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Experimental investigation of the reduction of NO_x species by CO and H_2 over $Pt–Ba/Al_2O_3$ lean NO_x trap systems

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ABSTRACT

In this paper the reactivity of NO_x stored at 350 °C onto $Pt–Ba/Al_2O_3$ LNT catalyst in the reduction by H_2, CO and CO/H_2O mixture is investigated by means of transient experiments and complementary FT-IR analyses.

Hydrogen is found to be the best reductant, being characterized by the highest NO_x removal efficiency in the range 150–350 °C. It is proposed that the reduction by hydrogen proceeds according to a dual-steps mechanism in which NO_x are first reduced to ammonia, which in turn further reacts with other nitrate species leading selectively to N_2.

Conversely, when CO is used as reducing agent under dry conditions only a part of the initially stored NO_x is removed as N_2, the other fraction being reduced to adsorbed cyanates/isocyanates species. It is proposed that the cyanate/isocyanate ad-species lead to the formation of nitrogen by oxidation involving other nitrate species; this reaction is self-poisoned by CO. In the presence of water, CO reduced nitrates into cyanates/isocyanates ad-species that were readily hydrolyzed to ammonia; this species is hence precursor in N_2 formation upon reaction with residual nitrate species. Alternatively, stored nitrates are reduced by H_2 formed via the water gas shift (WGS) reaction.

1. Introduction

Diesel engines are becoming very popular in the most developed countries, and particularly in Europe, since they guarantee reduced fuel consumptions and a decrease of CO_2 production. However, Diesel vehicles are characterized by higher pollutant emissions if compared to stoichiometric gasoline-powered engines, since they are blamed for soot and NO_x emissions. In Europe, to meet the current Euro V regulations for soot emissions, Diesel engines are equipped with particulate filters. However, the next coming Euro VI rules will impose a drastic reduction in the NO_x emissions as well. This will not be obtained with the traditional three-way-catalysts commonly used in stoichiometric engines since they cannot achieve high NO_x removal efficiency in the presence of excess oxygen. Accordingly, different after treatment solutions are now being considered: among these, the NO_x storage-reduction catalysts (or lean NO_x trap systems) are a viable solution for passenger cars and light duty applications [1–3].

Lean NO_x traps (LNTs) or NO_x storage-reduction (NSR) catalysts are constituted by a NO_x storage component (an alkaline or earth–alkaline metal oxide), which stores the NO_x under lean condition, and by a noble metal (Pt) that catalyzes the NO_x storage and operates the NO_x reduction as well, under a short rich period. One typical example of this class of catalysts is $Pt–Ba/\gamma\text{-}Al_2O_3$ [2,3].

Several studies were published on the mechanisms of both the NO_x storage [2–8] and reduction [2,9–14], but a complete understanding of these processes has not yet been achieved. In previous studies [9–12] we have analyzed the reduction process by hydrogen over $Pt–Ba/Al_2O_3$ and $Pt–K/Al_2O_3$ catalysts: it was found that the reduction under isothermal conditions is not initiated by thermal decomposition of stored NO_x ad-species, but a catalytic pathway involving Pt is instead operating [9,10]. It was also showed that the reduction of stored NO_x occurs through a two-steps in series molecular pathway in which NH_3 is intermediate in N_2 production [11,12].

The reduction of stored NO_x by CO has not been deeply investigated so far [15–20]. In a recent work, a preliminary analysis of the reduction by CO of NO_x stored over a model $Pt–Ba/Al_2O_3$ sample and on the pathways involved in N_2 formation has been carried out [15]. It has been observed that under dry conditions cyanates/isocyanates ad-species are produced by reaction of CO with surface nitrates; these species are involved in the formation of nitrogen upon oxidation by other adsorbed nitrate species. In the presence of water cyanates/isocyanates ad-species are readily hydrolyzed to ammonia; as in the case of H_2-reduction, it is suggested that this species is the precursor in N_2 formation upon

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reaction with residual nitrate species. However, a pathway in which hydrogen (formed through the WGSR reaction) is the actual reducing agent of the stored nitrates could not be ruled out.

With the aim of obtaining new insight in the reduction with CO of NO_x stored over a model Pt–Ba/Al_2O_3 NSR catalysts sample, an investigation has been undertaken in our labs by the complementary transient reactive experiments and FT-IR analyses. In particular a series of experiments have been performed in which NO_x has been stored on the catalyst surface at 350 °C and then its reduction has been carried out by admission of a sequence of pulses of CO at different temperatures. This allowed the analysis of the dynamics of the reduction of the stored NO_x ad-species. Experiments have been performed both under dry and wet conditions (i.e. with CO/H_2O mixtures), and with H_2 as well for comparison purposes, and results are discussed below.

2. Materials and methods

2.1. Materials

A model, homemade Pt–Ba/Al_2O_3 (1/20/100, w/w) catalyst was considered in this study. The γ-alumina support was obtained by calcination at 700 °C of a commercial alumina material (Versal 250 from UOP). At first, the Pt/γ-Al_2O_3 (1/100, w/w) sample was prepared by incipient wetness impregnation of the calcined alumina support with aqueous solutions of dinitro-diammina platinum (Stream Chemicals, 5% Pt in ammonium hydroxide); the powder was dried overnight at 80 °C in air and then calcined at 500 °C for 5 h (heating and cooling rate = 1 °C/min). Then, the Pt–Ba/γ-Al_2O_3 catalyst was prepared by incipient wetness impregnation of the Pt/γ-Al_2O_3 powder with an aqueous solution of barium acetate (Stream Chemical, 98.5%). The powders were dried overnight at 80 °C in air and calcined at 500 °C for 5 h. Typical values of surface areas and pore volumes were 137 m^2/g and 0.81 cm^3/g, while Pt dispersion, determined by H_2 chemisorption at room temperature was close to 70% [11]. The alumina support is almost completely covered by Ba, as indicated out by FT-IR data previously reported [8].

2.2. Transient reactive experiments

The transient experiments were performed in a flow microreactor system directly connected to a mass spectrometer (Balzers QMS 200). 60 mg of powder catalyst (sieved at 70–100 μm) and a total flow rate of 100 cc/min (at 1 atm and 0 °C) were used in each run. Two four-port valves were used to perform the abrupt switches between different phases: this guarantee that the overall flow rate in the reactor is always constant since an inert flow entering the reactor is substituted by an equal flow containing the reactant. Care was also taken to avoid all possible dead volumes in the lines before and after the reactor; this allowed a good step shape of the pulses. Finally, a backpressure positioned at the outlet of switching valves allowed the minimization of pressure changes upon switching of the feed gases. Argon, contained in the CO and H_2 cylinders, was used as inert tracer to track the pulses.

The reactor was inserted into an electric furnace whose temperature was controlled by using a K-type thermocouple directly immersed in the catalyst bed. The mass-spectrometer data were quantitatively analysed using the fragmentation patterns and the response factors determined experimentally from calibration gases. Relevant interferences in the mass-to-charge signals were taken into account in determining the products composition. A gas chromatograph (HP 6890) equipped with a Poraplot Q and a 5 Å molecular sieve capillary column was also used for the analysis of CO_2, N_2O, and H_2O, and of O_2, N_2, and CO, respectively. Further details about the experimental apparatus can be found elsewhere [9–12].

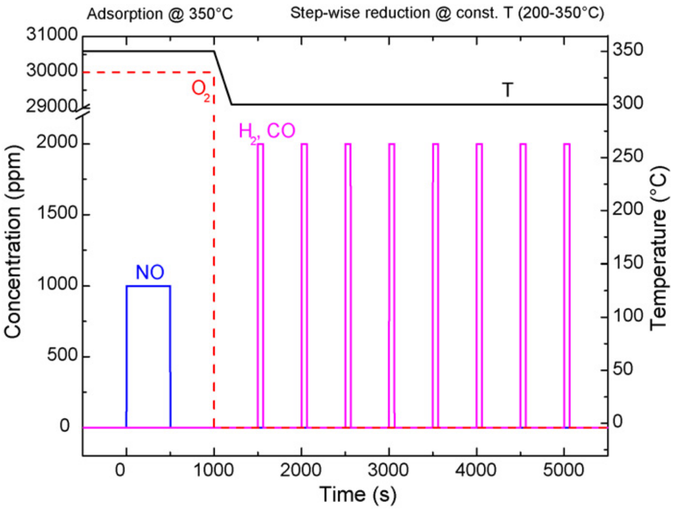

Fig. 1. Typical transient reactive experiment: inlet concentrations of reactants and temperature profile.

A typical transient reactive experiment is shown in Fig. 1, where the inlet concentration of the reactants and the catalyst temperature are sketched as a function of time. NO_x adsorption was carried out at 350 °C by imposing a single step change in the inlet concentration of NO (0–1000–0 ppm) in a stream of He + 3% (v/v) O_2. Then, the oxygen flow was removed from the feed and the temperature was set at the desired value, in the range 200–350 °C. The reduction of the NO_x adsorbed species was then carried out by feeding a sequence of H_2 or CO pulses (2000 ppm in He, pulse length roughly 60 s) at constant temperature. When the reduction process was complete (i.e. when the concentration of the products exiting the reactor was negligible), the sequence of pulses was stopped and the catalyst was heated at 350 °C under He flow. Eventually, an H_2 step (2000 ppm in He) was fed to the reactor at 350 °C to complete the reduction of the residual amounts of nitrates left after the previous reducing treatment, if any. This procedure allowed us to quantify the extent of nitrate reduction during the sequence of H_2 or CO pulses, that is to estimate the efficiency in the reduction of the stored NO_x at the selected temperature (percent fraction of stored NO_x reduced to N_2 and NH_3 during the rich phase). Also, the selectivity to N_2 of the reduction process has also been estimated. Since the N_2 selectivity changes during the pulses, a time-weighted N_2 averaged selectivity has been calculated according to Eq. (a):

$$S_{N_2} = \frac{2n_{N_2}}{2n_{N_2} + n_{NO} + n_{NH_3}} \qquad \text{(a)}$$

where n_{N_2}, n_{NO} and n_{NH_3} are the total molar amounts of N_2, NO and NH_3, respectively, evolved during the rich phase, and calculated by the integrals of the corresponding concentration vs. time curves. N_2O concentration has always been found negligible and accordingly this species has not been included in Eq. (a).

Notably, since the concentration of H_2 or CO was kept low, the reduction process was not accompanied by significant thermal effects, i.e. the reduction of the stored nitrates was carried out under nearly isothermal conditions [9]. In fact, a temperature increase below 2–3 and 1–2 °C was revealed by the thermocouple placed in the catalyst bed in the case of H_2 and CO admission, respectively. Experiments were also performed in the presence of water during the CO pulses: in this case, after NO_x adsorption at 350 °C under dry conditions, the catalyst temperature was set at the desired value and water (1%, v/v in He) was fed to the reactor. Once the mass spec signals were stabilized, a sequence of CO pulses (2000 ppm in flowing He + H_2O 1%, v/v) was admitted to the reactor.

2.3. IR analyses

The reduction of the stored NO_x species was also investigated in parallel by FT-IR *in situ* analyses. IR spectra were collected on self-supporting discs ($10\,mg\,cm^{-2}$) placed in a commercial cell (Aabspec), allowing thermal treatments in controlled atmospheres (in static conditions) and simultaneous registration of spectra up to 600 °C. FT-IR spectra were collected in absorption–transmission on a PerkinElmer FT-IR System 2000 spectrophotometer.

Before the NO_x storage, the samples were submitted to the following steps: (i) outgassing at 550 °C for 30 min; (ii) four or five conditioning cycles consisting of NO_2 adsorption at 350 °C, followed by outgassing at 550 °C, necessary to transform the bulky $BaCO_3$ present on calcined powder into a BaO dispersed phase [21]; (iii) oxidation at 550 °C for 30 min; (iv) cooling in oxygen down to the temperature requested. NO_x storage was carried out at 350 °C by admitting freshly prepared NO/O_2 mixtures ($p_{NO_2} = 5$ mbar, $p_{O_2} = 20$ mbar) for 20 min, outgassing at the same temperature for few seconds and cooling down to RT. The reduction was accomplished both in H_2 ($p = 5$ mbar) or in CO ($p = 5$ mbar) at increasing temperature.

3. Results and discussion

3.1. NO_x adsorption

The results, here not reported for brevity, are similar to those presented elsewhere [8–10]. Upon NO admission to the reactor, the NO outlet concentration presented a dead time and then rapidly increased with time, reaching a steady state value. The evolution of NO_2, due to NO oxidation, was also observed. It was estimated that at the end of the run roughly $3 \times 10^{-4}\,mol/g_{cat}$ of NO_x were adsorbed onto the catalyst surface. Previous FT-IR experiments collected under similar conditions [8] indicated that NO_x were stored primarily in the form of nitrates.

3.2. Reduction by hydrogen

At first the reactivity of hydrogen at 200, 250, 300 and 350 °C with NO_x stored at 350 °C was investigated. For the sake of brevity, Fig. 2A and B shows the results of experiments carried out at 300 and at 200 °C, respectively, in terms of outlet concentration profiles of hydrogen, nitrogen and ammonia.

In the case of the experiment performed at 300 °C (Fig. 2A), from the figure it appears that during the first five pulses H_2 was completely consumed and N_2 (along with water, not shown) was observed at the reactor outlet. The observed N_2 concentration (near 400 ppm) is in agreement with the overall stoichiometry of nitrates reduction by H_2 (reaction (1)):

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + Ba(OH)_2 + 4H_2O \quad (1)$$

During the sixth pulse, hydrogen appeared into the gas phase and its concentration slowly increased approaching the inlet value after 12 pulses. In the meantime the concentration of nitrogen decreased, and evolution of small amounts of ammonia were also detected. Quantitative analysis of data indicated that at the end of the run all the stored NO_x species were reduced to N_2 and/or NH_3 (see Fig. 3), with a selectivity to nitrogen close to 90%.

Fig. 2B shows the results obtained upon reduction at 200 °C of the nitrates stored at 350 °C. In this case a sharp hydrogen peak was observed during the first H_2 pulse, followed by nitrogen evolution. During the subsequent few pulses H_2 is completely consumed and N_2 is formed; the initial H_2 concentration is restored after a few pulses, i.e. 8–9 pulses. Besides, larger amounts of NH_3 were detected at the reactor outlet if compared to those measured at 300 °C. At the end of the pulse sequence the reduction of the stored nitrates was not yet completed as indicated by N_2 formation (and the corresponding H_2 consumption) which was observed during the final H_2 treatment at 350 °C. As a matter of fact, as indicated in Fig. 3, a NO_x removal efficiency as low as 75% was measured in this case, while the selectivity to nitrogen was slightly higher than 80%. N_2O formation was never observed, as documented by the trace of mass-to-charge signal 44 and by direct GC analysis.

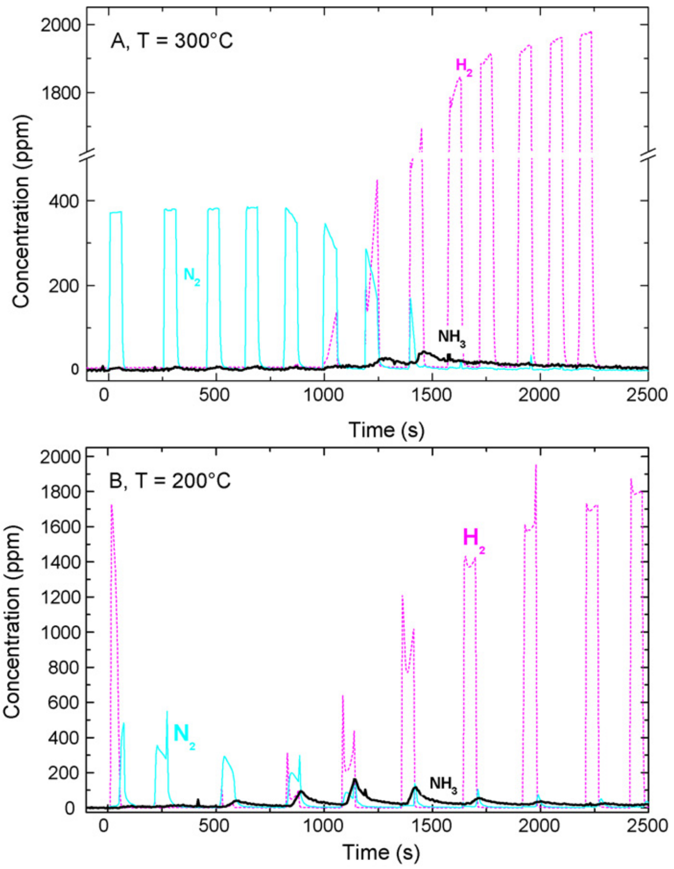

Fig. 2. Transient reactive experiments with H_2 (2000 ppm) at 300 and 200 °C over the $Pt–Ba/Al_2O_3$ catalyst after NO/O_2 adsorption at 350 °C.

These data are fully consistent with those reported in [11] where NO_x adsorbed at 350 °C were reduced at different temperatures in the range 100–350 °C by feeding hydrogen with a single, long pulse:

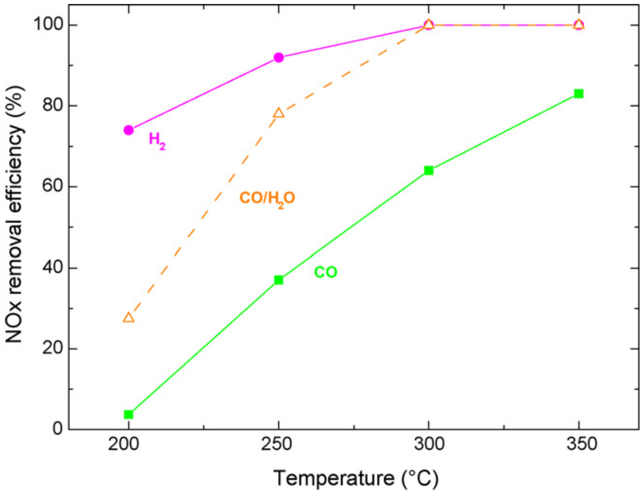

Fig. 3. NO_x reduction efficiency evaluated from transient experiments at different temperatures with H_2, CO and $CO + H_2O$.

indeed also in this case N_2 was initially formed, followed by NH_3 evolution. Furthermore, also in that case an induction period in the hydrogen consumption was observed, possibly associated with an initial adsorption and activation of H_2 on the catalyst surface at this low temperature or with an activation of surface nitrate species. Besides, similar NO_x removal efficiency and N_2 selectivity values were obtained.

The observed results are in line with the in-series two-steps pathway for nitrogen formation suggested elsewhere [11,12] and involving the fast formation of ammonia upon the reaction of nitrates with H_2 (reaction (2)), followed by the slower reaction of so-formed ammonia with the stored nitrates leading to N_2 (reaction (3)):

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + Ba(OH)_2 + 4H_2O \qquad (2)$$

$$3Ba(NO_3)_2 + 10NH3 \rightarrow 8N_2 + 3Ba(OH)2 + 12H_2O \qquad (3)$$

The sum of reactions (2) and (3) leads to reaction (1). Both reactions are catalyzed by Pt, as discussed in [11,12].

Such a scheme, along with the integral "plug-flow" behavior of the reactor, also explains the temporal evolution of reactants and products observed in the experiments shown in Fig. 2. In fact, considering the experiment carried out at 300 °C (Fig. 2A), only nitrogen formation was observed during the first H_2 pulses. This can be explained by considering that the hydrogen fed to the reactor during a pulse is entirely consumed in the initial part of the catalyst bed to give ammonia (reaction (2)); the so-formed ammonia then travels along the reactor where it reacts with nitrates stored downstream, leading to N_2 (reaction (3)). The overall H_2 consumption and N_2 formation is hence explained by the occurrence in series of reactions (2) + (3), i.e. reaction (1).

After several H_2 pulses, the trap becomes almost entirely regenerated and nitrates are left in minor amounts only at the end of the catalyst bed: accordingly ammonia which is formed in this case leaves the trap unreacted, giving the observed NH_3 slip. Of course, a delay in the detection of ammonia due to its adsorption on the lines of the analyzer cannot be excluded.

At low temperature (200 °C, Fig. 2B) a similar picture is evident, but due to the lower reactivity of ammonia towards nitrate species [8], a lower N_2 selectivity was measured.

The reduction of nitrates by hydrogen was also studied by FT-IR by admitting hydrogen at RT on the catalyst sample saturated with NO_x and contacting them for 10 min at increasing temperature. The collected spectra are reported in Fig. 4: no reduction was observed at $T < 150$ °C, hydrogen becomes active toward NO_x reduction only around 150 °C. This is apparent from spectrum b of Fig. 4, showing slight changes in the intensity of the bands with respect to spectrum associated with stored NO_x (spectrum a). In particular a decrease of the band at 1550 cm^{-1} (due to bidentate nitrates [22,23]) and a slight increase of the band at 1420 cm^{-1} (due to ionic nitrates [22,23]) is observed at 150 °C, and this can be taken as proof of the NO_x reduction. However, it is hard to evaluate the actual entity of the reduction, because these changes are the results of two different phenomena, that is (i) the NO_x reduction, producing water, and (ii) the simultaneous hydration of the surface producing a rearrangement of nitrate species, in particular a decrease of bidentate nitrate band accompanied by an increase of bands of the ionic ones. This point was analyzed in dedicated experiments (not reported) during which the interaction of water with the NO_x stored species was investigated. It was found that admission of water to the catalyst on which NO_x were pre-adsorbed leads to a decrease of the bands of bidentate nitrate species accompanied by an increase of the bands of the ionic nitrates.

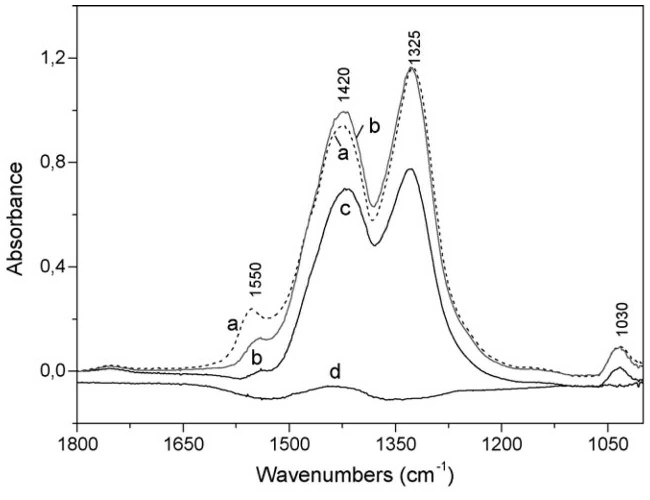

Fig. 4. FT-IR spectra of NO_x reduction in H_2 (5 mbar) at increasing temperatures over the Pt–Ba/Al_2O_3. Curve a, NO_x stored by NO/O_2 adsorption at 350 °C; curves b–d, after 10 min in H_2 at 150, 200 and 250 °C, respectively.

Upon further increasing the temperature, a significant reduction of the stored nitrates was observed, so that NO_x was completely removed at 250 °C (spectrum d in Fig. 4).

FT-IR reduction experiments carried out under isothermal conditions in the 100–350 °C range (not reported), pointed out that at 100 °C the reduction was very slow and not complete even after 1 h of contact, while at 250 °C, the NO_x was completely reduced in the few minutes.

It is worth noticing that no reduction intermediates were detected by FT-IR spectroscopy, nor by running the reduction at low temperature, nor using lower hydrogen pressures, and neither cooling down the sample without outgassing after the reduction to favor the adsorption on catalyst surface of possible intermediate species. In particular, no gaseous NH_3 could be detected, at variance with that observed during microreactor flow experiments (Fig. 2), nor adsorbed NH_3. However, the expected NH_3 amounts produced during the reduction are low, so that they are hardly detectable in gaseous phase by FT-IR spectroscopy, due to the short optical path of the IR cell. Besides, as pointed out by dedicated FT-IR experiments of adsorption (here not reported), NH_3 adsorbs very weakly on Pt–Ba/Al_2O_3 catalyst and thus it could be hardly detected as adsorbed species.

3.3. *Reduction by CO*

The reactivity of CO at 200, 250, 300 and 350 °C with NO_x stored at 350 °C was then investigated. Fig. 5A and B shows the results of the reduction experiments carried out at 300 and at 250 °C, respectively, in terms of outlet concentration profiles of CO, CO_2, nitrogen and ammonia.

At 300 °C (Fig. 5A) during the first four pulses CO was completely consumed and less than 100–150 ppm of N_2 and roughly 1400 ppm of CO_2 were formed. Notably, a nitrogen sharp peak of 500–750 ppm was detected upon the CO shut off: this N_2 peak significantly contributed to the overall N_2 production. Worth of note that dedicated blank experiments, and experiments carried out at different temperatures as well, proved that the observed N_2 peak is not an artifact but originates from a truly catalytic process.

Then, after the forth CO pulse, both the nitrogen and CO_2 concentrations decreased and CO appears at the reactor outlet, slowly recovering the inlet value. A decrease in the nitrogen peak observed at the end of the CO pulse was also observed.

It is worth noticing that nitrogen formation and CO consumption did not obey the stoichiometry of the expected reduction of nitrates by CO, reaction (4):

$$Ba(NO_3)_2 + 5CO \rightarrow BaCO_3 + N_2 + 4CO_2 \qquad (4)$$

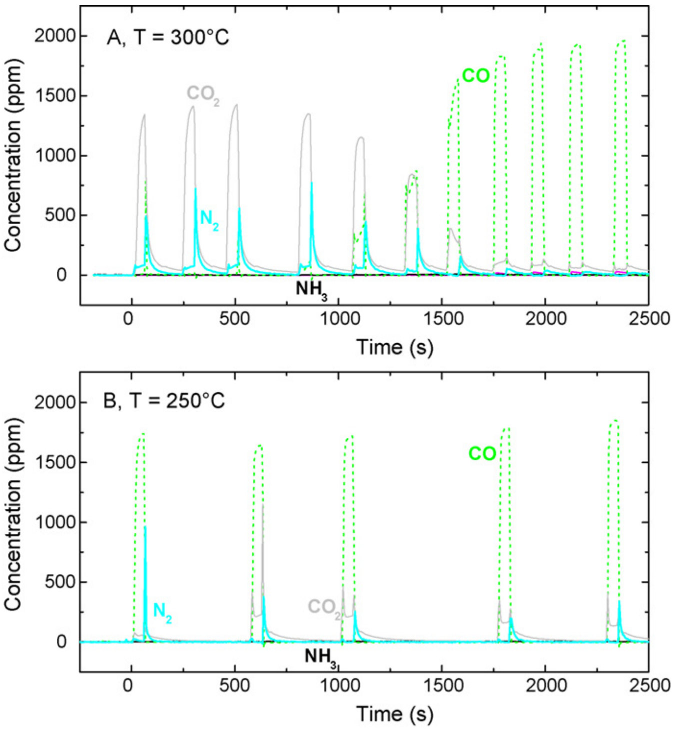

Fig. 5. Transient reactive experiments with CO (2000 ppm) at 300 and 250 °C over the Pt–Ba/Al_2O_3 catalyst after NO/O_2 adsorption at 350 °C.

In fact the amounts of N_2 released during the CO pulses experiment were lower than those expected from reaction (4). This point will be discussed below. Besides, as shown in Fig. 3, the stored nitrates were not completely removed at the end of the reducing phase, and the estimated overall NO_x removal efficiency (i.e. the fraction of NO_x stored at 350 °C that is reduced to N_2 and NH_3 during the whole regeneration period) was slightly higher than 80%.

In the case of the run performed at 250 °C (Fig. 5B), a different picture was apparent: in fact, N_2 was not produced during the CO pulse, but only upon CO shut off, along with small amounts of CO_2. Accordingly the data indicate that at such a low temperature CO is poorly reactive and indeed a NO_x removal efficiency lower than 40% was evaluated in this case (Fig. 3).

To gain additional information on the reactivity of CO towards the adsorbed nitrates, FT-IR studies have been performed by admitting CO at 200, 250, 300 and 350 °C on the catalyst with adsorbed NO_x species, and contacting them for 10 min. Fig. 6 shows the results of experiments carried at 250 and 300 °C: both carbonate-like (bands at 1557, 1350 and 1060 cm^{-1} [24–26]) and cyanate/isocyanate-like (band at 2230 cm^{-1} and shoulder at 2175 cm^{-1} [27]) species sensibly increase by reduction at 250 °C while nitrates (bands at 1557, 1420, 1325 cm^{-1}) decrease (spectrum b). At 300 °C the nitrates were almost completely absent (spectrum c) and the bands related to cyanate/isocyanate species were strongly increased in intensity and shifted, as expected, at lower wavenumbers (2222 and 2165 cm^{-1}), as result of the increased surface coverage.

It is also worth noticing that in all the experiments, after CO admission FT-IR spectra showed a band related to the stretching modes of linear carbonyls adsorbed on Pt sites, with intensity and frequency (2070–2035 cm^{-1}) depending from the temperature and time of contact. In fact, the vibration frequency is strictly related to the extent of the reduction of the Pt phase [28] and to the CO coverage of the Pt particles [29].

The information derived by the combined analysis of transient reactive experiments and FT-IR spectra pointed out that during the reduction of stored NO_x by CO different reactions occur: nitrates are indeed reduced to nitrogen (revealed by transient experiments) according to overall stoichiometry (4), but they are also reduced to isocyanate species (whose formation was evidenced by FT-IR) according to reaction (5):

$$Ba(NO_3)_2 + 8CO \rightarrow Ba(NCO)_2 + 6CO_2 \quad (5)$$

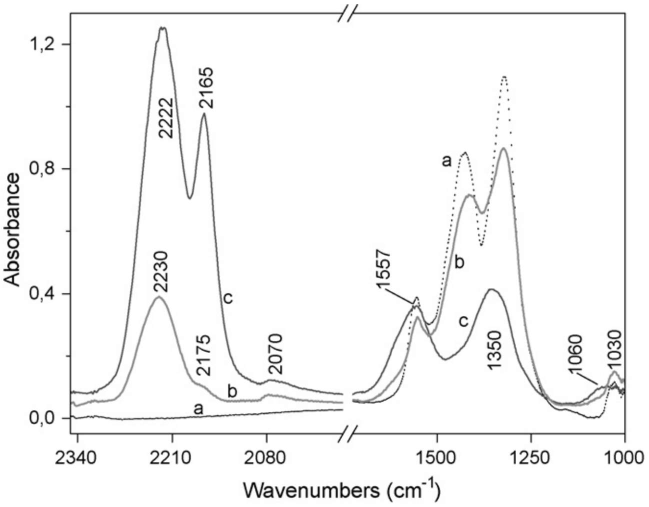

Fig. 6. FT-IR spectra of NO_x reduction by dry CO (5 mbar) at increasing contact temperature over the Pt–Ba/Al_2O_3. Curve a, NO_x stored by NO/O_2 adsorption at 350 °C; curves b and c, after 10 min in CO at 250 and 300 °C, respectively.

Notice that in reactions (4) and (5) the participation of Ba bulky species was considered for simplicity, but the involvement of surface species is most likely. Isocyanate/cyanate species are stable and remain adsorbed on the catalyst surface after the end of the reducing procedure.

Reactions (4) and (5) are able to describe the transient experiments presented in Fig. 5. In fact the N_2 production is lower than CO consumption according to the stoichiometry of reaction (4), due to the simultaneous formation of isocyanate/cyanate ad-species according to reaction (5). For instance in the run carried out at 300 °C, 0.63 10^{-4} mol/g_{cat} of nitrogen were produced; based on the amounts of CO_2 produced and of CO consumed, it is calculated that roughly 1.24×10^{-4} mol/g_{cat} of NCO species were simultaneously formed.

Concerning N_2 formation via reaction (4), it is speculated that NCO ad-species are intermediate in this reaction. It may be argued that nitrates are reduced by CO to NCO species (reaction (5)), which eventually lead to nitrogen formation by oxidation with unreacted nitrate species adsorbed close-by or spilling over the surface (reaction (6)):

$$5Ba(NCO)_2 + 3Ba(NO_3)_2 \rightarrow 8N_2 + 8BaCO_3 + 2CO_2 \quad (6)$$

It is indeed well known that NCO species are easily oxidized to N_2 and CO_2 by oxidant molecules like O_2 [18–20]; in line with previous suggestions reported by Szailer et al. [20], the oxidation of cyanates to N_2 could be carried out by other oxidants like surface NO_x species, this step being rate determining in N_2 formation. The occurrence of reaction (6) is also in line with the well known capability of O_2 to oxidize NCO species to N_2 [16,18–20].

Notably, a N_2 peak is also observed at the end of the CO pulse (see Fig. 5). This is a genuine N_2 production, as pointed out by blank experiments and by the observation that it changes during the various pulses and with temperature as well. As discussed elsewhere [15], this can be explained on the basis of self-poisoning effect of CO on the Pt active sites. As a matter of fact, IR data showed the formation of bands attributed to carbonyls species on

Pt sites (2070–2056–2035 cm^{-1}), which poisoned the active Pt sites [16,17]. It is hence speculated that at 300 °C the N_2 formation is self-inhibited by CO-poisoning of Pt at the beginning of the CO pulse. However, at the end of each CO pulse, upon CO shut off the Pt-carbonyls decompose and the reactivity of Pt is restored, possibly leading to the N_2 peak observed in Fig. 5. Such explanation is consistent with the fact that the nitrogen production upon CO shut off was observed to increase with decreasing temperature in the range 150–350 °C (compare for example experiments at 300 and 250 °C in Fig. 5) due to the increased stability of Pt-carbonyls at lower temperature. It turns out that reaction (6) is catalyzed by Pt: due to the participation of cyanate/isocyanate species and of nitrate species related to Ba, it is expected that the Pt–Ba interaction is relevant in the reaction. These points are presently under investigation in our labs.

3.4. Reduction by CO in the presence of water

Finally the effect of the presence of water in the feed stream was investigated when CO was used as reducing agent. For this purpose, transient reactive experiments analyzing the reduction of nitrates stored at 350 °C over the Pt–Ba/γ-Al_2O_3 catalyst were performed at different temperatures (in the range 150–350 °C) by feeding pulses of CO in a flow of He + 1% (v/v) water. Fig. 7A and B shows the results of the reduction carried out at 300 and at 250 °C, taken as example.

At 300 °C (Fig. 7A) CO was totally consumed during the first pulses and the evolution of N_2 (roughly 360 ppm) and CO_2 (not reported) was observed. Then, after a few pulses, the N_2 concentration started to decrease and H_2 evolution was observed, followed by small amounts of ammonia. Notably, no significant evolution of CO was observed, being almost completely transformed into H_2 via water gas shift (WGS) reaction. Quantitative analysis of data indicated that at the end of the run all NO_x adsorbed species were removed (see Fig. 3).

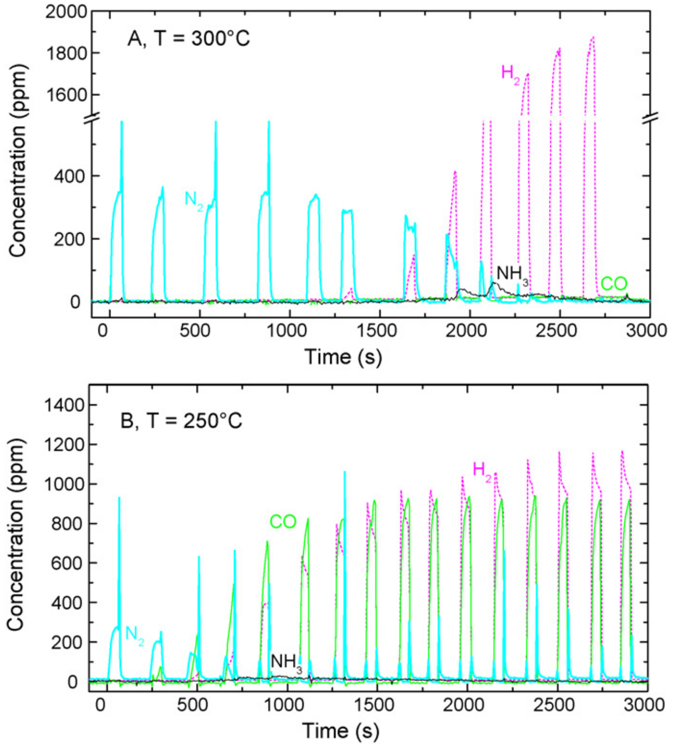

Fig. 7. Transient reactive experiments with CO (2000 ppm) + H_2O (1%, v/v) at 300 and 250 °C over the Pt–Ba/AlO_3 catalyst after NO/O_2 adsorption at 350 °C.

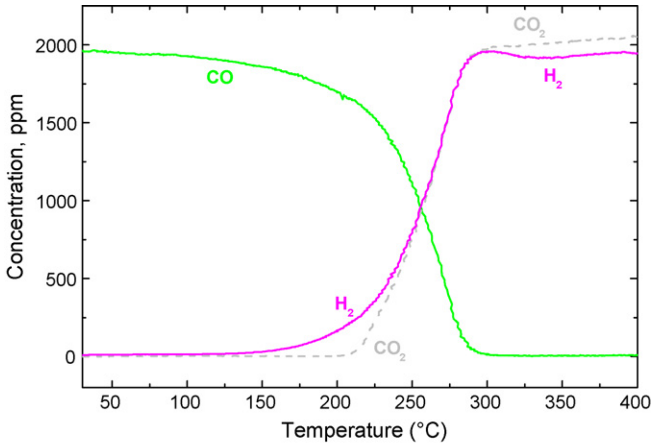

Fig. 8. TPR run in 2000 ppm CO + 1% (v/v) H_2O over the Pt–Ba/Al_2O_3 catalyst.

A different situation is apparent when the reduction of the nitrates stored at 350 °C was carried out at 250 °C (Fig. 7B). Indeed in this case unreacted CO was observed at the reactor outlet already from the second pulse, along with hydrogen. The CO and H_2 concentration progressively increased with the pulse number and eventually reach a steady concentration where the CO conversion is near 50%. N_2 formation was also observed, with amounts decreasing with the pulse number, so that after four pulses the N_2 formation was small. Notably, after the fourth CO pulse, N_2 evolution occurs preferentially upon CO shut off. Quantitative analysis of data indicated that at the end of the runs 80% of the initially NO_x adsorbed species were removed as N_2/NH_3 (see Fig. 3).

A comparison of Fig. 7 with Fig. 5 clearly show that water has a significant impact on the reduction of the stored NO_x by CO, particularly above 250 °C. This is likely related to the formation of H_2 according to the water gas Shift (WGS) reaction (7):

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (7)$$

As pointed out above, H_2 is by far a better reductant than CO. Accordingly, to better analyse the reactivity of the selected catalyst sample in the WGS reaction and the related formation of H_2, an experiment was performed by feeding CO (2000 ppm) and water (1%, v/v) at RT and then increasing linearly the temperature (10 °C/min) up to 400 °C. Aim of this run was to point out the temperature threshold of the WGS reaction. The results, shown in Fig. 8, clearly pointed out that CO is consumed starting from 150 °C, with the simultaneous production of hydrogen in line with the stoichiometry of the Water Gas Shift reaction (7). CO_2 evolution is also observed, as expected according to the stoichiometry of reaction (7), with a delay possibly related to the adsorption on the Ba sites with formation of Ba carbonate. Almost complete CO conversion is obtained at 280 °C.

Accordingly, it appears that the WGS reaction proceed very efficiently and already at low temperature on the Pt–Ba/Al_2O_3 sample. It is speculated that the reactivity of CO in the reduction of stored NO_x in the presence of water is enhanced due to the occurrence of the WGS reaction, leading to the formation of H_2 which, as previously shown, is much more reactive than CO. As a matter of fact, Fig. 3 points out that the NO_x removal efficiency values with CO in the presence of water are similar at high temperature to those measured with hydrogen, possibly suggesting that due to CO self-poisoning of the Pt active sites the reaction is controlled by the reactivity of the catalyst in the WGS reaction. Accordingly it is suggested that hydrogen, produced via WGS reaction, operates the reduction of the stored nitrates when the reduction is carried out by CO in the presence of water. However, other pathways may also operate, as discussed in the following.

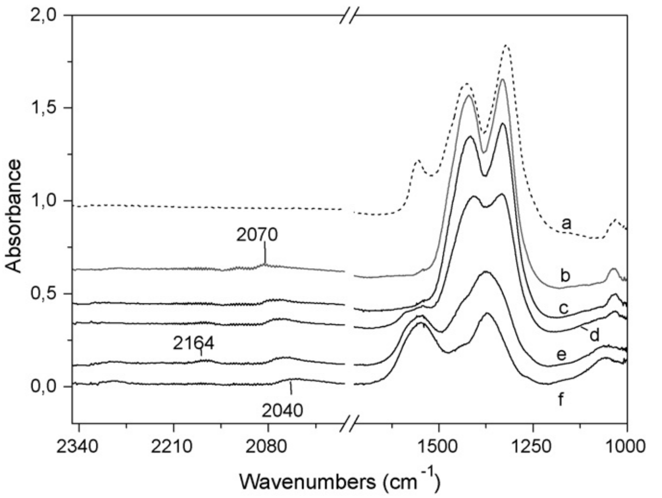

Fig. 9. FT-IR spectra of NO_x reduction by wet CO (p_{CO} = 5 mbar, p_{H_2O} = 10 mbar) at increasing temperatures over the Pt–Ba/Al_2O_3. Curve a, NO_x stored by NO/O_2 adsorption at 350 °C; curves b–f, after 10 min in wet CO at 150, 200, 250, 300 and 350 °C, respectively. Curves a–e were shifted for sake of clarity.

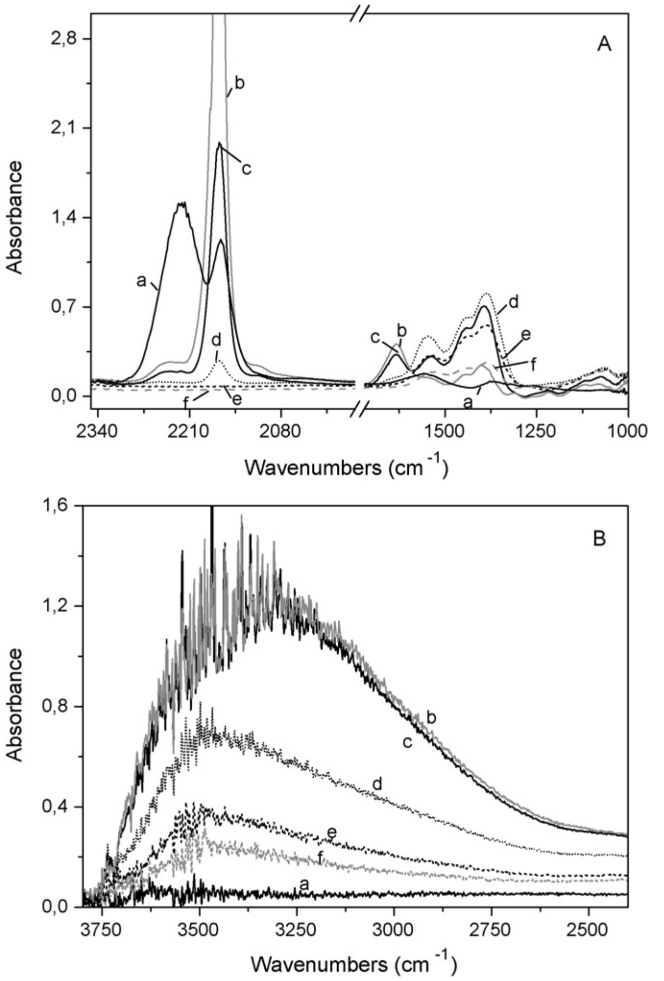

Fig. 10. FT-IR spectra of the surface cyanate/isocyanate evolution by interaction with water. Curve a, cyanate/isocyanate species formed by reduction at 350 °C in dry CO (5 mbar, 1 min of contact), evacuated at 350 °C for 10 min and cooled down to RT. Curves b and c, 1 min and 1 h at RT, respectively, after admission of water (10 mbar); curves d–f, subsequent heating in water for 10 min at 150, 250 and 360 °C, respectively.

The reduction of nitrates by CO in the presence of water was also investigated by FT-IR analyses. Fig. 9 shows the spectra collected admitting simultaneously CO and water (p_{CO} = 5 mbar, p_{H_2O} = 10 mbar) over a catalyst pre-saturated with nitrates and contacting them for 10 min at increasing temperature from 150 °C up to 350 °C. At 150 °C the bands due to bidentate nitrates (band at 1550 cm^{-1}) completely disappeared, while those related to the ionic nitrates sensibly increased (bands at 1420, 1325 cm^{-1}). Two process can be taken into account for these changes: the hydration of the surface producing the re-arrangement of the nitrate species, as discussed above, and a certain degree of reduction of bidentate species that is not possible to evaluate from this experiment. Then, starting from 200 °C, the reduction of ionic nitrates was evident: it increased with temperature and was complete at 350 °C. However, only bands related to the formation of carbonates and no bands related to cyanates/isocyanates species appeared, if one exclude a very weak bands at 2230 cm^{-1} present after reduction at 300 °C. Also in this case FT-IR spectra showed a band (2070–2030 cm^{-1}) related to the stretching mode of linear Pt-carbonyls.

Such behaviour is consistent with the effect of water on isocyanates species, that was analyzed separately by dedicated FT-IR experiments and illustrated in Fig. 10. After the formation of isocyanates by reduction at 350 °C in dry CO, the catalyst was evacuated at 350 °C for 10 min and cooled down to RT (curve a in Fig. 10A). Then it was contacted with water (10 mbar) at RT at increasing times (curves b and c); eventually the temperature was increased at 150, 250 and 350 °C the contact times being 10 min at each temperature (curves d–f).

Two processes can be observed. The first one, completed during the first 60 s of contact at RT (Fig. 10A, curve b), was the complete transformation of isocyanates species responsible for the band at 2230–2222 cm^{-1} into the ones responsible for the band at 2175 and 2165 cm^{-1}. These last ones are characteristic of an high hydrated surface, such as that obtained in this condition (see the presence of a band at 1630 cm^{-1} due to the bending mode of the molecular water; see also the broad band at about 3300 cm^{-1} in Fig. 10B due to the stretching of the molecular water and of surface hydroxyls).

The second process, slower than the first one (Fig. 10A, curve c: recorded after 1 h of contact at RT), was responsible for the decrease of the isocyanate/cyanate bands and for the simultaneous increase of bands in the 1550–1000 cm^{-1} region. The main bands at 1540, 1440, 1381 and 1060–70 cm^{-1}, which increases with contact time, are assigned to carbonate-like species, in particular the 1440 cm^{-1} one to ionic and the others ones to mono-dentate carbonates [26]. This process was almost complete at 150 °C (Fig. 10, curve d), simultaneously with the marked decrease of the band at 1630 cm^{-1} of the molecular water. The dehydration was also well visible in the OH stretching region. At 250 and 350 °C the surface dehydration continued, and at the same time the bands in the 1550–1000 cm^{-1} region sensibly decreased (Fig. 10, curves e and f) indicating a also carbonate desorption.

The results of FT-IR experiments are in nice agreement with data reported in literature [18] for NCO species adsorbed on Ag/Al_2O_3 catalyst: it was found that water hydrolyses NCO species very rapidly and already at very low temperature, according to reaction (8), producing CO_2 and ammonia:

$$Ba(NCO)_2 + 3H_2O \rightarrow BaO + 2NH_3 + 2CO_2 \qquad (8)$$

These results suggest that in the presence of water a pathway for nitrate reduction by CO is operating which involves the intermediate formation of NCO species. In the presence of water these species are readily hydrolyzed by water to ammonia, as opposite to what observed under dry conditions where a fraction of isocyanate/cyanate species were oxidized to nitrogen by the stored nitrates. Accordingly ammonia may play as intermediate (as in the case of the reduction by H_2) in the formation of N_2, according to the stoichiometry of reactions (8) + (3). However, a role played by water in increasing the reactivity of isocyanates/cyanates that in turn can react more readily with nitrates to give nitrogen, cannot be ruled out.

Hence, it appears that different routes may be active in the reduction of NO_x species by CO under wet conditions. A pathway involves hydrogen, formed via the WGS reaction. As a matter of fact, it has been shown that the $PtBa/Al_2O_3$ catalyst sample is very active in the WGSR (see Fig. 8). A different pathway may involve the reduction of nitrates by CO leading to the formation of isocyanates: these species are readily hydrolyzed to ammonia, which is eventually involved in the reduction of residual nitrates to N_2. Additional pathways can be suggested, possibly involving other N-containing reduced intermediates; besides a role of water in favoring the reactivity of isocyanates with nitrates to give nitrogen can also be invoked. These aspects are currently under investigation in our labs with the aim of identifying which of the different pathways is prevailing under realistic operating conditions.

4. Concluding remarks

In this paper the reactivity of NO_x stored at 350 °C over a model $Pt–Ba/Al_2O_3$ catalyst with different reducing agents, hydrogen and CO, was studied at different temperatures by means of transient reactivity experiments and FT-IR.

It was found that the admission at 350 °C of several H_2 pulses to the catalyst pre-saturated with NO_x at the same temperature results in the complete consumption of the reductant, and in the immediate selective formation of N_2. After few pulses, hydrogen appeared into the gas phase and the concentration of nitrogen decreased, while evolution of ammonia was observed. When the regeneration of the nitrates stored at 350 °C is carried out at lower temperatures, the ammonia formation is increased, and the removal of the stored NO_x is not complete. These results are in line with the previously proposed reaction scheme for the reduction of the stored NO_x involving a in-series two-steps pathway for nitrogen formation with an initial fast formation of ammonia upon the reaction of nitrates with H_2, followed by a slower reaction of so-formed ammonia with the stored nitrates leading to N_2.

When the reduction of the nitrates stored at 350 °C was carried out using CO as reducing agents, it was found that the admission of CO at the same temperature under dry conditions resulted in the production of nitrogen and CO_2. Calculations showed that N-containing species were still left onto the catalyst at the end of the reduction. Based on FT-IR analysis, it was found that, besides carbonates, $^{-}N{=}C{=}O$ (isocyanates) and/or $N{\equiv}C{-}O^{-}$ (cyanates) were formed. Also, bands relative to carbonyls species on Pt sites were identified. Accordingly when CO is used as reducing agent, the stored nitrates were reduced in part to N_2, and in part to adsorbed cyanates/isocyanate species.

It was also speculated that formation of NCO species is intermediate in formation of nitrogen as well: indeed cyanate/isocyanate species could lead to nitrogen formation via oxidation by other nitrate species, as suggested in the literature.

The use of CO as reducing agent was also addressed in the presence of water in the feed stream. Reactivity data showed that water enhanced the reactivity of CO: indeed, at 350 °C the NO_x removal efficiency was almost complete. Besides, along with nitrogen and CO_2, significant amounts of ammonia and hydrogen were found among the reaction products. FT-IR spectra confirmed the beneficial effect of water on the NO_x removal by CO; besides, in the presence of water NCO species were not observed.

It is suggested that in the presence of water the reduction of the stored NO_x may be accomplished by different pathways. It may be argued that NCO species are formed upon reaction of nitrates with CO; these species are readily hydrolyzed to CO_2 and ammonia, which is a very good reducing agent of nitrates and is eventually involved in the reduction of residual nitrates to N_2. However, a role played by water in increasing the reactivity of isocyanates that in turn can react more readily with nitrates to give nitrogen, cannot be ruled out.

A different pathway may also be invoked. Indeed, the formation of large amounts of H_2 during the reduction of nitrates by CO under a wet environment pointed out that the $Pt–Ba/Al_2O_3$ catalyst effectively catalyzes the water gas shift reaction at temperature as low as 175 °C, as pointed out by dedicated $CO + H_2O$ experiments. Accordingly it may be speculated that the reduction of the stored nitrates by CO under wet conditions involves hydrogen, formed via the WGSR, as actual reductant.

Finally it is worth mentioning that the pathways previously suggested for the formation of N_2 during the reduction of NO_x adsorbed species with hydrogen, CO or CO/H_2O mixtures shows a common peculiarity, i.e. the formation of N-containing key intermediates in which the N formal oxidation state equal to -3 (NH_3 in the case of the reduction by hydrogen and CO/H_2O mixtures, cyanates/isocyanates in the case of CO under dry conditions). Note that in this last case, only the involvement of adsorbed species is likely involved in the reduction of the stored nitrates. Mechanistic aspects involved in the formation of N_2 in the reduction of stored NO_x over LNT catalysts are presently under investigation in our labs, and results will be reported in a forthcoming paper.

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