas phase. However, in the presence of  $\text{CO}_2$  the

adsorbed carbonates and carboxylates could not be completely replaced by nitrates even after a long  $\text{NO}_x$  exposure. Moreover, the amount of pre-adsorbed  $\text{CO}_2$  released during  $\text{NO}_x$  storage correlated well with the amount of  $\text{NO}_x$  stored on the catalyst with 20 wt.% Ba, but not on the samples with Ba loadings of 8 and 4 wt.%.

Weiss et al. [13] investigated the adsorption of  $\text{NO}/\text{NO}_2/\text{CO}_2$  mixtures on  $\text{BaO}/\text{Al}_2\text{O}_3$  and  $\text{Pt-BaO}/\text{Al}_2\text{O}_3$  in the temperature range 150-400 °C. They found that nitrites form rapidly upon exposure of  $\text{NO}/\text{NO}_2$  mixtures, but the presence of  $\text{CO}_2$  limits the  $\text{NO}_x$  uptake equilibrium due to the unfavorable thermodynamics. This eventually indicates that nitrite formation is an impractical strategy for  $\text{NO}_x$  removal from  $\text{CO}_2$ -rich combustion effluent streams. These conclusions have been obtained with  $\text{NO}/\text{NO}_2$  mixtures and therefore it is also of interest to analyze the effect of  $\text{CO}_2$  during  $\text{NO}_x$  uptake from  $\text{NO}/\text{O}_2$ .

The effect of  $\text{CO}_2$  on the  $\text{NO}_x$  storage from  $\text{NO}_2$  and  $\text{NO}/\text{O}_2$  mixture has also been investigated previously by *in situ* FT-IR spectroscopy and pulse reactor experiments at 350 °C [14]. It has been found that upon adsorption of  $\text{NO}_x$  from  $\text{NO}/\text{O}_2$  both in the presence of gas-phase  $\text{CO}_2$  and over  $\text{CO}_2$  pre-covered  $\text{Pt-Ba}/\text{Al}_2\text{O}_3$  catalysts the  $\text{NO}_x$  breakthrough is significantly shortened if compared to the  $\text{CO}_2$ -free experiments. Besides, FT-IR experiments showed a less pronounced nitrite formation. However the  $\text{NO}_x$  storage capacity of the catalyst after prolonged contact with  $\text{NO}_2$  and  $\text{NO}/\text{O}_2$  mixtures was only slightly affected both in the presence of gas-phase  $\text{CO}_2$  and over the  $\text{CO}_2$  pre-covered catalysts.

Based on these findings, in order to better clarify the role of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on the  $\text{NO}_x$  storage and particularly on the formation of nitrite and nitrate adspecies via the *nitrite* and *nitrate* pathways,  $\text{NO}_x$  adsorption experiments have been carried out starting from  $\text{NO}/\text{O}_2$  mixtures in the presence and in the absence of  $\text{CO}_2$  and/or  $\text{H}_2\text{O}$  over a model  $\text{Pt-Ba}/\text{Al}_2\text{O}_3$  catalyst sample in the temperature range 150-350°C. *Operando* FTIR spectroscopy and transient flow pulse reactor experiments have been used as

complementary techniques to analyze the pathways involved in the storage of NO<sub>x</sub> and the effects produced by the presence of CO<sub>2</sub> and H<sub>2</sub>O in the feed stream.

## 2. EXPERIMENTAL

The Pt-Ba/Al<sub>2</sub>O<sub>3</sub> (1/20/100 w/w) catalyst sample used in this work was prepared by incipient wetness impregnation of  $\gamma$ -alumina (Versal 250 from UOP) with aqueous solution of dinitro-diamine platinum (Strem Chemicals, 5% Pt in ammonium hydroxide) and then with a solution of barium acetate (Aldrich, 99%). After each impregnation step, the powder was dried overnight in air at 80 °C and calcined at 500 °C for 5 h.

Textural, morphological and structural characterization was already reported in previous works [10, 14-16]. Here, we only recall some information of interest. The specific surface area and pore volume measured by N<sub>2</sub> adsorption-desorption at 77 K were 137 m<sup>2</sup>/g and 0.81 cm<sup>3</sup>/g, respectively. The Pt dispersion, as determined by H<sub>2</sub> chemisorption at 0 °C, was about 70%, in line with the mean Pt particle size measured by HRTEM (1.5 nm) [16]. XRD patterns of the calcined sample showed the presence of micro-crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and crystalline BaCO<sub>3</sub> whiterite phase.

The NO<sub>x</sub> storage has been investigated in the presence and in the absence of CO<sub>2</sub> and H<sub>2</sub>O by transient experiments wherein rectangular step feeds of NO (1000 ppm) have been admitted in Ar + O<sub>2</sub> (3% v/v) flowing into a IR reactor cell (Aabspec CX cell) directly connected to a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a MCT detector for the analysis of the surface species. Experiments have been performed at 150 °C, 200 °C, 250 °C and 350 °C; when CO<sub>2</sub> and H<sub>2</sub>O were present in the feed stream their concentration was 1% v/v and 2% v/v, respectively. The cell was loaded with 15 mg of catalyst powder compressed in self-supporting discs (diameter = 13 mm, thickness = 0.1 mm); a total flow of 25 cm<sup>3</sup> min<sup>-1</sup> (at 1 atm and 0 °C) has been used. The IR reactor cell was also directly



connected to a quadrupole mass spectrometer (Omnistar GSD 301 with a 1 s time-resolution), and a chemiluminescence analyzer (Model 42i-HL MEGATEC) for the analysis of the gas phase.

In order to evaluate the amount of NO<sub>x</sub> (as mol/g<sub>cat</sub>) stored at each temperature on the catalyst surface, from the gas phase has been calculated the difference between the NO<sub>x</sub> inlet concentration and the outlet NO<sub>x</sub> concentration at steady-state conditions. Then, by combining the results of quantitative analysis of the gaseous species with those of the synchronous operando FT-IR spectroscopy, the molar absorption coefficient of the bands related to nitrite and nitrate vibration modes could be evaluated. The same procedure described in [11] has been adopted to evaluate the amount of nitrites (adsorption at 150°C) and of nitrates (adsorption at 350°C).

To allow an accurate analysis of the dynamics of the storage phase, dedicated experiments have been performed in a plug-flow microreactor loaded with 60 mg of catalyst powder (70–100 μm) and operating under the same experimental conditions used in FT-IR experiments. A total flow of 100 cm<sup>3</sup> min<sup>-1</sup> (at 1 atm and 0 °C) has been used in these experiments, so that the Gas Hourly Space Velocity (GHSV) was exactly the same for both FT-IR and microreactor experiments (10<sup>5</sup> cm<sup>3</sup> g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>). The microreactor was directly connected to a mass spectrometer (Balzers QMS 200) and a FT-IR Multigas 2030 (MKS instrument) for the complete analysis of the reaction products.

Before both FTIR and flow-microreactor experiments, the catalyst was conditioned with several lean-rich cycles with NO/O<sub>2</sub> (1000 ppm NO + O<sub>2</sub> 3% v/v) and H<sub>2</sub> (2000 ppm) at 350 °C, with an inert purge in Ar between the lean and rich phase. Several cycles were run until a reproducible behavior was obtained, which corresponds to the transformation of the Ba carbonate phase into a well-dispersed nanosized BaO phase [16].

Finally, the thermal stability of the surface species involved in the storage in the presence of CO<sub>2</sub>, i.e. nitrites, nitrates and carbonates, was investigated by *in situ* FT-IR spectroscopy. For this purpose adsorption of NO/O<sub>2</sub> (1/10 mixture), NO<sub>2</sub> (2 mbar) and CO<sub>2</sub> (2 mbar) was performed at 100 °C to form

surface nitrites (the mixture used and the low temperature ensure the formation of only nitrites and not nitrates), nitrates and carbonates, respectively. Then the sample was evacuated at increasing temperature in the range 100-400 °C to investigate the thermal stability of the different species.

To better appreciate the spectral features of surface species, the IR spectra are reported in the figures after subtraction of a spectrum chosen as a background; the subtracting spectrum is always indicated in the figure captions.

### 3. RESULTS AND DISCUSSION

#### 3.1. CO<sub>2</sub> adsorption

Before addressing the effect of CO<sub>2</sub> on the NO<sub>x</sub> storage, it is important to investigate the surface species formed upon contacting CO<sub>2</sub> in the range 150-350 °C over a conditioned catalyst sample, i.e. subjected to several adsorption-reduction cycles in H<sub>2</sub> in order to remove the carbonates present on the freshly calcined sample. The final step of the conditioning treatment was the reduction by H<sub>2</sub> of the stored NO<sub>x</sub>, so that the surface is clean from any adsorbed NO<sub>x</sub> species. The results obtained upon contacting the sample with CO<sub>2</sub> at different temperatures are shown in Figure 1. A relevant point is that the surface species formed upon CO<sub>2</sub> adsorption exhibit spectral features completely different from those of crystalline BaCO<sub>3</sub> present on the fresh sample before the conditioning cycles, as already shown by some of us in ref. [14]. At 150 °C, 200 °C and 250 °C absorptions at 1555, 1372 and 1056 cm<sup>-1</sup>, characteristic of surface bidentate carbonate species adsorbed on the Ba phase ( $\nu(\text{C}=\text{O})$ ,  $\nu_{\text{asym.}}(\text{OCO})$  and  $\nu_{\text{sym.}}(\text{OCO})$ , respectively) [14, 17] are present. The shoulder at 1435 cm<sup>-1</sup> is related to the  $\nu_{\text{asym.}}(\text{CO}_3)$  mode of carbonates, adsorbed on the Ba phase, herein indicated as ionic carbonates and

not as monodentate carbonates, as suggested in our previous works [14, 16]. This new assignment has been enlightened by dedicated experiments performed on the basis of the results that we obtained about the water effect on nitrates stored onto Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst [18]: the dissociative chemisorption of water causes the transformation of bidentate nitrates into highly symmetric species that we call ionic nitrates. As a matter of fact, the effect of water on the adsorbed carbonates is the same observed for nitrates. These experiments have shown that the carbonate band at 1435 cm<sup>-1</sup> is correlated to another one at 1390 cm<sup>-1</sup> deriving from the splitting of corresponding double degenerate  $\nu_{\text{asym.}}(\text{CO}_3)$  mode of free carbonates. The very low separation between the two bands suggests the presence of highly symmetric surface species that we call ionic carbonates. Under actual working conditions, the band at 1390 cm<sup>-1</sup> is covered by the band related to  $\nu_{\text{asym.}}(\text{OCO})$  mode of bidentate carbonate species, mainly present on the surface. Notably, no surface species typical of alumina support, such as organic-like and hydrogen carbonates were observed [19], confirming an extensive spreading of the barium oxide phase, as previously shown [15, 16].

At 350 °C (Fig. 1, curve d) the bands related to bidentate carbonates are red-shifted to 1546 and 1357 cm<sup>-1</sup>. Reasonably, also the band at 1435 cm<sup>-1</sup> related to ionic carbonates is red-shifted in a way that makes it no more visible due to the superimposition with the band at 1357 cm<sup>-1</sup> that becomes highly asymmetric. The red-shift of carbonate bands can be related to the decrease of surface coverage and to the spreading of carbonates on the surface due to the temperature increase. The coverage decrease on increasing temperature is evidenced by the intensity loss of the bands.

Similar observations have been reported in a previous paper by Epling et al. [20], who studied the adsorption of CO<sub>2</sub> on Pt-Ba/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage-reduction catalyst. Similar features have been described regarding carbonate species except in that organic-like carbon species on alumina have been observed in that case.

Specific experiments have been performed in order to quantify the amount of CO<sub>2</sub> adsorbed over the catalyst surface at different temperature. For this purpose, a flow of CO<sub>2</sub> (1% v/v) has been admitted to the flow microreactor over a conditioned catalyst at 150 °C, 200 °C, 250 °C and 350 °C until saturation has been achieved. Then the catalyst has been cooled down to RT in inert atmosphere and finally heated up to 500 °C (10 °C/min). Accordingly the amounts of CO<sub>2</sub> stored on the catalyst surface at different temperatures could be evaluated; these amounts range from 2.0 10<sup>-4</sup> mol/g<sub>cat</sub> at 350 °C to 4.5 10<sup>-4</sup> mol/g<sub>cat</sub> at 150 °C. The largest amount of adsorbed CO<sub>2</sub> corresponds roughly to 30% of the overall Ba loading (considering the formation of BaCO<sub>3</sub>), and decreases on increasing the temperature, as expected: at 350 °C roughly 13% of the overall Ba loading is involved in carbonate formation. Taking into account that the BaO phase is well dispersed on the surface and that the amount of Ba is close to that of a monolayer, it is reasonable to consider that almost all the Ba sites are exposed at the surface. Accordingly, the large fraction of surface sites not available for carbonate adsorption (greater than 70%) is likely due to steric hindrance and electrostatic repulsion between carbonate species.

### ***3.2. NO<sub>x</sub> adsorption in the absence and in the presence of CO<sub>2</sub>***

In Figure 2 the FT-IR spectra recorded during the NO<sub>x</sub> storage at 150 °C in the different atmospheres are shown. In the absence of CO<sub>2</sub> (Fig. 2A), the storage proceeds with the initial formation of chelating nitrites ( $\nu_{\text{sym.}}(\text{NO}_2)$  and  $\nu_{\text{asym.}}(\text{NO}_2)$  at 1360 and 1210 cm<sup>-1</sup>, respectively), as already evidenced in our previous work [11]. The surface concentration of these species continues to increase with the NO/O<sub>2</sub> exposure until 20 min (Fig. 2A, curve d). Then a band at 1546 cm<sup>-1</sup> related to  $\nu(\text{N}=\text{O})$  mode of bidentate nitrates, formed by very slow nitrite oxidation, is also present. These data hence indicate that at 150 °C only the nitrite route is effective in the storage of NO<sub>x</sub>.

The analysis of the corresponding gas phase allows the quantification of the total amount of NO<sub>x</sub> stored at the end of the adsorption step. This amount is near  $3.7 \cdot 10^{-4}$  mol/g<sub>cat</sub>, corresponding to 15% of the overall Ba loading by assuming the formation of Ba(NO<sub>2</sub>)<sub>2</sub> species.

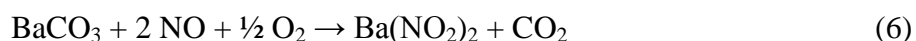
In the presence of CO<sub>2</sub>, negative bands appear in the FT-IR spectra (Fig. 2B). In fact the background spectrum is that recorded before NO admission, i.e. under a CO<sub>2</sub>/O<sub>2</sub>/Ar flow, and accordingly the negative bands are related to the surface carbonate species which are displaced upon NO<sub>x</sub> adsorption. Formation of nitrites is observed also in the presence of CO<sub>2</sub>; because of the carbonate presence, the evolution of nitrites is observable only through the behavior of the band at 1210 cm<sup>-1</sup> attributed to the  $\nu_{\text{asym.}}(\text{NO}_2)$  mode. Notably, the increase in intensity of the negative bands related to the displacements of carbonates parallels the increase of the bands of nitrites. It is also worth to note that the time evolution of the nitrite band is similar to that observed without CO<sub>2</sub> (compare Fig. 2A and 2B). In this case the gas phase analysis revealed that the total amount of stored NO<sub>x</sub> is near  $2.4 \cdot 10^{-4}$  mol/g<sub>cat</sub> (10% of the overall Ba loading), i.e. lower than those measured in the absence of CO<sub>2</sub>.

Finally in Figure 2C the results obtained in the presence of both CO<sub>2</sub> and H<sub>2</sub>O are reported. The catalytic behavior closely resembles that previously described in the presence of CO<sub>2</sub> only. FT-IR data pointed out that at low temperature (150°C) nitrites are observed, with amounts that increase with time of stream. The analysis of the region 1700-1280 cm<sup>-1</sup> also shows the displacement of carbonates during the formation of NO<sub>x</sub>, as observed in the case of the presence of CO<sub>2</sub> only. In this case near  $3.0 \cdot 10^{-4}$  mol/g<sub>cat</sub> (12% of the overall Ba loading) of NO<sub>x</sub> are stored at the end of the storage phase.

As explained in the Experimental section, to allow an accurate analysis of the dynamics of the storage phase, experiments have been performed in a plug-flow micro-reactor under the same experimental conditions used for the operando FT-IR. The results of the experiments carried out at 150°C are reported in Figure 3 in terms of outlet NO<sub>x</sub> concentration as a function of time, while the NO<sub>2</sub> / NO ratio measured at steady state (i.e. at the end of the NO pulse) is reported in Table 1.

As clearly appears in the Figure 3, upon NO admission in the absence of CO<sub>2</sub> and H<sub>2</sub>O (trace a), a dead time near 30 sec is observed in the NO<sub>x</sub> breakthrough. In the presence of CO<sub>2</sub> and of both CO<sub>2</sub>+H<sub>2</sub>O the dead time is reduced, i.e. the NO<sub>x</sub> breakthrough is observed at the reactor outlet after few seconds. The outlet NO<sub>x</sub> concentration increases reaching the inlet value more rapidly in the presence (curve b) than in the absence of CO<sub>2</sub>, indicating that the NO<sub>x</sub> uptake is slower. Only negligible amounts of NO<sub>2</sub> are observed at the reactor outlet (Table 1), pointing out that the NO oxidation reaction is very slow at this temperature. Note that the presence of water (curve c) in the feed further decreases the NO<sub>2</sub> / NO ratio (Table 1), in line with literature data [21-23] showing that water inhibits the oxidation of NO to NO<sub>2</sub>.

When CO<sub>2</sub> is present in the feed, the adsorption of NO<sub>x</sub> is also accompanied by the evolution of CO<sub>2</sub> (not shown in the Figure) due to the displacement of carbonates by nitrites. This is in line with FT-IR spectra showing the appearance of negative bands. The overall amount of CO<sub>2</sub> exiting the reactor is in line with the occurrence of the following reaction:



where a 2:1 ratio is expected between the amounts of stored nitrites and desorbed CO<sub>2</sub>, close to the measured value..

Experiments have also been performed at 200°C, 250°C and 350°C; for the sake of brevity only experiments performed at 250°C and 350°C are illustrated in the following.

Figure 4 shows FT-IR spectra obtained as a function of time during the NO/O<sub>2</sub> storage at 250°C in the absence (Fig. 4A), in the presence of CO<sub>2</sub> (Fig. 4B) and in the presence of both CO<sub>2</sub> and water (Fig. 4C). In the absence of CO<sub>2</sub>, FT-IR spectra show that mainly nitrites (band at 1210 cm<sup>-1</sup>) are present after 2 min (Fig. 4A, curve a). After 5 min (Fig. 4A, curve b) nitrites continue to increase and both ionic nitrates (ν<sub>asym.</sub>(NO<sub>3</sub>) mode split at 1415 and 1326 cm<sup>-1</sup> and ν<sub>asym.</sub>(NO<sub>3</sub>) mode at 1035 cm<sup>-1</sup> [15]) and bidentate nitrates (ν(N=O) mode at 1540 cm<sup>-1</sup>, the only one visible) start to form. After 20 min

(Fig. 4A, curve d), the band at  $1210\text{ cm}^{-1}$  related to nitrites decreases in intensity due to the oxidation of nitrites into nitrates and the nitrate bands increase monotonically. Hence these results show that at  $250\text{ }^{\circ}\text{C}$  the nitrite pathway is the prevalent route for  $\text{NO}_x$  storage since nitrates are observed only after nitrite formation. At this temperature nitrates can be formed by nitrite oxidation and by  $\text{NO}_2$  dismutation (reactions (2) + (3)). From the gas phase analysis, the total amount of  $\text{NO}_x$  stored at the end of the storage phase is near  $3.6 \cdot 10^{-4}\text{ mol/g}_{\text{cat}}$  (14% of the overall Ba loading).

In the presence of  $\text{CO}_2$ , in the FT-IR spectra (Fig. 4B) the analysis of the region  $1700\text{-}1280\text{ cm}^{-1}$  is complicated by the presence of negative bands related to displaced carbonates, as observed at  $150\text{ }^{\circ}\text{C}$ , but now superimposed to increasing absorptions related to nitrates. However it is still possible to follow the evolution of nitrites through the band at  $1210\text{ cm}^{-1}$ . The maximum intensity of this band is reached after 5 min and maintained after 10 min (Fig. 4B, curve b and c). The intensity of such band is lower of that reached after 10 min in the absence of  $\text{CO}_2$  (Fig. 4A, curve c). After 20 min (Fig. 4B, curve d) the intensity of nitrite band starts to decrease, as observed in the absence of  $\text{CO}_2$ . The presence of  $\text{CO}_2$  in the feed decrease the total amount of stored  $\text{NO}_x$  down to  $3 \cdot 10^{-4}\text{ mol/g}_{\text{cat}}$  (12% of the overall Ba loading)

When both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are present (Fig. 4C), again the catalytic behavior closely resembles that previously described in the presence of  $\text{CO}_2$  only at  $250^{\circ}\text{C}$ , showing also in this case the formation of nitrites at the beginning of the storage, followed by their oxidation to nitrates. The formation of nitrites and nitrates is accompanied by the displacement of carbonates. The amount of  $\text{NO}_x$  stored in this case is very similar to that calculated in the presence of  $\text{CO}_2$  only, i.e. near  $2.6 \cdot 10^{-4}\text{ mol/g}_{\text{cat}}$  (11% of the overall Ba loading).

The results of the gas phase analysis performed on the flow micro-reactor are shown in Figure 5. Under inert atmosphere, a dead time of about 95 sec in the  $\text{NO}_x$  breakthrough is observed (curve a), while in the presence of  $\text{CO}_2$  it decreases at about 17 sec. The  $\text{NO}_2/\text{NO}$  ratio at the reactor outlet at steady-state

(Table 1) is quite similar in the presence and in the absence of CO<sub>2</sub>, thus pointing out the negligible role of CO<sub>2</sub> in the NO to NO<sub>2</sub> oxidation, whereas is decreased by the presence of water as already observed. In all cases, the stationary level reached by NO and NO<sub>2</sub> are far from chemical equilibrium of NO oxidation to NO<sub>2</sub>, thus indicating that the reaction is kinetically controlled. Also at 250°C the total amount of desorbed CO<sub>2</sub> approaches the theoretical amount expected from the replacement of BaCO<sub>3</sub> with Ba(NO<sub>2</sub>)<sub>2</sub> and Ba(NO<sub>3</sub>)<sub>2</sub>.

Finally, Figure 6 shows the FT-IR spectra recorded as a function of time on stream during the NO<sub>x</sub> storage at 350 °C in the absence (Fig. 6A) in the presence of CO<sub>2</sub> (Fig. 6B) and of CO<sub>2</sub>+H<sub>2</sub>O (Fig. 6C). In the absence of CO<sub>2</sub> (Fig. 6A), IR spectra show that both nitrites (band at 1210 cm<sup>-1</sup>) and nitrates (bands at 1415, 1320 and 1027 cm<sup>-1</sup>) are almost simultaneously formed (Fig. 6A curve a). After 10 min (Fig. 6A, curve c) the band at 1210 cm<sup>-1</sup> related to nitrites is no more visible due to their oxidation into nitrates, while the nitrate bands continue to increase. In fact at this temperature the nitrate route is also active, as pointed out by the significant formation of NO<sub>2</sub> which is detected at the reactor outlet (Table 1). Near 4.3 10<sup>-4</sup> mol/g<sub>cat</sub> (18% of the overall Ba loading) of NO<sub>x</sub> are stored at the end of the storage phase.

When NO<sub>x</sub> adsorption is carried out in the presence of CO<sub>2</sub>, again the analysis of the region 1700-1280 cm<sup>-1</sup> in the FT-IR spectra (Fig. 6B) is complicated by the presence of negative bands related to the displacement of carbonates, superimposed to those of nitrates, as previously mentioned. Indeed, the bands at 1415 and 1312 cm<sup>-1</sup> are related to ionic nitrates, but their intensity and in some extent also their position are invalidated by the negative bands related to carbonates. Notably, the band at 1210 cm<sup>-1</sup> due to nitrites is hardly visible in this case, indicating that the amount of nitrites is much lower with respect to that observed without CO<sub>2</sub> at any time of contact. About 4.2 10<sup>-4</sup> mol/g<sub>cat</sub> (18% of the overall Ba loading) of NO<sub>x</sub> are stored at the catalyst surface.



The presence of both CO<sub>2</sub> and H<sub>2</sub>O does not change significantly the catalyst behavior and FT-IR spectra if compared to the presence of CO<sub>2</sub> only (compare Fig. 6B and Fig. 6C) Indeed, also in the presence of CO<sub>2</sub> and H<sub>2</sub>O nitrites can be hardly identified. In these conditions 4.2 · 10<sup>-4</sup> mol/g<sub>cat</sub> (18% of the overall Ba loading) of NO<sub>x</sub> are stored at the end of the storage phase.

The results of the gas phase analysis obtained with the powder plug-flow micro-reactor (Fig. 7) point out a significant dead time (120 sec) in the NO<sub>x</sub> breakthrough under inert atmosphere (trace a), while a significant decrease of the dead time is observed in the presence of CO<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>O (15 sec). In all cases, the concentrations of NO and NO<sub>2</sub> increase up to a steady state value. The NO<sub>2</sub>/NO ratio (Table 1) is not significantly affected by the presence of CO<sub>2</sub> whereas it is decreased by the presence of water as already discussed.

As for the other investigated temperatures, also at 350 °C the total amounts of released CO<sub>2</sub> (not shown) well agree with those expected from the stoichiometry of nitrate formation on Ba carbonates.

### ***3.3. Impact of CO<sub>2</sub> and water on the nitrite and nitrate routes for the NO<sub>x</sub> storage.***

It has been previously shown that the nitrite route, i.e. the adsorption of NO<sub>x</sub> at a Pt-Ba couple leading to the formation of nitrite species, is the unique route active at low temperature (e.g. 150 °C) where selective formation of nitrites has been observed and where oxidation of NO to NO<sub>2</sub> is poor. At higher temperatures formation of nitrates has also been observed, as well as of NO<sub>2</sub> in the gas phase. Accordingly at these temperatures the nitrate pathway, involving the disproportionation of NO<sub>2</sub> and leading to nitrate adspecies and NO, is also active in the storage of NO<sub>x</sub>, although nitrates may also be formed by nitrite oxidation, formed in turn according to the so-called nitrite route.

CO<sub>2</sub> and NO<sub>x</sub> compete for the same adsorption sites, being carbonates displaced during NO<sub>x</sub> adsorption. As mentioned in section 3.1, CO<sub>2</sub> adsorption allows to evaluate the overall fraction of surface sites available for carbonate formation, showing a maximum near 30% at 150 °C. Notably, the

fraction of Ba sites involved in NO<sub>x</sub> adsorption is always lower than that used for CO<sub>2</sub> adsorption and increases with temperature, at variance with what observed in the case of carbonate formation. At low temperature NO<sub>x</sub> adsorption is limited by the slow rate of nitrite and nitrate formation, whereas at high temperature to the decrease of nitrate thermal stability.

The presence of CO<sub>2</sub> (and of CO<sub>2</sub> and water as well) has an impact on the formation of nitrites, as pointed out by the different intensity of the band at 1210 cm<sup>-1</sup> (ν<sub>asym.</sub>(NO<sub>2</sub>) mode of nitrite species) in the presence and in the absence of CO<sub>2</sub> (and water). This is displayed in Figure 8 (left side) which shows the amount of stored nitrites (evaluated from the linear intensity of the 1210 cm<sup>-1</sup> band, i.e. the intensity of the band maximum, and using linear molar absorption coefficient reported in Ref. [11]) as a function of time in Ar (curves a), in Ar/CO<sub>2</sub> (curves b) and in Ar/CO<sub>2</sub>/H<sub>2</sub>O (curves c). Note that due to the overlap of bands of carbonates and of nitrates in the region 1300-1650 cm<sup>-1</sup> the concentration of nitrates could not be followed directly.

In the absence of CO<sub>2</sub> the nitrite concentration shows the typical behavior of intermediate species [11]. In fact the nitrite concentration monotonically increase with time at low temperatures (150°C), where almost only nitrites have been detected on the catalyst surface (if one neglect the small amounts of nitrates formed after prolonged contact), and show maxima at higher temperatures (250°C and 350°C), when nitrates are also observed. In particular at 350°C nitrites are observed only at the very beginning of the storage, and after prolonged contact with NO only nitrates are present on the catalyst surface (see Figure 4A).

Similar trends are apparent in the presence of CO<sub>2</sub>, although differences are clearly visible in the nitrite concentration evolution with time. At 150 °C the influence of CO<sub>2</sub> on the nitrite concentration is negligible at the beginning of the exposure. After prolonged exposure the presence of CO<sub>2</sub> decreases the amount of nitrites stored at steady state, possibly due to the presence of residual carbonate species with high stability that nitrites are not able to displace. At 250 °C a small decrease of the maximum

amount of stored nitrites is observed in the presence of CO<sub>2</sub>; a much more pronounced effect is observed at 350 °C, although at this temperature the nitrite surface concentration is much lower even in the absence of CO<sub>2</sub>. In fact at this temperature the maximum amount of nitrites measured in the presence of CO<sub>2</sub> is about 60% lower than that observed in the absence of CO<sub>2</sub>.

It is of interest to compare the nitrite surface concentration estimated from FTIR data (Figure 8, left side) with the total amounts of stored NO<sub>x</sub> estimated from gas-phase analysis (Figure 8, right side). At 150 °C the nitrite concentration and the total amounts of stored NO<sub>x</sub> show similar behavior, in line with the observation that almost only nitrites are present at this temperature. The presence of CO<sub>2</sub> reduces the amounts of stored NO<sub>x</sub> (i.e.  $2.4 \cdot 10^{-4}$  mol/g<sub>cat</sub> vs.  $3.7 \cdot 10^{-4}$  mol/g<sub>cat</sub>), in line with the decreased amount of stored nitrites (see Figure 8, left panel). Water addition, along with CO<sub>2</sub>, seems to have a slight beneficial effect in that it reduces the impact of CO<sub>2</sub>.

At 250 °C the nitrite concentration exhibits a different behavior if compared to the total stored NO<sub>x</sub>, being nitrates formed along with nitrites. Also in this case the stored NO<sub>x</sub> are reduced in the presence of CO<sub>2</sub> (i.e.  $3.0 \cdot 10^{-4}$  mol/g<sub>cat</sub> vs  $3.6 \cdot 10^{-4}$  mol/g<sub>cat</sub> at the end of exposure); the effect is even more evident in the presence of water as well. The observation that the total amounts of stored NO<sub>x</sub> (i.e. nitrites + nitrates) is affected by the presence of CO<sub>2</sub> more than the nitrite concentration suggests that the nitrate formation is influenced by the presence of CO<sub>2</sub> as well. The presence of water further reduces the amounts of stored NO<sub>x</sub> (but not of nitrites) possibly due to H<sub>2</sub>O negative impact on the nitrate pathway (water inhibits the NO oxidation to NO<sub>2</sub>).

Finally, at 350°C nitrites represent only a minor fraction of the stored NO<sub>x</sub>, being nitrates the dominant species; at such temperature the total amounts of NO<sub>x</sub> stored at steady state is very similar at 350 °C in the presence of CO<sub>2</sub> and of H<sub>2</sub>O and CO<sub>2</sub> as well. Considering that nitrite formation at this temperature is strongly inhibited by the presence of CO<sub>2</sub> (see Figure 8, left side) whereas the amounts of stored NO<sub>x</sub>

is not apparently affected, it is concluded that the nitrate pathway is not affected by CO<sub>2</sub> (and water as well) at 350°C, as already pointed out in a previous work of some of us [14].

The presence of CO<sub>2</sub> also impacts the dead time for NO<sub>x</sub> breakthrough. Inspection of Figures 3, 5 and 7 and of Table 1 clearly points out that in the absence of CO<sub>2</sub> the dead time for NO<sub>x</sub> breakthrough is significant and increases with temperature, whereas in the presence of CO<sub>2</sub> (and of water as well) the dead time for NO<sub>x</sub> breakthrough is not present or very short at any temperature. This picture is consistent with earlier proposal from some of us [14] where the dead time for NO<sub>x</sub> breakthrough has been associated with the occurrence of the nitrite route and to the integral behavior of the reactor. In fact when the storage occurs via the nitrate route, i.e. according to the stoichiometry of the following disproportion reaction:



the dead time for NO<sub>x</sub> breakthrough is expected to be small being the NO<sub>x</sub> storage accompanied by the evolution of NO. This is not the case of the “nitrite” pathway which implies the step-wise oxidation of NO to a surface nitrite over a Pt-Ba couple according to the stoichiometry of the overall reaction (6) [11]. In this light, the decrease of the dead time which is observed upon addition of CO<sub>2</sub> may be tentatively ascribed to the inhibiting effect of CO<sub>2</sub> on the nitrite pathway, mostly at high temperatures.

The inhibition effect of CO<sub>2</sub> on the nitrite route could be ascribed to the different thermal stability of the surface species involved in the storage, i.e. nitrites, nitrates and carbonates, and particularly to the ability of nitrites and nitrates to displace carbonates from surface sites.

In order to investigate the thermal stability of the involved surface species, nitrites, nitrates and carbonates have been individually adsorbed at 100 °C, and evacuated at increasing temperature in the range 100-400 °C (see experimental). Figure 9 shows the integrated intensities of IR absorptions of nitrites (Fig. 9A), nitrates (Fig. 9B) and carbonates (Fig. 9C) in the range 1700-1100 cm<sup>-1</sup> as a function of the evacuation temperature. The integrated intensity of the bands in the presence of the gas phase at

100 °C has been set at 100%. In order to compare thermal stabilities of nitrites, nitrates and carbonates the slopes of the curves in Figure 9 are compared: the greater the slope, the lower the thermal stability is in the considered temperature range. For this purpose, it is important to underline that nitrates and carbonates are present on the catalyst with different geometries (bidentate and ionic) that reasonably show different absorption coefficients. This is not the case for nitrites that show only one geometry. Different absorption coefficients of the different species may invalidate this kind of evaluation if during the desorption process the relative population of the different species changes. This is not the case: during the desorption process at increasing temperature the relative population of different species do not change in a relevant way (spectra not reported for sake of brevity).

As apparent from Figure 9B, nitrates are very stable up to 350 °C: accordingly these species, when formed, are able to displace the less stable carbonate species, being decomposed starting from 100°C (see Fig. 9C). A different picture is apparent in the case of nitrites (Fig. 9A). At low temperature nitrites show comparable stability with respect to carbonates, so nitrites are almost quantitatively formed at the expenses of carbonates. However, at high contact time the displacement of the most stable carbonate species is more difficult, resulting in a lower total amount of stored NO<sub>x</sub> at steady state. On the other hand, at high temperature the nitrite stability is lower than that of carbonates, so nitrites are not able to displace these species. In fact the formation of nitrites results strongly inhibited by CO<sub>2</sub> that lowers of about 60% the maximum amount of nitrites with respect to the case in the absence of CO<sub>2</sub> at 350 °C (Fig. 8).

In summary, the ability of nitrites to displace carbonates from the catalyst surface decreases with increasing temperature, while nitrates are able to displace carbonates at high temperature as well being more stable.

Concerning the role of water, Szanyi et al. [24] demonstrated that in the presence of water surface Ba-nitrates convert to bulk Ba-nitrates. Nevertheless, they showed that the amount of NO<sub>x</sub> taken up at 300

K by the storage material is essentially unaffected by the presence of water. Some of us in a recent paper [25] showed that surface hydroxylation is responsible for the conversion of bidentate nitrates into ionic ones. In the present paper, concerning the role of water (along with CO<sub>2</sub>) on the nitrite formation, inspection of Figure 8 points out that at low temperature water slightly increases the total amount of stored NO<sub>x</sub> with respect to the presence of CO<sub>2</sub> only. This is reasonably due to the transformation of bidentate carbonates into ionic ones operated by water, as mentioned in section 3.1. It is expected that ionic carbonates show different thermal stability with respect to bidentate ones, modifying the total amount of stored NO<sub>x</sub> at steady state. At 250 °C the amount of nitrites is not sensibly modified by water (Fig.8, left side), but the total amount of stored NO<sub>x</sub> (Fig. 8, right side) is significantly lower with respect Ar and CO<sub>2</sub> only, since water inhibits the oxidation of NO to NO<sub>2</sub> and, as a consequence, inhibits the nitrate route. The inhibitor effect of water onto NO oxidation decreases on increasing temperature due to the higher rate of NO oxidation. Accordingly at 350 °C the water effect on the total amount of stored NO<sub>x</sub> is negligible.

#### 4. CONCLUSIONS

The data herein presented converge in indicating that over Pt-Ba/Al<sub>2</sub>O<sub>3</sub> LNT catalyst the storage of NO<sub>x</sub> in the presence of oxygen and CO<sub>2</sub> under dry and wet conditions occurs through two pathways operating simultaneously, as in the absence of CO<sub>2</sub> and H<sub>2</sub>O, i.e. the nitrite and the nitrate pathways. The nitrite route is the unique pathway operating at low temperature (i.e. 150 °C) and involves the formation of surface nitrites only; the nitrate route, operating at higher temperature (i.e. ≥200 °C) along with the nitrite pathway, involves NO oxidation to NO<sub>2</sub> over Pt and its subsequent adsorption on Ba phase in the form of nitrates. Nitrates may also form upon nitrite oxidation.

The combined use of *operando* FT-IR spectroscopy and the transient response method has provided additional information which allowed to highlights the influence of CO<sub>2</sub> and H<sub>2</sub>O on the NO<sub>x</sub> storage.

In particular, the presence of  $\text{CO}_2$  does not significantly affect the  $\text{NO}_x$  storage at low temperature (150 °C) where formation of nitrites only has been observed. This indicates that at low temperatures the nitrite route for  $\text{NO}_x$  storage is not affected by the presence of  $\text{CO}_2$ . On the other hand, the nitrite route is progressively inhibited by  $\text{CO}_2$  upon increasing the temperature, and this results in a decrease of the dead time for the  $\text{NO}_x$  breakthrough that has been associated to the occurrence of the nitrite route. However, since the presence of  $\text{CO}_2$  does not affect the NO oxidation to  $\text{NO}_2$  and the occurrence of the nitrate route with nitrates well able to displace carbonates, the amounts of stored  $\text{NO}_x$  are only slightly decreased by  $\text{CO}_2$  at 350 °C where NO oxidation to  $\text{NO}_2$  is fast. On the other hand, on the basis of gas phase analysis at 250 °C and 150 °C the presence of  $\text{CO}_2$  decreases the amounts of stored  $\text{NO}_x$ . The change with temperature of the inhibition of  $\text{CO}_2$  on the nitrite route can be related to the different thermal stability of nitrites and carbonates on varying temperature, with nitrite ability to displace carbonates that decreases on increasing temperature.

The results obtained during the  $\text{NO}_x$  storage in the presence of  $\text{CO}_2$  in wet conditions are very similar to those obtained in dry conditions at all the temperatures studied, pointing out only a minor effect of water on the  $\text{NO}_x$  storage.

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