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Catalysis Today 126 (2007) 162–168
CATALYSIS TODAY
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MS-FTIR reduction stage study of NSR catalysts

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Abstract

A FTIR ‘‘home-made’’ cell is used to study the evolution of surface species and gas phase coupled with a mass-spectrometer (MS) for time-resolved analysis in static and dynamic conditions in order to gain further information about the variables that influence the mechanism of reduction of NO_x stored. A preliminary IR study with simultaneous gas and surface spectra of Pt-Ba-Al_2O_3 and free-Pt catalysts implies that the platinum is necessary for the regeneration in the appropriate temperature range (200–400 °C). The use of different reducing gases (H_2, C_3H_6 or C_3H_8) shows that the distribution of reduction products and the temperature reaction window are correlated with the reducing molecule. Secondly, an *operando* MS-FTIR technique permits us to compare a Pt-Ba-Al_2O_3 and Pt-K-Al_2O_3 catalysts under flow conditions during a complete NSR cycle, showing that barium containing catalyst allows better NSR performance.

Keywords: NSR; NO_x-Storage-Reduction; Lean-NO_x-Trap; NO_x regeneration stage; *Operando* MS-FTIR

1. Introduction

The growing environmental regulation has developed the use of lean-burn engines that operate in excess of oxygen, offering better fuel economy than traditional engines, minimizing the fuel consumption and reducing CO_2 and nearly all contaminant emissions. The oxygen excess in the exhaust gas increases the NO_x emitted and reduces the efficiency of the classic TWC; so NO_x abatement and mineralization under these lean fuel conditions is a challenge [1–7].

A promising approach called NO_x-Storage-Reduction (NSR), also referred as Lean-NO_x-Trap (LNT), is a smart process that promotes and develops catalytic materials that can effectively reduce NO and NO_2 in oxygen excess conditions of the exhaust gas. This multi-stage process is the result of lean-rich fuel operation in cyclic conditions. During oxygen excess conditions, the NO_x are stored onto catalyst surface (lean stage). When storage capacity is close to NO_x saturation, the conditions change to a short stage in rich-fuel composition, which begins the reduction of the NO_x stored species, thus providing the catalyst regeneration (reduction or regeneration stage) [2,6]. The standard formulation of NSR-catalysts is based on Ba and Pt as active elements and was developed and marketed by Toyota [8]. The different components have been chosen to achieve the dual-function in the NO_x-traps and the mineralization process. The alkaline-earth oxide is included in the catalyst formulation due to its efficiency as NO_x potential adsorbent and noble supported metal is involved in the oxidation-reduction processes.

Nowadays, there are different studies about the NO_x storage route during lean stages with different compositions (NO, NO_2, NO + O_2, adding H_2O, CO_2 and others additional components), changing the catalyst formulation or the technical method used for analyzing this primary storage step [9–13]. However, there are few bibliographic references about the regeneration process in rich fuel conditions [14], being always studied as a part of the NSR process [15–17]. The conditions of selectivity, catalytic formulation, the reducing gas employed and the temperature range are variables not well studied by IR *operando* technique.

A FTIR ‘‘home-made’’ cell is used to study the evolution of surface species and gas phase coupled with a mass-spectrometer (MS) for time-resolved analysis in static and dynamic

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doi:10.1016/j.cattod.2007.05.014

conditions in order to gain further information about the variables that influence the mechanism of reduction of NO_x stored. In a first step, a thermal evolution study with simultaneous gas analysis and surface spectra, introducing different reducing gases (H_2, C_3H_6 or C_3H_8) is employed over a Pt-Ba-Al_2O_3 and free-Pt catalyst in order to elucidate the role of the components, the reduction products and the temperature window. Secondly, the use of *operando* MS-FTIR technique, obtaining IR spectra of the catalyst surface and of the gas phase under dynamic conditions during a complete NSR cycle, would provide a general understanding of the reduction stage. Finally, the study is complemented with a new catalytic formulation considering the substitution of barium by potassium in order to analyze the effect of a formulation change.

2. Experimental

2.1. Catalyst synthesis

A set of catalysts labelled as Pt/M/Al_2O_3, where "M" is the alkaline metal used in the formulation (Ba or K), were synthesized. The overall metal loading was expressed as surface atomic density (atoms per square nanometre, at/nm^2) and the value was kept constant at 0.4 at-Pt/nm^2 ($\approx$2 wt%) and 4 at-M/nm^2 (13.7 wt% of Ba, 3.9 wt% of K). The alumina used as support is a commercial γ-alumina ($A_{BET} = 150\ m^2/g$, $V_p = 0.23\ cm^3/g$, Alpha-Aesar). The metal incorporation onto alumina support was made by incipient wetness impregnation method using solutions of diamminedinitritoplatinum (II) and alkaline-earth or alkaline acetate precursors. The preparation procedure involves two sequential impregnation steps: first, Pt was dispersed onto the support, dried overnight at 90 °C and calcined in air at 300 °C for 3 h. Then, the corresponding alkaline (-earth) metal was incorporated by an impregnation of the activated Pt/Al_2O_3; the sample was then dried and calcined in air at 500 °C for 2 h [6].

2.2. FTIR study

The reduction stage has been studied by IR over Pt-Ba-Al_2O_3 and Ba-Al_2O_3 catalysts. Changes of adsorbed species and products distribution have been analyzed in surface and gas cell spectra. The samples were pressed on self-supported disk, placed in the cell equipped with KBr windows and activated in vacuum at 500 °C during 1 h. Spectra were recorded with a Nicolet Avatar 360 spectrometer (100 scans, 4 cm^{-1} resolution) and the quartz-cell is permanently coupled to a vacuum line (residual pressure $\approx 1.10^{-4}$ torr). After the evacuation process, the samples were saturated with NO_x, introducing $NO + O_2$ ($NO:O_2$ ratio, 1:10 torr) in the cell at 300 °C for 10 min of contact time. Consecutively, the gas was evacuated from the cell and the temperature was decreased to room temperature (r.t.). Then, it was introduced a reducing pulse (H_2, 10 torr) in the cell and during this time there was no evacuation of the gas. Surface and gas spectra were recorded almost simultaneously from room temperature up to 400 °C (with 100 °C steps). The figures represent the subtraction spectra corresponding to the surface (1000–2000 cm^{-1}) and to the gas in the cell (400–4000 cm^{-1}) as function of absorbance (absorbance units, a.u.) at each temperature. Additionally, other reducing molecules (C_3H_6 and C_3H_8) were tested to analyze the reduction stages over Pt-Ba-Al_2O_3, following the same experimental method described with H_2.

2.3. Operando MS-FTIR

The *Operando* system is composed by a quartz-cell placed in the IR spectrometer compartment and the effluents are analyzed with an online mass spectrometer (MS, Mass Spectrometer, Balzers QMS 200). Gas feed into the cell is tuned by mass-flow controllers with lean (1000 ppm NO, 3% O_2 in He) or rich (5000 ppm H_2 in He) feed gas mixtures, respectively. A fixed amount of argon is fed as an internal standard during dynamics runs. Samples are activated (vacuum, 500 °C, 1 h) previously to introduce the reaction mixture. Then, the temperature was decreased at 200 °C and it remained constant during all the tests. NO_x Storage-Reduction process is simulated by alternating the lean and rich feeds every 20 min. Gas analysis is performed following the m/e 2 (H_2), 12 (C), 15 (NH_3), 18 (H_2O), 28 (N_2), 30 (NO), 32 (O_2), 40 (Ar), 44 (N_2O or CO_2) and 46 (NO_2). Finally, the Pt-Ba-Al_2O_3 activity is compared with a new formulated catalyst, labelled as Pt-K-Al_2O_3.

3. Results and discussions

3.1. FTIR study

IR response for Ba-Al_2O_3 (A and C) and Pt-Ba-Al_2O_3 (B and D) is shown in Fig. 1. Panels A and C (Fig. 1) represent the surface and gas spectra for Ba-Al_2O_3, and B and D (Fig. 1) the surface and gas spectra for Pt-Ba-Al_2O_3, respectively. The activation procedure (vacuum, 500 °C, 1 h) does not eliminate the carbonates from the catalytic surface. The modes associated to carbonates species (1400–1500 cm^{-1}) overlap with those of nitrates and the quality of the spectra is low. NO_x saturated surfaces ($NO + O_2$ spectra) on both catalyst (Fig. 1A and B) show modes associated with Ba-nitrites at 1225 and 1100 cm^{-1} and Ba-nitrates at 1555, 1628 and 1775 cm^{-1} [6,7,9,10,12,15,17–19]. After NO_x surface saturation, a pulse of H_2 was introduced in the cell at room temperature. The samples evolution was analyzed in the 100–400 °C range. Ba-Al_2O_3, catalyst (Fig. 1A), shows the same trend below 300 °C. The mode associated to nitrite species (c.a. 1225 cm^{-1}) disappears and the intensity of nitrates signals (1300–1400 and 1500–1650 cm^{-1}) decreases at 400 °C. The spectrum of Pt-Ba-Al_2O_3 catalyst (Fig. 1B, spectrum $NO + O_2$) shows similar nitrite and nitrate modes than the Pt-free catalyst. But after the H_2 pulse, the surface regeneration begins at 200 °C where signals localized at 1225, 1550 and 1775 cm^{-1}, associated to nitrites and nitrates, disappear.

The thermal decomposition of the adsorbed NO_x species (nitrites and nitrates) occurs above 350 °C, in agreement with TPD runs (not shown) [6]. On Pt-free catalyst, the nitrate decomposition in H_2 atmosphere is also observed at

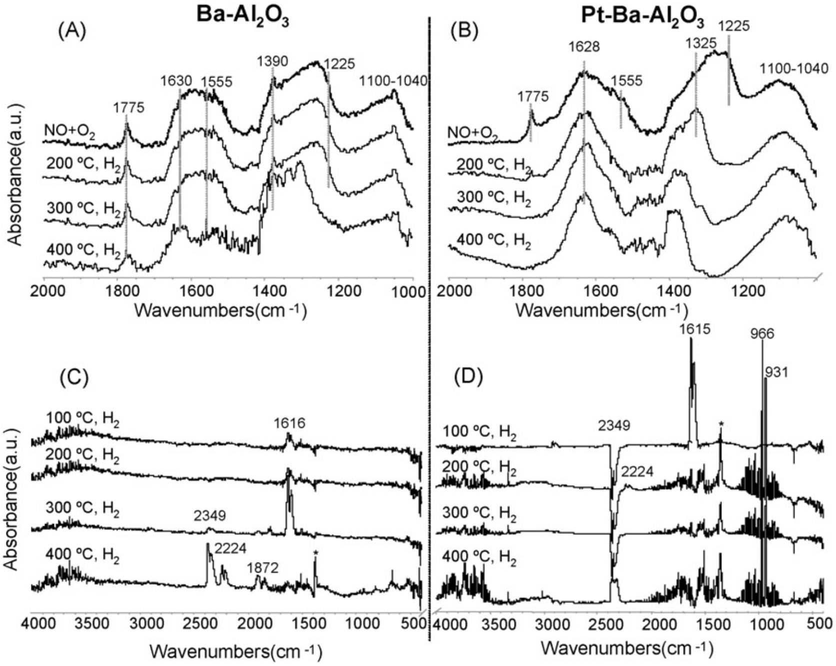

Fig. 1. FTIR spectra of surface catalyst and gas in the cell during reduction stage conditions. (A) Subtraction spectra of NO + O_2 adsorption over Ba-Al_2O_3 catalyst at 300 °C (NO + O_2 spectrum) and after subsequent interaction with H_2 at 200 °C, 300 °C and 400 °C. (B) Subtraction spectra of NO + O_2 adsorption over Pt-Ba-Al_2O_3 catalyst at 300 °C (NO + O_2 spectrum) and after subsequent interaction with H_2 at 200 °C, 300 °C and 400 °C. (C) Spectra of gas in the cell during the interaction of Ba-Al_2O_3 with H_2 at 100 °C, 200 °C, 300 °C and 400 °C. (D) Spectra of gas in the cell during the interaction of Pt-Ba-Al_2O_3 with H_2 at 100 °C, 200 °C, 300 °C and 400 °C. (*potassium nitrate on cell windows).

temperature above 350 °C [14]. In agreement to Nova et al., the surface nitrates reduction on Pt-Ba-Al_2O_3 in H_2 environment occurs before its thermal decomposition. This experimental feature implies that thermal decomposition is not a previous step for surface regeneration. Pt-Ba-Al_2O_3 catalysts show lower temperature for NO_x reduction than Ba-Al_2O_3; so platinum is necessarily involved in the rich cycle. This fact is indirectly observed in the gas phase spectra. Fig. 1C (Ba-Al_2O_3) shows the NO_2 mode (1616 cm^{-1}) when the evacuation temperature rises to 200 °C and it is more defined at 300 °C. It is associated to a NO_2 release and not to nitrate decomposition, because no change in surface spectra was registered at these temperatures (Fig. 1A). At 400 °C, the gas spectrum shows modes associated to N_2O (2224 cm^{-1}), NO (1875 cm^{-1}) [19–22], H_2O and CO_2 (2349 cm^{-1}).

Fig. 1D shows the gas phase spectra for Pt-Ba-Al_2O_3 experiment. It is worth to notice that the modes of N-species are presented at lower temperatures than the Pt-free catalyst. At 100 °C in the spectrum, NO_2 partial desorption (1615 cm^{-1}) is apparent because no appreciable changes are detected on the catalytic surface (Fig. 1B). However, modes associated to reduction products of the nitrates and nitrites are registered at 200 °C. This is in accordance with the decrease of the intensity of surface signals at 200 °C. The major components detected are N_2O (2224 cm^{-1}) as intermediate reduction product [17,23], NH_3 (3333, 966 and 931 cm^{-1}) and H_2O. N_2O is completely disappeared at 300 °C. NH_3 and H_2O are still present at 400 °C. It is well known that N_2 is not easily IR-active, although it is reported a weak vibration mode of (N≡N) at 2331 cm^{-1} [19,22]. The perturbation of the CO_2 signal (2349 cm^{-1}) could be related to the overlap with this N_2 mode. This experiment established that the surface regeneration begins at 200 °C only with the Pt-containing catalyst. This reaction temperature range for Pt-Ba-Al_2O_3 catalyst is also confirmed by flow test over powder and monolithic catalysts.

Similar runs were performed on Pt-Ba-Al_2O_3 using C_3H_8 and C_3H_6 as reducing agents. The specific reducing molecule determines the temperature at which regeneration begins. In situ IR regeneration cycles carried out with H_2 show that the reduction process begins at 200 °C. When C_3H_6 is used, it is necessary to have at least 10 min of contact at 300 °C and 40 min with propane to detect reduction products [6]. Fig. 2 shows the gas phase spectra for H_2, C_3H_6 and C_3H_8 at the

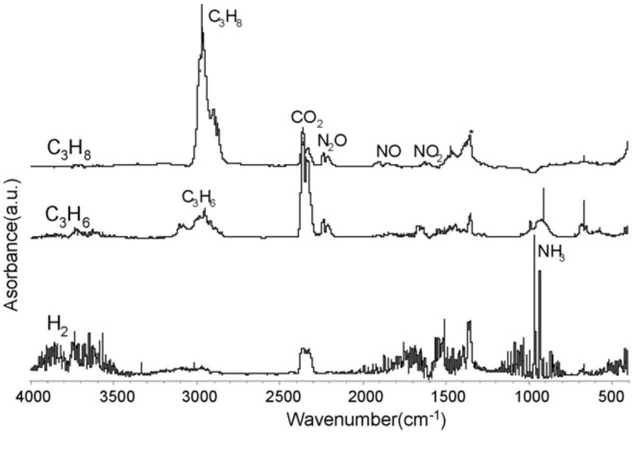

Fig. 2. FTIR spectra of gas in the cell at 400 °C with different reducing gases (*potassium nitrate on cell-windows).

highest temperature tested (400 °C). IR spectra depend on the gas feed. The signals registered are associated to products of the surface regeneration. The reduction routes of nitrites and nitrates depend on the reducing agent used for: NH_3 (930–970 cm^{-1}), H_2O, N_2 (2331 cm^{-1}) and CO_2 (2349 cm^{-1}) are detected when H_2 is used; N_2O (2223 cm^{-1}), NO (1875 cm^{-1}) and NO_2 (1616 cm^{-1}) are evident under C_3-hydrocarbons. Similar product distributions are reported by other authors [20,21,23]. These observations are in agreement with Abdulhamid et al. [24] who report the same temperature range on a Pt-Ba-Al_2O_3 catalyst in flow conditions. Therefore, both the temperature range and the extension of the reduction cycle should be correlated with the reduction capacity of the molecule employed [25].

3.2. *Operando* FTIR-MS

Lean-Rich cycling isothermal experiments are performed (IR-MS) over Pt-Ba-Al_2O_3 and Pt-K-Al_2O_3 catalysts. Fig. 3 shows the results of the NO_x-storage cycle at 200 °C using Pt-Ba-Al_2O_3 sample. Panel A (Fig. 3) shows IR of the activated sample (previous to NO + O_2 pulse) and the temporal evolution of the surface during the NO_x storage (registered at 2, 10 and 20 min of contact). Panel B (Fig. 3) illustrates the gas phase spectra in the cell; and Panel C (Fig. 3) represents the outlet gas profile monitored by MS during the lean phase.

NO adsorption in the presence of oxygen at low temperature (200 °C) produces a relatively fast surface saturation by formation of nitrites (1220 cm^{-1}) and ionic nitrates species (1300–1400 cm^{-1}) [6,15,20,21,23]. A perturbation between 1500 and 1600 cm^{-1} is also visible, that could be associated to the formation of bidentate nitrates overlapping with carbonate signals. Besides, temporal evolution of gas in the cell evidenced modes associated to NO and N_2O that become more intense during the test run. NO_2 and rotovibrational H_2O modes are appreciable after 10 min and these remain after 20 min of reaction (Fig. 3B). There is no significant change between spectra recorded at 10 and 20 min; during the lean stage the catalyst presents an acceptable storage and oxidizing capacity and it is saturated after 10 min of contact.

NO_x breakthrough profile during lean phase (bottom panel, Fig. 3C) shows a practically complete NO_x storage. The delay time registered for NO_2 outlet (panels B and C, Fig. 3) confirms that it is more easily adsorbed than NO. During the run (performed in dry conditions), H_2O signal (m/e18) presents a delay time with respect to NO. It is associated to hydroxyls participating in the NO_x storage process. In parallel, the m/e 44 signal (CO_2 or N_2O) is also apparent. Coupling IR and MS allows determining that the m/e 44 corresponds to a CO_2 release because the m/e12 (C) is also monitored. Therefore, that involves the $BaCO_3$ species as NO_x-storage sites [16]. The m/e 44 is also assigned to the formation of N_2O because it is evidenced by IR (2223 cm^{-1}, Fig. 3B). It should be associated to a disproportionate reaction of NO ($3NO \leftrightarrow N_2O + NO_2$) [20].

Fig. 4 shows the results corresponding to the regeneration cycle at 200 °C using H_2 as reducing agent (5000 ppm H_2 in He). Fig. 4A shows a gradual surface regeneration with time and after 20 min the spectrum resembles that of the activated surface before the NO_x-storage stage. Gas phase spectra (Fig. 4B) show signals associated to H_2O production after the first minute, as it was expected due to use of H_2 as reducing agent ($BaNO_3 + H_2 \rightarrow N_2 + H_2O + BaO$). N_2O and a weak signal at 1850–1900 cm^{-1}, related to NO, are also observed due to an incomplete reduction. These compounds are the non-selectivity products detected during the early stage of the rich cycle; similar results are reported in bibliography [16–18,24]. All reduction products are detected during the first minute of the stage, so regeneration could be considered fast. N_2 is monitored by MS. Fig. 4C represents the outlet concentrations versus time of the species produced during the rich cycle. The

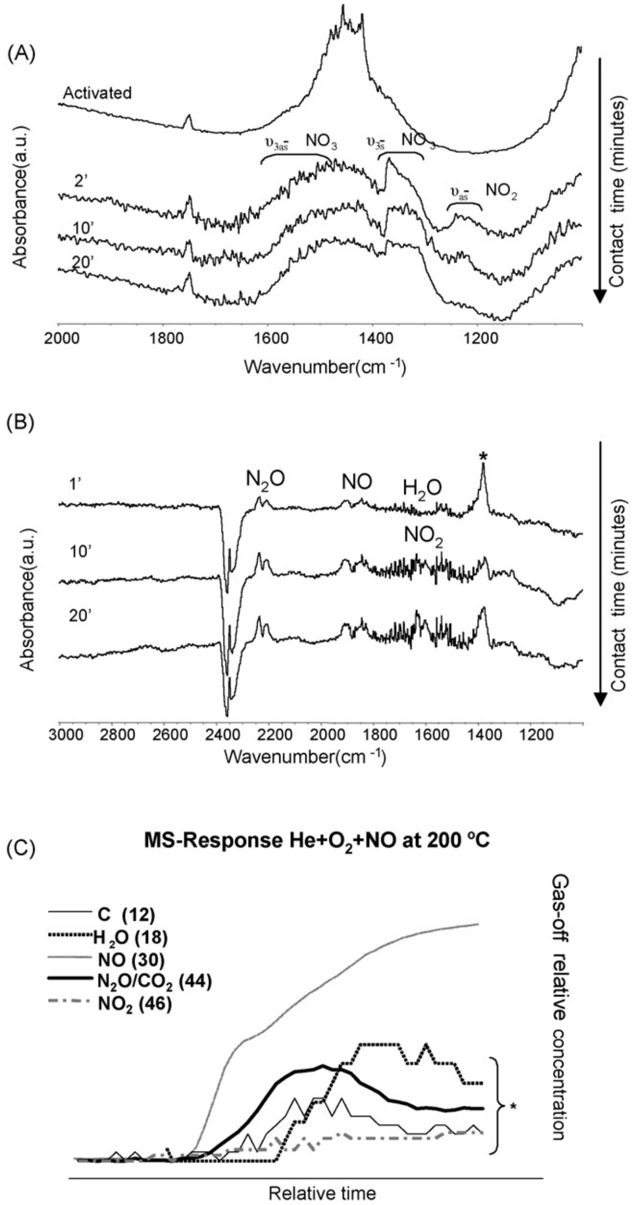

Fig. 3. *Operando* MS-FTIR response during lean cycle (NO + O_2 in He pulse at 200 °C) over Pt-Ba-Al_2O_3: (A) temporal evolution of the surface spectra, (B) temporal evolution of the gas spectra and (C) outlet concentrations of the main products registered by MS during lean conditions (*Enlarged signals).

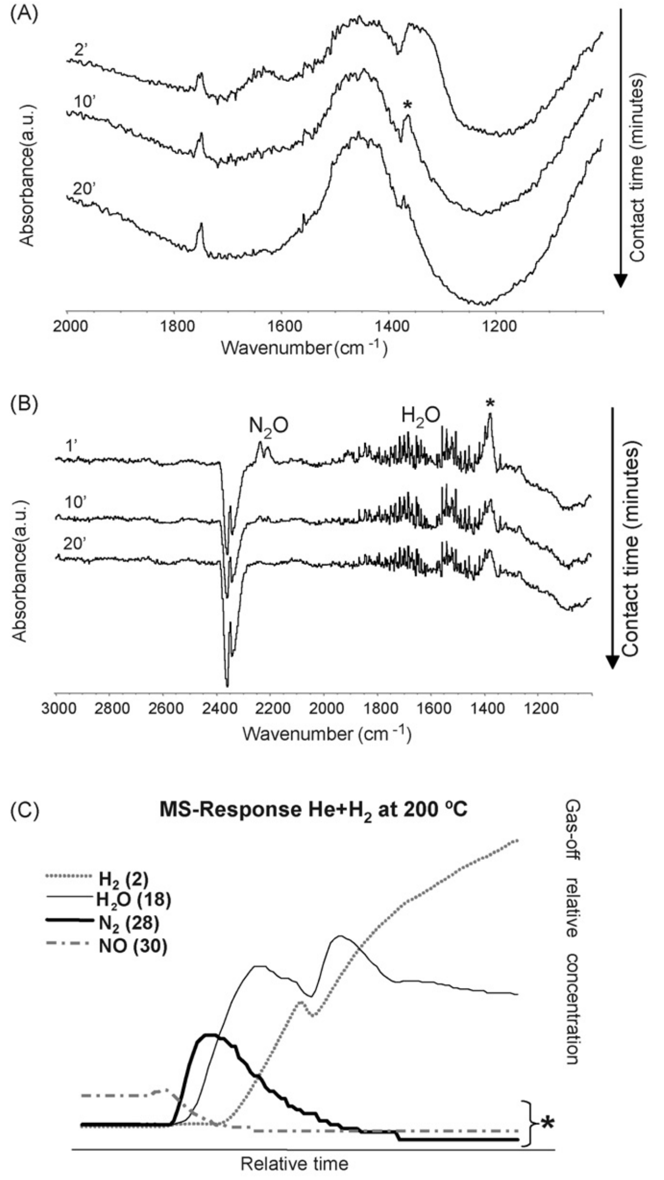

Fig. 4. *Operando* MS-FTIR response during reduction stage (H_2 in He pulse at 200 °C) over Pt-Ba-Al_2O_3: (A) temporal evolution of the surface spectra, (B) temporal evolution of the gas spectra and (C) outlet concentrations of the main products registered by MS during reduction conditions (*Enlarged signals).

reduction of retained NO_x is accompanied by the release of H_2O and N_2 as major products and by a weak NO desorption. During N_2 formation, H_2 is consumed by surface reducible species. The regeneration cycle is almost finished when N_2 outlet concentration decreases and H_2 signal increases. A delay time is observed for H_2O outlet concentration respect to N_2 signal, which is usually associated to a hydroxylation of the regenerated surface [16]. Finally, it is noticed that N_2O outlet signal was not detected by MS although is clearly observed in gas phase spectra; maybe the presence of H_2 provokes its reduction before MS detection.

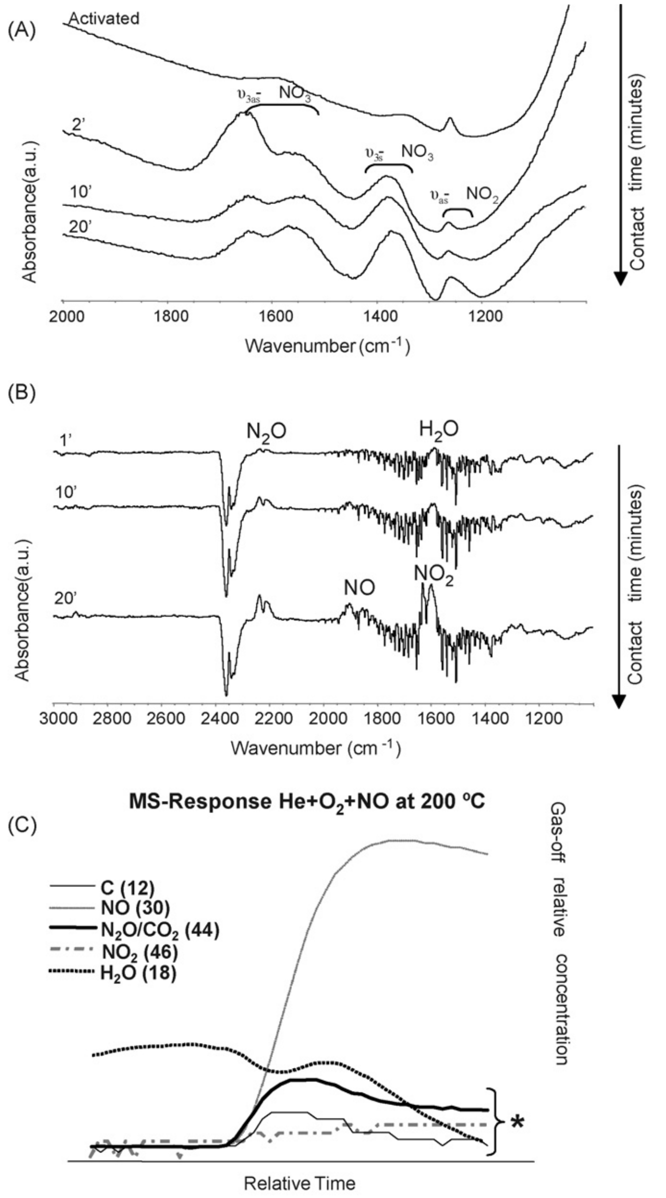

Fig. 5. *Operando* MS-FTIR response during lean cycle (NO + O_2 in He pulse at 200 °C) over Pt-K-Al_2O_3: (A) temporal evolution of the surface spectra, (B) temporal evolution of the gas spectra and (C) outlet concentrations of the main products registered by MS during lean conditions (*Enlarged signals).

K-containing catalyst has been tested in order to obtain additional information about the NSR process. Figs. 5 and 6 show the catalytic behaviour of Pt-K-Al_2O_3 system during a lean-rich cycle at 200 °C, respectively. Surface catalyst spectra are presented in Fig. 5A, which exhibits modes associated to K-nitrites (1230–50 cm^{-1}) and K-nitrates (1380, 1550 and 1650 cm^{-1}) [6,26,27] that become more intense with time. The absence of carbonates bands facilitates the study of the K-containing sample. Initially, gas phase spectra (Panel B, Fig. 5) show modes associated to H_2O and N_2O. Weak signals of NO_2 and NO become apparent after 10 min and reach a maximum after 20 min. MS profiles (Fig. 5C) show a very close breakthrough times for NO, CO_2/N_2O, NO_2 and H_2O. The water base line signal is apparently not stabilized as a consequence of the continuous water release [16,18] and a hydroxylation equilibrium is promoted by K-substitution in the catalyst formulation. The m/e 44 (CO_2/N_2O) is associated to both compounds due to the presence of m/e 12 (C) signal by MS and the N_2O detection by IR. N_2O production during lean cycle

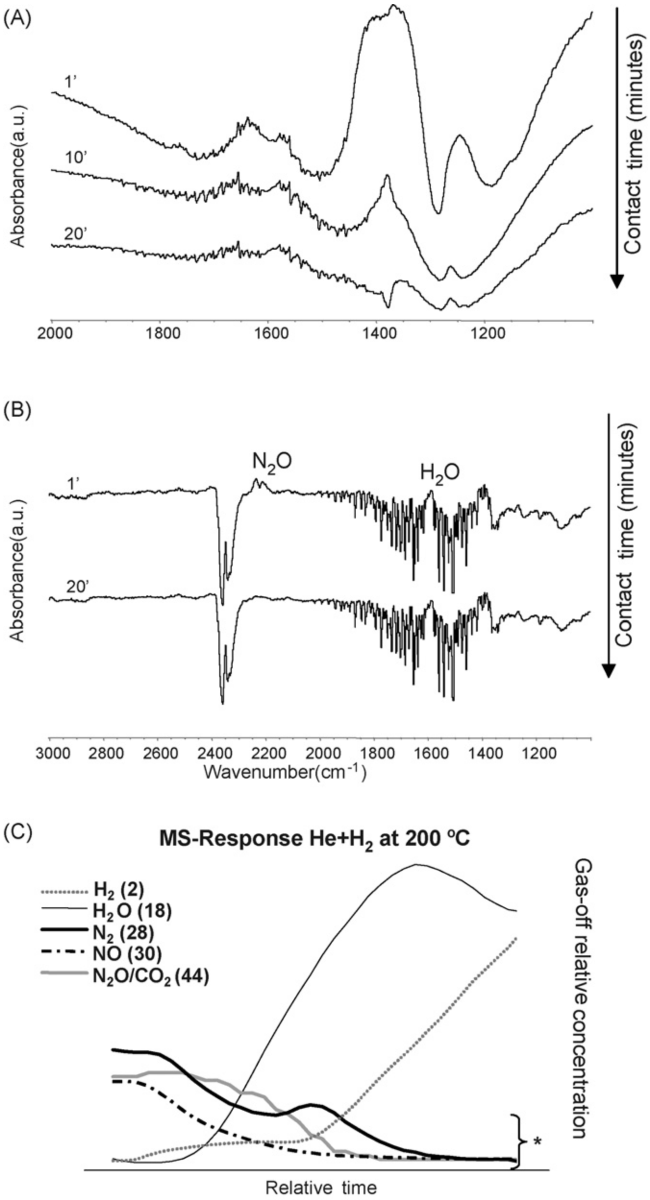

Fig. 6. *Operando* MS-FTIR response during reduction stage (H_2 in He pulse at 200 °C) over Pt-K-Al_2O_3: (A) temporal evolution of the surface spectra, (B) temporal evolution of the gas spectra and (C) outlet concentrations of the main products registered by MS during reduction conditions (*Enlarged signals).

could be related to a NO disproportionation probably consequence of the relative high NO pressure in the cell during storage process or even in the cylinder. NO outlet concentration reaches a saturation value faster than Pt-Ba-Al_2O_3. Most of potassium sites for storage are related to an oxide form because CO_2 and H_2O release are negligible. On the contrary, BaO, $Ba(OH)_2$ and $BaCO_3$ seems to be important storage sites due to the detection of CO_2 and H_2O during lean cycle with Pt-Ba-Al_2O_3 catalyst, as it is well established in previous works [6,16,18]. These results suggest that the overall storage capacity is lower for K-containing catalyst, even with a similar metal density.

Results corresponding to the regeneration stage with H_2 in He over Pt-K-Al_2O_3 at 200 °C are presented in Fig. 6. Surface spectra (Fig. 6A) show a gradual decrease of modes associated to nitrite and nitrate species. The last spectrum registered does not resemble the activated surface; not even after 20 min in rich conditions. A weak and broad signal associated to potassium nitrate monodentate (1380 cm^{-1}) [6,26,27] remains on the surface indicating an incomplete surface regeneration. On the contrary, barium-containing catalyst is completely regenerated before the end of the rich stage. Temperature could be an important variable that influence the level of storage and reduction. Actually barium seems to have better performance at 200 °C. In Fig. 6B, gas phase spectra show modes associated to H_2O released by the reduction process. N_2O is also registered due to an incomplete reduction of adsorbed species. The relative outlet concentrations of the reduction products are presented in Fig. 6C. MS-response shows NO and N_2O presence at the beginning of H_2 pulse, besides H_2O and N_2. It is possible to distinguish two consecutive N_2 formation, and two associated H_2 perturbations, apparently related to a non-effective reduction process. It has to be pointed out that there is not ammonia production with any catalysts in these conditions.

Significant differences have been registered during lean-rich isotherm cycling experiment at 200 °C. The storage capacity is lower with K-containing catalyst and this implies that a similar surface atomic density (4 at/nm^2) does not guarantee the same storage capacity per site. Taking into account that 4 at-K/nm^2 is 3.9 wt% and 4 at-Ba/nm^2 is 17 wt%, different support coverage will be reached. This fact has already been reported about other metals on different supports [28–30].

Lesage et al. [26] reported a higher NO_x adsorption capacity with a sample containing potassium than with a Ba-containing catalyst. The content of potassium is 20 wt% over an alumina with a 150 m^2/g; it supposes a metal density around 20 at-K/nm^2. The adjustment of this variable seems to be important for a new formulated catalyst with proper storage capacity. So, the metal loading has to be adjusted depending on the metal used as support. That means that the effectiveness in the retention-regeneration processes not only depends on the capacity per site; but also on the support coverage and on the interaction with the noble metal.

4. Conclusions

The reduction stage in cyclic NSR process does not need thermal decomposition (ca. 400 °C) of adsorbed species as a previous step in the presence of platinum. Ba-Al_2O_3 catalyst presents a limited NO_x-storage capacity and needs a higher temperature in the regeneration stage to decompose the surface species, with independence of the reducer used. The reducing agents modify the routes of nitrates (and nitrites) reduction (*via* N_2 and NH_3 using H_2; *via* N_2O, NO and NO_2 with C_3-hydrocarbons). The temperature necessary to begin the regeneration depends on the molecule used like $H_2 > C_3H_6 > C_3H_8$.

Even at 200 °C (low temperature in typical NSR range) during the NO_x-storage cycle, hydroxyl and carbonate sites are evidenced as storage sites due to the detection of CO_2 and H_2O releases during the nitrate surface formation. This effect is more important with barium-containing catalyst. The surface regeneration is complete with Ba-containing catalyst but some species still remains onto surface with potassium due to an incomplete reduction. This effect could affect the overall storage capacity of Pt-K-Al_2O_3 during the subsequent cycle because not all sites are regenerated. At this temperature no ammonia production is detected unlike other works.

For the design of a new formulated catalyst for NSR process it is necessary to take into account the coverage of different metals over a support, in order to reach a proper storage capacity.

Acknowledgements

This work is financially supported by Spanish Science and Education Ministry (MEC, PPQ2003-01656) and by Junta de Andalucia for PhD-Grant.

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