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Reaction pathway of the reduction by CO under dry conditions of NO_x species stored onto Pt—Ba/Al_2O_3 Lean NO_x Trap catalysts

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ABSTRACT

The reduction by CO under dry condition of NO_x species stored at 350 °C onto a Pt—Ba/Al_2O_3 Lean NO_x Trap catalyst is investigated by means of transient response methods (CO-TPSR and CO-ISC experiments) and complementary FTIR spectroscopy. It is shown that the reduction by CO under nearly isothermal conditions of nitrates stored onto Pt—Ba/Al_2O_3 occurs through a Pt-catalyzed pathway which leads mainly to nitrogen and does not proceeds via the thermal decomposition of stored nitrates with release of NO_x in the gas phase. The CO-TPSR and CO-ISC experiments and the combined FTIR study show that (i) the reduction of nitrates by CO occurs via a consecutive reaction scheme with formation of nitrites and then of surface isocyanate/cyanate species followed by the reaction of these species with residual nitrites to give nitrogen; (ii) the reaction of NCO species with nitrites to give nitrogen is slower than the reduction of nitrates to give nitrites and then NCO species; (iii) upon contact with oxygen at increasing temperature, NCO species can be re-oxidized to surface nitrites at first and then to surface nitrates; (iv) the formation of nitrogen is observed during the reduction of stored NO_x by CO, and during the oxidation of surface NCO species upon oxygen addition and upon admission of NO in the presence of excess O_2. In all cases, the formation of nitrogen can be explained by the reaction between surface NCO species and nitrites. The mechanism for the reduction of stored NO_x by CO under dry and near isothermal conditions is discussed.

1. Introduction

Lean NO_x Traps (LNTs), also referred to as NO_x storage-reduction (NSR) catalysts, represent a viable technology for the reduction of NO_x emissions from light duty diesel engines and lean burn gasoline engines [1–3]. Their operation comprises a lean period of 30–90 s during which the NO_x emitted in the exhaust gases are adsorbed on the catalyst surface in the form of nitrites and nitrates, followed by a short 3–5 s rich period during which the stored NO_x are reduced by H_2, CO and unburned hydrocarbons to give N_2. The LNT catalysts typically consist of a NO_x storage component, such as Ba or K, and of a noble metal such as Pt. This latter catalyzes the oxidation of NO and the combustion of CO and unburned hydrocarbons during the lean period, and the reduction of stored NO_x during the rich period; the catalysts components are dispersed on high surface area support like alumina.

Several studies were published on the reduction of stored NO_x using hydrogen as reducing agent [3–17]. In previous works, some of us have shown that the reduction by H_2 under near isothermal conditions of nitrates stored onto Pt—Ba/Al_2O_3 and Pt—K/Al_2O_3 is not initiated by the thermal decomposition of nitrates/nitrites ad-species with release of NO_x in the gas phase but involves a Pt-catalyzed pathway which is active at low temperature and leads to nitrogen [4,5]. It has also been proposed that under near isothermal conditions N_2 is formed exclusively via a consecutive reaction scheme which involves the fast reaction of H_2 with stored NO_x to give ammonia followed by the slower reaction of ammonia with residual stored NO_x to give N_2 [6–8]. On the opposite, Pihl et al. [9] and Cumaranatunge et al. [10] suggested that upon switch from lean to rich conditions the stored NO_x are at first released to the gas phase. In the operation of a real system, the NO_x release is caused primarily by the exotherm generated by the reaction between fuel and excess oxygen in the gas phase or oxygen stored in the catalyst upon the rich spike. However, the decrease in O_2 and NO_x gas-phase concentrations, which destabilizes the stored nitrates, may also contribute to the NO_x release. Then, the regeneration of the NO_x Trap occurs via dissociative adsorption of gaseous NO and of hydrogen at metal Pt to form Pt—N, Pt—O and Pt—H species followed by recombination of surface Pt—N species to give nitrogen and by recombination of surface Pt—N and Pt—H species to give ammonia according to a parallel pathway. However, the selective catalytic reduction of NO_x with ammonia and the oxidation of ammonia to give nitrogen are also considered in the schemes.

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Several authors have also postulated a spillover mechanism involving oxygen from Pt to Ba during the NO_x storage and a reverse spillover involving nitrites/nitrates from Ba to Pt during the reduction [11–13]. This explains why the NO_x storage and reduction is improved when the Pt is in close proximity to the Ba [11,14–16] and also accounts for the participation to NSR of a large percentage of Ba [17].

The reduction by CO of NO_x stored on LNT catalysts has attracted lower interest. It has been reported that stable isocyanates/cyanates are formed during the reduction of stored NO_x by CO; these species are hydrolyzed into ammonia which then react with NO or stored NO_x in the presence of oxygen to give nitrogen [18–20]. The reactivity of isocyanates/cyanates with O_2 to give N_2 and CO_2 was observed over Pt—Rh/Ba/Al_2O_3 and Ag/Al_2O_3 catalysts by Daturi and coworkers using FTIR spectroscopy [20,21] and by Scholz et al. over a Pt—Ba/γ-Al_2O_3 catalyst performing lean-rich cycling experiments [22]. The hydrolysis of surface NCO species to give ammonia and carbon dioxide has been also reported by Daturi and coworkers [20]. Furthermore, FTIR analysis performed at low temperatures (i.e. 150 °C) over Pd/Al_2O_3 catalysts showed that isocyanate/cyanate species react upon adding NO/O_2 mixtures to the feed flow. The mechanism of the reduction of stored NO_x by H_2 and by CO over LNT catalysts under dry conditions has been discussed by Szailer et al. [19]. The proposed mechanism assumes as a first step the thermal decomposition of stored NO_x with release of NO_x in the gas phase followed by dissociative re-adsorption onto the Pt sites with rearrangement, formation of adsorbed NCO species which eventually react with NO_x to give nitrogen.

In this paper, a systematic and quantitative study of the reduction by CO under dry conditions of NO_x stored onto a Pt—Ba/Al_2O_3 LNT catalyst is carried out to clarify the reaction pathway and the mechanism of the reaction. Transient reactivity methods and complementary FTIR spectroscopy are employed to obtain information on the nature, reactivity and evolution of reagents, intermediates and products both in the gaseous phase and at the catalyst surface. In order to prevent the thermal decomposition of nitrates with release of NO_x in the gas phase during the lean/rich switches that complicates the description of the reacting system, experiments have been performed under nearly isothermal conditions, i.e. in the absence of significant temperature effects during cycling. This has been accomplished using low CO concentration and by separating the lean and the rich phases by an inert purge in between. Accordingly, a more precise rationalization of the catalytic behavior and a better understanding of the chemical processes occurring during the lean/rich cycling could be obtained.

2. Experimental

2.1. Materials

Ba/Al_2O_3 and Pt—Ba/Al_2O_3 catalysts were prepared by the incipient wetness impregnation method, using aqueous solutions of $Ba(CH_3COO)_2$ (Strem Chemical, 99%) and $Pt(NH_3)_2(NO_2)_2$ (Strem Chemicals, 5% Pt in ammonium hydroxide) to impregnate the γ-alumina support calcined at 700 °C (Versal 250 from La Roche Chemicals, surface area of 200 m^2/g and pore volume of 1.2 cm^3/g). In the case of the Pt—Ba/Al_2O_3 catalyst, the impregnation was carried out in sequential manner: the alumina support was first impregnated with the Pt-containing solution and then with the Ba acetate solution. After each impregnation step, the catalysts were dried at 80 °C overnight and then calcined at 500 °C for 5 h. The final loading was 20/100 w/w for the Ba/Al_2O_3 catalyst and 1/20/100 w/w for the Pt—Ba/Al_2O_3 catalyst. The following surface areas and pore volumes were measured by N_2 adsorption–desorption at 77 K: 133 m^2/g and 0.82 cm^3/g for the Ba/Al_2O_3 sample; 137 m^2/g and 0.81 cm^3/g for the Pt—Ba/Al_2O_3 sample. The Pt dispersion, as determined by H_2 chemisorption at 0 °C, was ~70% [24].

2.2. Reactivity tests

The reactivity tests were performed over the Pt—Ba/Al_2O_3 and the Ba/Al_2O_3 samples previously conditioned. In the case of the Pt—Ba/Al_2O_3 sample, conditioning involves a few adsorption/reduction cycles with NO/O_2 (1000 ppm NO and 3% v/v O_2 in He) and H_2 (2000 ppm in He) at 350 °C, respectively, with an inert purge (He) between the two phases. Conditioning was done until a reproducible behavior was obtained and this typically required 2 or 3 cycles [4,7]. For the Ba/Al_2O_3 binary catalyst, which does not adsorb significant amounts of NO [25] and do not react with H_2, the adsorption was carried out with NO_2 (1000 ppm in He), and the adsorbed NO_x were removed by heating at 500 °C. Like Pt—Ba/Al_2O_3, also in the case of Ba/Al_2O_3 large amounts of NO_x are stored on the catalyst surface in the form of nitrate species [25].

Temperature-programmed surface reaction experiments (TPSR) were carried out in the presence of CO as reducing agent to analyze reactivity of adsorbed nitrates. Before performing TPSR runs, the catalysts were saturated with NO_x at 350 °C by imposing a rectangular step feed of NO (0 → 1000 ppm → 0) in flowing He + 3% v/v O_2. For the Ba/Al_2O_3 catalyst, the adsorption was carried out with NO_2 (1000 ppm in He) instead of NO + O_2. The NO + O_2 (or NO_2) flow was maintained up to catalyst saturation and then the inlet NO + O_2 (or NO_2) concentration was decreased to zero. The samples were then kept under inert He flow for about 1 h at 350 °C to provoke the desorption of weakly adsorbed species (He purge). The samples were then cooled down to RT under flowing He [4,7] and then heated at 15 °C/min up to 400 °C in He + 2000 ppm CO (CO-TPSR).

The storage/reduction of NO_x over Ba/Al_2O_3 and Pt—Ba/Al_2O_3 was also performed at constant temperature by imposing stepwise changes in the inlet concentration of the reagents (Isothermal Step Concentration experiments, ISC), according to the following sequence. After catalyst conditioning, the storage of NO_x (lean phase) was accomplished at 350 °C for about 150 s using the same conditions reported for CO-TPRS experiments. After storage, the NO + O_2 (or NO_2) concentration was decreased to zero, while maintaining the same temperature (He purge). The reduction of the stored NO_x was then carried out by imposing a stepwise change in the CO inlet concentration (0 → 2000 ppm → 0) in flowing He (Rich phase). Three or four cycles have been carried out until a steady cyclic catalytic behavior was obtained.

The experiments were carried out in a flow micro-reactor system consisting of a quartz tube reactor (7 mm internal diameter) directly connected to a mass spectrometer (Balzers QMS 200). In order to minimize intra- and inter-particle diffusion limitations, 60 mg of catalyst with small particle diameter (100–120 μm) and a total flow rate of 100 cc/min (at 1 atm and 0 °C) were used in each run. The flow rates of the gases were measured and controlled by mass-flow controllers (Brooks 5850 TR), and the gases were mixed before entering the reactor. The reactor was inserted into an electric furnace driven by a PID temperature controller/programmer (Eurotherm 2408). A K-type thermocouple (outer diameter 0.5 mm) directly immersed in the catalyst bed was used to measure and control the catalyst temperature. The following mass-to-charge (m/e) ratios were used to monitor the concentration of products and reactants: 2 (H_2), 14 (N_2), 17 (NH_3), 18 (H_2O), 28 (CO), 30 (NO), 32 (O_2), 44 (N_2O or CO_2), and 46 (NO_2). The mass-spectrometer data were quantitatively analyzed 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 and procedures can be found elsewhere [4,6,7].

2.3. FTIR study

Absorption/transmission IR spectra were run on a Perkin-Elmer FTIR System 2000 spectrophotometer equipped with a Hg—Cd—Te cryo-detector, working in the range of wavenumbers 7200–580 cm^{-1} at a resolution of 1 cm^{-1} (number of scans ~10). For IR analysis, powder samples were compressed in self-supporting discs (10 mg cm^{-2}) and placed in a commercial heated stainless steel cell (Aabspec), allowing thermal treatments *in situ* under vacuum or controlled atmosphere and the simultaneous registration of spectra at temperatures up to 600 °C.

Before the NO_x storage, the samples were fully conditioned, i.e. submitted to: (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 [26], (iii) oxidation at 550 °C for 30 min, 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} = 5 mbar, p_{O2} = 20 mbar) on Pt—Ba/Al_2O_3 discs, or NO_2 (p_{NO2} = 5 mbar) on Ba—Al_2O_3 discs, up to catalysts saturation (ca. 20 min), followed by outgassing at the same temperature for few seconds. The ratio O_2/NO used during storage is rather small compared to real operation. The spectra of the stored NO_x were collected at 350 °C or after cooling down the discs at the chosen temperature. The reduction was accomplished with CO (P_{CO} = 10 mbar) and was performed at: (i) 350 °C, at increasing exposure times or (ii) increasing temperature in the range 150–350 °C.

NO (Praxair, purity $\geqslant$99.0%) was freshly distilled before use. Conversely, NO_2 (Praxair, purity $\geqslant$99.5%), O_2 (Praxair, purity $\geqslant$99.999%) and CO (Praxair, purity $\geqslant$99.9%) were directly used.

3. Results and discussion

3.1. Reduction of NO_x stored onto Ba/Al_2O_3

3.1.1. CO-TPSR experiments

The reactivity toward CO of NO_x species stored at 350 °C over the Ba/Al_2O_3 sample was investigated at first by performing a CO-TPSR experiment. The results are presented in Fig. 1 and show that CO is consumed to a very limited extent above ~330 °C (minimum concentration near 1800 ppm) and that CO_2 and NO are simultaneously formed along with trace amounts of N_2 and NO_2. The concentrations of the products increase up to 400 °C and then slowly decrease to 0 ppm while the system is hold at this temperature (400 °C); in the meantime, the concentration of CO slowly recovers the inlet value of 2000 ppm.

The moles of CO consumed and of the different products formed during CO-TPSR over Ba/Al_2O_3 were calculated from Fig. 1 and are reported in Table 1 together with those obtained during CO-TPSR over Pt—Ba/Al_2O_3 that will be discussed later on. It appears that only a fraction of the NO_x originally stored as nitrates onto the catalyst is removed during the CO-TPSR experiment (2.91×10^{-4} gmoles/g_{cat} of NO_x released as N_2 + NO + NO_2 vs. 13.1×10^{-4} gmoles/g_{cat} stored NO_x, which corresponds to ~22% of the initial NO_x loading).

It is worth noticing that CO is able to react at ca. 330 °C with NO_x stored at 350 °C. This temperature value is near to the onset temperature for nitrates thermal decomposition (~360 °C) [25] and accordingly the presence of CO in the feed does not affect significantly the temperature threshold of nitrate thermal decomposition.

3.1.2. CO-ISC experiment and FTIR study

The reduction by CO of nitrates stored onto Ba/Al_2O_3 was also studied by transient experiment under isothermal conditions (CO-ISC experiment) at 350 °C. After adsorption of NO_2 at the same temperature, 2000 ppm of CO was admitted to the catalyst. After CO admission, the outlet concentration of CO approaches quickly the feed level, indicating a very limited reaction between adsorbed nitrates and CO and thus indicating that stored NO_x are poorly reactive in the presence of CO at the adsorption temperature of 350 °C. Also very small amounts of CO_2 are formed that confirmed the poor activity of CO toward nitrates, along with very few ppm of NO_x.

The interaction of CO at 350 °C with the NO_x species stored on Ba/Al_2O_3 catalyst was also followed by FTIR spectroscopy and the results are presented in Fig. 2: (i) curve a is the spectrum of NO_x species previously stored at 350 °C, i.e. mainly ionic nitrates (related bands at 1410, 1320 and 1030 cm^{-1}, the splitted $\nu(NO_3)_{asym}$ and the $\nu(NO_3)_{sym}$ modes, respectively) and minor amounts of bidentate nitrates (ν(N=O) mode at 1550 cm^{-1}, the only one visible) [25,26]; (ii) curves b–e correspond to the spectra recorded during the interaction with CO at increasing exposure times at 350 °C. Carbonate species (the related bands expected at 1560, 1350 and 1060 cm^{-1}, corresponding to ν(C=O), $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$, respectively [24,27]) along with small amounts of isocyanate and/or cyanate species (weak bands at 2164 and 2222 cm^{-1}) [28] are detected. Owing to the strong overlapping of the bands related to nitrates and carbonates, it is not easy to evaluate the extent of nitrates reduction. However, even after 1 h of exposure (curve e), the reduction of nitrates is not complete; indeed, the broad and asymmetric band at 1345 cm^{-1} is due to the superposition of the two $\nu(NO_3)_{asym}$ modes of the ionic nitrates and the $\nu(OCO)_{asym}$ mode of the carbonates.

In line with CO-TPSR and CO-ISC data, FTIR data show that the reduction by CO of nitrates stored onto the Ba/Al_2O_3 is very slow at 350 °C and occurs to a rather limited extent. The reaction leads to the formation of mainly carbonate species and of minor amounts of isocyanate and/or cyanate species.

It is worth noticing that isocyanates/cyanates present after 1 h of exposure, as well as residual nitrates and carbonates, are stable after 10 min of evacuation at 350 °C (not shown).

3.2. Reduction of NO_x stored onto Pt—Ba/Al_2O_3

3.2.1. CO-TPSR experiment and FTIR study

The reactivity toward CO of NO_x species previously stored at 350 °C over the Pt—Ba/Al_2O_3 sample was investigated by performing a CO-TPSR experiment and the results are presented in Fig. 3. CO consumption is seen starting from ~180 °C and is complete in the temperature range 270–320 °C. The formation of CO_2 is detected simultaneously with the consumption of CO, showing a maximum of ~1500 ppm in the temperature range where CO consumption is complete. Very small amounts of NO are observed at low temperatures but well above 180 °C, namely at 215–250 °C. At 250 °C, the concentration of NO diminishes to zero. At the same time, nitrogen is formed and its concentration shows a sharp increase from 200 to 250 ppm at 250 °C, it keeps at this level up to 290 °C and then slowly decreases. Above ~320 °C, the CO concentration increases and tends to recover the inlet value of 2000 ppm while non negligible quantities of ammonia are formed (with an upper concentration of 50–60 ppm). From ~350 °C, when the nitrogen concentration decreases to zero, hydrogen is detected in the gaseous products together with a shoulder in the CO_2 trace

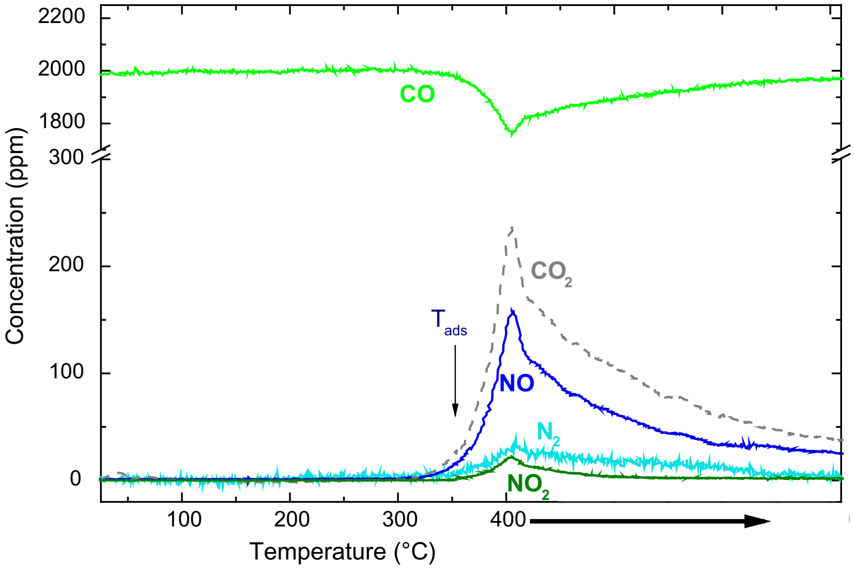

Fig. 1. CO-TPSR (2000 ppm CO in He) after NO_2 adsorption at 350 °C over the Ba/Al_2O_3 catalyst.

Table 1
Moles/g_{cat} of CO consumed and of products formed during CO-TPSR over Ba/Al_2O_3 and $Pt—Ba/Al_2O_3$.

Catalyst/reagent – product species	Temperature range	
	RT-250 °C	RT-400 °C with hold at 400 °C
Ba/Al_2O_3; NO_x stored: 13.1×10^{-4}		
CO consumed	–	4.62×10^{-4}
CO_2 formed	–	3.59×10^{-4}
N_2 formed	–	0.464×10^{-4}
NO formed	–	1.82×10^{-4}
NO_2 formed	–	0.159×10^{-4}
$Pt—Ba/Al_2O_3$; NO_x stored: 5.76×10^{-4}		
CO consumed	1.43×10^{-4}	20.7×10^{-4}
CO_2 formed	0.427×10^{-4}	14.8×10^{-4}
N_2 formed	–	0.935×10^{-4}
NO formed	0.0301×10^{-4}	0.086×10^{-4}
NH_3 formed	–	0.507×10^{-4}
H_2 formed	–	0.475×10^{-4}

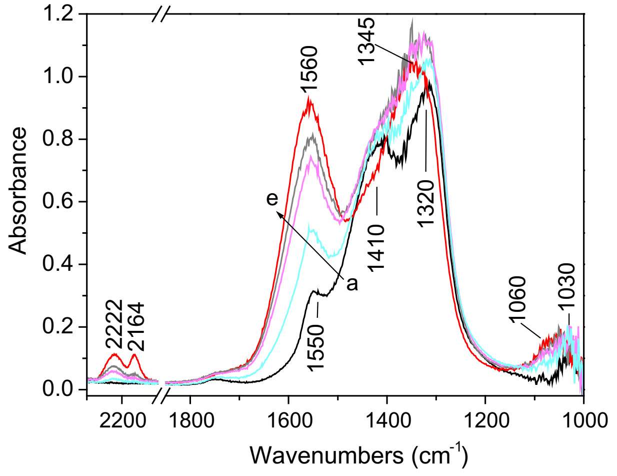

Fig. 2. FTIR spectra of NO_x reduction at 350 °C in CO (5 mbar) at increasing exposure time over the Ba/Al_2O_3 catalyst. Curve a, spectrum of NO_x stored at 350 °C by NO_2 adsorption; curves b–e, spectra after reduction for 2 min, 5 min, 10 min and 1 h, respectively.

centered at $T = 400$ °C. The presence of ammonia and H_2 among the reaction products is likely associated with the presence of trace amounts of water in the feed and/or of surface hydroxyls (*vide infra*).

It is worth noticing that over the $Pt—Ba/Al_2O_3$ sample, the consumption of CO occurs at temperatures well below that of NO_x thermal desorption over the same catalyst. Indeed, the He-TPD experiment performed after NO_x adsorption at 350 °C, already published elsewhere [4] and shown in the insert of Fig. 3 for comparison purpose, indicates that nitrates are stable up to 350 °C, i.e. up to the NO_x adsorption temperature. Accordingly, the CO-TPSR data clearly prove that CO is able to reduce the nitrate species stored onto $Pt—Ba/Al_2O_3$ catalyst at temperature well below that of their thermal decomposition (~180 °C vs. 350 °C).

The moles of CO consumed and of the different products formed during CO-TPSR up to 400 °C with hold at this temperature for 30 min over $Pt—Ba/Al_2O_3$ were calculated from Fig. 3 and are reported in Table 1. In total, 2.46×10^{-4} gmoles/g_{cat} of NO_x are released in the gas phase as $N_2 + NO + NH_3$ while 5.76×10^{-4} gmoles/g_{cat} of NO_x species have been stored previously onto the catalyst. The much higher amount of NO_x stored over Ba/Al_2O_3 starting from NO_2 (13.1×10^{-4} gmoles/g_{cat}) with respect to that measured over the $Pt—Ba/Al_2O_3$ from NO/O_2 mixture (5.76×10^{-4} gmoles/g_{cat}) can be explained by considering that the higher adsorption capability of NO_2 if compared to NO/O_2. In any case, over the $Pt—Ba/Al_2O_3$ sample only ~43% of the stored nitrates are reduced to gaseous N-containing products and consequently N-containing species are still present at the catalyst surface at the end of the CO-TPSR experiment. Besides, the C mass balance between CO_x at the inlet and outlet does not close since 2.07×10^{-3} moles/g_{cat} of CO are consumed and only 1.48×10^{-3} moles/g_{cat} of CO_2 are produced. This indicates that C-containing species are also stored onto the catalyst surface at the end of the CO-TPSR experiment.

Worth of note, the C balance is not satisfied also in the low-temperature region, below 250 °C (1.43×10^{-4} moles/g_{cat} of CO consumed vs. 0.427×10^{-4} moles/g_{cat} of CO_2 produced), where only a very small quantity of N-containing species is released in the gas phase (0.031×10^{-4} moles/g_{cat} of NO). This points out that in this temperature range, the stored nitrates are reduced with formation of C-containing species which remain adsorbed on the surface. This is indeed confirmed by the results of FTIR measurements,

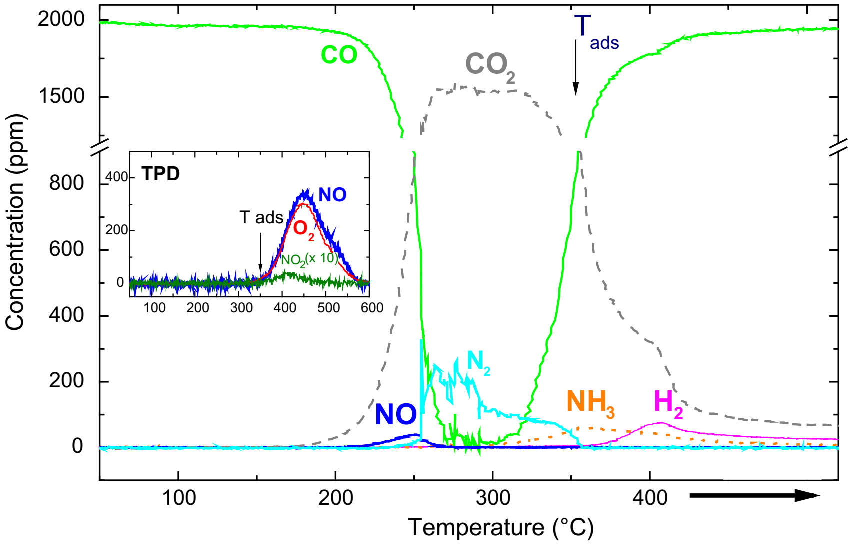

Fig. 3. CO-TPSR (2000 ppm CO in He) after NO/O_2 adsorption at 350 °C over the Pt—Ba/Al_2O_3 catalyst. The results of the TPD run in He after NO/O_2 adsorption at 350 °C over the same catalyst is shown in the insert.

where the reduction by CO of NO_x species previously stored at 350 °C onto the Pt—Ba/Al_2O_3 catalyst has been investigated (Fig. 4A). In this figure, curve a is the spectrum of NO_x species previously stored at 350 °C and cooled down to 150 °C. The stored nitrates are not perturbed by interaction with CO at 150 °C (not shown); curves b–e correspond to the spectra recorded during interaction with CO at increasing temperature in the 200–350 °C range after 10 min of exposure at each temperature. The bands of the stored nitrates slightly decrease at 200 °C (spectrum b) and almost completely disappear in the range 300–350 °C (curves d and e). Starting from 200 °C, very small amounts of NCO species are formed, as revealed by the two related bands at 2230 and 2170 cm^{-1}, whose intensity increases markedly with temperature, while the position shifts to lower frequency (2222 and 2164 cm^{-1}, respectively). Simultaneously, surface carbonates are formed, whose related bands (1555, 1350 an 1060 cm^{-1}) are well evident only starting from 300 °C (spectra d and e), when the intensity of the bands related to nitrates is strongly decreased. From this temperature, a shoulder at about 1250 cm^{-1} indicates the presence of small amounts of nitrites. Actually, the partial superposition of the bands related to nitrates, nitrites and carbonates makes difficult to track the contemporaneous NO_x removal and carbonates formation. In any case, the results point out that nitrates are reduced by CO to nitrites and to NCO species, while CO_2 produced during the reduction is adsorbed at the catalyst surface forming carbonate species. The two bands at 2222 and 2164 cm^{-1} have been assigned in the literature to isocyanate species coordinated to Al^{3+} in tetrahedral coordination and on the barium phase, respectively [19,21,29]. However, our results obtained from experiments performed for assignment purposes do not match with literature. We found that both the bands are related to isocyanate/cyanate species on the Ba-phase surface [30,31]. We have also observed that carbonates and isocyanates/cyanates present after reduction at 350 °C are stable under 10 min of evacuation at 350 °C (not shown).

In line with TPSR data, FTIR experiments confirm that nitrates stored onto Pt—Ba/Al_2O_3 catalyst are reduced by CO at temperatures much lower than that of their thermal decomposition (200 °C vs. 350 °C).

It is also worth noticing that, after CO interaction at 200 °C, FTIR spectrum showed two weak bands at 2110 cm^{-1} and at 2084 cm^{-1} related to the stretching modes of linear carbonyls adsorbed on Pt^{+} and $Pt^{\delta+}$ sites, indicating that the platinum is only partially reduced at this temperature. At higher temperatures only a band shifting

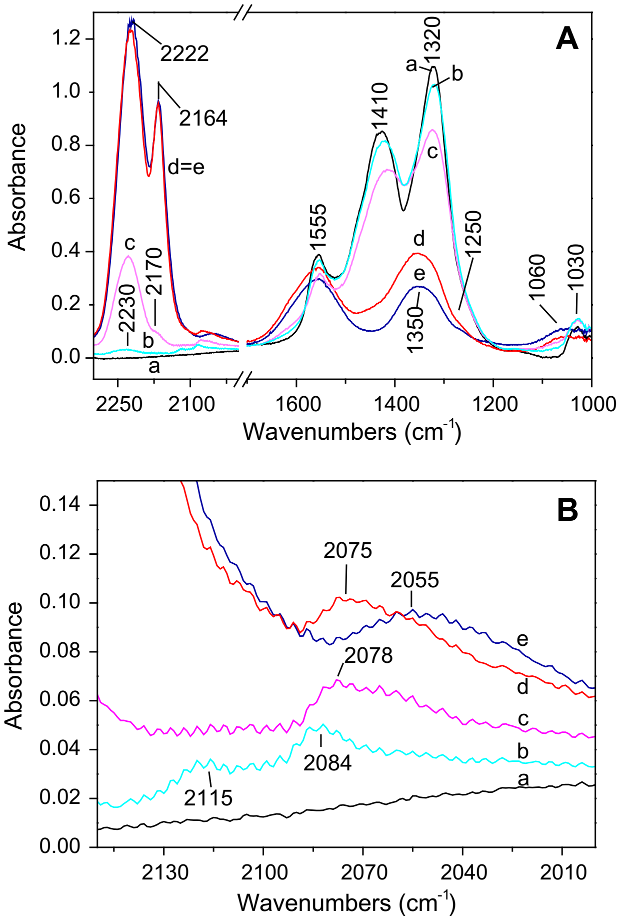

Fig. 4. FTIR spectra of NO_x reduction in CO (5 mbar) at increasing temperature over the Pt—Ba(16)/Al_2O_3 catalyst. Curve a, spectrum of NO_x stored at 350 °C by NO/O_2 adsorption; curves b–e, spectra after reduction at 200, 250, 300 and 350 °C, respectively. Each spectrum was run after 10 min of exposure to CO. Section B is an expansion of the spectra in the 2130–2010 cm^{-1} region.

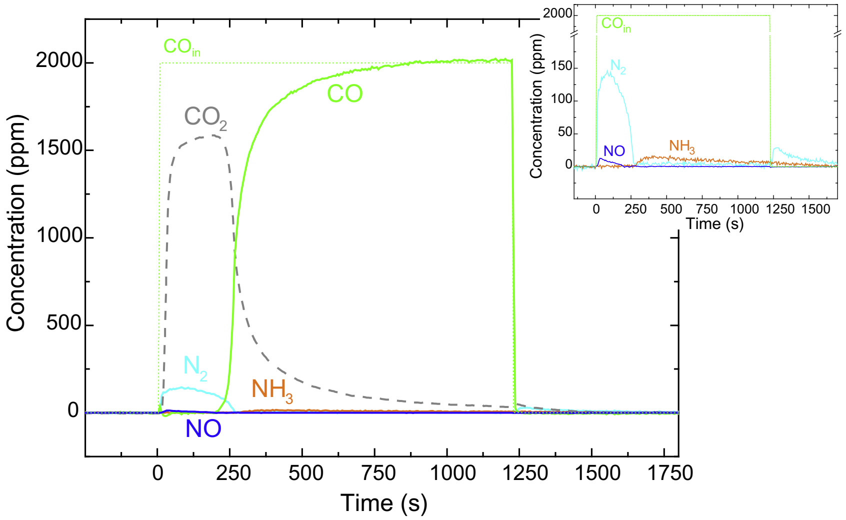

Fig. 5. ISC experiments with CO (2000 ppm in He) at 350 °C over the Pt—Ba/Al_2O_3 catalyst after NO/O_2 adsorption at the same temperature.

from 2078 to 2055 cm^{-1} is present (see Fig. 4B). Actually, the vibration frequency is strictly related to the extent of the reduction of the Pt phase and to the CO coverage of the Pt sites [32,33]. In particular, the frequency shifts to lower value upon increasing the reduction extent and, on the reduced Pt particles, upon decreasing the coverage, i.e. increasing the interaction temperature.

3.2.2. CO-ISC experiment and FTIR study

The reactivity toward CO of NO_x stored at 350 °C over the Pt—Ba/Al_2O_3 sample was also investigated by performing isothermal reactivity experiments at the same temperature.

The results of a CO-ISC experiment run at 350 °C reported and discussed in the following are collected over a sample that showed stable cyclic behavior, i.e. after performing several lean-rich cycles (i.e. NO_x storage and reduction by CO with an inert purge in between) at 350 °C until the amounts of NO consumed during the lean phase equals the amounts of N-containing species evolved in the entire lean-rich cycle. This occurs in correspondence to the third or fourth lean/rich cycle, as will be discussed later on.

Table 2
Moles/g_{cat} of CO consumed and of different products formed during CO-ISC carried out at 350 °C over Pt—Ba/Al_2O_3: 2000 ppm stepwise CO admission (t = 0–1250 s); 2000 ppm stepwise CO shut off (t = 1250–1750 s).

Reagent-product species	CO admission (t = 0–1250 s)	CO shut off (t = 1250–1750 s)
NO_x stored: 1.53×10^{-4}		
CO consumed	7.74×10^{-4}	–
CO_2 formed	6.15×10^{-4}	2.5×10^{-6} *
N_2 formed	3.96×10^{-5}	8.18×10^{-6}
NO formed	1.87×10^{-6}	–
NH_3 formed	7.43×10^{-6}	–

* The contribution of the CO_2 tailing in Fig. 5 has been subtracted.

Fig. 5 shows the results of a CO-ISC experiment over the Pt—Ba/Al_2O_3 catalyst by admitting in a stepwise manner 2000 ppm of CO at 350 °C after NO_x adsorption at the same temperature. Upon admission of CO, ~150 ppm of N_2 and ~1550 ppm of CO_2 are immediately produced, together with negligible amounts of NO (see insert). CO is completely consumed for about 200 s; afterward CO is detected at the reactor outlet and its concentration increases and reaches the inlet value within less than 1000 s. After CO breakthrough, the N_2 concentration decreases, and the evolution of very small amounts of ammonia is observed, while the CO_2 concentration decreases. The presence of small amounts of ammonia among the reaction products is likely associated with the presence of trace amounts of water in the feed and/or of surface hydroxyls (*vide infra*). It is worth of note that a negligible increase in the catalyst temperature of $\leqslant$2–3 °C is measured upon CO admission, so that the reduction is performed under nearly isothermal conditions. When the CO feed is stopped (at 1250 s), a small amount of nitrogen is produced, along with CO_2 (not shown in the insert of Fig. 5).

The moles of CO consumed and of the different products formed during CO-ISC experiment over Pt—Ba/Al_2O_3 were calculated from Fig. 5 and are listed in Table 2. It appears that also during the CO-ISC experiment the C and N balances in the gas phase are not satisfied: in fact, upon CO admission, 7.74×10^{-4} moles/g_{cat} of CO are consumed while 6.15×10^{-4} moles/gcat of CO_2 are formed. Also, a total amount of 0.88×10^{-4} gmoles/g_{cat} of NO_x are released in the gas phase as $N_2 + NO + NH_3$ while 1.53×10^{-4} gmoles/g_{cat} of NO_x species were stored onto the catalyst before reduction (see Table 3): accordingly both N- and C-containing species are present

Table 3
Moles/g_{cat} of NO consumed and different species released in the NO_x storage phase during a lean-rich cycle after the reduction phase presented in Fig. 5 over a fully conditioned catalyst: 3% O_2 stepwise addition (t = 0–500 s); 1000 ppm NO stepwise admission (t = 500–650 s); 1000 ppm NO stepwise removal (t = 650–900 s).

Reagent-product species	3% O_2 stepwise addition (t = 0–500 s)	1000 ppm NO stepwise admission (t = 500–650 s)	1000 ppm NO stepwise removal (t = 650–900 s)
NO stored	–	1.53×10^{-4}	-2×10^{-6}
N_2 released	1.7×10^{-5}	5.52×10^{-6}	–
NO evolved	1.35×10^{-6}	1.54×10^{-5}	1.5×10^{-6}
NO_2 evolved	2.06×10^{-6}	4.94×10^{-6}	3.3×10^{-7}
CO_2 released	3.39×10^{-5}	2.7×10^{-5}	

at the catalyst surface at the end of the CO-ISC experiment (i.e. after 1250 s from CO admission). It is noted that in the CO-ISC experiment, the amount of stored NO_x is much lower than that measured over the same catalyst up to saturation during the CO-TPSR experiment (1.53×10^{-4} vs. 5.76×10^{-4} gmoles/g_{cat}) due to the shorter adsorption time adopted during the CO-ISC experiment (150 s vs. 1000 s).

Finally, upon CO shut off, 8.18×10^{-6} moles/g_{cat} of N_2 are released together with 7.7×10^{-6} moles/g_{cat} of CO_2 (*vide infra*).

The interaction of CO at 350 °C with the NO_x species stored on Pt—Ba/Al_2O_3 catalyst was also followed by FTIR spectroscopy, and the results are presented in Fig. 6A: curve a is the spectrum of NO_x species previously stored at 350 °C; curves b–d correspond to the spectra recorded during interaction with CO at increasing exposure times at 350 °C.

The reduction of nitrates by CO is very fast since the intensity of the nitrate bands at 1340, 1420 and 1550 cm^{-1} is reduced markedly after 30 s of CO contact (curve b) and even more after 1 min of CO contact (curve c). Simultaneously, the carbonate species appear, due to the adsorption of CO_2 produced during the reduction, along with NCO species. After 2 min, nitrate species have almost disappeared (spectrum d) as mostly carbonate bands are evident. A careful inspection of Fig. 6A also reveals the presence of nitrite species, as it can be appreciated from a weak shoulder at 1250 cm^{-1} in curves c and d. This confirms that also in this case nitrates are reduced by CO to give nitrites and NCO species. Furthermore, FTIR spectra also show, after CO interaction, the presence of a weak band at 2070 cm^{-1} related to the presence of linear carbonyls onto Pt sites.

The prolonged outgassing at 350 °C (see Fig. 6B) indicates that NCO species are very stable at this temperature; notably, a fraction of these species is still present after 2 h 30 min of outgassing (curve c).

It is now of interest to make a comparison between the results described in Fig. 6A with those obtained by interaction of CO at 350 °C with the NO_x species stored on Ba/Al_2O_3 catalyst, shown in Fig. 2. For this reason, we can take as a measure of the amounts of the nitrate species stored the integrated intensity (I_{NO3}) of the bands at 1555, 1420, 1310 cm^{-1} and, for the isocyanate/cyanate species, the integrated intensity (I_{NCO}) of the bands at 2222 and 2164 cm^{-1}. The same should be made for the carbonate species, the related bands being at 1560, 1350 and 1060 cm^{-1}, but owing to the superposition of these bands to those of nitrates, if still present, we will take only the integrated intensity of the band at 1560 cm^{-1}, I_{CO3}, as measure of the amounts of the carbonates. Actually, the band at 1555 cm^{-1} due to bidentate nitrates, if present, is always very weak.

On one hand, we observe that (i) for Pt—Ba/Al_2O_3, the ratio between the amounts of nitrates originally stored onto the catalyst and the amounts of isocyanates/cyanates formed after 2 min of exposure to CO, I_{NO3}/I_{NCO}, is 1.39; (ii) for Ba/Al_2O_3, the I_{NO3}/I_{NCO} ratio estimated after the same exposure time to CO is 100 and 22 after 1 h of exposure to CO, i.e. still very high. On the other hand, (i) for Pt—Ba/Al_2O_3, the ratio between the amounts of nitrates originally stored onto the catalyst and the amounts of carbonate species formed after 2 min of exposure to CO, I_{NO3}/I_{CO3}, is 6.3; (ii) for Ba/Al_2O_3 the I_{NO3}/I_{CO3} ratio is 9 after 2 min of exposure to CO (and 2.5 after 1 h of exposure to CO). It is worth to note that for 2 min of exposure to CO, the surface nitrates are completely disappeared for the Pt—Ba/Al_2O_3 catalyst, while they prevail on the carbonates on the Ba/Al_2O_3 catalyst and are still present after 1 h of exposure. The previous observations show that the reduction of stored NO_x is very effective in the presence of Pt leading to both isocyanates/cyanates and carbonates, the ratio of their amounts (I_{NCO}/I_{CO3}) being 4.5 at the end of the reduction process after ca. 2 min of exposure. In the absence of Pt, the reduction of the stored nitrates is still incomplete after 1 h of exposure to CO at 350 °C, and again, both isocyanates/cyanates and carbonates are formed. However, the ratio of their amounts (I_{NCO}/I_{CO3}) is now very low, i.e. 0.12. This indicates that the reduction leading to isocyanates/cyanates is catalyzed by Pt.

3.3. Reaction network in the reduction by CO of nitrates stored onto Pt—Ba/Al_2O_3

The results collected during CO-TPSR over Ba/Al_2O_3 (Fig. 1) and over Pt—Ba/Al_2O_3 (Fig. 3) highlight that in the presence of Pt the reduction of nitrate species by CO is faster considering that the temperature of onset of the reaction is much lower (~180 °C vs. 330 °C), and the conversion of CO is much higher and in fact is limited by the concentration of the reducing agent. Besides, it does not require as first step the thermal release of NO_x in the gas phase since the reaction is seen at temperatures well below that of the thermal decomposition of adsorbed NO_x (350 °C). The results collected during CO-ISC experiment over Ba/Al_2O_3 and over Pt—Ba/Al_2O_3 (Fig. 5) are in line with the results of CO-TPSR experiments and further indicate that the reduction at 350 °C by CO of NO_x stored onto the Pt—Ba/Al_2O_3 catalyst is very fast and controlled by the concentration of CO, while it is almost negligible over Ba/Al_2O_3. It is possible to conclude that the reduction by CO under

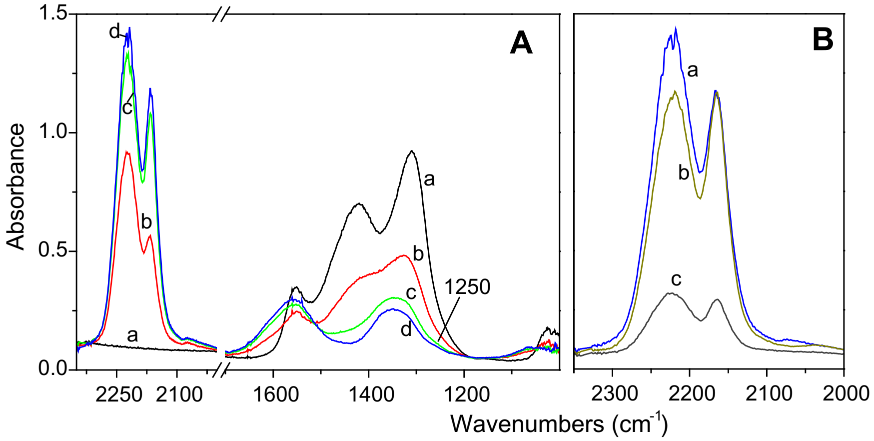

Fig. 6. (A) FTIR spectra of NO_x reduction in CO (5 mbar) at 350 °C at increasing exposure time over the Pt—Ba/Al_2O_3 catalyst. Curve a, spectrum of NO_x stored at 350 °C by NO/O_2 adsorption; curves b–d, spectra after reduction for 30 s, 1 min and 2 min, respectively. (B) FTIR investigation on the stability of NCO species under evacuation at 350 °C. Curve a, the same spectrum reported as curve d in section A; curves b and c, spectra after evacuation for 30 min and 2 h 30 min, respectively.

nearly isothermal conditions of nitrates stored onto Pt—Ba/Al_2O_3 catalyst at high temperature (i.e. 350 °C) occurs according to a Pt-catalyzed pathway. Such a pathway does not involve as first step the thermal decomposition of stored NO_x species with release of NO_x in the gas phase and is effective already at low temperature. As it is apparent from Figs. 3 and 5, this catalytic route of nitrates reduction by CO leads mainly to nitrogen and CO_2 in the gas phase.

It is worth noticing that a low-temperature Pt-catalyzed pathway has already been demonstrated for the reduction by H_2 of NO_x stored over the same catalyst used in this study [4], leading mostly to nitrogen; hydrogen is more effective than CO since the onset temperature of the reduction is lower (140 °C vs. 180 °C). This suggests that the reduction of stored NO_x with H_2 and with CO might present analogies that are worth to be investigated, the onset temperature of the process depending from the reactivity of the reducing agent toward the stored NO_x species.

Besides the results of CO-TPSR and CO-ISC experiments over Pt—Ba/Al_2O_3 (Figs. 3 and 5) and of the complementary FTIR study, (Figs. 4 and 6) indicate that the reduction by CO of nitrates stored onto the Pt—Ba/Al_2O_3 catalyst occurs according to the stoichiometry of the following overall reactions:

$$Ba(NO_3)_2 + 2CO \rightarrow Ba(NO_2)_2 + 2CO_2 \qquad (1)$$

$$Ba(NO_3)_2 + 8CO \rightarrow Ba(NCO)_2 + 6CO_2 \qquad (2)$$

$$Ba(NO_3)_2 + 5CO \rightarrow BaCO_3 + N_2 + 4CO_2 \qquad (3)$$

Reactions (1)–(3) account for the consumption of CO and of nitrates, and for the formation of CO_2. In particular, reaction (1) represents the reduction of the nitrates to nitrites; this reaction is not clearly apparent from FTIR data when nitrate species are still abundant at the surface, but it is evident both by Figs. 4A and 6A when nitrates are almost disappeared. Reactions (2) and (3) account for the consumption of nitrates with formation of cyanates/isocyanates, N_2 and CO_2; they also explain the fact that the N balance and the C balance in the gas phase do not close at the end of both CO-TPSR and CO-ISC experiments. Reaction (3) also accounts for the formation of carbonates at the catalyst surface, as revealed by FTIR. Notice that reaction (1) is incorporated into reactions (2) and (3). Also, note that in reactions (1)–(3) the participation of Ba bulky species has been considered for simplicity, but the involvement of surface species is most likely. The same comment applies for the other reactions discussed in the following.

The consumption of nitrates and the formation of NCO species, according to reaction (2), are revealed by the FTIR spectra which have been collected at $T \geqslant 200$ °C, and is in line with the fact that the C and N balances in the gas phase are not closed in the overall range of low temperatures examined (180–250 °C). This suggests that reaction (2), i.e. formation of NCO species, is effective in the 180–250 °C temperature range; in the same temperature range reaction (3) does not occur since N_2 is not detected. Our results compare well with those previously reported by Szailer et al. [19]: these authors observed the formation of surface NCO species near 150 °C and an appreciable reduction of nitrates above 200 °C upon storage of NO_x at RT onto a Pt—Ba/Al_2O_3 catalyst and using CO as the reducing agent. The formation of NCO species during the reduction of NO_x by CO was previously reported also by Unland [18] and Lesage et al. [20].

It is worth mentioning that in reaction (3) the formation of $BaCO_3$ has been envisaged upon reduction of the stored nitrates with formation of N_2. This is consistent with FTIR data shown in Fig. 4 (where carbonate species are detected already in small amounts by reduction at 250 °C) and in Fig. 6 (by reduction at 350 °C). However, BaO can also be present due to incomplete reaction with CO_2 (reaction 4):

$$BaO + CO_2 \rightarrow BaCO_3 \qquad (4)$$

The formation of N_2 (and of CO_2) is also apparent in CO-ISC experiment of Fig. 5 upon CO shut off and cannot be explained by reaction (3) due to the absence of CO. In this case, a reaction between NCO adsorbed species with residual amounts of nitrates is suggested, following the stoichiometry of the overall reaction (5):

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

It is noted that the amount of CO_2 formed in correspondence with the CO shut off and reported in Table 2 (2.5×10^{-6} moles/g_{cat}) well corresponds to that expected from reaction (5) based on the amount of N_2 formed (i.e. $8.18 \times 10^{-6} \times 2/8$ moles/$g_{cat} = 2.045 \times 10^{-6}$ moles/g_{cat}).

Notably, also formation of N_2 by global reaction (3) during CO-TPSR and CO-ISC may involve the reaction of NCO species formed by reaction (2) with adsorbed NO_x species according to reaction (5). NCO species are not completely consumed during the rich phase of the CO-ISC experiment; their presence at the surface was pointed out by their reaction toward gaseous oxygen and NO_x during the subsequent lean phase of a lean-fuel rich cycle, as will be shown in the next paragraph. This fraction of NCO species accumulated on the catalyst surface do not react with nitrates either because they are not reactive being not close to nitrate species and/or to vacant Pt sites or because residual nitrates are few [11,14].

In our opinion, the occurrence of reaction (5) is pointed out by the N_2 formation at the shut off of the CO feed (insert of Fig. 5), due to the availability of vacant Pt sites which were partially poisoned by CO during the CO feed, i.e. in the presence of gaseous CO (self-inhibition by CO). As a matter of fact, CO-ISC and pulse experiments performed at lower temperatures and reported elsewhere [31,34] showed that the nitrogen peak is always visible upon the CO shut off, and that the peak is greater at lower temperatures. This is in line with the hypothesis of a self-inhibition of CO due to its strong adsorption on the Pt active sites.

Finally to explain the formation above 300 °C of ammonia (5.07×10^{-5} moles/g_{cat} in Table 1) and of hydrogen (4.75×10^{-5} moles/g_{cat} in Table 1) during CO-TPSR as well as the formation of very small amounts of ammonia during the CO-ISC experiment (7.43×10^{-6} moles/g_{cat} in Table 2), the presence of small amounts of water in the feed and/or of surface hydroxyl species must be invoked. The formation of ammonia is likely due to hydrolysis of surface NCO species [21], reaction (6):

$$Ba(NCO)_2 + 3H_2O \rightarrow BaO + 2NH_3 + 2CO_2 \qquad (6)$$

Notice that the temperature of onset of ammonia formation in Fig. 3 may be slightly lower than 300 °C due to a delay in the dynamic response of ammonia in our apparatus. Such a delay has been observed during dedicated ammonia transient experiments and is likely due to ammonia adsorption–desorption in the capillary of the MS, maintained at 90 °C.

On the other hand, the formation of hydrogen is likely due to the WGS reaction, reaction (7):

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

and/or to ammonia decomposition above 350 °C, reaction (8):

$$NH_3 \rightarrow 1/2N_2 + 3/2H_2 \qquad (8)$$

Indeed the occurrence of the WGS reaction was experimentally observed over this catalyst from a CO/H_2O mixture. Also, the decomposition of ammonia and the associated formation of N_2 and H_2 in a 1/3 ratio were observed during NH_3–TPSR of NO_x stored onto Pt—Ba/Al_2O_3 above 350 °C [7] and the formation of H_2 in Fig. 3 is seen together with a shoulder in the CO_2 trace centered at $T = 400$ °C.

3.4. Lean phase over Pt—Ba/Al_2O_3 catalyst

Fig. 7 displays the results of O_2 interaction after the reduction phase (Fig. 5); the subsequent NO admission (NO_x storage phase) is also shown. Upon admission of 3% v/v O_2 (Fig. 7, $t = 0$ s), the evolution of CO_2 with maximum concentration of ~850 ppm and of nitrogen with maximum concentration of ~450 ppm is observed, along with that of NO and NO_2 in minor amounts with maximum concentration of ~80 and ~50 ppm respectively. These species are produced by the oxidation of surface NCO groups that remain adsorbed at the catalyst surface after reduction with CO, as discussed earlier.

The oxidation of NCO species by oxygen was also investigated by means of FTIR. After NO_x storage, the NCO species were accumulated on Pt—Ba/Al_2O_3 by contacting the sample for 5 min with CO at 350 °C: after that the catalyst was outgassed for few minutes and cooled down to RT. Then, the NCO species were contacted with an excess of oxygen (10 mbar) and the temperature was progressively increased. The corresponding FTIR spectra are shown in Fig. 8. No changes are observed till 150 °C, when the bands corresponding to NCO species begin to decrease; by rising the temperature the oxidation proceeds, and after 10 min at 350 °C of contact the bands at 2222 and 2164 cm^{-1} completely disappear. In parallel, the bands in the region of 1700–1000 cm^{-1} reveal the formation of mainly carbonate (bands at 1555 and 1350 cm^{-1}) and nitrite species (band at 1230 cm^{-1}) in the 150–300 °C range and, mainly nitrate species at 350 °C. As a result, the spectrum recorded at 350 °C after interaction of NCO with oxygen (spectrum e) perfectly matches in the region 1700–1000 cm^{-1} the spectrum recorded at the same temperature during the reduction of the stored NO_x by CO 1 min after its admission (spectrum f, see insert of Fig. 8). This indicates that in the presence of oxygen the NCO species can be oxidized to nitrate and carbonate species; besides nitrates formation involves nitrites as intermediate.

The results shown in Figs. 7 and 8 can be explained by the following overall reactions (9)–(11):

$$Ba(NCO)_2 + 3/2O_2 \rightarrow N_2 + BaO + 2CO_2 \quad (9)$$

$$Ba(NCO)_2 + 3O_2 \rightarrow Ba(NO_2)_2 + 2CO_2 \quad (10)$$

$$Ba(NCO)_2 + 4O_2 \rightarrow Ba(NO_3)_2 + 2CO_2 \quad (11)$$

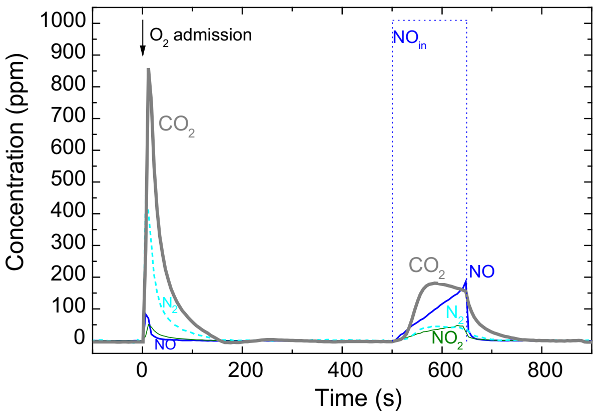

Fig. 7. Lean phase at 350 °C over the Pt—Ba/Al_2O_3 catalyst following NO_x adsorption at 350 °C and reduction with CO (2000 ppm in He) at the same temperature. $t = 0$: O_2 admission (3% v/v in He); $t = 500$ s: NO admission (1000 ppm in He + 3% v/v O_2); $t = 650$ s: NO shut off.

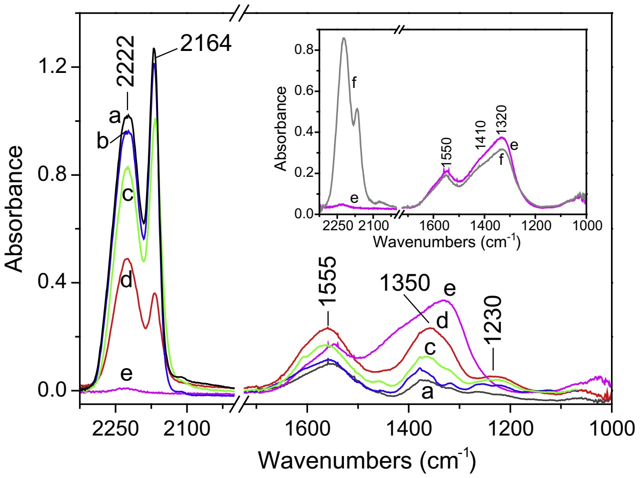

Fig. 8. FTIR investigation into the reactivity of NCO species toward oxygen. Curve a, spectrum of NCO species formed at 350 °C and cooled down to RT; curves b–e: spectra after admission of O_2 and heating for 10 min at 150, 250, 300 and 350 °C, respectively. In the inset curve e is compared with the spectrum of NO_x reduction with CO at 350 °C after 30 s of contact (curve f).

Reactions (9)–(11) account for the consumption of NCO species with oxygen and for the formation of CO_2. Reaction (9) also accounts for the evolution of N_2 upon oxygen admission. The reaction of isocyanates/cyanates with O_2 to give N_2 and CO_2 was previously reported by Lesage et al. over a Pt—Rh/Ba/Al_2O_3 catalyst [20], by Scholz et al. over a Pt—Ba/Al_2O_3 catalyst [22] and by Bion et al. over a Ag/Al_2O_3 catalyst [21]. Reaction (10) is incorporated into reaction (11); reactions (10) and (11) account for the formation of nitrite and nitrate species revealed by FTIR. Formation of N_2 according to reaction (9) may occur via the interaction of nitrates or nitrites with residual isocyanate/cyanate species according with reaction (5) and (12), respectively:

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

$$Ba(NCO)_2 + Ba(NO_2)_2 \rightarrow 2N_2 + 2BaCO_3 \quad (12)$$

The amounts of the different species released upon the oxygen addition were calculated from Fig. 7 and are presented in Table 3. Upon oxygen addition, 3.39×10^{-5} moles/g_{cat} of CO_2 are released, along with 1.7×10^{-5} moles/g_{cat} of N_2. This is in nice agreement with the occurrence of reaction (9). Formation of BaO according to reaction (9) is documented by the results of subsequent NO step addition at $t = 500$ s (Fig. 7). Indeed after the NO addition CO_2 evolution is observed, with a delay of about 15 s. As already reported in [17], over a fully carbonated surface CO_2 evolution is observed with no delay with respect to NO admission. The death time here observed in the CO_2 evolution is due to the adsorption of NO_x at BaO sites still present at the surface after the oxidation phase. From the delay in the CO_2 evolution it is calculated that the number of BaO sites involved in the storage of NO_x to give $Ba(NO_2)_2$ or $Ba(NO_3)_2$ is 1.86×10^{-5} gmoles/g_{cat}, corresponding to 0.76% of the Ba catalyst loading. This number compares well to 1.7×10^{-5} gmoles/g_{cat} of N_2 generated in the previous oxidation phase of NCO species by oxygen (see Table 3), that according to reaction (9) should be equal to the gmoles/g_{cat} of BaO.

Notably, reactions (9)–(11) do not account for the release of small quantities of NO_x upon oxygen addition reported in Table 3 (3.41×10^{-6} moles/g_{cat}). However, this NO_x quantity is of minor importance since the N_2 selectivity during the O_2 addition calculated from Table 3 is ~91% (3.41×10^{-6} moles/g_{cat} of NO + NO_2 vs. 1.7×10^{-5} moles/gcat of N_2). Considering that nitrogen is formed only by reaction (9), it is possible to estimate that 1.7×10^{-5} moles/g_{cat} of $Ba(NCO)_2$ are decomposed upon admission of oxygen to give N_2.

The oxidation of NCO species with O_2 at 350 °C does not lead to the consumption of all NCO species present at the catalyst surface.

This is demonstrated by the results also displayed in Fig. 7 showing that, upon the subsequent admission of NO to the reactor at $t = 500$ s, small amounts of N_2 are formed, with a time delay of about 15 s. In fact the formation of N_2 during NO_x storage under lean conditions can be explained by the oxidation of residual NCO species present at the catalyst surface by means of surface nitrites, nitrates, NO/O_2 and/or NO_2, according to reactions (5) and (12)–(14):

$$5Ba(NCO)_2 + 3Ba(NO_3)_2 \rightarrow 8N_2 + 8BaCO_3 + 2CO_2 \tag{5}$$

$$Ba(NCO)_2 + Ba(NO_2)_2 \rightarrow 2BaCO_3 + 2N_2 \tag{12}$$

$$Ba(NCO)_2 + 3/2NO + 3/2O_2 \rightarrow 5/2N_2 + BaCO_3 + CO_2 \tag{13}$$

$$Ba(NCO)_2 + 3/2NO_2 \rightarrow 5/2N_2 + BaCO_3 + CO_2 \tag{14}$$

The moles of NO_x stored and of the gaseous species released or evolved during the NO_x storage phase ($t = 500$–650 s in Fig. 7) were calculated from Fig. 7 and are shown in Table 3. It appears that 5.52×10^{-6} moles/g_{cat} of N_2 are released so that the number of $Ba(NCO)_2$ species oxidized according to reactions (5) and (12)–(14) is between 2.21×10^{-6} and 3.45×10^{-6} moles/g_{cat}; these quantities are calculated in case only reaction (13) (or reaction (14)) or only reaction (5) is effective, respectively. These data confirm that surface NCO species are still present after oxygen addition and are oxidized during the subsequent NO_x storage phase because of the superior oxidizing capability of $NO + O_2$, NO_2, surface nitrites and/or surface nitrates as compared to O_2 alone. The oxidation of isocyanates/cyanates over Pd/Al_2O_3 at low temperature (150 °C) following switch to a flow containing 500 ppm NO + 5% O_2 was previously documented by Macleod and Lambert [23].

In fact, the final situation detected during the FTIR study carried out on the oxidation of NCO species by O_2 (Fig. 8) is slightly different from that observed in Fig. 7 and discussed earlier because NCO species completely disappear in the former case whereas they are still present after oxygen addition during the lean phase of Fig. 7. It is speculated that the formation of nitrites/nitrates together with the total consumption of NCO species in the FTIR study is likely due to the different and more severe conditions employed in this case (e.g. the longer time of contact with oxygen). This is also consistent with the role of reactive intermediates of nitrite/nitrate species in reactions (12) and (5).

On the basis of the results previously discussed, it is worth of note that when CO is used as reducing agent, the stored NO_x species are reduced to N_2 both during the lean and the rich phases. This is well illustrated in Fig. 9, which compares the gmoles/g_{cat} of NO consumed from the gas phase during NO storage (lean phase) with the gmoles/g_{cat} of gaseous N-containing species (mostly N_2) released or evolved during both the lean and the rich phases in a series of four consecutive lean-rich cycles, starting from a lean phase over a conditioned catalyst sample (i.e. a catalyst sample cycled using H_2 as reductant, see experimental). As shown in Fig. 9, the amount of NO consumed during the lean phase at 350 °C (open triangles) is greater during the first cycle (1.75×10^{-4} gmoles/g_{cat}) and decreases to the value of 1.53×10^{-4} gmoles/g_{cat} when the catalyst reaches reproducible cyclic operation. Besides during the first lean/rich cycle only a fraction (roughly 50%) of the NO consumed during the lean phase is released as gaseous N-containing species (full circles), almost entirely as N_2 during the rich phase. Indeed starting from a catalyst that has been previously conditioned with H_2, no N_2 is observed both upon O_2 admission and during the NO_x storage. In the subsequent cycles, the amount of released N-containing products increases since N_2 is formed during the lean phase as well. At the fourth cycle, the amount of NO consumed from the gas phase in the lean phase equals that of the evolved N-containing species during the whole cycle and accordingly a reproducible cyclic behavior is attained with the closure of the N balance.

These results indicate that the changes in the catalyst behavior during CO pulses are primarily associated to the buildup of surface NCO species during reduction of stored NO_x by CO. These species are subsequently released or evolved upon oxygen addition, upon NO addition and upon the shut off of the NO feed.

A quantitative analysis of NCO species still present onto the catalyst at the end of the reduction phase was performed in a dedicated experiment. It is well known [20] that cyanates and isocyanates decompose to ammonia and CO_2 through reaction with water, according to the following reaction:

$$Ba(NCO)_2 + 4H_2O \rightarrow Ba(OH)_2 + 2NH_3 + 2CO_2 \tag{15}$$

Accordingly, water was admitted to the reactor following the reduction of nitrates with CO at 350 °C. Ammonia and CO_2 production was observed and calculations confirmed that ammonia and CO_2 production was in line with the reaction (15). The amounts of NCO species present onto the catalyst evaluated from the produced ammonia were in line with what estimated by N_2 formation during the lean phase.

3.5. Reaction pathway and mechanism in the reduction by CO of nitrates stored onto Pt—Ba/Al_2O_3

3.5.1. Reaction pathway

Based on the previous discussion, the reaction pathway for the reduction by CO of nitrates stored over Pt—Ba/Al_2O_3 under dry conditions can be suggested as shown in Fig. 10. It is likely that the reduction of the stored nitrates proceeds according to an in series reaction scheme through the subsequent formation of nitrites (path ***a***) and of NCO species (path ***b***), followed by the reaction of these species with nitrates/nitrites and/or O_2, $NO + O_2$ and NO_2 to give N_2, CO_2 and $BaCO_3$ (path ***c***).

The conversion of $Ba(NO_3)_2$ into $Ba(NO_2)_2$ and $Ba(NCO)_2$ during reduction by CO with the corresponding evolution of CO_2 (paths ***a*** and ***b***) has been derived from the analysis of CO-TPSR and CO-ISC experiments over Pt—Ba/Al_2O_3 and from the complementary FTIR investigation. These reactions were observed to a much lower extent over Ba/Al_2O_3 and accordingly they are catalyzed by Pt, but they also require the presence of Ba.

The oxidation of NCO species in the presence of O_2, NO/O_2 and/or NO_2 to give N_2 and CO_2 in the gas phase and $Ba(NO_2)_2$, $Ba(NO_3)_2$

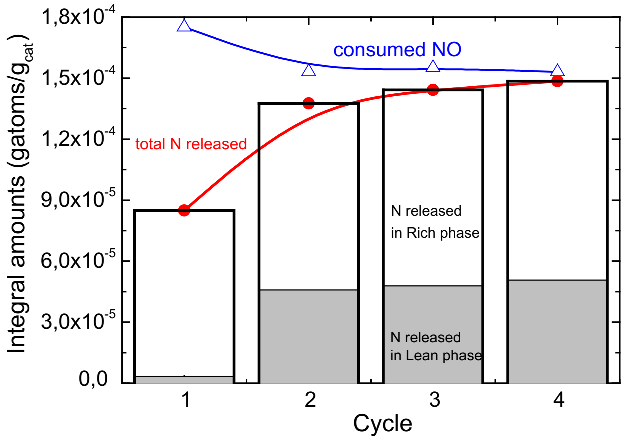

Fig. 9. Integral amounts of NO consumed from the gas phase (open triangles) and of N released into the gas phase (as N_2, NH_3, etc., filled circles) during four lean/rich cycles. Filled columns represent the total N released during the lean phase; empty columns show the amounts of N released during the rich phase.

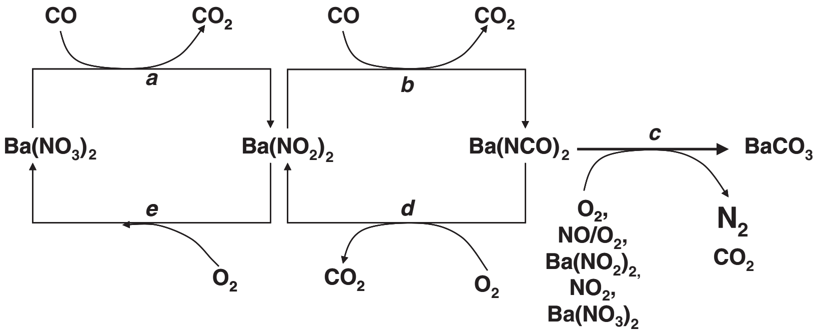

Fig. 10. Reaction pathway in the reduction by CO of nitrates stored onto Pt—Ba/Al_2O_3 catalyst.

and $BaCO_3$ at the catalyst surface (paths ***c***, ***d***, ***e***) has been revealed during the experiment over Pt—Ba/Al_2O_3 shown in Fig. 7 upon admission of O_2 and of NO/O_2 and by the complementary FTIR study. The oxidation of NCO species by means of $Ba(NO_3)_2$ and/or $Ba(NO_2)_2$ (again path ***c***) has also been invoked to explain the release of nitrogen during the CO-ISC experiment upon the shut off of CO. All these reactions have been observed only in the presence of Pt.

The CO-TPSR experiment over Pt—Ba/Al_2O_3 has shown that the reaction of surface nitrates to give nitrogen is slower than that responsible for the initial reduction of nitrates to give either nitrites or NCO species. In fact, the formation of nitrogen is observed only above 250 °C while evidence for the formation of NCO species and of nitrites from 180 °C is provided by the consumption of CO and by the simultaneous evolution in the gas phase of CO_2 with no N-containing species. In fact both the C and N balances do not close in the temperature interval 180–250 °C (Fig. 3 and Table 1).

The formation of nitrogen via the reduction of nitrates by CO has been revealed during the CO-ISC experiment in Fig. 5 and the complementary FTIR study in Fig. 6. In fact under the CO-ISC conditions, this reaction is explained as the sum of the reduction of nitrates by CO to give surface NCO species [reaction (2)] and the subsequent oxidation of these species by surface nitrates to give nitrogen [reaction (5)], while this last reaction is controlled by the presence of reactive nitrate species as the reduction of nitrates proceeds to a significant extent. The results in Fig. 7 and the complementary FTIR study in Fig. 8 have demonstrated that NCO species are left at the catalyst surface after reduction of CO; these species can be oxidized to give N_2 during the subsequent lean phase either by oxygen or by NO + O_2, NO_2, surface nitrites and/or surface nitrates. Finally, the oxidation of surface NCO species observed upon O_2 addition in Fig. 7 with formation of N_2 is also quantitatively explained by the reaction between nitrates (or nitrites), obtained by oxidation of NCO species, with residual NCO species [reaction (5) or reaction (12)]. Indeed the FTIR study has also shown that surface nitrites and nitrates are reformed by oxidation of NCO species (paths ***d*** and ***e***). Thus, it appears that the formation of nitrogen either during the reduction of stored NO_x by CO, or during the oxidation of NCO species upon oxygen addition or during the storage of NO_x upon admission of NO in the presence of excess oxygen is always explained by the reaction between NCO species and surface nitrates (or nitrites), where NCO species, nitrites and nitrates can be transformed ones into the others via oxidation or reduction.

3.5.2. Mechanistic considerations

The mechanism of the reduction of stored NO_x by H_2 and by CO over Pt—Ba/Al_2O_3 catalyst under dry conditions has been previously discussed by Szailer et al. [19] and also reported by other authors [22]. Szailer et al. proposed that when hydrogen is used as reductant, vacant Pt sites (Pt*) are formed by reaction of hydrogen with adsorbed oxygen atom ($Pt\cdots O_a$) left on the Pt surface forming water. The water thus formed destabilizes surface nitrates which could then decompose on the Pt surface with release of NO_x in the gas phase.

Vacant Pt sites are also generated upon reaction of adsorbed oxygen with CO. Although the destabilization of surface nitrates in the case of only CO and under dry conditions is not discussed by the authors, it could be explained assuming that at first nitrates spill over from the Ba particles to the Pt particles and are decomposed in the presence of CO with release of NO_x species in the gas phase, which then are dissociated on vacant Pt particles to form adsorbed nitrogen atoms ($Pt\cdots N_a$). At low temperature, the primary reaction with CO is the removal of adsorbed oxygen atoms from the Pt particles to form CO_2. The vacant Pt sites become available for the adsorption of CO, which can then react with adsorbed nitrogen atoms to form NCO species (Pt—NCO).

NCO formed on the Pt particles spill over to the oxide component of the catalyst. The reaction to form nitrites and eventually NCO species is faster than the reaction of adsorbed nitrogen atoms to give N_2 ($2Pt\cdots N_a \rightarrow 2Pt^* + N_2$). Accordingly, at low temperature the formation of nitrites, NCO species and CO_2 but not of N_2 is observed (viz. at 180–250 °C during CO-TPSR in Fig. 3).

At higher temperatures, these NCO species can readily react with the NO_x species stored by the catalyst ($NCO_a + NO_x \rightarrow N_2 + CO_2$). It is not clear whether this reaction does involve adsorbed or gas-phase NO_x; however, the authors observed that the onset of this reaction corresponds to the onset of nitrate decomposition, suggesting a possible intermediation of gaseous NO_x.

This mechanistic proposal appears consistent with the typical behavior of LNT systems, characterized by long lean phases and short rich periods during which the stored nitrates (and nitrites) decompose to gaseous NO_x due to the relevant exothermicity that takes place upon lean/rich switch. This mechanism is also consistent with several features of the reaction pathway depicted in Fig. 10 and of the transient reactivity data presented in this paper. However, it does not seem fully consistent with all the features pointed out in the present study, and in particular:

(i) all the nitrogen containing species involved in the reaction pathway in Fig. 10 are adsorbed at the catalyst surface so that one could expect that the mechanism responsible for the formation of nitrogen proceeds entirely through adsorbed species. It is worth noting that in the present study the reduction of stored NO_x is accomplished at 350 °C under near isothermal conditions with limited concentration of CO to prevent thermal decomposition of nitrates with release of NO_x in the gas phase; accordingly there is no need to invoke, as a preliminary step, the decomposition of nitrates or nitrites with release of NO_x into the gas phase which are then re-adsorbed onto the catalyst with decomposition and further rearrangement to give nitrogen (via surface NCO species);

(ii) along similar lines the assistance of CO in the decomposition of nitrates which results in the release of NO_x species in the gas phase must account for the very large decrease of the onset temperature of the reduction by CO of stored NO_x from 350 °C (seen during thermal desorption) down to 180 °C (observed during CO-TPSR). An even larger effect is seen in the case of H_2 [7], with a decrease of the onset temperature from 350 °C down to 70 °C;

(iii) N_2 is formed primarily according to an in series two steps process where NCO species are formed first and then are converted to nitrogen upon reaction with $NO_{x,a}$ species. Accordingly, the alternative route to form nitrogen based on the reaction of adsorbed nitrogen atoms to give N_2 is believed to be poorly active not only at relatively low temperature but also at higher temperature, which seems not in line with literature reports on the NO reduction by hydrogen over Pt—Ba/Al_2O_3 [14];

(iv) the mechanism responsible for the formation of nitrogen through oxidation of NCO species upon admission of oxygen during the lean phase of the cycle implies that NCO species that are formed by reduction of stored NO_x can undergo reoxidation to give nitrogen. This feature, along with the reaction of NCO species with either NO/O_2, NO_2 or nitrites/nitrates to form nitrogen, is not consistent with the mechanism proposed by Szailer et al. [19].

A possible alternative mechanism is presented in the following for the reduction of surface nitrates by CO to give nitrogen over Pt—Ba/Al_2O_3 under dry conditions.

The first step in the reaction scheme is represented by the reduction of nitrates by CO adsorbed at a Pt site ($Pt\cdots CO_a$) to give nitrites with evolution of CO_2 (reaction I):

$$\text{—Ba—ONO}_2 + \text{Pt}\cdots\text{CO}_a \rightarrow \text{—Ba—ONO} + \text{CO}_2 + \text{Pt}^* \tag{I}$$

This reaction has been demonstrated by the FTIR data in Figs. 4 and 6, where the reduction of nitrates upon contact with CO has been studied at increasing temperature and at increasing time of contact and constant temperature. It has also been proved that the reaction is catalyzed by Pt.

The present study has shown that surface nitrites are then reduced by CO to give surface NCO species and that this reaction is much faster over Pt—Ba/Al_2O_3 than over Ba/Al_2O_3 and therefore is catalyzed by Pt as well. Due to the large variation in the oxidation state of N associated with the overall reaction from nitrites to NCO species (i.e., from formal oxidation state +3 to −3), it is most likely that this reaction proceeds in a stepwise manner. Accordingly, the following stepwise reduction of nitrites to give NCO species is speculated that seems consistent on a chemical ground and where only intermediate species already detected or synthesized are formed (reactions II–IV):

$$\text{—Ba—ONO} + \text{Pt}\cdots\text{CO}_a \rightarrow \text{—Ba—OCONO} + \text{Pt}^* \tag{II}$$

$$\text{—Ba—OCONO} + \text{Pt}\cdots\text{CO}_a \rightarrow \text{—Ba—OCNO} + \text{CO}_2 + \text{Pt}^* \tag{III}$$

$$\text{—Ba—OCNO} + \text{Pt}\cdots\text{CO}_a \rightarrow \text{—Ba—NCO} + \text{CO}_2 + \text{Pt}^* \tag{IV}$$

Reaction (II) describes the reduction of nitrites to give a CO_2NO^- ions by CO insertion. The experimental observation of the covalent bonded CO_2NO^- ion produced by co-condensation of laser-ablated metal atoms and electrons with NO and CO_2 mixtures in excess Ar and at 11 K has been reported in [35]. Matrix isolation FTIR combined with theoretical calculations has been employed to identify the anion. The anion assignment was further supported by photolysis and CCl_4 doping experiments.

Reaction (III) accounts for the subsequent reduction step to form oxyisocyanate ions. The trimer of hydroxamic acid HO—N=C=O was synthesized and characterized in solid state by IR, MS, and TG analysis and in DMSO-d_6 solutions by NMR and in aqueous solution by IR as well to prove its chemical structure, to reveal a number of physico-chemical properties related to hydroxamate moieties and to indicate hydroxylisocyanate as a possible degradation product in [36]. Theoretical studies on the oxyisocyanate negative ions are also available in the literature [37].

Reaction (IV) describes the successive reduction of oxyisocyanate ions to give NCO species.

All reactions II–IV, catalyzed by Pt, require the spillover of the species from the Ba component onto the Pt particles at the Pt—BaO interface. According to these scheme nitrates are reduced to NCO species in a stepwise manner, so that the formal oxidation number of nitrogen is reduced progressively from +5 (in nitrate ad-species) to −3 (for NCO ad-species) according to a process which involves the transfer of two electrons in each step. Notably, the intermediates involved in reactions I–IV have been spectroscopically detected or synthesized previously. In particular, nitrates, nitrites and NCO species have been observed in the present study by FTIR. Besides CO_2NO^- ions have been synthesized at very low temperature (11 K) and under dilute conditions while hydroxyisocyanate has been observed only upon decomposition of the more stable cyclic trihydroxamic acid. Accordingly, these intermediates are expectedly very reactive and indeed they are not detected in the present study. As a consequence, the reduction of nitrates to give NCO species is likely controlled by the reduction of nitrates to give nitrites. On the other hand, considering that the steps involved in the reduction of nitrites to give NCO species are fast they can proceeds through reactive intermediates different from those proposed in reactions II and III, but generated via the same or a similar chemical route.

The formation of NCO species is then followed by their reaction with residual nitrites to give nitrogen, reaction (V):

$$\text{—Ba—NCO} + \text{—Ba—ONO} \rightarrow \text{—Ba—O—Ba—} + \text{N}_2 + \text{CO}_2 \tag{V}$$

Reaction (V) is consistent with the data in Figs. 3 and 4 and in Figs. 5 and 6 showing that the reduction of nitrates to give N_2 during CO-TPSR and during the CO-ISC experiment always proceeds with formation of nitrites. It is also consistent with the data in Figs. 7 and 8 which show that NCO species are oxidized to give N_2 upon oxygen admission and subsequent admission of NO in the presence of excess oxygen and that the oxidation of NCO species leads to the formation of nitrites as intermediate species.

Indeed once NCO species are formed they are very susceptible to nucleophilic attack and therefore they can react with nitrite ions with intra-molecular rearrangement, internal redox process and CO_2 loss to give dinitrogen molecule as described by reaction (V). An example of this chemistry is provided by the reaction of aryl isocyanates with nitrite ion, as reported in [38].

This reaction has also strict analogies with that of amide species with NO to give nitrosoamide [39,40] or that of ammonium ion with nitrite ion to give ammonium nitrite [41,42]. Both nitrosamide and ammonium nitrite have been proposed as the key intermediates responsible for the production of nitrogen in the SCR of NO_x by ammonia over V- and W-based oxide catalysts [40,43] and Fe- and or Cu-exchanged zeolites [44–46] indeed are known to decompose easily and with full selectivity to nitrogen and water [47].

4. Conclusions

In this paper, the reactivity of NO_x stored at 350 °C onto Pt—Ba/Al_2O_3 LNT catalyst in the reduction by CO under dry conditions was investigated by means of transient experiments (CO-TPSR and isothermal CO-ISC) and complementary FTIR study.

It was shown that the reduction by CO of nitrates stored onto Pt—Ba/Al_2O_3 at high temperature under nearly isothermal conditions occurs through a Pt-catalyzed pathway, which does not involve the thermal decomposition of stored NO_x with release of NO_x in the gas phase and leads mainly to nitrogen and CO_2.

Transient experiments performed both under temperature programming (CO-TPSR) and under isothermal conditions (CO-ISC) and the complementary FTIR study have suggested that (i) the reduction of nitrates by CO occurs through a consecutive reaction scheme which includes the reduction of nitrates into nitrites and then into NCO species followed by the reaction of these species with residual nitrates/nitrites to give nitrogen; (ii) the reaction of surface nitrates/nitrites with NCO species to give nitrogen is slower than the reduction of nitrates to give either nitrites or NCO species; (iii) the formation of nitrogen that is, observed during the reduction of stored NO_x by CO and during the oxidation of NCO species upon oxygen/NO + O_2 addition, can be explained in all cases by the reaction between NCO species and surface nitrates and nitrites.

A mechanism was proposed for the reduction of surface nitrates by CO under dry conditions, which proceeds through a stepwise reduction of nitrates in the order into nitrites, CO_2NO^- ions, oxyisocyanate ions and finally NCO ions and involves the transfer of two electrons in each step. As opposite to other mechanisms previously proposed in the literature, the suggested scheme involves only adsorbed species.

It was noted that NCO species, nitrites and nitrates can be transformed into the others upon oxidation or reduction. This provides a unifying view to explain the production of nitrogen in the reduction by CO of NO_x stored as nitrites and/or nitrates, as well as in the reduction by isocyanates and in the oxidation of NCO species under dry conditions.

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