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Influence of platinum and barium precursors on the NSR behavior of $Pt–Ba/Al_2O_3$ monoliths for lean-burn engines

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ABSTRACT

The influence of platinum and barium precursors on the catalytic performance of monolithic $Pt–Ba/Al_2O_3$ NO_x storage catalysts was studied. The precursors used in the preparation were: tetraammineplatinum nitrate [$Pt(NH_3)_4(NO_3)_2$] and hexachloroplatinic acid [$H_2Pt(Cl)_6$] for incorporation of platinum by adsorption from solution (ion exchange); and barium acetate [$Ba(CH_3–COO)_2$] and barium nitrate [$Ba(NO_3)_2$] for incorporation of barium by dry impregnation. The prepared samples were characterized by XRD, H_2 chemisorption and thermogravimetry, to determine the distribution and dispersion of the metallic phases. The catalytic activity of the prepared monolithic catalysts was tested for lean/rich NO_x storage and reduction in a flow reactor using hydrogen as reducing agent. The catalyst prepared from tetraammineplatinum nitrate and barium acetate was the most active in the NO_x storage during the lean period. NO_x storage capacity (NSC) and selectivity were dependent with temperature. The higher NSC was obtained at temperature 330–350 °C. About 80% selectivity to nitrogen was achieved with catalysts prepared from tetraammineplatinum nitrate, versus 70% when the platinum was incorporated from hexachloroplatinic acid.

1. Introduction

The demand to improve the fuel efficiency of vehicles and the need to decrease the CO_2 emissions has recently led to the introduction of lean-burn engines, operating in the presence of excess of oxygen. However, the presence of excess oxygen under lean-burn conditions strongly decreases the efficiency to reduce the NO_x gases with the three-way catalysts normally used after engines operated under stoichiometric conditions.

One promising strategy to solve the problem is the use of NO_x storage and reduction (NSR) catalysts. This technique was proposed by Takahashi et al. in the 1990s [1]. The basic concept of the NSR catalyst is a cycled process during which the storage of NO_x is accomplished under lean conditions and the subsequent catalyst regeneration is carried out during a short period under rich conditions. The NSR catalyst consists of a storage component, mainly BaO, and a precious metal, generally Pt, dispersed on γ-Al_2O_3 as the washcoat on a ceramic monolith.

The catalytic behavior of Pt–Ba model systems in the reduction of NO_x under NSR conditions is object of many papers in the literature. It is notable that the catalysts studied were prepared in different ways. This probably affects the behavior of the catalysts and may influence the conclusions about the performance of the NSR catalysts. Pt is introduced via impregnation of suitable support materials with aqueous solutions of different precursors, e.g. $Pt(NH_3)_4(OH)_2$ [2–4], $Pt(NH_3)_2(NO_2)_2$ [4,5–12], $H_2Pt(Cl)_6$ [4,13,14], and $Pt(NO_3)_2$ [4,15–17] with the loading varying between 0.5 and 3 wt%. Dawoody et al. [16] studied the influence of the Pt-precursors on the catalytic performance of $Pt–Ba/Al_2O_3$. Barium is usually introduced as $Ba(CH_3–COO)_2$ [5–12,18] or $Ba(NO_3)_2$ [2–4,13–17,19] which, after subsequent calcinations in air, forms BaO/$BaCO_3$ phases. Table 1 shows the main references corresponding to different preparation methods for $Pt–BaO/Al_2O_3$ powder or monolith NSR catalysts.

Recently, Lindholm et al. [19] have varied the order of the impregnation steps in the preparation procedure, either by adding Pt to the catalyst before impregnating it with Ba or by adding Ba before adding Pt to the sample. The results clearly show that the preparation procedure influences the behavior of NO_x storage and reduction catalysts both during lean and rich conditions. The storage increased as much as 54% when impregnating Pt/Al_2O_3 with Ba, specially at higher temperatures.

The most common method to deposit the active materials is by wet impregnation (filling the monolith channels). However, we have previously reported that incorporation of Pt by adsorption

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Table 1
Preparation of Pt–Ba/Al_2O_3 catalysts in the literature and values of platinum dispersion.

Ref.	Sample type	Composition	Pt precursor	Ba precursor	Incorporation order	Pt dispersion
[2,3]	Monolith	2 wt% Pt 20 wt% BaO γ-Al_2O_3	$Pt(NH_3)_4(OH)_2$	$Ba(NO_3)_2$	Pt to Ba/Al_2O_3	<1%
[4]	Monolith	2 wt% Pt 20 wt% BaO γ-Al_2O_3	H_2PtCl_6 $Pt(NH_3)_4(OH)_2$ $Pt(NH_3)_2(NO_2)_2$ $Pt(NO_3)_2$	$Ba(NO_3)_2$	Pt to Ba/Al_2O_3	3% 9% 2% 16%
[5,8,9,11]	Powder γ-Al_2O_3	0.7–1 wt% Pt 0–30 wt% Ba	$Pt(NH_3)_2(NO_2)_2$	$Ba(CH_3–COO)_2$	Ba to Pt/Al_2O_3	82% (0 wt% Ba) 40% (30 wt% Ba)
[6,7,12]	Powder γ-Al_2O_3	0.7–1 wt% Pt 0–28 wt% Ba	$Pt(NH_3)_2(NO_2)_2$	$Ba(CH_3–COO)_2$	Ba to Pt/Al_2O_3	n.a.
[10]	Powder γ-Al_2O_3	0.5 wt% Pt 11.8 wt% BaO	$Pt(NH_3)_4(NO_3)_2$	$Ba(CH_3–COO)_2$	Pt to Ba/Al_2O_3	21% (0 wt% Ba) 5% (12 wt% BaO)
[13]	Powder γ-Al_2O_3	1.3–1.7 wt% Pt 8–26 wt% BaO	H_2PtCl_6	$Ba(NO_3)_2$	Pt to Ba/Al_2O_3	n.a.
[14]	Powder γ-Al_2O_3	0.5 wt% Pt 10 wt% $Ba(NO_3)_2$	H_2PtCl_6	$Ba(NO_3)_2$	Ba to Pt/Al_2O_3	n.a.
[15]	Monolith	n.a.	$Pt(NO_3)_2$	$Ba(NO_3)_2$	Pt to Ba/Al_2O_3	3%
[16]	Monolith	2.5 wt% Pt 20 wt% BaO γ-Al_2O_3	$Pt(NO_3)_2$	$Ba(NO_3)_2$	Pt to Ba/Al_2O_3	20–30% (comparison of methods to determine Pt dispersion)
[17]	Monolith	2.9 wt% Pt 20.8 wt% Ba γ-Al_2O_3	$Pt(NO_3)_2$	$Ba(NO_3)_2$	Ba to Pt/Al_2O_3	18%
[18]	Monolith (dipped into γ-Al_2O_3 + $Ba(Ac)_2$ slurry)	n.a.	Amine-based Pt-precursors	8% Ba/γ-Al_2O_3	Pt to Ba/Al_2O_3	n.a.
[19]	Monolith	2.9 wt% Pt 20.8 wt% Ba γ-Al_2O_3	$Pt(NO_3)_2$	$Ba(NO_3)_2$	Ba to Pt/Al_2O_3	18%
[19]	Monolith	3.2 wt% Pt 20.7 wt% Ba γ-Al_2O_3	$Pt(NO_3)_2$	$Ba(NO_3)_2$	Pt to Ba/Al_2O_3	25%
[20]	Monolith	1 wt% Pt 20 wt% BaO γ-Al_2O_3	$Pt(NH_3)_4(NO_3)_2$	$Ba(CH_3–COO)_2$	Ba to Pt/Al_2O_3	35% (adsorption) 13% (impregnation)

n.a.: not available.

from a $Pt(NH_3)_4(NO_3)_2$ solution in basic medium (ion exchange) achieved higher platinum dispersion and homogeneous metal distribution than when using wet impregnation procedure [20]. Barium was incorporated afterwards as suggested by Lindholm et al. [19], by dry impregnation from a $Ba(CH_3–COO)_2$ solution resulting in the Ba uniformly dispersed and distributed. This facilitates that Pt and Ba are in close proximity on the catalyst surface, which allows Pt to catalyze the reduction of N_xO_y species adsorbed over Ba-containing sites, which is one of the mechanistic features of the NSR process.

The chemical properties of the metal precursor used in the catalyst preparation play an important role in the interaction of the metals with each other and with the surface. This interaction influences the metal particle size and distribution on the surface. This paper, which follows the preparation procedure as in Ref. [20], studies the influence of the use of different precursors, i.e. hexachloroplatinic acid and barium nitrate, on the Pt and Ba dispersion and distribution and consequently on the NO_x storage behavior of the catalyst. Following the motivation of Ref. [20], we try to consolidate the best way in which NSR monolithic catalysts have to be prepared by studying the precise roles of the catalyst constituents for NO_x storage, the reaction mechanism involved over each of them, and the subsequent decomposition of the stored species under rich conditions.

2. Experimental

2.1. Catalyst preparation

Several cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) monoliths, 20 mm in length and diameter, were cut from a commercial sample supplied by Corning, with cell density of 400 cells per square inch and wall thickness of 150 μm. After calcination in air at 1000 °C to remove possible impurities, the monoliths were washcoated with γ-alumina SA6173 supplied by Saint-Gobain. This alumina was previously stabilized by calcination at 700 °C in air for 4 h. Several immersions were done in the γ-Al_2O_3 slurry until $\approx$450 mg of alumina were washcoated as reported elsewhere [20]. Afterwards, the platinum was incorporated by adsorption from solution to obtain $\approx$1.2 wt% Pt relative to the amount of washcoat.

The precursors used for platinum incorporation were hexachloroplatinic acid (HCPA) or tetraamine platinum(II) nitrate (TAPN) supplied by Alfa Aesar. To promote the adsorption (ion exchange), the pH of the solution was set at 11.6 by addition of

Table 2
Precursor used and composition in the catalysts used in this study.

Sample name	Platinum precursor	Barium precursor	Catalyst weight (mg)	γ-Al_2O_3 weight (mg)	Pt (wt%)	Ba (wt%)
A	TAPN	BaAc	3520	468	1.24	15.2
B	TAPN	BaN	3480	453	1.27	13.3
C	HCPA	BaAc	3490	458	0.86	14.5
D	HCPA	BaN	3480	458	0.88	11.6

TAPN = tetraamine platinum(II) nitrate; HCPA = hexachloroplatinic acid; BaAc = barium acetate; BaN = barium nitrate.

ammonia (25% NH_3, Panreac) in the case of TAPN, while the pH was not altered (2.6) when HCPA was used as precursor. The monoliths were maintained in contact with the precursor solution for 24 h to reach the adsorption equilibrium. Then, the samples were dried for 24 h, calcined in air at 500 °C for 4 h and reduced in 5% H_2/N_2 stream for 1 h.

The barium was incorporated from barium acetate (BaAc, Aldrich) or barium nitrate (BaN, Aldrich) aqueous solutions by dry impregnation. The target nominal loading was 15 wt% Ba. The monoliths were immersed in the solution for 10 s and then the excess of liquid was blown out with compressed air. Multiple impregnation steps were employed in the samples prepared with BaN due the low solubility of this salt. Later, the samples were calcined at 500 °C for 4 h. Thus, the four samples shown in Table 2 were prepared.

2.2. Characterization techniques

X-ray diffractograms were recorded for the prepared samples in order to identify different barium phases, using a Philips PW1710. The instrument was operated in step mode between 5° and 100° 2θ with a step of 0.02° 2θ and 1 s/step.

The thermogravimetric analysis (TGA) of the samples was carried out in a Setaram, SETSYS Evolution instrument. The samples (around 20 mg) were placed in a Pt crucible and loaded into the TGA sample tray. Data were obtained by heating up the sample from 25 to 1000 °C in 100 mL min^{-1} air flow with a constant rate of 5 °C min^{-1}.

The quantitative analysis of Pt and Ba in the catalyst was made in a quadrupole mass spectrometer Q-ICP-MS (Thermo, XSERIES 2), preparing solutions from the direct digestion of the catalysts.

The particle size of the Pt crystallite was measured by hydrogen chemisorption. Before chemisorption, 120 mL min^{-1} of pure H_2 was flowed through the samples at 450 °C for 2 h. Afterwards, the samples were degasified at the same temperature for 4 h. The adsorption isotherm was obtained at 30 °C and repeated after 1 h of evacuation.

2.3. Activity measurements

The experiments were performed in a downflow stainless steel reactor [20]. The reaction temperature was varied from 250 to 400 °C, in the proximity of the usual operation temperature in the automobile practice.

The NO_x storage and reduction activity of the monolithic catalysts were tested carrying out successive cycles composed of a 150 s-long lean period followed by a 20 s-rich period. The composition of the lean and rich gas mixture was 380 ppm NO/6% O_2/N_2 and 380 ppm NO/2.3% H_2/N_2, respectively. Gases were fed via mass flow controllers and the total flow rate was set at 3365 mL min^{-1}, which corresponded to a space velocity of 32,100 h^{-1}. The outlet gas concentration was continuously measured by chemiluminescence (NO_x), paramagnetic (O_2) and infrared (N_2O, NH_3) detectors (Rosemount Analytical). Prior to NO_x storage experiments, the samples were pretreated at 250 °C for 10 min with pure nitrogen, followed by reduction in 4% H_2/N_2 for 20 min.

The activity of the catalysts during the lean and rich periods, was evaluated by the three following parameters:

- NO_x storage capacity (NSC) calculated as:

$$\mathrm{NSC}(\mu\mathrm{mol\ NO}_x) = \int_0^{t_L} [F^0_{\mathrm{NO}} - F_{\mathrm{NO}_x}(t)]dt \tag{1}$$

where F^0_{NO} is the NO molar flow (mol min^{-1}) at the inlet, F_{NO_x} is the NO_x molar flow (mol min^{-1}) at the outlet and t_L (min) is the length of the lean cycle.

- NO_x reduction conversion (X_R) during the reduction period:

$$X_R(\%) = 100 \times \frac{\mathrm{NO}^{\mathrm{in}} - \mathrm{NO}_x^{\mathrm{out}}}{\mathrm{NO}^{\mathrm{in}}} \tag{2}$$

$$\mathrm{NO}^{\mathrm{in}} = \int_0^{t_L} [F^0_{\mathrm{NO}} - F_{\mathrm{NO}_x}(t)]dt + F^0_{\mathrm{NO}} t_R \tag{3}$$

$$\mathrm{NO}_x^{\mathrm{out}} = \int_{t_L}^{t_R} F_{\mathrm{NO}_x}(t)dt \tag{4}$$

$\mathrm{NO}^{\mathrm{in}}$ computed the NO_x moles stored during the lean period and released in the rich period (first term) and those in continuous addition during the rich period (second term).

- Selectivity to ammonia (S_{NH_3}) was defined as the amount of NH_3 at the reactor outlet whenever was detected, mainly during the rich period and subsequent time of the next lean period in which concentration is reduced practically to zero, related to the total amount of $\mathrm{NO}^{\mathrm{in}}$, i.e. NO_x mmol calculated by Eq. (3). As only traces of N_2O was detected it can be said that nitrogen is the other component present during the release period, making $S_{\mathrm{N}_2}(\%) = 100 - S_{\mathrm{NH}_3}(\%)$.

3. Results and discussion

3.1. Catalyst characterization

The composition of the monolithic samples used for NO_x storage and reduction is given in Table 2. As it can be seen, samples prepared with the same precursor resulted in practically the same Pt loading, 1.25 wt% when the incorporation was carried out with TAPN and 0.87 wt% when HCPA was used. Barium loading around 15 wt%, (Cat. A) and (Cat. C), was achieved with only one immersion of the monolith in the BaAc solution, whereas 3 immersions in the BaN solution were needed to obtain 13.3 and 11.6 wt% Ba, (Cat. B) and (Cat. D), respectively.

Fig. 1 shows the X-ray diffractograms corresponding to powder samples of catalysts A and B, prepared from different barium precursors, barium acetate (BaAc) and barium nitrate (BaN), respectively. A distinct signal at 24.3° (2θ) and several other peaks associated with crystallite $BaCO_3$ (orthorhombic whiterite) could be identified in the sample prepared with BaAc. The intensity of the pattern due to $BaCO_3$ at 24.3° (2θ) was 20 times stronger in a sample prepared by mechanical mixture of $BaCO_3$ and Pt/Al_2O_3 having the same virtual composition of $Pt–BaO/Al_2O_3$ than in the

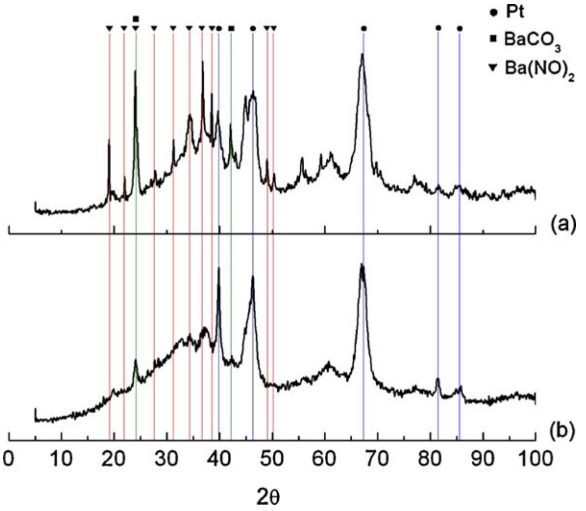

Fig. 1. XRD spectra recorded over Pt–Ba/Al_2O_3 prepared by (a) barium nitrate and (b) barium acetate.

catalyst. This means that near 95% of Ba was not detected by XRD, being uniformly dispersed on the surface. On the other hand, the sample prepared with BaN showed several peaks associated with $Ba(NO)_2$ (nitrobarite). The intensity of these peaks were notably higher comparing to those found for $BaCO_3$, suggesting that less amount of barium was uniformly dispersed on the surface. The background signal in both samples corresponded to a semi-amorphous alumina, and the low intensity of the diffraction peaks corresponding to platinum, suggested that the metallic phase was uniformly distributed and well dispersed over the catalyst surface, in agreement with the results obtained from chemisorption experiments.

Decomposition of model acetate/nitrate precursors in impregnated Pt–Ba(20%)/Al_2O_3 samples was analyzed by thermogravimetry. The derivative of the weight loss versus temperature provides some information of the decomposition of the phases during the calcination. While the decomposition temperature of pure barium acetate was found at 430 °C, in the case of BaAc–Pt/Al_2O_3 the decomposition of the salt occurred at lower temperature. As reported by Piacentini et al. [6] the presence of the alumina support and the Pt loading affected the decomposition of BaAc. We suggest that the proximity between barium and platinum may also affect the decomposition pattern. In that sense, we found two decomposition steps, at 200 and 250 °C associated with the proximity of the Pt–Ba couple. The weight loss recorded around 200 °C is related to the decomposition of barium assisted by a proximal Pt whereas the weight loss at higher temperatures is related to bulk barium far enough from a Pt so that the oxidation could not be assisted by the metal. On the other hand, thermogravimetric experiments over BaN–Pt/Al_2O_3 sample revealed that barium nitrate is very stable and decomposes only around 550 °C. This means that a calcination temperature of 500 °C was not enough to decompose completely the precursor, this being confirmed by the presence of $Ba(NO)_2$ in XRD measurements. Higher calcination temperature in the catalyst preparation step would make possible the total decomposition of the precursor. In contrast, it has been confirmed that temperatures above 500 °C reduce notably the Pt dispersion in the sample from 46 to 19% [20], making unacceptable the NSR behavior of the resulting catalyst.

Hydrogen chemisorption experiments were carried out over Pt/Al_2O_3 samples. Both platinum precursors led to dispersion values of 46% (TAPN) and 51% (HCPA). The decrease in Pt dispersion upon addition of barium has been widely discussed in literature [5,6,20]. This is likely due to the fast and exothermic decomposition of the barium precursors, eventually leading to the sintering of Pt crystallites, and/or to the masking of Pt crystallites by the Ba component. In fact, Pt–BaO/Al_2O_3 prepared by impregnation with BaAc solution resulted in a decrease in Pt dispersion with respect to Pt/Al_2O_3 from 46 to 35%.

3.2. NO_x storage and reduction behavior

As an example, two consecutive storage-reduction cycles are shown in Fig. 2a for (Cat. A) at different temperatures up to 350 °C. The cycles for (Cat. B), (Cat. C) and (Cat. D) were similar in shape, although quantitatively different. During the first seconds of the lean period the NO fed to the reactor is completely stored on the surface of the catalyst, and during the next 150 s significant amounts of NO_x are stored as indicated by the area between the inlet and the outlet NO_x concentration. The NSC values, as μmol NO_x, can be calculated by Eq. (1).

Alternatively, during the rich period the stored NO_x are released, being transformed into N_2/NH_3 as N_2O was not practically detected at the reactor outlet at any time. Fig. 2b shows the evolution of NH_3 concentration. While 2.3% of hydrogen was fed to the reactor, the ammonia concentration increased rapidly up to a maximum at the end of the rich period. Afterwards, when the feedstream changed again to lean conditions, the outlet concentration decreased until no ammonia was detected at the end of the lean period. It is worth noticing that the coexistence of NO, NH_3 and O_2 could make the SCR reaction possible. The extension of the SCR reaction with temperature is subject of further study in our laboratories for different catalyst formulations.

The NO_x storage profiles shown in Fig. 2a indicated that the storage capacity increased with temperature until 350 °C. On the other hand, Fig. 2b shows that the ammonia profiles are clearly temperature dependant, at low temperatures (250 °C), the maximum concentration of ammonia detected at the end of the rich cycle was 1100 ppm, decreasing to 400 ppm at the temperature of 350 °C. At this temperature, although larger amount of NO_x were stored, less amount of NH_3 was detected.

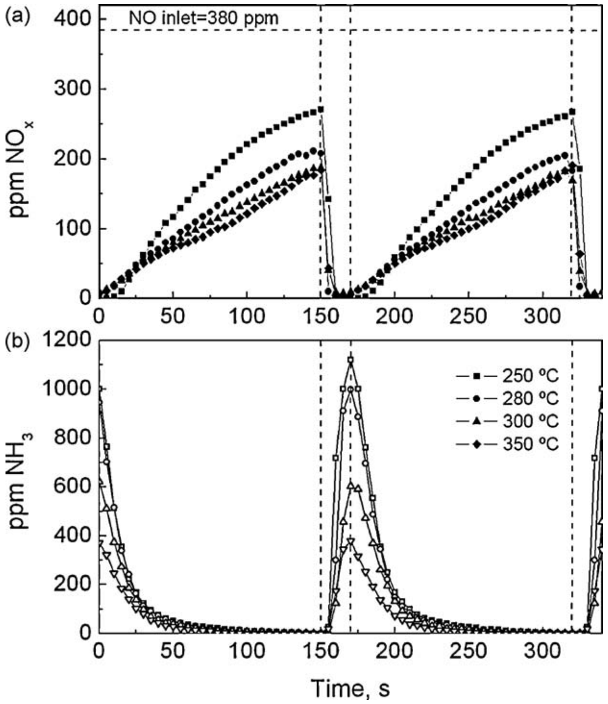

Fig. 2. Outlet concentration of NO_x (a) and NH_3 (b) with time during lean and rich period, for temperatures from 250 to 350 °C.

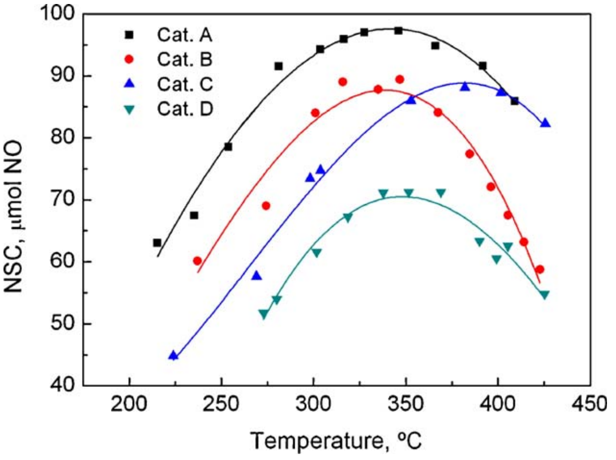

Fig. 3. NO_x storage capacity as a function of temperature for the prepared catalysts.

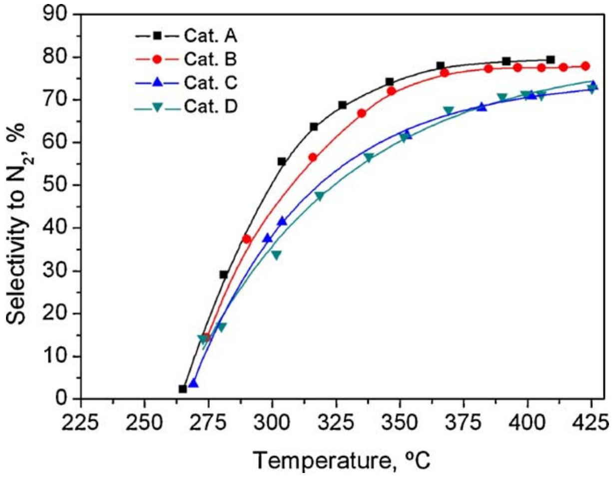

Fig. 4. Selectivity to nitrogen as a function of temperature for the prepared catalysts.

The influence of temperature on the NSC (μmol NO_x), calculated by Eq. (1), is shown in Fig. 3 for the studied catalysts. The NO_x storage capacity of the catalysts followed the next trend, from the most to the least active: (Cat. A) > (Cat. B) > (Cat. C) > (Cat. D). This order can be related to the physicochemical characteristics of the catalysts due to the precursors used in preparation. In our previous work [20] we suggested that when both Pt and Ba are uniformly dispersed and distributed, this facilitates that Pt and Ba are in close proximity on the catalyst surface, which allows Pt to catalyze the reduction of N_xO_y species adsorbed over Ba-containing sites, which is one of the mechanistic features of the NSR process.

(Cat. A) and (Cat. B) were prepared with TAPN precursor achieving practically the same Pt content (1.25 wt% Pt). The NSC of the (Cat. A) was higher at all temperature, and it was even more pronounced at higher temperatures (see difference at 420 °C in Fig. 3). Thus, the advantageous behavior of (Cat. A) can be mainly attributed to the barium phase characteristics, or even in its interaction with platinum. As determined by XRD, barium was less dispersed when incorporated from BaN than when BaAc was the precursor. Furthermore, the calcination temperature of 500 °C was not enough to completely decompose the first precursor. These observations are in agreement with the best activity of (Cat. A) relative to (Cat. B). On the other hand, the increase of the catalyst capability to adsorb NO with the Ba loading has been also associated with the involvement in the NO_x storage process of Pt–Ba neighboring species [5]. The authors have previously reported that the addition of Ba increases the number of Pt–Ba neighboring species, which could also favor the NO_x storage process, resulting in a better utilization of the Ba component. This is also in good agreement with our experimental results, as the barium content in (Cat. A) is slightly larger with respect to (Cat. B). Discussion is similar when comparing NSC behavior of (Cat. C) and (Cat. D).

Comparison between (Cat. A) and (Cat. C), or (Cat. B) and (Cat. D) allows discussing the effect of the platinum precursor. One of the most important characteristics involved in the NO_x storage capacity is the particle size of Pt [20]. The Pt/Al_2O_3 (without barium) samples presented similar dispersion when TAPN or HCPA were used as precursors, 46 and 51%, respectively. The addition of barium decreased the platinum dispersion by around 20%, whatever barium precursor was used. Thus, the platinum dispersion cannot be considered in this case as a key parameter for comparison of NO_x storage behavior of the catalysts. However, (Cat. A) showed better storage capacity in relation to (Cat. C), or (Cat. B) in relation to (Cat. D), which should be related to the higher loading of platinum and better proximity with barium. Here we found values as different as 1.25 wt% Pt when TAPN was used, (Cat. A) and (Cat. B), and 0.87 wt% Pt with HCPA (Cat. C) and (Cat. D). Besides, when HCPA is used as platinum precursor, the Pt is incorporated to the alumina by electrostatic forces between the anion $[PtCl_6]^{2-}$ and the positively charged alumina. In that case, the basic properties needed to improve the NO_x storage may be altered negatively [21]. On the other hand, it could be observed (Fig. 3) that at higher temperatures (>400 °C) the NSC depends on the barium precursor and not on the platinum precursor, neither Pt loading. Barium nitrate precursor led to the storage of 55 μmol of NO whereas BaAc stored 82 μmol NO.

The selectivity to nitrogen is represented in Fig. 4 for different temperatures. When the storage is carried out below 250 °C, almost all NO_x released during the regeneration step, will react with hydrogen to form ammonia (selectivity to NH_3 ≈100%). When increasing the temperature, the ammonia concentration at the reactor exit decreases significantly, and when the maximum storage capacity is reached (350 °C) the selectivity to N_2 is above 60% for all the prepared catalysts. On the other hand, it could be seen in Fig. 4 that (Cat. A) and (Cat. B), prepared from TAPN and with the same Pt loading (1.25 wt%) led to a similar selectivity, although different barium precursors were used and different barium loadings were incorporated. The same occurs with (Cat. C) and (Cat. D), prepared from HCPA and with 0.87 wt% Pt. At higher temperatures, (Cat. A) and (Cat. B) gave $S_{N_2} \approx 80\%$ versus 70% obtained with (Cat. C) and (Cat. D). This difference in selectivity can be attributed mainly to the Pt loading. It clearly appears that the reduction process seems to be catalyzed by Pt particles, which play an important role in the decomposition of surface nitrate species. As suggested by Fanson et al. [13] the primary role of platinum should be allowing the reduction agent (H_2) to bond the surface, which can then react with stored nitrates. A comprehensive and detailed picture explaining the mechanism of the reduction process and in particular of its selectivity has not been completed in literature, and it is under investigation.

4. Conclusions

In this work we have studied the influence of the precursors used to incorporate platinum and barium during the preparation of monolithic $Pt–Ba/Al_2O_3$ NSR catalysts. For the incorporation of platinum, we have used tetraammineplatinum nitrate and hexachloroplatinic acid, and for the impregnation of barium we have used barium acetate and barium nitrate. Platinum was incorporated by adsorption from solution (ion exchange) and barium by dry impregnation.

From the results of the characterization measurements we can conclude that both platinum precursors could lead to highly dispersed catalysts. XRD measurements suggested that less amount of barium was uniformly dispersed on the catalyst surface when this phase was incorporated from barium nitrate than barium acetate. Platinum dispersion was reduced by about 20% upon incorporation of barium.

The catalytic activity measurements revealed that the catalyst prepared by tetraammineplatinum nitrate and barium acetate showed the highest activity for NO_x storage and reduction. This behavior can be attributed to the good distribution of barium and to highest accessible amount of Pt sites, which causes an increase in the amount of storage sites available and also an increase in the interfacial area between Ba and Pt. The maximum NO_x storage capacity was obtained in the range 330–350 °C for all the studied catalysts.

The selectivity towards NH_3/N_2 formation was temperature dependent, i.e. lower temperatures favor the NH_3 production and higher temperatures led mainly to N_2 formation. The higher selectivity towards nitrogen obtained with the catalysts prepared by tetraammineplatinum nitrate, and practically independent of the method of barium impregnation, was attributed to the higher Pt loading. It clearly appears that the reduction process seems to be catalyzed by Pt particles, which play an important role in the decomposition of surface nitrate species.

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