The NO$_x$ Reduction by CO on a Pt−K/Al$_2$O$_3$ Lean NO$_x$ Trap Catalyst[†]

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The reduction by CO under dry conditions of NO$_x$ species stored at 350 °C onto a Pt−K/Al$_2$O$_3$ lean NO$_x$ trap catalyst is investigated by means of transient response methods (CO-TPSR and CO-ISC experiments) and complementary FT-IR spectroscopy. The results show that the pathway for the reduction of stored NO$_x$ by CO under dry and near isothermal conditions (and in the absence of CO$_2$) is the same as that proposed by some of us in a previous work for a Pt−Ba/Al$_2$O$_3$ catalyst. In particular, (i) the reduction of stored NO$_x$ by CO occurs according to a Pt-catalyzed surface pathway that does not involve, as a first step, the release of NO$_x$ in the gas phase, is effective already at low temperature, and leads to nitrogen; (ii) the reaction scheme implies the formation of surface isocyanate species, followed by the reaction of these species with residual NO$_x$ to give nitrogen; and (iii) the reaction of NCO species with nitrates to give nitrogen is slightly slower than the reduction of nitrates to give NCO species; but on the Pt−K/Al$_2$O$_3$ catalyst, this last step is faster than on the Pt−Ba/Al$_2$O$_3$ system. As a consequence, the amount of isocyanate species present on the surface at the end of the reduction is lower for Pt−K/Al$_2$O$_3$ than for the Pt−Ba/Al$_2$O$_3$ catalyst.

1. Introduction

Commercial vehicles and diesel passenger cars will be subjected in the near future to very stringent emission regulations regarding nitrogen oxides (NO$_x$). In fact, EU emission standards coming into force in 2014 (Euro 6), as similar legislation already in force in the U.S., impose strict emission limits on these pollutants, in addition to hydrocarbon, carbon monoxide, and particulate matter (soot): accordingly, improved and viable solutions for NO$_x$ reduction under lean conditions are required.

Different strategies have been proposed to handle the strict NO$_x$ limits in lean-burn automotive emissions. One such strategy is the NO$_x$ storage-reduction (NSR) system, or lean NO$_x$ traps (LNTs).[1−3] This technique is based on the use of a catalyst containing precious metals, such as Pt, Pd, and Rh, for the reduction and oxidation reactions, and alkali or alkaline-earth metal components, such as Ba or K, that store NO$_x$ as nitrite and nitrate species.[4,5] Overall, NO$_x$ are reduced to N$_2$ over an NSR catalyst by alternating lean and rich periods, that is, a lean period of 30−90 s during which the NO$_x$ emitted in the exhaust gases are stored on the catalyst surface and a short 3−5 s rich period during which the stored NO$_x$ are reduced to N$_2$ by H$_2$, CO, and unburned hydrocarbons.

Several studies deal with the reactivity and characteristics of Ba-containing catalysts (see, for example, refs 6−9), but reports on the specific behavior of K-based catalysts are scarce in the literature, particularly on the reduction step. In this respect, the reactivity of different reducing agents (e.g., H$_2$, CO, C$_3$H$_6$, and C$_3$H$_8$) has been investigated in the case of Ba-containing

catalysts; these studies indicate that hydrogen is the most effective reductant for lean NO$_x$ traps.[10−14]

In recent papers of various research groups, including ours, mechanistic aspects of the reduction of NO$_x$ stored over Ba-based NSR catalytic systems have been reported when H$_2$ is used as a reductant.[15−17] It has been shown that the reduction by H$_2$ under near isothermal conditions of NO$_x$ stored onto Pt−Ba/Al$_2$O$_3$ (and onto Pt−K/Al$_2$O$_3$ as well) is not initiated by the thermal decomposition of nitrates/nitrites ad-species with the release of NO$_x$ in the gas phase but involves a Pt-catalyzed surface pathway that is active at low temperature and leads to nitrogen.[18,19]

However, at temperatures higher than 350 °C, where substantial nitrate decomposition is observed, there is a possibility that the reduction occurs also via a desorption process.

It has also been proposed that, under near isothermal conditions, N$_2$ is formed exclusively via a consecutive reaction scheme that 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$_2$.[15−17,20] However, it has been also pointed out that the reaction of ammonia with residual stored NO$_x$ to give N$_2$ is slower over Pt−Ba/Al$_2$O$_3$ than over Pt−K/Al$_2$O$_3$.

In general, the reduction by CO of NO$_x$ stored on LNT catalysts has attracted lower interest. In a very recent paper, some of us have performed a systematic and quantitative study of the reduction by CO under dry conditions of NO$_x$ stored onto a Pt−Ba/Al$_2$O$_3$ LNT catalyst in order to clarify the reaction pathway and the mechanism of the reaction.[21] By using transient reactivity methods and complementary FT-IR spectroscopy, it was shown that, also in the case of CO and under nearly isothermal conditions, the reduction of nitrates stored onto Pt−Ba/Al$_2$O$_3$ occurs through a Pt-catalyzed surface pathway.

A mechanism was proposed for the reduction of surface nitrates by CO under dry conditions, which proceeds through a stepwise reduction of nitrates with the formation of nitrites and then of surface isocyanate/cyanate species, followed by the reaction of these species with residual nitrites to give nitrogen. This last reaction is slower than the reduction of nitrates to give nitrites and then NCO species. Dedicated experiments have also shown that NCO species can be reoxidized to surface nitrites at first and then to surface nitrates upon contact with oxygen at increasing temperature. This explains the formation of nitrogen 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.

The work presented here focuses on the study of the reduction steps when K replaces Ba as the storage component and CO is used as a reductant. For this purpose, the reduction with CO under dry conditions (and in the absence of CO_2) of NO_x stored onto a model Pt−K/Al$_2$O$_3$ catalyst has been analyzed. For this purpose, NO_x have been adsorbed on the catalyst surface starting from NO/O$_2$; then the reactivity of the stored NO_x with CO has been investigated by means of temperature-programmed surface reaction (TPSR) experiments. Isothermal step concentration (ISC) experiments have also been performed in which the storage and the reduction phases have been carried out under nearly isothermal conditions, that is, in the absence of significant temperature effects during cycling. These conditions have been accomplished by using a 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 uncontrolled thermal effects could be obtained.

In parallel with reactivity experiments, FT-IR spectroscopy has been employed as a complementary technique to obtain information about the nature, reactivity, and evolution of surface species. The results collected over the Pt−K/Al$_2$O$_3$ catalyst sample in this study have been compared with those collected in the case of a Pt−Ba/Al$_2$O$_3$ catalyst[21] in order to highlight possible similarities and differences.

2. Experimental Section

2.1. Materials. K/Al$_2$O$_3$ and Pt−K/Al$_2$O$_3$ catalysts were prepared by the incipient wetness impregnation method, using aqueous solutions of CH$_3$COOK (Sigma Aldrich, 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 UOP, surface area of 207 m^2/g and pore volume of 0.96 cm^3/g). In the case of the Pt−K/Al$_2$O$_3$ catalyst, the impregnation was carried out in a sequential manner: the alumina support was first impregnated with the Pt dinitrodiammine solution and then with the K 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 5.4/100 w/w for the K/Al$_2$O$_3$ catalyst and 1/5.4/100 w/w for the Pt−K/Al$_2$O$_3$ catalyst. The following surface areas and pore volumes were measured by N$_2$ adsorption−desorption at 77K: 179 m^2/g and 0.84 cm^3/g for the K/Al$_2$O$_3$ sample and 176 m^2/g and 0.9 cm^3/g for the Pt−K/Al$_2$O$_3$ sample. The Pt dispersion, as determined by H$_2$ chemisorption at 0 °C, was ∼65%. The mean Pt particle size measured by HRTEM was 1.5 nm,[22] in good agreement with the mean Pt particle size (d_{Pt}) calculated from the empirical relationship often used for monometallic catalysts, d_{Pt} (nm) = 1.1/(H/Pt), where H/Pt is the Pt dispersion measured from H$_2$ chemisorption.

2.2. Reactivity Tests. The reactivity tests were performed over the Pt−K/Al$_2$O$_3$ and the K/Al$_2$O$_3$ samples previously conditioned. In the case of the Pt−K/Al$_2$O$_3$ catalyst, conditioning involved 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 two or three lean−rich cycles.[19,20] For the K/Al$_2$O$_3$ binary catalyst, which does not adsorb significant amounts of NO, in line with previous observations for the homologous Ba/Al$_2$O$_3$,[9] and does 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 400 °C. Like Pt−K/Al$_2$O$_3$, also in the case of K/Al$_2$O$_3$, NO_x are stored on the catalyst surface in the form of nitrates.[20,22]

Temperature-programmed surface reaction (TPSR) experiments were carried out in the presence of CO as a reducing agent to analyze the reactivity of adsorbed nitrates. For this purpose, NO_x were stored at 350 °C with NO/O$_2$ mixtures (1000 ppm NO, 3% v/v O$_2$ in He). For the K/Al$_2$O$_3$ catalyst, the adsorption was carried out with NO$_2$ (1000 ppm in He). The NO + O$_2$ (or NO$_2$) flow was maintained up to adsorption equilibrium; then the inlet NO + O$_2$ (or NO$_2$) concentration was decreased to zero. After storage, the samples were kept under an inert He flow at the same temperature to provoke the desorption of weakly adsorbed species (He purge). Afterward, the samples were cooled to RT under flowing He and the CO-TPSR experiment was started by heating the catalyst at 10 °C/min up to 400 °C in He + 6500 ppm CO.

The storage/reduction of NO_x over Pt−K/Al$_2$O$_3$ was also investigated at constant temperature by imposing stepwise changes in the inlet concentration of the reagents (isothermal step concentration (ISC) experiments), according to the following sequence. After catalyst conditioning (see above), the storage of NO_x (lean phase) was accomplished at 300 °C by admitting NO (1000 ppm) in He + 3% v/v O$_2$. After storage, the NO + O$_2$ concentration was decreased to zero, while maintaining the catalyst at 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 were carried out until a reproducible catalytic behavior was attained.

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d.) directly connected to a mass spectrometer (Omnistar 200, Pfeiffer vacuum) and to a micro GC (Agilent 3000A) for the online analysis of the outlet gases (N$_2$, O$_2$, CO, CO$_2$, N$_2$O). The outlet NO, NO$_2$, and NH$_3$ concentrations were also detected by a UV analyzer (Limas 11HW, ABB).

A 60 mg portion of the catalyst with a small particle diameter (100−120 μm) and a total flow rate of 100 cc/min (at 1 atm and 0 °C) was used in each run in order to minimize intra- and interparticle diffusion limitations. 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. A K-type thermocouple (outer diameter of 0.5 mm) directly immersed in the catalyst bed was used to measure and control the catalyst temperature.

Further details about the experimental apparatus and procedures can be found elsewhere.[8,9,15,20,21]

2.3. FT-IR Study. Absorption/transmission IR spectra were run on a Perkin Elmer FT-IR System 2000 spectrophotometer equipped with a Hg−Cd−Te cryo-detector, working in the range of wavenumbers of 7200−580 cm^{-1} at a resolution of 2 cm^{-1}. For IR analysis, powder samples were compressed in self-

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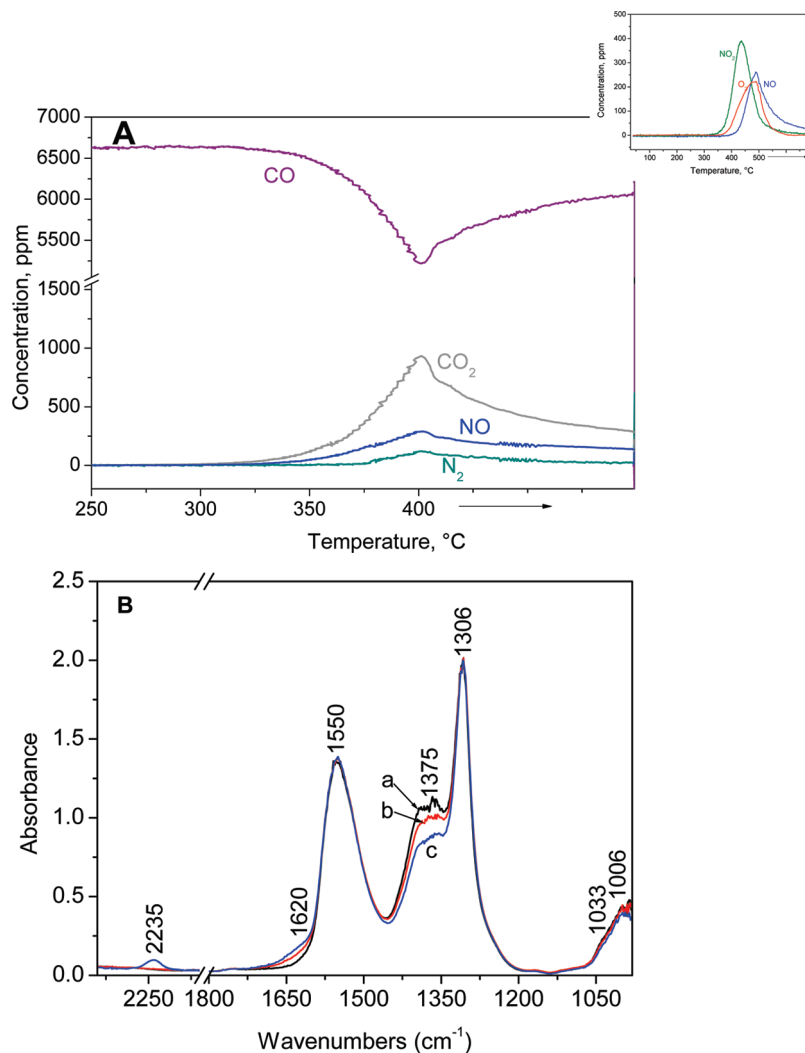
Figure 1. (A) CO-TPSR (6500 ppm CO in He) after NO$_2$ adsorption at 350 °C over the K/Al$_2$O$_3$ catalyst. The results of the TPD run in He after NO$_2$ adsorption at 350 °C over the same catalyst are shown in the inset. (B) FT-IR spectra of NO$_x$ reduction at 350 °C in CO (10 mbar) at increasing exposure times over the K/Al$_2$O$_3$ catalyst. Curve a: spectrum of NO$_x$ stored at 350 °C by NO$_2$ adsorption. Curves b and c: spectra after reduction for 40 min and 3 h, respectively.

supporting disks (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 conditioned (i) by outgassing at 500 °C for 30 min, (ii) with one or two cycles consisting of NO$_2$ adsorption at 350 °C and reduction with H$_2$ at 350 °C (for the Pt−K/Al$_2$O$_3$ catalyst) or outgassing at 500 °C (for the K/Al$_2$O$_3$ sample), necessary to eliminate the carbonates present on calcined powder,[22] and (iii) by oxidation at 500 °C for 30 min and cooling in oxygen down to the temperature requested.

NO$_x$ storage was carried out at 350 °C by admitting, on the Pt−K/Al$_2$O$_3$ disk, freshly prepared NO/O$_2$ mixtures (p_{NO} = 5 mbar, p_{O_2} = 20 mbar) or, on the K−Al$_2$O$_3$ disk, NO$_2$ (p_{NO2} = 5 mbar) up to catalyst saturation (ca. 20 min), and outgassing at the same temperature. The spectra of the stored NO$_x$ were collected at 350 °C or after cooling the disks at the chosen temperature. The reduction was accomplished in CO (p_{CO} = 10 mbar) and was performed both in isothermal conditions and at increasing temperature. The reduction in isothermal conditions was accomplished at 280 and 350 °C: at each temperature, the spectra were run at increasing exposure times. For the reduction

experiments at increasing temperature, the samples were cooled down to 100 °C under vacuum, then heated in CO in the range of 100−400 °C.

NO (Praxair, purity $\geq$ 99.0%) was freshly distilled before use. Conversely, NO$_2$ (Praxair, purity $\geq$ 99.5%), O$_2$ (Praxair, purity $\geq$ 99.999%), and CO (Praxair, purity $\geq$ 99.9%) were directly used.

3. Results and Discussion

3.1. K/Al$_2$O$_3$ Sample. *3.1.1. CO-TPSR Experiments and FT-IR Study.* The reactivity of CO toward NO$_x$ species stored at 350 °C onto K/Al$_2$O$_3$ was investigated by performing a CO-TPSR experiment, and the results are presented in Figure 1A.

CO is consumed above ∼330 °C while CO$_2$ and NO are simultaneously formed, along with trace amounts of N$_2$. The concentrations of the products increase up to 400 °C and then slowly decrease to 0 ppm while the system is held at this temperature (400 °C); in the meantime, the concentration of CO slowly approaches the inlet value.

It is worth noticing that CO reacts with stored NO$_x$ at temperatures (330 °C) near the onset temperature for the thermal decomposition of nitrates (∼340 °C), as appears from the He-TPD experiment reported in the inset of Figure 1A. In this

experiment, the thermal decomposition of nitrate species present on the catalyst surface results in the initial evolution of NO_2, followed by O_2 and NO. The process is not complete at temperatures as high as 500 °C; the catalyst was then kept at 500 °C until desorption of NO_x was complete. The comparison between He-TPD and CO-TPSR experiments points out that the presence of CO in the feed does not affect appreciably the temperature threshold of nitrate thermal decomposition. In contrast, decomposition under a reducing atmosphere leads to a different product distribution, with the lack of any significant NO_2 evolution, and a corresponding increase in NO concentration. Besides, also oxygen evolution was not observed, whereas the formation of nitrogen was seen together with that of CO_2. These results well parallel those obtained in the case of the Ba/Al_2O_3 catalyst.[18,21]

The reduction of the NO_x stored onto the K/Al_2O_3 catalyst at 350 °C with CO has also been investigated by in situ FT-IR spectroscopy, and the spectra obtained at increasing exposure times are reported in Figure 1B. In particular, curve a is the spectrum of NO_x species previously stored at 350 °C, that is, ionic nitrates (related bands at 1375 and 1033 cm^{-1}, assigned to $\nu(NO_3)_{asym}$ and $\nu(NO_3)_{sym}$ modes, respectively) and bidentate nitrates (related bands at 1550, 1306, and 1006 cm^{-1}, assigned to $\nu(N=O)$, $\nu(NO_2)_{asym}$, and $\nu(NO_2)_{sym}$ modes, respectively).[20,22] Curves b and c correspond to the spectra recorded during the interaction with CO at increasing exposure times at 350 °C. The extent of nitrate reduction is nihil after 20 min of exposure (not reported). After 40 min of exposure (curve b), small amounts of ionic nitrates are consumed and it needs 3 h of exposure (curve c) to further reduce the ionic nitrates and to reveal minor amounts of reaction products (carbonate species, shoulder at 1620 cm^{-1}, corresponding to $\nu(C=O)$ mode,[22]) along with minor amounts of isocyanate species (weak band at 2235 cm^{-1}).[23]

In line with CO-TPSR experiment reported in Figure 1A, FT-IR data show that the reduction by CO of nitrates stored onto the K/Al_2O_3 sample is extremely slow at 350 °C and only occurs to a rather limited extent.

3.2. Pt−K/Al_2O_3 Catalyst. *3.2.1. CO-TPSR Experiment and FT-IR Study.* The reactivity of CO toward NO_x species previously stored at 350 °C over the Pt−K/Al_2O_3 sample was investigated by performing a CO-TPSR experiment (CO inlet 6500 ppm), and the results are presented in Figure 2A. CO consumption starts near 210 °C: the CO trace shows a minimum of ∼4150 ppm at 270 °C and then slowly increases, approaching at 340 °C an asymptotic value that is slightly below the inlet concentration. A shoulder in the CO consumption peak is observed near 315 °C. The formation of CO_2 is detected simultaneously with the consumption of CO, showing a maximum of ∼1420 ppm in the temperature range where the CO trace shows its minimum. At the same time, nitrogen is formed at a slightly higher temperature, starting from 230 °C; its concentration gradually increases up to 340 ppm at 280 °C, then slowly decreases. A shoulder in N_2 and CO_2 traces is observed corresponding to the shoulder of the CO peak at 315 °C. Finally, very small amounts of NO are also detected near 235 °C.

From ∼330 °C, when the nitrogen concentration is close to zero, hydrogen is detected in the gaseous products together with CO_2. The production of H_2 and CO_2 at high temperature, jointly with a constant consumption of CO, suggests the occurrence of the water gas shift (WGS) reaction:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (1)$$
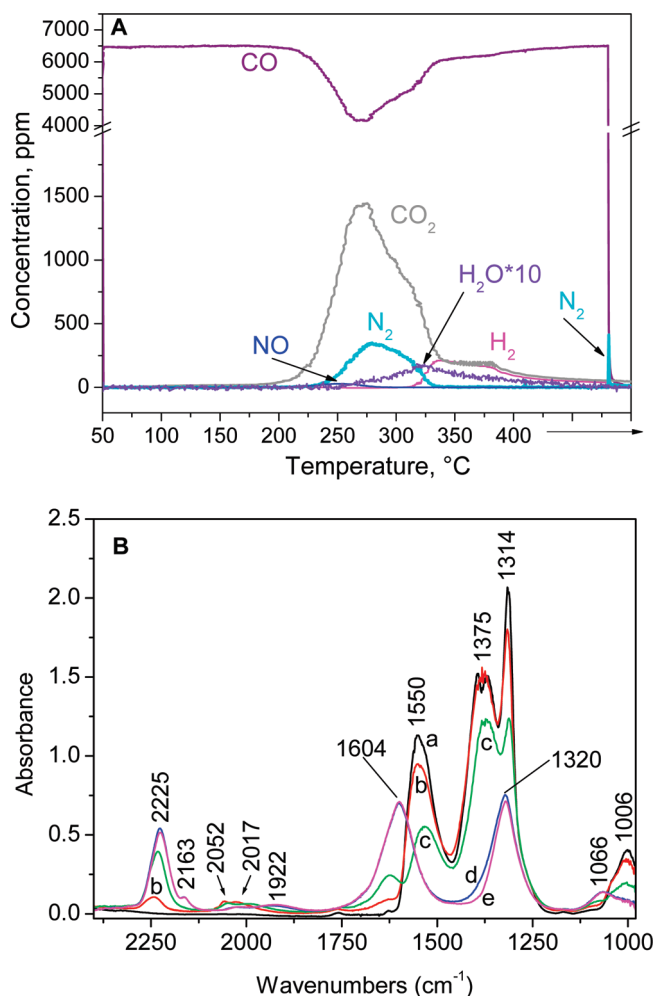
Figure 2. (A) CO-TPSR (6500 ppm CO in He) after NO/O_2 adsorption at 350 °C over the Pt−K/Al_2O_3 catalyst. (B) FT-IR spectra of NO_x reduction in CO (10 mbar) at increasing temperatures over the Pt−K/Al_2O_3 catalyst. Curve a: spectrum of NO_x stored at 350 °C by NO/O_2 adsorption. Curves b−e: spectra after reduction at 250, 300, 350, and 400 °C, respectively.

Indeed, inspection of Figure 2A shows the presence of small amounts of water starting from 250 °C; according to that observed during the He-TPD (not reported), the water concentration trace increases with temperature, suggesting that it is likely related to a desorption from the catalyst surface. The desorption of H_2O could be likely associated with the presence of trace amounts of water in the feed that causes the surface catalyst rehydration at low temperatures (RT−200 °C) and is released at high temperature (250−350 °C). It is worth noting that the WGS reaction occurs over the Pt−K/Al_2O_3 sample starting from 180 °C in the absence of stored nitrates (data not reported) but is observed at higher temperature (330 °C) when the stored nitrates are almost completely depleted. A similar behavior has been observed over the Pt−Ba/Al_2O_3 sample.[21] In addition, it has also been shown in the past that the catalyst promotes the reverse water gas shift (RWGS) reaction as well, and also in this case, the reaction was seen to take place after stored NO_x groups have been depleted.[8]

It is concluded that, over Pt−K/Al_2O_3, the consumption of CO occurs at temperatures well below that of NO_x thermal desorption over the same catalyst. In fact, in the absence of CO, nitrates stored at 350 °C decompose only starting from the temperature of adsorption, as pointed out by dedicated

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TABLE 1: mol/g$_{cat}$ of CO Consumed and of Products Formed during CO-TPSR over Pt−K/Al$_2$O$_3$[a]

reagent and product species (mol/g$_{cat}$)	temperature range	
	RT−250 °C	RT−330 °C
CO consumed	2.91×10^{-4}	14.7×10^{-4}
CO$_2$ formed	1.49×10^{-4}	9.05×10^{-4}
N$_2$ formed	0.08×10^{-4}	1.90×10^{-4}
NO formed		0.12×10^{-4}
H$_2$ formed		1.63×10^{-4}
NH$_3$ formed		

[a] NO_x stored at 350 °C in NO/O$_2$ is 4.33×10^{-4} mol/g$_{cat}$.

He-TPD experiments where the stability of nitrates stored at 350 °C over the Pt−K/Al$_2$O$_3$ sample has been investigated (data not reported). Moreover, a comparison with the results of CO-TPSR experiments carried out over the Pt-free sample (Figure 1) pointed out that the reduction of the stored nitrates is catalyzed by Pt because, over K/Al$_2$O$_3$, the reduction is only observed starting from the temperature of the thermal decomposition of stored NO_x. This clearly indicates that, over Pt−K/Al$_2$O$_3$, a Pt-catalyzed surface route is responsible for the reduction of the stored nitrates, similar to the case of Pt−Ba/Al$_2$O$_3$.[15,21]

Notably, the CO trace is complex, with a first peak at about 270 °C and a shoulder near 315 °C. This may suggest the involvement of stored NO_x species with different reactivities. These features have been observed also when H$_2$ is used as a reductant instead of CO:[19,20] also in that case, two major H$_2$ consumption peaks were apparent in the TPSR experiments, associated with the formation of different products, that is, N$_2$ in the first peak and NH$_3$ in the shoulder at higher temperature. As will be discussed later on, FT-IR measurements pointed out that this is possibly related to the presence of NO_x adsorbed species having different reactivities, that is, ionic and bidentate nitrates.

The moles of CO consumed and of the different products formed during CO-TPSR were calculated from Figure 2A and are reported in Table 1 for different temperature ranges. During the whole TPSR run, 1.90×10^{-4} mol/g$_{cat}$ of N$_2$ and 0.12×10^{-4} mol/g$_{cat}$ of NO are released in the gas phase. Because 4.33×10^{-4} mol/g$_{cat}$ of NO_x species has been previously stored onto the catalyst, ∼90% of the stored nitrates are reduced to gaseous N-containing products. Accordingly, small amounts of N-containing species could be present at the catalyst surface at the end of the CO-TPSR experiment. In fact, as it will be shown in the following, FT-IR spectra show that NCO species still remain onto the catalyst surface at the end of the reduction phase.

The features herein discussed suggest that the reduction of stored NO_x species primarily occurs according to the reactions

$$2KNO_3 + 5CO \rightarrow K_2CO_3 + N_2 + 4CO_2 \qquad (2)$$

$$2KNO_3 + 8CO \rightarrow 2KNCO + 6CO_2 \qquad (3)$$

Close inspection of Figure 2A shows that, in the low-T region (below 250 °C), the consumption of CO is accompanied by the evolution of CO$_2$ and of a very small quantity of N-containing species (0.08×10^{-4} mol/g$_{cat}$ of N$_2$, Table 1). This points out that the initial step in the reduction of stored nitrates is described by reaction 3, as is also confirmed by FT-IR study (see below).

A similar TPSR experiment performed over the Pt−Ba/Al$_2$O$_3$ catalyst demonstrated that, at the end of the CO-TPSR experiment, only ∼43% of the stored nitrates were reduced to gaseous N-containing products and, consequently, N-containing species were still present at the catalyst surface.[21] Also, in that case, in the low-temperature region (below 250 °C), the CO consumption is higher than that expected from N$_2$ and CO$_2$ production and the formation of isocyanates species has been pointed out by FT-IR experiments, according to the stoichiometry of the following reaction:

$$Ba(NO_3)_2 + 8CO \rightarrow Ba(NCO)_2 + 6CO_2 \qquad (4)$$
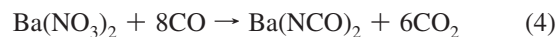
As shown in the following, FT-IR measurement reveals that the formation of isocyanates ad-species is effective in the case of the Pt−K/Al$_2$O$_3$ catalyst as well. However, opposite to the homologous Pt−Ba/Al$_2$O$_3$ catalyst,[21] over Pt−K/Al$_2$O$_3$, the amounts of NCO species left onto the catalyst surface at the end of the reduction are small, in line with the observation that ∼90% of the stored nitrates are reduced to gaseous N-containing products (see above).

The reduction by CO of NO_x species previously stored at 350 °C onto the Pt−K/Al$_2$O$_3$ catalyst investigated by means of in situ FT-IR spectroscopy is reported in Figure 2B. In this figure, curve a is the spectrum of NO_x species stored at 350 °C and cooled to 100 °C, and curves b−e correspond to the spectra recorded during interaction with CO at increasing temperatures up to 400 °C. The stored nitrates are not perturbed in the range of 100−200 °C (not reported); at 250 °C, the bidentate nitrates begin to be reduced (curve b, bands at 1550, 1314, and 1006 cm^{-1}) and are completely removed at 350 °C (curve d). Starting from 300 °C (curve c), also, the ionic nitrates (bands at 1375 and 1033 cm^{-1}) start to be reduced, and their reduction is complete at 400 °C. It is worth noting that ionic nitrates are more resistant to the reduction with respect to the bidentate ones, but ionic nitrates start to react before the complete removal of bidentate species: this justifies the presence of the two contributions of CO consumption in the TPSR measurement (Figure 2A), with a minimum near 270 °C and a shoulder at 315 °C.

Simultaneous to the nitrate reduction, increasing amounts of NCO surface species (band at 2225 cm^{-1} and a very weak one at 2163 cm^{-1}) and of surface carbonates (bands at 1604, 1320, and 1066 cm^{-1}, corresponding to $\nu(C=O)$, $\nu(CO_2)_{asym}$, and $\nu(CO_2)_{sym}$ modes, respectively[22]) are also revealed. Actually, up to 350 °C, the $\nu(CO_2)_{asym}$ mode of carbonates is superimposed with some of nitrate modes. The NCO species responsible for the band at 2163 cm^{-1} appear only by reduction at 350 °C. The two bands at 2225 and 2163 cm^{-1} are in the same positions of the bands related to isocyanate species formed in a similar experiment (i.e., reduction with CO of stored NO_x) accomplished on a Pt−Ba/Al$_2$O$_3$ catalyst.[21] In the literature, these bands have been assigned to isocyanate species coordinated to Al^{3+} in tetrahedral coordination and on the Ba phase, respectively.[24−26] However, our results obtained from experiments performed with assignment purposes do not match with the literature. We found that both the bands are related to different isocyanate species on the Ba phase.[21,27,28] For the same reasons, and on the basis of dedicated experiments (not reported because it is out of the aim of this work), we assign both the bands found on the Pt−K/Al$_2$O$_3$ catalyst to different NCO species on the K phase.

In line with TPSR data, FT-IR experiments confirm that nitrates stored onto the Pt−K/Al$_2$O$_3$ catalyst are reduced by CO at temperatures lower than that corresponding to their thermal decomposition. However, FT-IR measurements reveal a begin-

ning of the reduction at temperatures slightly higher (250 °C) than that found in the TPSR experiment (210 °C). This can be related to the different operating conditions: vacuum pretreatment and static conditions for FT-IR measurements and flow conditions for TPSR ones. Moreover, FT-IR experiments confirm that, on the Pt−K/Al$_2$O$_3$ catalyst, a certain amount of nitrogen is still present on the surface as isocyanate species after reduction of stored nitrates with CO up to 400 °C. As already mentioned, the formation of strongly adsorbed NCO species justifies the absence of N$_2$ evolution at the beginning of the TPSR experiment, while CO is being consumed. NCO species might be involved in N$_2$ formation, as pointed out by a close inspection of the bands in Figure 2B, which shows that increasing the temperature, keeping constant the erosion rate of nitrate bands, the growing rate of NCO absorption at 2225 cm^{-1} decreases. This point will be further addressed below.

Isocyanate species formed on the Pt−K/Al$_2$O$_3$ catalyst at the end of the reduction (see Figure 2B, curve e) are in very low amounts if compared with those formed in similar conditions by reduction with CO of NO$_x$ stored on the Pt−Ba/Al$_2$O$_3$.[21] This statement needs some considerations. The more correct mode to support the statement should be an evaluation of the ratio between the integrated intensities of absorption bands related to NCO at the end of the reduction and of nitrate absorption bands before the reduction. In this way, it should be possible to evaluate the ratio between the total amount of nitrogen stored as nitrates and of nitrogen that remains at the surface after the reduction step on the two catalysts. However, whereas on the Pt−Ba catalyst, practically only ionic nitrates are present, on the Pt−K catalyst, both ionic (with different spectroscopic features with respect to the Pt−Ba system) and bidentate nitrates are present. The different distributions of nitrate types with different absorption coefficients on the two systems makes this kind of evaluation not feasible.

Conversely, having the NCO species the same spectroscopic features on the Pt−K/Al$_2$O$_3$ and Pt−Ba/Al$_2$O$_3$ systems, it is reasonable to assume that they have the same absorption coefficients. Moreover, we have to take into account the following: (i) the molar amounts of K and Ba per gram of catalyst are similar on both the systems; (ii) the dispersion of the basic phase is high on both the catalysts;[22,29] (iii) we used disks with comparable weights; (iv) the ratio between the specific surface areas of Pt−K/Al$_2$O$_3$ (176 m^2/g) and Pt−Ba/Al$_2$O$_3$ (137 m^2/g) is 1.3; and (v) the amounts of NO$_x$ stored at 350 °C on the two systems are comparable (4.33 × 10^{-4} mol/g$_{cat}$ for Pt−K/Al$_2$O$_3$ and 5.8 × 10^{-4} mol/g$_{cat}$ for Pt−Ba/Al$_2$O$_3$).[20,21] On the basis of these considerations, it is possible to directly compare the integrated intensities (normalized to the surface areas of the catalysts) of the bands related to isocyanate species formed in similar experiments to make an evaluation of the difference in the amounts of isocyanates formed on the two systems. These calculations suggest that the amount of isocyanates formed on the Pt−K catalyst is roughly 5 times lower than that formed on the Pt−Ba catalyst.

Another possibility is considering the ratio between the integrated intensities of the bands related to isocyanate species and to the carbonate species formed at the end of the reduction. In this case, no assumptions about surface areas, disk weights, and the amount and dispersion of the storage phase are necessary. However, it is necessary to assume (i) the same absorption coefficients for the carbonates on the surface of Pt−K and Pt−Ba systems (this is reasonable because they show the same spectroscopic features for the two catalysts) and (ii) a similar equilibrium between CO$_2$ in the gas phase and CO$_2$

adsorbed as carbonates on the surface of Pt−K/Al$_2$O$_3$ and Pt−Ba/Al$_2$O$_3$. Another crucial assumption is that the carbonate amounts per gram of catalyst should be the same, even if carbon consumed from CO to form NCO species is surely higher for Pt−Ba than for the Pt−K catalyst. However, the reaction pathway proposed (see below) shows the formation of a high CO$_2$ excess with respect to isocyanates, ensuring a negligible error in the evaluation proposed here. On the basis of these considerations, the ratio between the amounts of NCO (in the range of 2330−2080 cm^{-1}) and CO$_3^{2-}$ species (in the range of 1800−1160 cm^{-1}) formed at the end of the nitrate reduction at increasing temperature is 0.27 for Pt−K/Al$_2$O$_3$ and 1.4 for Pt−Ba/Al$_2$O$_3$. This calculation suggest that, assuming constant the amount of carbonates formed on the two catalysts, the quantity of isocyanates on the Pt−K system is roughly 5 times lower than that on the Pt−Ba one, perfectly in line with the previous evaluation.

The calculated values are in agreement with data obtained from TPSR experiments over both Pt−K/Al$_2$O$_3$ and Pt−Ba/Al$_2$O$_3$ catalysts. In fact, for the Pt−Ba/Al$_2$O$_3$ catalyst,[21] 43% of the stored nitrates are reduced to gaseous N-containing products and, consequently, 57% of nitrogen remains on the surface as isocyanates, whereas for Pt−K/Al$_2$O$_3$, 90% of the stored nitrates are reduced to gaseous N-containing products and, consequently, only 10% of nitrogen remains on the surface as isocyanates. This means that the quantity of isocyanates present on the Pt−K system is roughly 5−6 times lower than that on the Pt−Ba one.

Finally, it is also worth noticing that, after CO interaction at 250 °C up to 300 °C, FT-IR spectra showed two weak bands at 2052 and 2017 cm^{-1} (Figure 2B) related to the stretching modes of linear carbonyls adsorbed on reduced Pt sites,[22] indicating that the platinum is already reduced by CO at 280 °C. Actually, these bands start to decrease at 350 °C for carbonyl desorption with a contemporary shift to lower frequencies, as expected on decreasing the CO coverage.

3.2.2. CO-ISC Experiment and FT-IR Study.
The reactivity toward CO of NO$_x$ stored at 300 °C over the Pt−K/Al$_2$O$_3$ sample was investigated by performing isothermal reactivity experiments.

The results of a CO-ISC experiment run at 300 °C reported and discussed in the following are collected over a sample that showed reproducible cyclic behavior, that is, after performing few lean−rich cycles (i.e., NO$_x$ storage and reduction by CO with an inert purge in between).

Figure 3 shows the results of a lean−rich cycle at 300 °C (storage and reduction) over the Pt−K/Al$_2$O$_3$ catalyst performed by admitting 1000 ppm NO in the presence of O$_2$ (3% v/v in He), followed by reduction of the stored NO$_x$ by admission of 2000 ppm CO (in He). A helium purge was fed between the lean and rich phases.

As shown in Figure 3, the admission of 3% v/v O$_2$ (Figure 3, $t = -1000$ s) causes the evolution of a small amount of N$_2$, produced by the oxidation of surface N-containing species that remain adsorbed at the catalyst surface after the previous reduction with CO. Upon the NO step addition (at $t = 0$ s), NO and NO$_2$ show a dead time of about 30 and 100 s, respectively; their concentration rapidly increases with time, approaching the asymptotic concentrations corresponding to the NO$_x$ feed concentration (NO + NO$_2$) after about 2000 s. Accordingly, significant amounts of NO$_x$ were stored (5.41 × 10^{-4} mol/g$_{cat}$). Formation of NO$_2$ in the gas phase indicates that Pt is active in the NO oxidation reaction; as indicated in a dedicated FT-IR analysis, nitrates are the major adsorbed species present after adsorption in NO/O$_2$ at 300 °C.[19,20]

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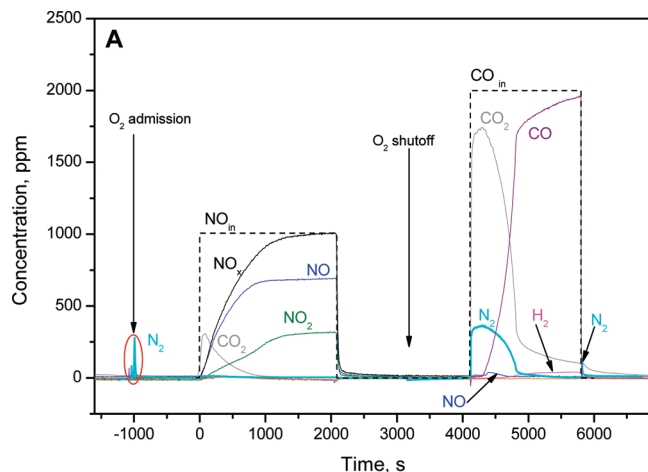
Figure 3. ISC experiments at 300 °C over the Pt−K/Al$_2$O$_3$ catalyst (storage phase, NO 1000 ppm + O$_2$ 3% v/v in He; reduction phase, CO 2000 ppm in He).

TABLE 2: mol/g$_{cat}$ of CO Consumed and of Different Products Formed during CO-ISC Carried Out at 300 °C over Pt−K/Al$_2$O$_3$[a]

| reagent and product species (mol/g$_{cat}$)	O$_2$ admission (t = −1000 s)	CO admission (t = 4114− 5770 s)	CO shutoff (t = 5770− 6600 s)
CO consumed		16.2 × 10^{-4}	
CO$_2$ formed		13.9 × 10^{-4}	0.334 × 10^{-4}
N$_2$ formed	0.035 × 10^{-4}	2.61 × 10^{-4}	0.024 × 10^{-4}
NO formed		0.09 × 10^{-4}	
NH$_3$ formed			

[a] NO$_x$ stored at 300 °C in NO/O$_2$ is 5.41 × 10^{-4} mol/g$_{cat}$.

Upon admission of CO (t = 4114 s), ∼360 ppm N$_2$ and ∼1730 ppm CO$_2$ are immediately produced, together with negligible amounts of NO (30 ppm). CO is completely consumed for about 200 s; afterward, CO is detected at the reactor outlet: its concentration increases and approaches the inlet value within ∼1700 s after CO admission. After CO breakthrough, the N$_2$ and CO$_2$ concentrations (and NO production) decrease. When the nitrogen concentration is close to zero (i.e., when stored NO$_x$ are almost depleted), H$_2$ production is observed, as in the case of the CO-TPSR experiment.

It is worth noting that a very small increase in the catalyst temperature (≤2 °C) is measured upon CO admission so that the reduction is performed under nearly isothermal conditions.

When the CO feed is stopped (after 1700 s from the CO admission), a small amount of nitrogen is produced, along with CO$_2$ (see Table 2).

The moles of CO consumed and of the different products formed during CO-ISC experiment over Pt−K/Al$_2$O$_3$ were calculated from Figure 3 and reported in Table 2. From the amounts of CO consumed and of evolved N$_2$ and CO$_2$, it appears that the reduction of the stored NO$_x$ roughly obeys the stoichiometry of reaction 2:

$$2KNO_3 + 5CO \rightarrow N_2 + K_2CO_3 + 4CO_2 \qquad (2)$$
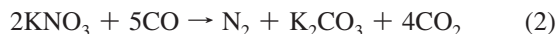
Besides, the N balance is almost satisfied, thus suggesting that almost all the stored NO$_x$ have been removed by CO. As a matter of fact, FT-IR results pointed out that only small amount of N-containing species remains onto the catalyst surface after reduction with CO (see below), but this is within the experimental error of our experiments.
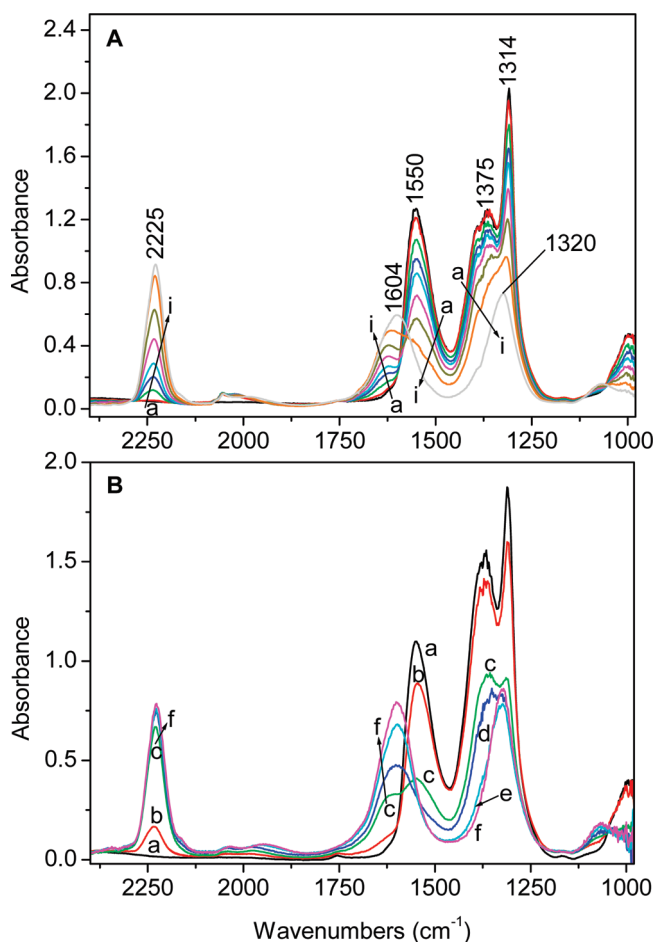
Figure 4. (A) FT-IR spectra of NO$_x$ reduction in CO (10 mbar) at 280 °C at increasing exposure times over the Pt−K/Al$_2$O$_3$ catalyst. Curve a: spectrum of NO$_x$ stored at 350 °C by NO/O$_2$ adsorption. Curves b−i: spectra after reduction at 280 °C for 30 s, 1 min, 2 min, 4 min, 8 min, 15 min, 30 min, and 2 h, respectively. (B) FT-IR spectra of NO$_x$ reduction in CO (10 mbar) at 350 °C at increasing exposure times over the Pt−K/Al$_2$O$_3$ catalyst. Curve a: spectrum of NO$_x$ stored at 350 °C by NO/O$_2$ adsorption. Curves b−f: spectra after reduction for 15 s, 30 s, 1 min, 2 min, and 4 min, respectively.

The interaction of CO with the NO$_x$ species stored on the Pt−K/Al$_2$O$_3$ catalyst under isothermal conditions, followed by FT-IR spectroscopy and obtained at 280 and 350 °C, is presented in Figure 4A and 4B, respectively. In Figure 4A, curve a is the spectrum of NO$_x$ species previously stored at 350 °C, whereas curves b−i correspond to the spectra recorded during interaction with CO at increasing exposure times at 280 °C. As expected on the basis of the results obtained at increasing temperatures, the reduction of bidentate nitrates starts before (after 30 s, Figure 4A, curve b, bands at 1550, 1314, and 1006 cm^{-1}) the reduction of ionic ones (after 1 min, Figure 4A, curve c, bands at 1375 and 1033 cm^{-1}). At 280 °C, the reaction evolves slowly and it is not completed even after 2 h (Figure 4A, curve i). This can be evidenced by the linear intensity of the carbonate band at 1320 cm^{-1} formed during the reduction: it should be almost the same of that of the band at 1604 cm^{-1} (as evidenced in the experiment at increasing temperature, Figure 2B); but this is not the case, revealing the contribution of residual ionic nitrates under the band at 1320 cm^{-1}. NCO species formed are practically only those responsible for the absorption at 2225 cm^{-1}. Furthermore, also in these kinds of FT-IR experiments, it is possible to observe the presence of bands in the region of 2090−1880 cm^{-1} related to the presence of carbonyls onto reduced Pt sites.

In Figure 4B, curve a is the spectrum of NO_x species previously stored at 350 °C, whereas curves b−f correspond to the spectra recorded during CO interaction at increasing exposure times at 350 °C. The reduction of nitrates is very fast because the band intensities of both bidentate and ionic nitrate are reduced markedly after 30 s of CO contact, even more after 1 min of contact (Figure 4B, curve c). Their consumption is complete after 4 min (Figure 4B, curve f), even if, already at 2 min of contact, their amounts are really low, being revealed by a very weak shoulder on the high wavenumber side of the carbonate band at 1320 cm^{-1}. Simultaneously to the nitrate reduction, the carbonate species appear due to the adsorption of CO_2 produced during the reduction, along with NCO species (bands at 2225 and 2163 cm^{-1}).

As observed for the FT-IR experiment at increasing temperature, also isothermal measurements confirm that, on the Pt−K/Al_2O_3 catalyst after NO_x reduction in CO, only small amounts of nitrogen are still present on the surface as isocyanate species. Indeed, isocyanate species formed on the Pt−K/Al_2O_3 catalyst at 350 °C (at 280 °C, the reduction is not complete) are in very low amounts if compared with those formed in the same conditions by reduction with CO of NO_x stored on the Pt−Ba/Al_2O_3 catalyst.[21] As already performed for experiments at increasing temperature, it is possible to coarsely evaluate the integrated intensities of absorption bands related to NCO, or the ratio between the integrated intensities of the NCO band (in the range of 2330−2080 cm^{-1}) and of CO_3^{2-} absorptions (in the range of 1800−1160 cm^{-1}), taking into account the same assumptions already mentioned. Whichever of the two methods of calculation is employed, the result is that the quantity of isocyanates on the Pt−K system is roughly 4 times lower than that on the Pt−Ba/Al_2O_3 catalyst. CO-ISC data performed on the Pt−Ba/Al_2O_3 catalyst[21] showed that 58% of the stored nitrates are reduced to gaseous N-containing products, and consequently, 42% of nitrogen remains on the surface as isocyanates. On this basis, we can estimate that about 10% of nitrogen, stored in the form of nitrates, remains on the surface as NCO species for Pt−K/Al_2O_3.

At the end of the FT-IR reduction experiment at 350 °C, the thermal stability of NCO species was also investigated by FT-IR analysis, and results are shown in Figure 5A. The prolonged outgassing at 350 and 400 °C (Figure 5A) indicates that NCO species are very stable at these temperatures; notably, on the basis of the integrated intensity of the band at 2225 cm^{-1}, 57% of the NCO species are still present after 2 h of outgassing at 350 °C (Figure 5A, curve d) and 39% after 1 h of outgassing at 400 °C (curve e). It is also possible to evaluate the carbonate thermal stability (bands at 1600, 1320, and 1064 cm^{-1}), which is lower than that of isocyanates: 31% of the carbonates remain on the surface after 2 h of outgassing at 350 °C (Figure 5A, curve d) and 24% after 1 h of outgassing at 400 °C (curve e).

Oxidation measurements of NCO species were also performed after NO_x reduction in CO at 280 °C (Figure 5B): after reduction, the sample was outgassed at 350 °C and then cooled down at 100 °C (Figure 5B, curve a). Oxygen was then admitted at 100 °C: the sample was heated in O_2 at 10 °C/min, and the spectra were run at intervals of 2 min up to 400 °C. The isocyanates are not perturbed in the range of 100−240 °C (not reported). Their erosion starts at 240 °C (curve b), and it is complete only at 400 °C (curve f). This justifies N_2 evolution in the ISC experiment, when oxygen is admitted after a reduction step in CO.

3.3. Mechanistic Aspects. The results collected during CO-TPSR over K/Al_2O_3 (Figure 1A) and over Pt−K/Al_2O_3 (Figure
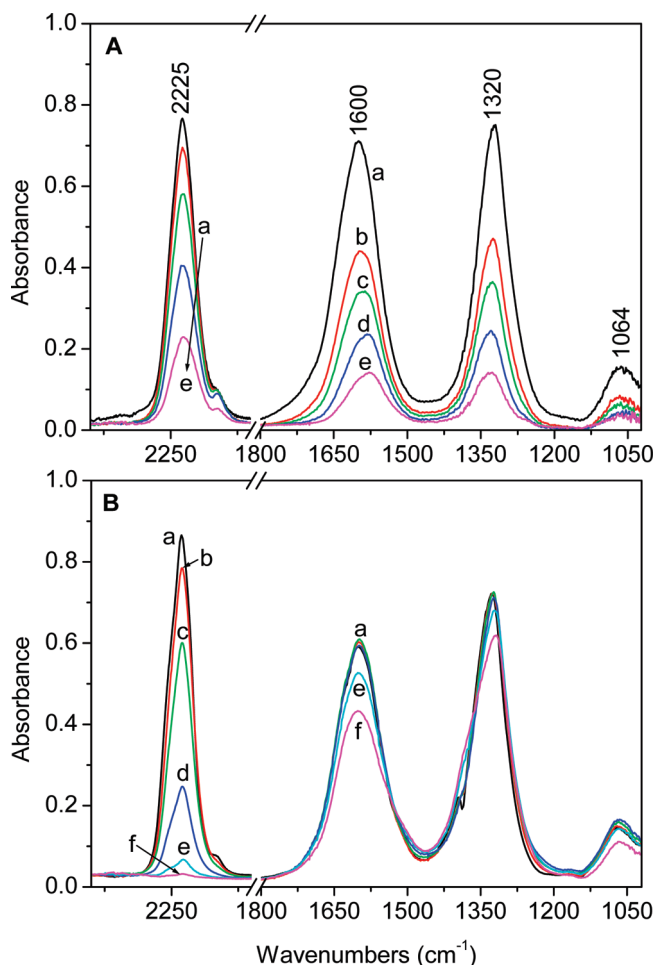
Figure 5. (A) FT-IR investigation of the thermal stability of NCO species under evacuation at 350 and 400 °C. Curve a: spectrum of NCO species formed in CO at 350 °C. Curves b−d: spectra after evacuation at 350 °C for 10 min, 30 min, and 2 h, respectively. Curve e: spectrum after evacuation at 400 °C for 1 h. (B) FT-IR investigation on the reactivity of NCO species toward oxygen. Curve a: spectrum of NCO species formed at 350 °C and cooled to 100 °C. Curves b−f: spectra during treatment in O_2 (10 mbar) at 240, 280, 320, 360, and 400 °C, respectively (heating at 10 °C/min, spectrum recording each 2 min).

2A) highlight that, in the presence of Pt, the reduction of nitrate species by CO is faster considering that the onset temperature of the reaction is lower (∼210 vs 340 °C), and the conversion of CO is higher. Besides, it appears that the reduction does not require as a first step the thermal release of NO_x in the gas phase because the reaction is seen at temperatures well below that of the thermal decomposition of adsorbed NO_x (340 °C).

The results collected during the CO-ISC experiment over Pt−K/Al_2O_3 (Figure 3) are in line with the results of CO-TPSR experiments and further indicate that the reduction at 300 °C by CO of NO_x stored onto the Pt−K/Al_2O_3 catalyst is very fast and controlled by the concentration of CO. It is possible to conclude that the reduction by CO under nearly isothermal conditions of nitrates stored onto the Pt−K/Al_2O_3 catalyst at high temperature (i.e., 300 °C) occurs according to a Pt-catalyzed surface pathway. As it is apparent from Figure 3, this catalytic route of nitrate reduction by CO leads mainly to nitrogen and CO_2 in the gas phase. At temperatures higher than 350 °C, where substantial nitrate decomposition is observed during TPD (data not reported), there is a possibility that desorption and then reaction can occur in addition to the surface reaction.

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It is worth noticing that a low-temperature Pt-catalyzed surface pathway has already been demonstrated for the reduction by H$_2$ of NO$_x$ stored over the same catalyst used in this study,[20] leading mostly to nitrogen; hydrogen is more effective than CO because the onset temperature of the reduction is lower (120 vs 210 °C). The same conclusions apply to a Pt−Ba/Al$_2$O$_3$ catalyst used in previous studies,[15,21] and this suggests that the reduction of stored NO$_x$ with H$_2$ and with CO over LNT catalysts might present analogies that are worth being investigated.

The results of CO-TPSR and CO-ISC experiments over Pt−K/Al$_2$O$_3$ (Figures 2A and 3) and of the complementary FT-IR study (Figures 2B and 4) indicate that the reduction by CO of nitrates stored onto the Pt−K/Al$_2$O$_3$ catalyst under dry conditions occurs according to the stoichiometry of the following overall reactions:

$$2KNO_3 + 5CO \rightarrow K_2CO_3 + N_2 + 4CO_2 \qquad (2)$$

$$2KNO_3 + 8CO \rightarrow 2KNCO + 6CO_2 \qquad (3)$$

Reactions 2 and 3 account for the consumption of CO and of nitrates, and for the formation of CO$_2$. In particular, reaction 3 accounts for the consumption of nitrates with the formation of isocyanates (revealed by FT-IR) and CO$_2$; reaction 2 accounts for the formation of N$_2$, CO$_2$, and carbonates at the catalyst surface, as revealed by FT-IR. The formation of isocyanates and carbonates at the surface explains the fact that the N balance and the C balance in the gas phase is far from 100% at the end of the CO-TPSR experiment. In particular, reaction 2 does not occur in the low-temperature range (210−250 °C) where N$_2$ is not detected.

FT-IR spectra reveal also that bidentate nitrates stored onto the catalyst surface are reduced at first and ionic ones start to be reduced later on, i.e. the ionic nitrates result more resistant to the CO reduction. Similar results have been obtained when H$_2$ was used as a reductant instead of CO;[19,20] also, in that case, FT-IR measurements put in evidence a different reactivity between ionic and bidentate nitrates toward H$_2$. These features agree well with TPSR data where two contributions of reductant (H$_2$ and/or CO) consumption are apparent.

The data discussed herein are consistent with the reaction pathway already proposed for N$_2$ formation in the case of Pt−Ba/Al$_2$O$_3$.[21,28] In that case, ISC, TPSR, and FT-IR results have demonstrated that large amounts of NCO species are left at the catalyst surface after reduction of CO under dry conditions; 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. N$_2$ is formed primarily according to an in-series two-step process, where NCO species are formed first and then are converted to nitrogen upon reaction with NO$_x$ stored species. In analogy with the reaction pathway for the reduction by CO of nitrates stored over Pt−Ba/Al$_2$O$_3$ under dry conditions, the reduction by CO of nitrates stored onto the Pt−K/Al$_2$O$_3$ catalyst occurs according to the stoichiometry of the following overall reactions:

$$2KNO_3 + 8CO \rightarrow 2KNCO + 6CO_2 \qquad (3)$$

$$6KNO_3 + 10KNCO \rightarrow 8N_2 + 8K_2CO_3 + 2CO_2$$
$$(5)$$
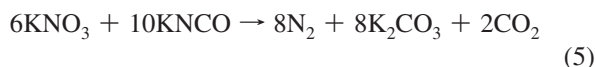
Hence, NCO species are considered intermediates in the formation of N$_2$, whose formation occurs exclusively according

to the stoichiometry of the reactions 3 + 5 (the sum giving the overall reaction 2).

Besides, analogies could be found for both the catalytic systems also with the reduction of stored nitrates by H$_2$, where an in-series two-step molecular pathway has been proposed for N$_2$ formation involving, at first, the formation of ammonia upon reaction of nitrates with H$_2$, followed by the reaction of the so-formed ammonia with the residual stored nitrates, leading to the formation of N$_2$.[15,16,19,20] The following overall reactions are involved:

$$2KNO_3 + 8H_2 \rightarrow 2NH_3 + KOH + 4H_2O \qquad (6)$$

$$6KNO_3 + 10NH_3 \rightarrow 8N_2 + 6KOH + 12H_2O \qquad (7)$$
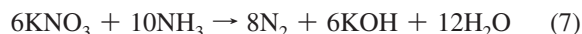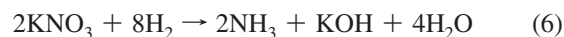
In the case of reduction by CO, NCO ad-species play as intermediates in the reduction instead of NH$_3$.

The reduction by CO of NO$_x$ stored over Ba- and K-containing catalysts shows slightly distinct features. Over Pt−Ba/Al$_2$O$_3$, only ionic nitrates were observed, giving during the CO reduction two FT-IR bands at 2222 and 2164 cm^{-1} related to NCO species, whereas both bidentate and ionic nitrates are present on Pt−K/Al$_2$O$_3$ and mainly the band at 2225 cm^{-1} is detected.

The CO-TPSR experiment over Pt−Ba/Al$_2$O$_3$ has shown[21,28] that the reaction of surface nitrates to give nitrogen (analogous to reaction 2) is slower than that responsible for the initial reduction of nitrates to give NCO species (analogous to reaction 3). The formation of nitrogen in this case via the reduction of nitrates by CO is explained as the sum of the reduction of nitrates by CO to give surface NCO species (analogous to reaction 3) and the subsequent oxidation of these species by surface nitrates to give nitrogen (analogous to reaction 5).

Also, in the case of Pt−K/Al$_2$O$_3$, the reaction of surface nitrates to give nitrogen seems to be slower than that responsible for NCO species formation. In fact, the formation of nitrogen is observed only above 250 °C, while evidence for the formation of N-containing species from 210 °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. Accordingly, FT-IR measurement shows that isocyanates are formed and their storage on the surface is higher in the low-temperature range. However, in this case, the reaction between surface nitrates and surface NCO species to give nitrogen is faster and more efficient than over the Ba-containing system. Accordingly, at the end of the CO-ISC experiments, both the C and the N balances are near 100% in the case of the K-containing catalyst (300 °C), but not over Pt−Ba/Al$_2$O$_3$ (350 °C).

The reason for the higher NO$_x$ reduction efficiency to N$_2$ pointed out by the Pt−K/Al$_2$O$_3$ catalyst may be related to the higher mobility of the adsorbed surface species. It has been speculated that the reduction of the stored NO$_x$ implies the surface mobility of these species toward Pt, where they are reduced by the reductant.[21] In the case of CO as a reductant, isocyanate species are formed as intermediates. In the suggested pathway of the reduction of stored NO$_x$ by CO, the rate-determining step is the slow reaction between nitrates and isocyanates (reaction 5), which involves two surface species; hence, the surface mobility of the species is expected to play a major role on the reaction. It is known that K-nitrates have a melting point lower than that of Ba-nitrates (334 vs 592 °C). Along this line, K-nitrates might have a higher surface mobility that facilitates their spillover from the K component onto the

Pt particles and, as a consequence, their reaction with K−NCO species. As a result, the CO reduction is more efficient over the Pt−K/Al$_2$O$_3$ catalyst than over the Pt−Ba/Al$_2$O$_3$ catalyst.

4. Conclusions

In this paper, the reactivity of NO$_x$ stored at 350 °C onto the Pt−K/Al$_2$O$_3$ LNT catalyst in the reduction by CO under dry conditions was investigated by means of transient experiments (CO-TPSR and isothermal CO-ISC) and a complementary FT-IR study.

It was shown that the reduction by CO of nitrates stored onto Pt−K/Al$_2$O$_3$ at high temperature under nearly isothermal conditions occurs through a Pt-catalyzed surface 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$_2$. The reaction scheme already proposed in the case of the Pt−Ba/Al$_2$O$_3$ catalyst operates also in the case of the Pt−K/Al$_2$O$_3$ system and implies the formation of surface isocyanate species, at first, and, in the second step, the reaction of these superficial species with residual nitrates to give nitrogen. Over the Pt−K/Al$_2$O$_3$ system, this last surface reaction is more efficient than over the Ba-containing catalyst, so at the end of the reduction, the amount of isocyanate species present on the surface is lower for Pt−K/Al$_2$O$_3$ than for the Pt−Ba/Al$_2$O$_3$ catalyst. A different mobility of the surface species involved in these reactions is invoked, with K-containing species having a higher mobility than Ba ones.

References and Notes

(1) Takahashi, N.; Shinjoh, H.; Iijima, T.; Suzuki, T.; Yamazaki, K.; Yokota, K.; Suzuki, H.; Miyoshi, N.; Matsumoto, S.; Tanizawa, T.; Tanaka, T.; Tateishi, S.; Kasahara, K. *Catal. Today* **1996**, *27*, 63–69.

(2) Epling, W. S.; Campbell, L. E.; Yezerets, A.; Currier, N. W.; Parks, J. E. *Catal. Rev.−Sci. Eng.* **2004**, *46*, 163–245.

(3) Shinojh, H.; Takahashi, N.; Yokota, K.; Sugiura, M. *Appl. Catal., B* **1998**, *15*, 189–201.

(4) Takeuchi, M.; Matsumoto, S. I. *Top. Catal.* **2004**, *28*, 151–156.

(5) Konsolakis, M.; Yentekakis, I. V. *Appl. Catal., B* **2001**, *29*, 103–113.

(6) Mahzoul, H.; Brilhac, J. F.; Gilot, P. *Appl. Catal., B* **1999**, *20*, 47–55.

(7) Prinetto, F.; Ghiotti, G.; Nova, I.; Lietti, L.; Tronconi, E.; Forzatti, P. *J. Phys. Chem. B* **2001**, *105*, 12732–12745.

(8) Lietti, L.; Forzatti, P.; Nova, I.; Tronconi, E. *J. Catal.* **2001**, *204*, 175–191.

(9) Nova, I.; Castoldi, L.; Prinetto, F.; Ghiotti, G.; Lietti, L.; Tronconi, E.; Forzatti, P. *J. Catal.* **2004**, *222*, 377–388.

(10) Poulston, S.; Rajaram, R. *Catal. Today* **2003**, *81*, 603–610.

(11) Liu, Z.; Anderson, A. *J. Catal.* **2004**, *228*, 243–253.

(12) Jozsa, P.; Jobson, E.; Larsson, M. *Top. Catal.* **2004**, *30*, 177–180.

(13) James, D.; Fourre, E.; Ishii, M. *Appl. Catal., B* **2003**, *45*, 147–159.

(14) Abdulhamid, H.; Fridell, E.; Skoglundh, M. *Top. Catal.* **2004**, *30*, 161–168.

(15) Lietti, L.; Nova, I.; Forzatti, P. *J. Catal.* **2008**, *257*, 270–282.

(16) Nova, I.; Lietti, L.; Forzatti, P. *Catal. Today* **2008**, *136*, 128–135.

(17) Forzatti, P.; Lietti, L.; Nova, I. *Energy Environ. Sci.* **2008**, *1*, 236–247.

(18) Nova, I.; Lietti, L.; Castoldi, L.; Tronconi, E.; Forzatti, P. *J. Catal.* **2006**, *239*, 244–254.

(19) Castoldi, L.; Lietti, L.; Nova, I.; Matarrese, R.; Forzatti, P.; Vindigni, F.; Morandi, S.; Prinetto, F.; Ghiotti, G. *Chem. Eng. J.* **2010**, *161*, 416–423.

(20) Castoldi, L.; Lietti, L.; Forzatti, P.; Morandi, S.; Ghiotti, G.; Vindigni, F. *J. Catal.*, in press. DOI:10.1016/j.jcat.2010.09.026. Published Online: Nov 4, 2010.

(21) Forzatti, P.; Lietti, L.; Nova, I.; Morandi, S.; Prinetto, F.; Ghiotti, G. *J. Catal.* **2010**, *274*, 163–175.

(22) Prinetto, F.; Manzoli, M.; Morandi, S.; Frola, F.; Ghiotti, G.; Castoldi, L.; Lietti, L.; Forzatti, P. *J. Phys. Chem. C* **2010**, *114*, 1127–1138.

(23) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: West Sussex, Great Britain, 1980.

(24) Szailer, T.; Kwak, J. H.; Kim, D. H.; Hanson, J. C.; Peden, C. H. F.; Szanyi, J. *J. Catal.* **2006**, *239*, 51–64.

(25) Bion, N.; Saussey, J.; Haneda, M.; Daturi, M. *J. Catal.* **2003**, *217*, 47–58.

(26) Bion, N.; Saussey, J.; Hedouin, C.; Seguelong, T.; Daturi, M. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4811–4816.

(27) Frola, F. Ph.D. Thesis, University of Turin, Italy, 2007.

(28) Nova, I.; Lietti, L.; Forzatti, P.; Frola, F.; Prinetto, F.; Ghiotti, G. *Top. Catal.* **2009**, *52*, 1757–1761.

(29) Frola, F.; Manzoli, M.; Prinetto, F.; Ghiotti, G.; Castoldi, L.; Lietti, L. *J. Phys. Chem. C* **2008**, *112*, 12869–12878.