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Alkaline- and alkaline-earth oxides based Lean NO_x Traps: Effect of the storage component on the catalytic reactivity

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ABSTRACT

The introduction of lean-burn engine technology has prompted the development of NO_x storage-reduction (NSR or Lean NO_x Traps, LNT) catalysts, which are currently based on a $PtBa/Al_2O_3$ system. Potassium is another element that has shown potentials as a storage component. This work explores the role of K during the NO_x storage phase and the subsequent reduction using transient activity data and FT-IR analyses over a PtK/Al_2O_3 powdered catalyst. The catalytic behaviour of a PtK/Al_2O_3 system has been compared with that of a $PtBa/Al_2O_3$ catalyst. NO_x storage experiments indicate similar storage efficiency in the two cases.

The storage pathways are similar on both the storage components: nitrites and nitrates are formed, the first ones only at the beginning of the storage, quickly transformed in nitrates.

The reduction of NO_x stored over both systems is also analyzed when H_2 is used as reductant. An in series 2-steps process is herein reported, involving at first the formation of NH_3 upon reaction of nitrates with H_2 (step 1), followed by the reaction of NH_3 with residual nitrates to give N_2 (step 2). The influence of the storage component on the Pt sites modifies the reactivity of H_2 towards stored nitrates.

1. Introduction

Lean NO_x adsorber catalysts or Lean NO_x Traps (LNTs) are emerging as a leading choice for reduction of NO_x in exhausts from diesel and gasoline lean-burn engines [1], due to the high NO_x removal efficiency which is guaranteed over a wide range of operating conditions. These catalytic systems work under cyclic conditions, alternating lean phases during which the NO_x produced by the engine are adsorbed on catalyst surface, with short rich phases during which the stored nitrate species are reduced to nitrogen.

LNT catalysts are usually constituted by an alkaline or alkaline-earth oxide as NO_x storage component, by a noble metal (Pt) which catalyses both the NO_x oxidation and reduction, and by a high surface area support like alumina. The most common formulations include barium as material for the NO_x storage, but potassium is gaining attention as storage component as well [2,3]. While several studies report on the reactivity and characteristics of Ba-containing catalysts [4–9 and references therein], investigations on the specific behaviour of K-based catalysts are still rather scarce in the literature. Toops et al. [10–12] analyzed by *in situ* DRIFT the NO_x storage on Pt–K/Al_2O_3, and the effect of H_2O and CO_2 on this step. They concluded that NO_x is stored primarily in the form of ionic nitrates on the K component; nitrites are also observed at low temperatures (below 200 °C), for short adsorption times. The nature of the NO_x stored species (i.e. nitrites and nitrates) and the proposed adsorption mechanisms parallel those already described in the case of Pt–Ba/Al_2O_3 catalysts. Investigations on the reduction of NO_x stored on K-containing catalysts are also very scarce in the literature, as opposite to Ba-based NSR catalytic systems [13–16]. Accordingly, objective of this work was the investigation of the effect of the nature of the storage component (i.e. K vs. Ba) on the nature and reactivity in the adsorption reduction processes of the stored NO_x species. For this purpose, transient activity experiments and FT-IR analyses were used as complementary techniques to study NO_x storage and reduction over homemade PtK/Al_2O_3 and $PtBa/Al_2O_3$ model catalysts under controlled operating conditions.

2. Experimental

2.1. Catalysts preparation and characterization

$PtBa/Al_2O_3$ (1/20/100, w/w) and PtK/Al_2O_3 (1/5.4/100, w/w) catalysts, with equal molar amounts of the storage component

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(0.146 mol K/ or Ba/100 g Al_2O_3) were prepared by incipient wetness impregnation of γ-alumina (Versal 250 from UOP) with aqueous solutions of dinitro-diammine platinum (Strem Chemicals, 5% Pt in ammonium hydroxide) followed by a solution of barium acetate or potassium acetate (Aldrich, 99%). After each impregnation step, the powders were dried overnight in air at 353 K and calcined at 773 K for 5 h.

XRD diffraction analyses were performed on the powder samples calcined at 773 K in air and collected with a Bruker D8 vertical goniometer diffractometer equipped with a monochromator. Surface area and pore size distribution were determined by N_2 adsorption–desorption at 77 K with the BET method using a Micromeritics TriStar 3000 instrument. The Pt dispersion of the samples was estimated by hydrogen chemisorption at 273 K, upon reduction in H_2 at 573 K using a TPD/R/O 1100 Thermo Fischer Instrument.

HRTEM analyses were performed using a side entry Jeol JEM 3010 (300 kV) microscope; for the analyses the powdered samples were deposited on a copper grid coated with porous carbon film. For HRTEM analysis freshly calcined samples were reduced in H_2 at 623 K.

Absorption/transmission IR spectra were run on a PerkinElmer FT-IR 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 (10–15 mg cm^{-2}) and placed in a commercial heatable stainless steel cell (Aabspec) allowing thermal treatments *in situ* under vacuum or controlled atmosphere. Pellets were activated by heating in vacuo at 773–823 K and subsequently submitted to the conditioning treatments, consisting of few cycles (actually only one for PtK catalyst) of heating in NO_2 at 623 K and outgassing at 823 K sufficient to eliminate the majority of carbonates. Pellets were thereafter oxidized in dry oxygen at 773–823 K, followed by cooling in oxygen down to the selected temperature. To characterize the Pt phase with CO as a probe molecule, the catalysts were reduced by heating in H_2 at 623 K and evacuating at the same temperature, followed by cooling down to room temperature (RT) and registering FT-IR spectra at RT before and after interaction with CO.

2.2. Reactivity tests

All reactivity tests were performed in a flow micro-reactor equipment, consisting of a quartz tube (7 mm i.d.) connected to a mass spectrometer (Thermostar 200, Pfeiffer) for the continuous on-line analysis of the outlet gases [7,8]. The outlet NO, NO_2, NH_3 concentrations were also analyzed by a UV detector (Limas 11HW, ABB). 60 mg of catalyst powder (75–100 μm) and a total flow of 100 Ncc/min (at 273 K and 1 atm, corresponding to a Gas Hourly Space Velocity (GHSV) of 10^5 $cm^3/h/g_{cat}$) were used in each run. The estimated contact time at 273 K is 3.6×10^{-2} s.

Prior to catalytic activity runs, the catalyst sample has been conditioned by performing few storage/reduction cycles (ISC, Isothermal Step Concentration experiments). For this purpose, a rectangular step feed of NO (1000 ppm) in He + O_2 (3%, v/v) and of hydrogen (2000 ppm) in He, separated by a He purge in between, were alternatively fed to the reactor at 623 K. Conditioning lasted until a reproducible behaviour was obtained; this typically required 2–3 adsorption/reduction cycles. The presence of the inert purge between the lean and rich phases prevents the occurrence of temperature and/or concentration spikes between the two phases, thus allowing the separate analysis of the NO_x adsorption and reduction steps under controlled conditions. Accordingly clean indications concerning the reactivity of the catalysts in these two steps could be obtained.

The reduction of NO_x species stored at 623 K was also investigated at different temperatures. Accordingly, after NO_x storage at 623 K followed by a He purge, the catalyst temperature was set at the desired value in the range 373–623 K and a rectangular step feed of H_2 (2000 ppm in He) was fed to the reactor, thus provoking the reduction of the stored NO_x. At the end of the reduction procedure the catalyst was heated up to 623 K under He flow and eventually hydrogen was added to the reactor to complete the reduction of unreacted stored NO_x, if any.

For FT-IR analysis, NO_x storage experiments were performed on fully conditioned oxidized catalysts by admitting freshly prepared NO/O_2 mixtures (P_{NO} = 5 mbar; $P_{O_2} = 20$ mbar) at 623 K. FT-IR spectra were recorded at the same temperature at increasing exposure times. After the storage phase the catalyst was evacuated at 623 K and cooled down to 373 K. The reduction of the stored NO_x was carried out by admitting H_2 (5 mbar) at increasing temperature.

Further details on experimental methods and apparatus can be found elsewhere [5,7,8].

3. Results and discussion

3.1. Catalyst characterization

The specific surface area of the pure γ-Al_2O_3 was near 200 m^2/g, while lower values were determined for the Ba-containing and K-containing samples (141 $m^2\,g^{-1}$ and 176 $m^2\,g^{-1}$, respectively). The surface area contraction was accompanied by a slight reduction of the pore volume (1 $cm^3\,g^{-1}$ for γ-Al_2O_3 down to 0.9–0.8 $cm^3\,g^{-1}$ for K- and Ba-containing sample, respectively); the pore radius was in the range of 90–110 Å.

In the XRD patterns of the freshly calcined $PtBa/Al_2O_3$ catalyst both the monoclinic (JCPDS 78-2057) and orthorhombic (Whiterite, JCPDS 5-378) polymorphic forms of $BaCO_3$ were detected in addition to γ-Al_2O_3 (JCPDS 10-425), as reported in Ref. [17]. Experiments recently performed on freshly PtK/Al_2O_3 catalyst [18] showed the characteristic peaks of γ-Al_2O_3; monoclinic K_2CO_3 (JCPDS 16-820) and cubic K_2O (JCPDS 23-493) phases were also hardly recognized.

The morphological and structural features of the calcined samples were also investigated by HRTEM. As already reported in the case of the $PtBa/Al_2O_3$ sample [17], the mean Pt particle sizes (1.5 nm) estimated from TEM were in good agreement with data obtained from H_2 chemisorption that indicates a Pt dispersion near 70%. Experiments recently performed on the PtK/Al_2O_3 catalyst [18] have still evidenced mean Pt particle size (1.5 nm) estimated from TEM in agreement with the Pt dispersion measured by H_2 chemisorption (near 65%).

To complete the characterization of the Pt phase and to gain information about its interaction with potassium or barium sites, the adsorption at RT of CO as probe molecule was studied by FT-IR spectroscopy on reduced Pt/Al_2O_3, PtK/Al_2O_3 and $PtBa/Al_2O_3$ catalysts [5,17,18] and the results are shown in Fig. 1. On Pt/Al_2O_3 two peaks appear (Fig. 1, curve a), a main one at 2090 cm^{-1}, assigned to ν_{CO} of linear carbonyls formed on Pt^0 particles, and a minor one at 1845 cm^{-1}, assigned to ν_{CO} of bridged CO. The ratio between the intensity of the two bands is that expected for this metal, which shows a preference for bonding of CO in linear configuration.

On the other hand, the spectral features observed on the K and Ba ternary catalysts (curves b and c, respectively) can be briefly summarized as follows: (i) a band is observed at 2045 cm^{-1} over both PtK/Al_2O_3 and $PtBa/Al_2O_3$ and is assigned to ν_{CO} of linear carbonyls on Pt metal particles. The pronounced red-shift with respect to ν_{CO} of linear carbonyls on Pt/Al_2O_3 is that expected for CO adsorbed on Pt particles supported on oxides with strong basic character

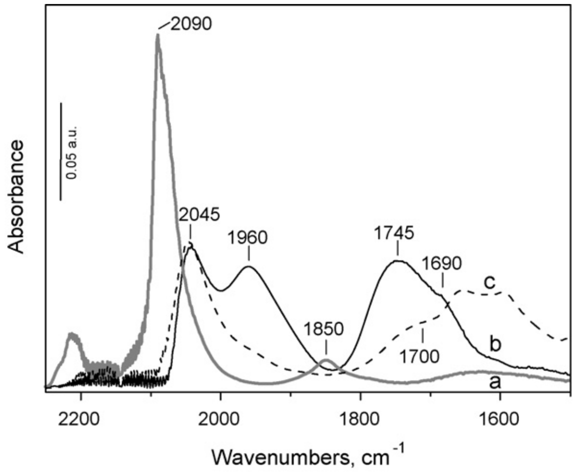

Fig. 1. FT-IR spectra after CO admission (2 kPa) at RT on reduced Pt/Al_2O_3, $Pt–K/Al_2O_3$ and $Pt–Ba/Al_2O_3$ (curves a, b and c, respectively). The spectra have been reported after subtraction of the spectrum before gas admission.

and is consistent with a strong interaction with the alkaline- or alkaline-earth phase; (ii) a shoulder at 1960 cm^{-1} is observed in the case of Ba-containing catalyst, while on Pt–K sample this feature shows an intensity comparable to that of the 2045 cm^{-1} band. This component was assigned to linear carbonyls formed on Pt atoms at the border of the basic phase, thus interacting much more strongly with the basic oxygen anions; (iii) a broad absorption is observed at 1745 cm^{-1} with shoulder at 1690 cm^{-1} in the case of K-containing catalyst assigned to ν_{CO} of bridged and/or multi-bridged CO markedly red-shifted in comparison with ν_{CO} of bridged carbonyls on Pt/Al_2O_3. In the same region only the shoulder at about 1700 cm^{-1} has been assigned to bridged and/or multi-bridged CO in the case of Ba-containing catalyst. Actually, the other two bands at 1655 cm^{-1} and 1598 cm^{-1} have been previously assigned to ketenic species formed on the BaO phase for CO dismutation [17]. The position of the ν_{CO} of bridged carbonyls is still in line with the strong interaction of Pt atoms with the basic phase; besides, their intensities compared to ones of ν_{CO} of linear carbonyls indicate the presence of Pt particles strongly negatively charged, particularly in the case of K-containing catalyst, and thus more able for bonding CO in bridged configuration [19]. We can conclude that the relative amount of metallic atoms more strongly interacting with the basic phase is much higher for Al_2O_3 supported PtK than PtBa samples.

3.2. Catalyst activity

3.2.1. NO_x storage phase

The results obtained during the three initial NO_x storage-reduction cycles carried out at 623 K over the freshly calcined PtK/Al_2O_3 catalyst are shown in Fig. 2. In the first NO_x storage cycle (Fig. 2A) upon the NO step addition at $t = 0$ s the NO_x outlet concentration presents a delay of about 140 s, and then slowly increases with time eventually reaching the inlet concentration value. An important evolution of CO_2 is also monitored with a time delay about 60 s, whereas very low amount of water have been detected with a delay near 50 s.

Previous studies performed at this temperature (623 K) on Ba- and K-free Pt/Al_2O_3 catalyst [8] showed the lack of any detectable NO dead time. As a matter of fact, in the absence of K or Ba only minor amounts of NO_x have been stored on the alumina surface upon NO admission, but these NO_x ad-species decompose when the NO concentration is decreased back to zero. Hence these results indicate that NO_x are stored on the alkaline component, and exclude the involvement of any chromatographic effect in the delay observed in the NO_x concentration traces. In line with earlier studies [7], the data suggests that NO_x are first adsorbed at K_2O, then at KOH (with release of water) and finally at K_2CO_3, with CO_2 release. Notably, the observed small evolution of water (Fig. 2) suggests that KOH sites are present in very low amounts. The second NO_x storage run (Fig. 2B) has been performed after reduction with diluted H_2 (2000 ppm in He) at the same temperature. The NO_x breakthrough in the second cycle is slightly increased (200 s vs. 140 s) and water evolution becomes more evident; it occurs with a time delay of 50 s. CO_2 evolution is also observed, although significantly reduced. Hence the data indicate that catalyst regeneration with H_2 restores the adsorption K sites; however K_2O and KOH are formed instead of K_2CO_3 (which was originally present) since H_2O (and not CO_2) is produced during reduction in the second (and third) cycle. Accordingly the amounts of K_2O and KOH species on the catalyst surface progressively increase at the expenses of K_2CO_3, which indeed is present in very small amounts during the third NO_x storage cycle (Fig. 2C) as pointed out by the very small CO_2 release which is observed in this case. Notably the results obtained in this third cycle closely resemble those obtained after the second cycle and hence the catalyst is almost fully conditioned after the third cycle.

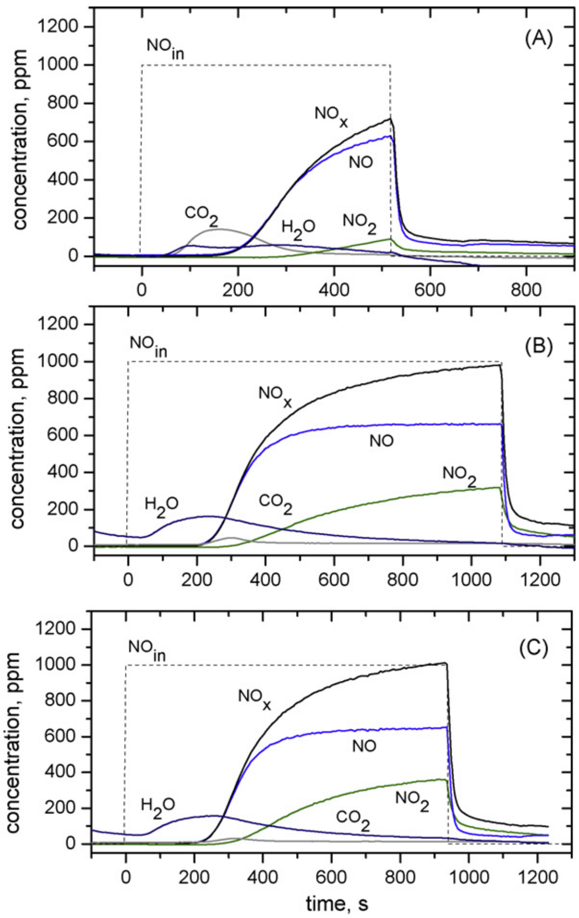

Fig. 2. Subsequent NO_x storage runs at 623 K on a fresh sample of PtK/Al_2O_3: NO, NO_2, NO_x, H_2O, CO_2 outlet concentration and NO inlet concentration (NO 1000 ppm, 3% (v/v) O_2 in He).

These results are in line with FT-IR spectra showing that vibration modes of carbonate species present on the fresh catalyst diminish during the NO_x uptake so that after 2 storage-reduction cycles they are no longer detectable, in line with that reported by Toops et al. [11] and by Lesage et al. [19].

The data recorded during the three conditioning cycles over K-containing catalyst parallels those obtained in the case of Ba-based system [7], showing that also in that case $BaCO_3$ was progressively transformed into BaO and $Ba(OH)_2$.

It is worth of note that conditioning process seems to be slightly faster on PtK/Al_2O_3 than on $PtBa/Al_2O_3$. This is in line with the different stability of carbonate species initially present at the catalyst surface. In fact, from FT-IR spectra (here not reported for brevity) on $PtBa/Al_2O_3$ bands characteristic of bulky $BaCO_3$ have been recognized; the features due to ionic $BaCO_3$ disappeared during the conditioning treatment consisting of few cycles of heating in NO_2 at 623 K and outgassing at 823 K as previously reported [5,17]. On the other hand, on PtK/Al_2O_3 only bidentate carbonates are identified (different from bulky ionic K_2CO_3, recorded for comparison); the bidentate carbonates are already removed to a large extent simply by outgassing at 823 K.

The storage phases performed at 623 K of both the fully conditioned PtK/Al_2O_3 and $PtBa/Al_2O_3$ catalysts have been compared in Fig. 3. For the PtK/Al_2O_3 system (Fig. 3A) upon the NO step addition (at $t = 0$ s) NO and NO_2 show a dead time of about 200 and 280 s respectively; then their concentration rapidly increases with time approaching the asymptotic concentrations. The NO pulse is stopped before the NO_2 concentration reached a steady level, indicating that saturation of the catalyst surface with NO_x is not yet completed after 800 s.

The area included between the NO inlet and NO_x ($NO + NO_2$) outlet concentration traces is proportional to the amount of NO_x that have been stored onto the catalyst surface: these amounts have been estimated near 2.7E−04 mol/g_{cat} up to NO_x breakthrough and 5.7E−04 mol/g_{cat} up to saturation, corresponding to a K utilization (i.e. the fraction of K sites involved in the storage of NO_x) close to 19.7% and 41.6%, respectively. These amounts are in line with those reported in literature for similar catalytic system [19].

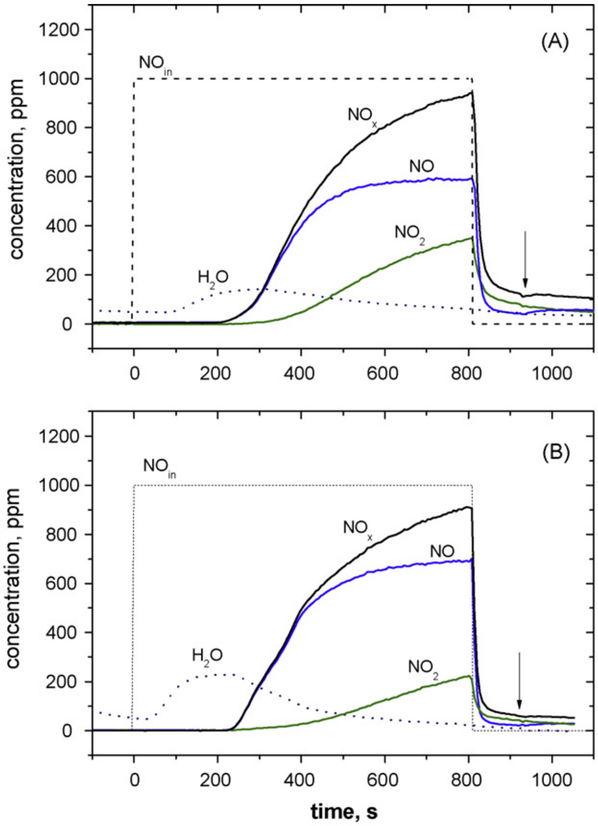

Fig. 3. NO_x storage phases on $Pt–K/Al_2O_3$ (A) and $Pt–Ba/Al_2O_3$ (B) catalysts at 623 K (NO 1000 ppm, 3% (v/v) O_2 in He).

Upon NO shutoff the concentrations of NO and of NO_2 decrease with time due to desorption of the NO_x weakly adsorbed. Upon switching from 3% O_2 in He to pure He (indicated by the arrow in Fig. 3A) the amount of NO desorbed increases. The prolonged tail shown by NO and NO_2 after both NO and O_2 shutoff indicates that some NO_x weakly adsorbed species decompose due to the decrease of the inlet NO concentration and due to the effect of oxygen partial pressure on the formation/stability of nitrate species formed onto the catalyst surface, in agreement with the same effect observed in the case of $PtBa/Al_2O_3$ catalyst [20]. This desorption process is very slow, as indicated by the NO reactor outlet concentration that slowly decreases with time.

In Fig. 3B is reported the storage phase of the fully conditioned $PtBa/Al_2O_3$ catalyst for comparison purpose. The NO_x shows a dead time of about 230 s and the stored amounts up to breakthrough are near 2.8E−04 mol/g_{cat} (5.6E−04 mol/g_{cat} up to saturation) corresponding to 11.5% (23% up to saturation) of the overall Ba loading. Notably, the amounts of stored NO_x are very similar to that of the K-based sample. Also in the case of the $PtBa/Al_2O_3$ catalyst, the release of water suggests that $Ba(OH)_2$ species are involved in the adsorption phase on a fully conditioned sample (when H_2 is used as reducing agent) [7]. Upon NO shutoff the concentrations of NO and of NO_2 decrease faster than in the case of PtK/Al_2O_3 system. Along similar lines, a minor NO_x desorption has been observed closing the oxygen feed gas (indicated by the arrow in Fig. 3B). This can be explained considering a higher stability of Ba-nitrate/nitrite species compared to K-one, as discussed below.

Comparison of Fig. 3A and B also points out a slightly higher NO oxidation capability of the K-based catalyst if compared to $Pt–Ba/Al_2O_3$. Indeed although the NO_2 concentration measured at the end of the NO pulse has not yet reached steady-state

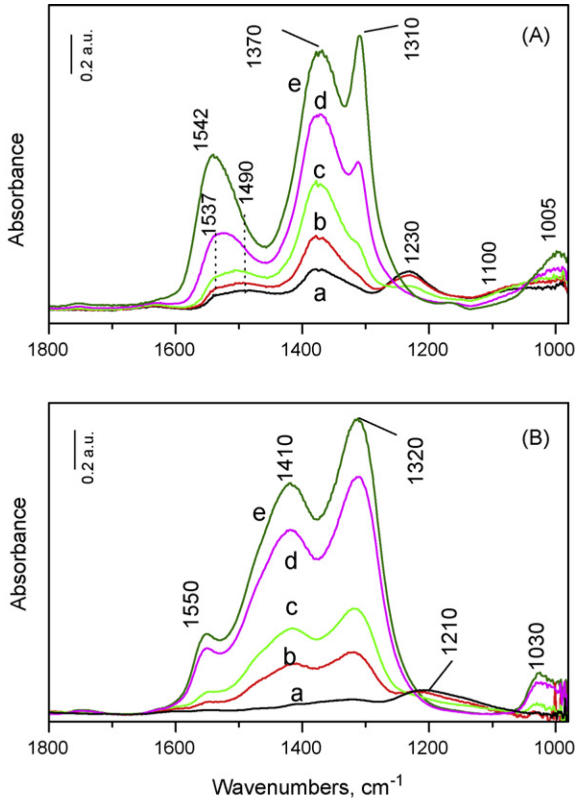

Fig. 4. FT-IR spectra upon admission of NO/O_2 mixtures (1:4, p_{NO} = 5 mbar) at 623 K at increasing exposure times on: (A) PtK/Al_2O_3 catalyst (contact time: curve a, 10 s; curve b, 30 s; curve c, 1 min; curve d, 5 min; curve e, 35 min); (B) $Pt–Ba/\gamma-Al_2O_3$ catalyst (contact time: curve a, 10 s; curve b, 30 s; curve c, 5 min; curve d, 10 min; curve e, 20 min).

conditions, higher NO_2 concentrations are obtained in the case of the Pt–K/Al_2O_3 sample (345 ppm vs. 218 ppm). The NO oxidation reaction is affected by several factors, including the Pt particle size, with larger Pt particle resulting in higher rates [21]. In our case, both K- and Ba-based catalyst samples show similar Pt dispersion (with mean Pt dimension close to 1.5 nm), and accordingly it is expected that this does not play a major role in explaining the different reactivity of the two samples. However, it has also been shown that the presence of Ba affects the reactivity of Pt in NO oxidation [22,23]. This has been related to the blocking of Pt sites by NO_x stored on BaO [22], but an increase of the electronic density of Pt by the alkaline-earth oxide has also been invoked. This would favour the formation of Pt oxides form Pt, hence decreasing the catalytic activity in the NO oxidation. As a matter of fact, it has been previously shown by CO adsorption experiments that both K and Ba strongly interact electronically with Pt, and that the interaction is different with K and Ba. Accordingly it is speculated that this may affect the activity of Pt in the NO oxidation reaction.

In situ FT-IR experiments of storage performed at 623 K on fully conditioned PtK/Al_2O_3 and PtBa/Al_2O_3 are compared in Fig. 4. Both the catalysts show an initial formation of nitrite species, which rapidly evolve to ionic and bidentate nitrates. In particular, over PtK/Al_2O_3 catalyst (Fig. 4A) at low exposure times (10 s, curve a) both linear nitrites ($\nu_{N=O}$ modes at 1490 and 1537 cm^{-1}; ν_{N-O} modes, broad band at 1100–1000 cm^{-1}), chelating nitrites ($\nu_{O-N-O,asym}$ mode at 1230 cm^{-1}) and ionic nitrates ($\nu_{NO_3,asym}$ mode at 1370 cm^{-1}; $\nu_{NO_3,sym}$ mode at 1040 cm^{-1} superimposed to the ν_{N-O} modes of linear nitrites) are present at catalyst surface. Upon increasing the exposure time the nitrite species decrease and eventually disappear after 5 min (line d), while ionic nitrates increase and bidentate nitrates appear ($\nu_{N=O}$ mode at 1540 cm^{-1}; $\nu_{O-N-O,asym}$ mode at 1310 cm^{-1}). Finally, after long exposures (30–35 min, line e) only nitrates, both of the ionic and bidentate types, are present on the catalyst surface. The assignments have been done on the basis of the correlation between the intensity of the bands and of literature data [12,19,24].

Similarly, in Fig. 4B spectra recorded upon NO/O_2 admission over PtBa/Al_2O_3 catalyst are shown [8]. Also in this case at low exposure time (curve a, 10 s) small amounts of chelating nitrites are formed (weak band at 1210 cm^{-1}); the nitrite band reaches its maximum intensity after 1 min of exposure to the NO/O_2 mixture and at this exposure time nitrate species are already detected in large amounts. After 3–5 min of exposure (curve c) only ionic nitrates ($\nu_{NO_3,asym}$ mode splitted in two peaks at 1410 cm^{-1} and 1320 cm^{-1}; $\nu_{NO_3,sym}$ mode at 1030 cm^{-1}) and in minor amounts, bidentate nitrates ($\nu_{N=O}$ modes at 1550 cm^{-1}) are present on the catalyst surface. After 20 min (curve e) the nitrate modes have reached their maximum intensity.

On the basis of these data, the reaction pathway already suggested for NO_x adsorption over alumina supported PtBa [8] is proposed also in the case of the PtK/Al_2O_3 catalyst sample. In the presence of NO/O_2 mixtures (the actual gases in the exhausts), NO_x are stored on the basic catalyst component in the form of nitrite ad-species ("nitrite route"). These species are then progressively oxidized to nitrates, possibly by O_2 and/or NO_2. In parallel with the occurrence of the "nitrite route", the oxidation of NO to NO_2 on Pt sites by gaseous oxygen also occurs. As previously shown in the case of Ba-containing catalyst samples [8,25], it is likely that over K-based catalysts NO_2 is stored in the form of nitrates according to the following disproportionation reaction, hereafter indicated as "nitrate route":

$$3NO_2 + K_2O \rightarrow 2KNO_3 + NO \qquad (1)$$

The occurrence of this pathway over the K-based catalyst is presently under investigation in our laboratories. It is worth of note that dedicated experiments performed at different temperature over PtBa/Al_2O_3 catalyst samples have shown that nitrites formation is favoured at low temperature, whereas nitrates at high temperature [25,26].

Finally, it is worth noting that nitrites formed on K-containing system at the beginning of the storage are both of bidentate and linear type and that the ratio between the amount of ionic nitrates and bidentate ones (as measured by the integrated intensities of their vibration modes) is higher on PtK/Al_2O_3 than on PtBa/Al_2O_3 [8].

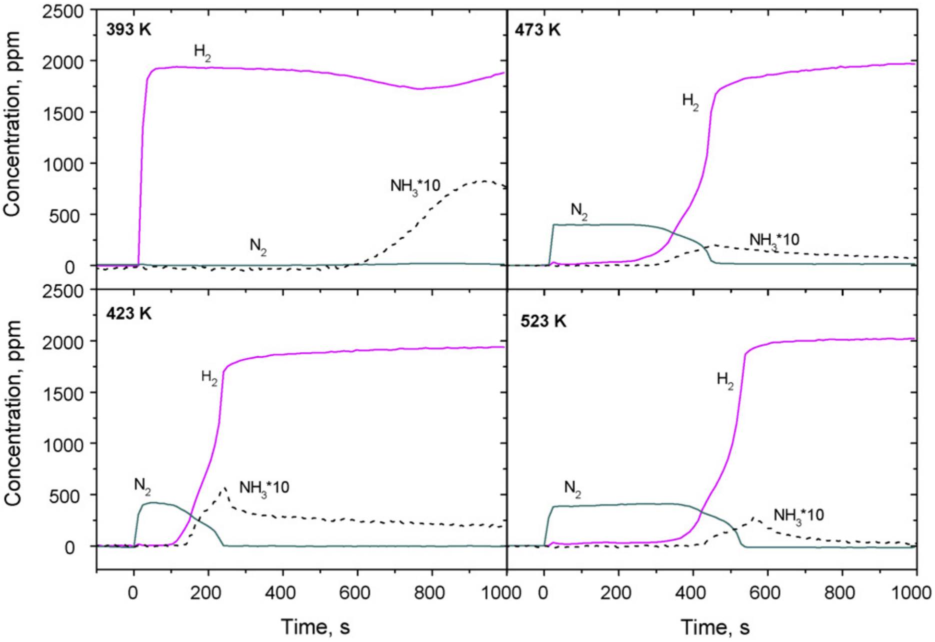

Fig. 5. Temporal evolution of H_2, N_2 and NH_3 outlet concentrations during reduction with H_2 (2000 ppm in He) at different temperature after NO/O_2 adsorption at 350 °C over the Pt–K/γ-Al_2O_3 catalyst (H_2-ISC experiment).

3.2.2. NO_x reduction

The nitrates stored at 623 K have been reduced under isothermal conditions at different temperatures, in the range 373–623 K. In Fig. 5 the concentration profiles of hydrogen, nitrogen and ammonia are displayed as a function of time in the case of PtK/Al_2O_3 catalyst. At the lowest investigated temperature (373 K, not shown in the figure) no reaction is observed. In the case of the experiment carried out at 393 K, the reaction shows a significant induction period. Indeed initially H_2 is detected unconverted at the reactor outlet; then, after 500 s, the H_2 concentration starts to decrease showing a minimum near 730–840 s. The decrease of the H_2 concentration is accompanied by the evolution of NH_3 and of minor amounts of N_2. The overall amount of ammonia that is detected at the reactor outlet (6.62E−05 mol/g_{cat}) and the corresponding H_2 consumption (3.01E−04 mol/g_{cat}) are in line with the occurrence of the reaction with the following stoichiometry:

$$2KNO_3 + 8H_2 \rightarrow K_2O + 2NH_3 + 5H_2O \quad (2)$$

A minor NO formation is also observed during reduction (not shown in the figure). NO evolution is likely related to the occurrence of an unselective NO_x reduction process.

Upon increasing the reaction temperature at 423 K, the induction period disappeared and a complete uptake of H_2 is initially observed. After 100 s, its concentration increases up to the inlet value (2000 ppm). Large amounts of nitrogen are detected at the reactor outlet in correspondence with H_2 consumption, whose amounts (8.98E−05 mol/g_{cat} of N_2 produced, 6.01E−04 mol/g_{cat} of H_2 consumed) are in line with the occurrence of the reaction with the following stoichiometry:

$$2KNO_3 + 5H_2 \rightarrow K_2O + N_2 + 5H_2O \quad (3)$$

Only minor amounts of ammonia are formed. A further increase of the reduction temperature favours the N_2 formation at the expenses of ammonia, so that the N_2 selectivity increases at this temperature, being near 76%. At the highest investigated temperature (623 K) only minor amounts of ammonia are detected and the stored NO_x are reduced almost exclusively to N_2 (selectivity close to 96%).

The reduction of the NO_x stored species in the same temperature range has also been studied by *in situ* FT-IR experiments. The evolution with temperature of the bands in the 1800–980 cm^{-1} region is shown in Fig. 6. At 423 K (Fig. 6A), upon H_2 admission, bidentate nitrates ($\nu_{N=O}$ mode at 1530 cm^{-1}, $\nu_{O-N-O,asym}$ mode at 1317 cm^{-1}) are slowly reduced, whereas bands related to ionic nitrates increase ($\nu_{NO_3,asym}$ mode at 1380 cm^{-1}). Simultaneously, a broad band at 3500–3800 cm^{-1} (region not reported in the figure) related to the stretching modes of surface hydroxyls appears, due to the adsorption of water produced during the reduction, according to reaction:

$$K_2O + H_2O \rightarrow 2KOH \quad (4)$$

The increase of ionic nitrate bands is related to the effect of water on their spectroscopic features. Indeed, studies presently ongoing in our labs pointed out that the presence of water increases the intensity of ionic nitrate modes.

Upon increase the temperature up to 473 K (Fig. 6B) the reduction rate sensibly increases but, while chelate nitrates are quickly destroyed (30 s), the ionic ones are still present in sensible amounts after 10 min in H_2. At higher temperature (523 K, Fig. 6C) both the nitrates are almost completely destroyed after 30 s. Note that also residual carbonates are removed (negative bands at 1567 cm^{-1} and 1324 cm^{-1}) by reduction at 473–523 K.

The reduction of the stored nitrates with H_2 has also been carried out on $PtBa/Al_2O_3$ catalyst in the same temperature range (373–623 K) after NO_x adsorption at 623 K.

The concentration profiles of hydrogen, nitrogen and ammonia are displayed as a function of time in Fig. 7 [27]. At lowest temperature (373 K, not shown) no reduction is observed. In the case of the experiment carried out at 423 K, the reaction shows a significant induction period. Indeed initially H_2 is detected unconverted at the reactor outlet; then, after 200 s, the H_2 concentration starts to decrease showing a minimum near 450–750 s. The decrease of the H_2 concentration is accompanied by the evolution of NH_3 and of negligible amounts of N_2; here the nitrogen selectivity is close to 14%.

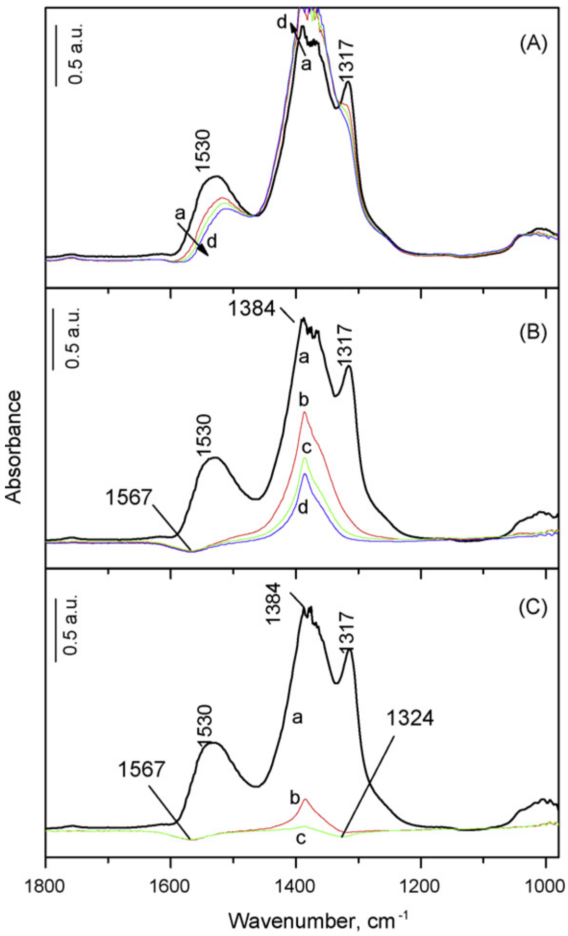

Fig. 6. FT-IR spectra of NO_x reduction with H_2 on Pt–K/γ-Al_2O_3 catalyst at increasing temperature: A, 423 K; B, 473 K and C, 523 K. Curves a, NO_x stored by NO/O_2 adsorption at 623 K; curves b, after 30 s in H_2; curves c, after 5 min in H_2; curves d, after 10 min in H_2.

Upon increasing the reaction temperature at 473 K, the induction period almost disappeared and a small and sharp H_2 peak is observed upon admission of H_2 to the reactor. N_2 formation is observed after the H_2 peak, followed by NH_3 evolution which is seen in correspondence of H_2 breakthrough. For further increases of the reduction temperature the initial H_2 peak is no more observed and N_2 formation is immediately observed upon H_2 addition, with no delay. Also in the case of Ba-containing catalyst, ammonia evolution always follows that of N_2 and is accompanied by the detection of unconverted H_2. NH_3 formation significantly decreases with temperature, so that at the maximum investigated temperature (623 K) only minor amounts of ammonia are detected. This leads to a significant increase of the selectivity of the reaction with temperature, reaching at higher temperature values near 94%.

In Fig. 8 are reported the FT-IR spectra recorded upon H_2 admission at different temperature over $PtBa/Al_2O_3$ catalyst. At 373 K (not shown) no reduction is observed. At 423 K the reduction starts, being the bidentate nitrates firstly reduced (curve b). Upon increasing the temperature the reduction proceeds faster and at 523 K

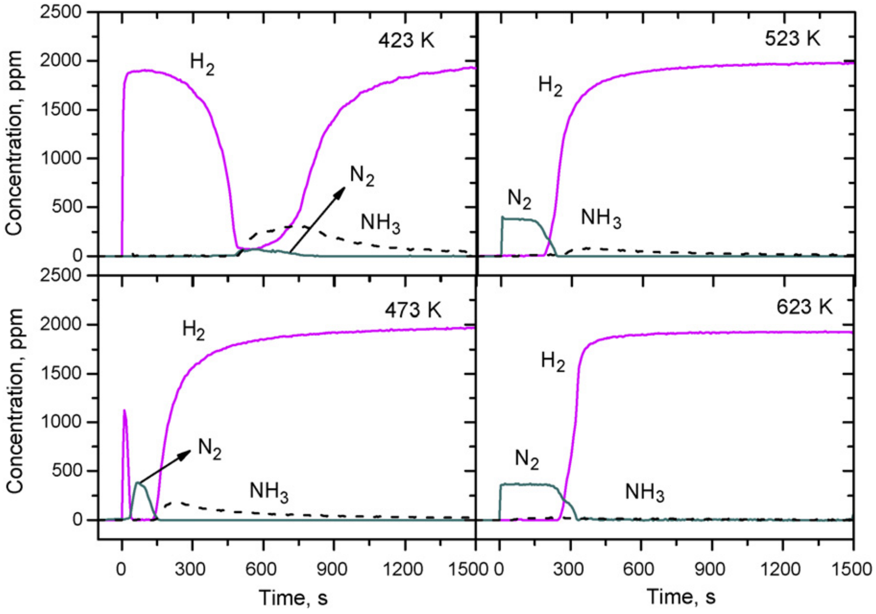

Fig. 7. Temporal evolution of H_2, N_2 and NH_3 outlet concentrations during reduction with H_2 (2000 ppm in He) at different temperature after NO/O_2 adsorption at 350 °C over the Pt–Ba/γ-Al_2O_3 catalyst (H_2-ISC experiment).

(curve d) the nitrates are completely removed. Also the residual carbonates are removed (negative bands in the figure), as in the case of PtK/Al_2O_3 catalyst.

From the data discussed above and partially reported in our recent papers [27,28] it appears that similar trends of NO_x removal efficiency and N_2 selectivity have been obtained in the case of PtK/Al_2O_3 and $PtBa/Al_2O_3$ catalyst, i.e. in the two cases both the amounts of reduced NO_x and selectivity to N_2 increases with temperature. However a higher reactivity has been observed at low temperature over the Ba-containing catalyst, along with a lower selectivity to N_2.

The observed dependence of the N_2 selectivity with temperature suggests that, as already proposed for the $PtBa/Al_2O_3$ catalyst sample [27], over the PtK/Al_2O_3 catalysts as well the reduction of stored nitrates by H_2 occurs via a two steps molecular pathway which involves a first step responsible for the formation of ammonia and for the consumption of hydrogen, fast even at low temperatures, followed by the slower reaction of ammonia with residual nitrates to form nitrogen. These overall molecular steps account to the overall stoichiometry of the reduction of nitrates by H_2:

$$\begin{array}{ll} M\text{-}(NO_3)_x + 8\ H_2 \rightarrow 2\ NH_3 + M(OH)_x + 4\ H_2O & \text{(a)} \\ M\text{-}(NO_3)_x + 10\ NH_3 \rightarrow 8\ N_2 + M(OH)_x + 12\ H_2O & \text{(b)} \\ \hdashline M\text{-}(NO_3)_x + 5\ H_2 \rightarrow N_2 + M(OH)_x + 4\ H_2O & \text{(c)} \end{array}$$

where M is K or Ba.

To further analyze these aspects, the reactivity of ammonia with nitrates has also been investigated and NH_3–ISC experiments have been performed after NO_x storage at 623 K over both the catalytic systems. The data, here not reported for brevity [27,28], show that ammonia is an effective reductant for stored NO_x. In the case of PtK/Al_2O_3 catalyst the ammonia reactivity at low temperatures is even greater than that of H_2 (greater reduction efficiencies could be obtained with NH_3 than with H_2), whereas in the case of $PtBa/Al_2O_3$ catalyst ammonia shows a reactivity always lower than in the case of K-containing system.

As previously discussed in the case of the $PtBa/Al_2O_3$ sample [27], the observed temporal evolution of products during the reduction (with nearly complete nitrogen selectivity at the beginning of the rich phase followed by ammonia formation near the end of the regeneration, see Fig. 7) is due to the development of an H_2 front which develops and travels along the reactor: accordingly NH_3 formed at the H_2 front reacts with NO_x stored downstream the front, leading to N_2 formation. However we note that the production of NH_3 is significantly smaller in the case of PtK/Al_2O_3 catalyst than on $PtBa/Al_2O_3$ catalyst: for this sample a very poor N_2 selectivity was measured at low temperatures. This is related to the high reactivity of NH_3 towards the stored nitrates observed in the case of the PtK/Al_2O_3 sample: accordingly when NH_3 is formed upon reaction of the stored NO_x with H_2, NH_3 readily reacts with the nitrates stored downstream the H_2 front and this drives the selectivity to NH_3. On the other hand, in the case of the $PtBa/Al_2O_3$ catalyst sample, the reactivity of H_2 is much higher if compared to

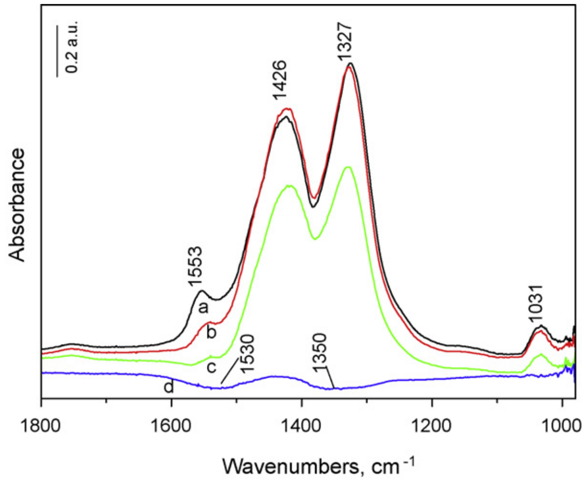

Fig. 8. FT-IR spectra of NO_x reduction with H_2 on Pt–Ba/γ-Al_2O_3 catalyst at increasing temperature: curve a, NO_x stored by NO/O_2 adsorption at 623 K; curve b, after 15 min in H_2 at 423 K; curve c, after 10 min in H_2 at 473 K; curve d, after 10 min in H_2 at 523 K.

that of NH_3, and at low temperatures NH_3 is the prevalent reaction product.

The different activity of H_2 and NH_3 in the reduction of NO_x stored over PtK/Al_2O_3 and PtBa/Al_2O_3 could be associated either to a different reactivity of the adsorbed NO_x species, or to a change in the activity of the Pt active sites in the reduction process due to the presence of the different storage component (K vs. Ba), or both. A comparison of the features of the NO_x species adsorbed over PtBa/Al_2O_3 with those stored on PtK/Al_2O_3 (see above) revealed that in both cases bidentate and ionic nitrate species are formed upon NO adsorption in the presence of O_2, although in different relative amounts. Besides, the FT-IR characterization previously reported by using CO as adsorbate to probe the state of the Pt sites on Pt/Al_2O_3, PtBa/Al_2O_3 and PtK/Al_2O_3, pointed out that the Pt sites were modified by the presence of the K- or Ba-phase, due to a strong electronic interaction between the basic oxide and the noble metal. This is revealed both by the red-shift of the Pt-carbonyl bands and by the relative increase of bridged carbonyls. However, a higher amount of the Pt atoms in strict contact with the basic phase is observed in the case of the Pt–K catalyst than in the case of the Pt–Ba catalyst and, by consequence, the presence of a major fraction Pt particles more negatively charged on the Pt–K catalyst than on the Pt–Ba catalyst.

4. Conclusions

A PtK/Al_2O_3 NSR model catalyst has been prepared, characterized and tested in the NO_x storage-reduction process and its behaviour has been compared with that of a PtBa/Al_2O_3 NSR model catalyst. Data collected by the different characterization techniques agree in indicating that (i) the platinum phase is well dispersed on the alumina support in form of nanosized particles having mean dimension equal to 1.5 nm; (ii) the Pt phase is strongly influenced by the presence of the storage component, more strongly by the potassium phase; (iii) the two catalysts show similar storage capacity, with initial formation of nitrites species and subsequent transformation into nitrates, but the ratio between the amount of ionic nitrates and bidentate ones is higher on PtK/Al_2O_3 than on PtBa/Al_2O_3; (iv) over both the catalytic systems during the reduction phase operates a 2-step in series process for N_2 formation, involving the participation of ammonia as an intermediate. The first step of the suggested two steps process is ammonia formation through the reaction of H_2 with stored nitrates; ammonia then reacts with the nitrates left downstream in the reactor leading to the formation of nitrogen. In the case of the K-containing catalyst the N_2 selectivity obtained upon reduction of stored nitrates is much higher than that measured over PtBa/Al_2O_3, particularly at low temperature. This is due to the higher reactivity of ammonia towards stored NO_x with respect to PtBa/Al_2O_3 or a minor reactivity of nitrates with hydrogen that reduces the temperature gap between hydrogen and ammonia reactivity. Accordingly once NH_3 is formed, it readily reacts with stored nitrates leading to the formation of N_2, and the NH_3 concentration keeps low. The different reactivity of hydrogen and ammonia towards nitrates over the investigated systems could be due the presence of alkaline or alkaline-earth metal oxide, which modify the nature of stored nitrates (different ionic/bidentate ratio) and the nature of Pt sites.

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