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**Effect of reducing agent (C<sub>3</sub>H<sub>6</sub>, CO, H<sub>2</sub>) on the NO<sub>x</sub> conversion and selectivity during representative lean/rich cycles over monometallic platinum-based NSR catalysts. Influence of the support formulation.**

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**Abstract**

NO<sub>x</sub> storage reduction efficiency was investigated on a Pt-10%BaO/Al<sub>2</sub>O<sub>3</sub> model catalyst using a complex gas feed including reductants and oxidants in both lean and rich mixtures. Three representative reductants have been studied, separately and blended: C<sub>3</sub>H<sub>6</sub>, CO, H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>. The influence of each reductant was evaluated with a special consideration to the N<sub>2</sub>O selectivity. The reductant /oxidant ratio was kept constant for the lean and the rich gas mixture, respectively. The N<sub>2</sub>O emission depends on the introduced reductant(s), and the nature of reductant acts differently depending on the temperature. At 200°C, H<sub>2</sub> mainly drives the N<sub>2</sub>O emission, whereas at 300°C, N<sub>2</sub>O yields is enhanced by C<sub>3</sub>H<sub>6</sub>. In addition, it is demonstrated that NO<sub>x</sub> reduction also occurs during the lean period, leading to significant amount of N<sub>2</sub>O. In fact, on Pt-10%BaO/Al<sub>2</sub>O<sub>3</sub> catalyst, 70 to 90% of the produced N<sub>2</sub>O come from the lean phase, except with CO as reductant which does not allow any NO<sub>x</sub> reduction in lean condition. Results were compared with a platinum/ceria-zirconia-based oxide (Pt/CZ) previously studied. Pt/CZ is generally more active at low temperature (200°C). At 300°C, significant differences appear between the two formulations depending on the used reductant, especially concerning the N-compound selectivities in the rich pulses.

**Keywords:** NO<sub>x</sub> reduction, selectivity, N<sub>2</sub>O, NH<sub>3</sub>, NSR, LNT

## 1. Introduction

Catalytic elimination of environmental pollutants from passenger car is a permanent challenge for researchers. Particularly, NO<sub>x</sub> reduction from exhaust gas of Diesel and lean-burn engines is still a problem for car manufacturers. Among the processes effective to reduce NO<sub>x</sub> in lean condition, two technologies are usually proposed: (i) the NO<sub>x</sub> Storage-Reduction (NSR) concept [1,2], working in transient conditions; and (ii) the Selective Catalytic Reduction (SCR). The SCR is described as a promising way to reduce NO<sub>x</sub>, with the possible use of a large variety of reductants including unburned hydrocarbons, ammonia, urea, hydrogen or alcohol for instance. Actually, under the impulse of environmental legislation, the urea-SCR process is considered as a possible technological issue to reduce NO<sub>x</sub> from light vehicles, as reported in numerous publications [1,3-11]. However, the NSR process has some interest since it does not require an additional reductant source. It works mainly in lean condition. NO<sub>x</sub> are then oxidized on precious metals and stored on basic compounds, mainly as nitrates. Periodically, the catalyst is submitted to rich conditions for a few seconds and the previously stored NO<sub>x</sub> are reduced into N<sub>2</sub> on the precious metals. Among the disadvantages of this system, the selectivity of the reduction may be problematic. Indeed, an incomplete reduction leads to the formation of N<sub>2</sub>O, a powerful greenhouse effect gas. The N<sub>2</sub>O emission is usually observed at low temperatures (200-300°C), whereas it tends to become zero at a higher temperature (400°C). Another by product can also be observed when a high reduction level is achieved, namely NH<sub>3</sub>. Both N<sub>2</sub>O and NH<sub>3</sub> emission during the NSR process must obviously be proscribed. However, ammonia produced during NSR cycles can be used *in-situ* with the association of an adequate NH<sub>3</sub>-SCR catalyst [12]. NH<sub>3</sub> and N<sub>2</sub>O can be observed during the NO<sub>x</sub> reduction [13-19]. Ammonia formation is favored when H<sub>2</sub> is used as reductant, whereas CO is claimed to be the major responsible for N<sub>2</sub>O emission [4,15,20].

Practically, the exhaust pipe usually contains a close-coupled catalyst which is placed in front of the NSR catalyst. This association is supposed to convert the three main pollutants, namely CO, unburned hydrocarbons (HC) and NO<sub>x</sub>. However, due to the high cost of precious metals, this previous catalyst is not supposed to convert all CO and HC. A part of this job is dedicated to the NSR catalyst, which also contains precious metals. In another words, the global precious metal loading is partitioned between both catalysts. As a consequence, untreated reductant can arrive on the NSR catalyst during the lean phases of the NSR process. Note that this precatalyst also strongly influences the composition of the rich mixture for the NO<sub>x</sub> trap regeneration. Fuel is initially used as reductant, but it is partially transformed over the precatalyst and the NSR catalyst is finally submitted to a mixture of hydrocarbons, CO and H<sub>2</sub> with various compositions.

In a previous work, the NO<sub>x</sub> conversion and selectivity over a ceria-zirconia based oxide supported platinum NSR catalyst was studied using C<sub>3</sub>H<sub>6</sub>, CO and H<sub>2</sub> as reductants, used separately or mixed [21]. Using complex gas mixtures including reductant(s) in both lean and rich media, it was showed that NO<sub>x</sub> conversion and selectivity strongly depend on the used reductant and the temperature test. Especially, the contribution of the lean phase can largely contribute to the global N<sub>2</sub>O formation, in accordance with the DeNO<sub>x</sub> activity measurement in excess of oxygen.

In this work, the same scientific approach was applied to a usual 1%Pt-10%BaO/Al<sub>2</sub>O<sub>3</sub> NSR model catalyst. The NO<sub>x</sub> reduction efficiency was evaluated at 200, 300 and 400°C with C<sub>3</sub>H<sub>6</sub>, CO and H<sub>2</sub> as reductants, with a special consideration for the NO<sub>x</sub> reduction selectivity.

These two platinum based catalysts exhibit very different redox behavior toward oxygen storage/mobility. The last part of this work puts in evidence the influence of the support formulation on the NO<sub>x</sub> reduction behaviors.

## 2. Experimental part

### 2.1 Catalyst preparation

10% BaO/Al<sub>2</sub>O<sub>3</sub> material was prepared by the precipitation of barium salt (Ba(NO<sub>3</sub>)<sub>2</sub>) on alumina powder. First, the alumina was added in ultra-pure water and the temperature was raised at 60°C. The pH was then increased to 10 by adding an ammonia solution, and the dry barium salt was added. After drying at 120°C, support was calcined 700°C for 4h under air. After calcination at 700°C, platinum (1 wt%) was impregnated using a Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> aqueous solution. After drying, the catalyst was pre-treated at 700°C for 4h under N<sub>2</sub>, and finally stabilized at 700°C for 4h under a mixture containing 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. As previously reported [ 22 ], the intermediate nitrogen treatment allows higher platinum and barium dispersions. The obtained catalyst is denoted Pt-Ba/Al.

In this study, the Pt-Ba/Al behaviors are compared to another platinum based catalyst supported over a modified ceria-zirconia oxide provided by Rhodia and denoted Pt/CZ. The preparation and characterizations of Pt/CZ are detailed in ref. [21]. Platinum (2.1 wt%) was added by impregnation. Catalyst was then calcined at 500°C for 4h under synthetic air and finally submitted to a hydrothermal treatment at 700°C for 25h.

### 2.2. Catalyst characterizations

The BET surface areas were deduced from N<sub>2</sub> adsorption at -196°C carried out with a Micromeritics apparatus. Prior to the measurement, the samples were treated at 250°C under

vacuum for 8 h in order to eliminate the adsorbed species.

X-ray powder diffraction was performed at room temperature with a Bruker D5005 using a  $K\alpha$  Cu radiation ( $\lambda=1.54056 \text{ \AA}$ ). The powder was deposited on a silicon monocrystal sample holder. The crystalline phases were identified by comparison with the ICDD database files.

Platinum accessibility was determined with a Micromeritics AutoChem II instrument. Typically, 200 mg of sample were reduced in hydrogen flowing ( $30 \text{ mL min}^{-1}$ ) at  $400^\circ\text{C}$  for 1h, then purged in ultrapure Ar ( $30 \text{ mL min}^{-1}$ ) for 2h and cooled down to room temperature. Pulses of  $\text{H}_2$  ( $0.5347 \text{ mL}$ ) were injected at  $-80^\circ\text{C}$ , every minute up to saturation (HC1). A new series of pulses was injected over the sample, after 10 min of purging under pure Ar, in order to determine the reversible part of the chemisorbed hydrogen (HC2). The irreversible part was taken as  $\text{HC} = \text{HC1} - \text{HC2}$ .

The redox properties of catalysts were evaluated by temperature programmed reduction (TPR) experiments. Prior to the TPR test, the catalyst (100 mg) was first pretreated *in situ* under oxygen at  $300^\circ\text{C}$  for 30 min and cooled to room temperature. After flushing under argon for 45 min, the reduction was carried out from room temperature up to  $800^\circ\text{C}$  under a  $1\% \text{H}_2/\text{Ar}$  mixture, using a  $5^\circ\text{C min}^{-1}$  heating rate. The sample was maintained at  $800^\circ\text{C}$  for 60 min before cooling under argon. Hydrogen consumption was followed by thermal conductivity.

Main characteristics of two studied catalysts are described thereafter. Pt-Ba/Al catalyst exhibits BET specific surface areas of  $161 \text{ m}^2\text{g}^{-1}$  and a platinum dispersion of about 16% deduced from  $\text{H}_2$  chemisorption measurements. XRD pattern of this sample (not shown) is consistent with previous reported analysis [22]. The main crystalline phase detected by XRD is  $\text{BaAl}_2\text{O}_4$ , and  $\text{BaCO}_3$  is slightly evidenced.  $\text{H}_2$ -TPR measurement shows no significant hydrogen consumption, as previously reported for Pt-20 %BaO/ $\text{Al}_2\text{O}_3$  catalyst [23].

To compare, Pt/CZ material exhibits a BET specific surface area of  $82 \text{ m}^2\text{g}^{-1}$ . The platinum dispersion was measured at 16%, as for Pt-Ba/Al. XRD analysis showed only one crystallized structure corresponding to a solid solution with a ceria cubic fluorite-like structure. The  $\text{H}_2$ -TPR characterization (not shown) evidenced a high reducibility, with a main reduction peak at around  $150^\circ\text{C}$ . It corresponds to both the platinum reduction and the easily reducible  $\text{Ce}^{\text{IV}}$  reduction in  $\text{Ce}^{\text{III}}$ . The related  $\text{H}_2$  consumption reaches  $557 \mu\text{mol H}_2/\text{g}_{\text{cata}}$ , whereas the total  $\text{H}_2$  consumption in the  $25\text{-}800^\circ\text{C}$  temperature range is  $938 \mu\text{mol H}_2/\text{g}_{\text{cata}}$ .

### 2.3. NO<sub>x</sub> storage capacity (NSC) measurement

Before measurements, the catalyst (70mg) was firstly pretreated *in situ* for 15 min at  $500^\circ\text{C}$ , under a  $10\% \text{O}_2$ ,  $10\% \text{H}_2\text{O}$ ,  $10\% \text{CO}_2$  and  $\text{N}_2$  mixture, and then cooled down to  $400^\circ\text{C}$  with the

same mixture. The catalyst was then submitted to a reducing treatment (4% CO, 1.33% H<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> and N<sub>2</sub>) for 15min and cool down to 200°C under the same mixture. After a purge under N<sub>2</sub>, the sample was then submitted to 500ppm NO, 10% O<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> and N<sub>2</sub> mixture. For measurements at 300°C and 400°C, the catalyst is treated in reducing mixture during the increase of the temperature. The total flow for the whole procedure is constant at 20 L.h<sup>-1</sup>. It corresponds to a gas hour space velocity (GHSV) of about 200.000 h<sup>-1</sup> for Pt-Ba/Al catalyst. It is a little higher with Pt/CZ since its apparent density is higher. The gas flow was introduced using mass-flow controllers, except for H<sub>2</sub>O which was introduced using a saturator. Gas analysis (NO, NO<sub>2</sub>) was performed by a Multigas MKS 2030 analyzer (FTIR). Long time storage is not representative of the NSR catalyst working conditions, since the lean periods are commonly around 1 min. The NO<sub>x</sub> storage capacity was then estimated by the integration of the recorded profile for the first 60 seconds, equal to the lean periods of the NSR test in cycling conditions (see below). The contribution of the reactor volume was subtracted. With the conditions used in this test, 99.2 μmol NO<sub>x</sub> per gram of catalyst were injected in 60s. Then, the NO<sub>x</sub> storage capacity for 60 s expressed in μmol<sub>NO<sub>x</sub></sub>/g almost corresponds to the storage rate (%).

In addition, the platinum oxidation activity was estimated as the NO<sub>2</sub>/NO<sub>x</sub> ratio (%) at saturation (usually after about 900s).

#### 2.4. NO<sub>x</sub> conversion in cycling conditions

Before measurements, the catalyst (70mg) was treated in situ 15 min at 500°C under the full gas lean mixture, displayed on Table 1. The sample was then cooled down to 200°C under the same mixture. The NO<sub>x</sub> conversion was studied in cycling condition by alternatively switching between lean (60s) and rich (4s) conditions using electro-valves. The lean and rich gas compositions are described in Table 1. Most gases (NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, CO, CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>...) were analyzed using a Multigas FTIR detector (MKS 2030), except H<sub>2</sub> which was analyzed by mass spectrometry. NO<sub>x</sub> reduction into N<sub>2</sub> is calculated assuming no other N-compounds than NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>, neither HNCO which was never detected. For each tested temperature (200, 300 and 400°C), the activity of the catalyst was followed until stabilization and calculations were done taking into account ten cycles after stabilization.

Supplementary tests were carried out with simplified gas mixtures, *i.e.* with only one reducing compound (C<sub>3</sub>H<sub>6</sub> or CO or H<sub>2</sub>), but with the same reductant/oxidant ratio as used with the full gas mixture (Table 1). The reductant/oxidant ratio (*i.e.* the redox stoichiometry of the gas mixture) is calculated using equation (1), and corresponds to 0.017 and 3.35 for the lean and

the rich gas mixture, respectively.

$$\text{red/ox} = (9*[\text{C}_3\text{H}_6]+[\text{CO}]+[\text{H}_2]) / ([\text{NO}]+2[\text{O}_2]) \quad (1)$$

Table 1: rich and lean gas compositions used for the NO<sub>x</sub> conversion test (60s lean/4s rich). Total flow rate: 20L h<sup>-1</sup> (GHSV= 200.000 h<sup>-1</sup>). The redox ratio is constant at 0.017 at 3.35 with lean and rich gas mixture, respectively.

Gas		Reductant			Oxidant		common gases		
		C <sub>3</sub> H <sub>6</sub>	CO	H <sub>2</sub>	NO	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>
Full gas	<i>Lean</i>	300	500	167	500	10			
	<i>(L)</i>	ppm	ppm	ppm	ppm	%	10	10	balance
	<i>Rich</i>	9000	4	1.33	100	2	%	%	
<i>(R)</i>	ppm	%	%	ppm	%				
Only C <sub>3</sub> H <sub>6</sub> as reductant	<i>Lean</i>	374	-	-	500	10			
	<i>(L)</i>	ppm	-	-	ppm	%	10	10	balance
	<i>Rich</i>	1.49	-	-	100	2	%	%	
<i>(R)</i>	%	-	-	ppm	%				
Only CO as reductant	<i>Lean</i>	-	3300	-	500	10			
	<i>(L)</i>	-	ppm	-	ppm	%	10	10	balance
	<i>Rich</i>	-	13.4	-	100	2	%	%	
<i>(R)</i>	-	%	-	ppm	%				
Only H <sub>2</sub> as reductant	<i>Lean</i>	-	-	3300	500	10			
	<i>(L)</i>	-	-	ppm	ppm	%	10	10	balance
	<i>Rich</i>	-	-	13.4	100	2	%	%	
<i>(R)</i>	-	-	%	ppm	%				

## 2.5. Light-off tests in lean mixture

The lean DeNO<sub>x</sub> behaviors of the catalysts were also examined using only the lean mixtures reported in Table 1. Before measurement, catalyst (70mg) was treated in situ 15 min at 500°C under the chosen lean mixture. The N-compounds concentration (NO<sub>x</sub>, N<sub>2</sub>O, NH<sub>3</sub>) were recorded from 500°C down to 200°C under the same mixture.

## 3. Results

In this part is depicted the catalytic properties of the Pt-Ba/Al NSR model catalyst depending on the operating conditions.

### 3.1. NO<sub>x</sub> storage capacities (NSC)

In order to have a good understanding of the NO<sub>x</sub> reduction efficiency in cycling condition, the NO<sub>x</sub> storage capacity of Pt-Ba/Al was evaluated at 200, 300 and 400°C using the lean mixture of the NSR test, but without any reductant in the feed stream. The amount of stored NO<sub>x</sub> for

60s ( $\mu\text{mol/g}$ ), length of the lean periods for the NSR test, is reported in Table 2. It increases with temperature, from  $9\mu\text{mol/g}$  to  $46\mu\text{mol/g}$  at  $200^\circ\text{C}$  and  $400^\circ\text{C}$ , respectively. In parallel, the NO oxidation rate, estimated by the  $\text{NO}_2/\text{NO}_x$  ratio after saturation, also increases with the temperature (Table 2), with a maximum of 60% obtained at  $400^\circ\text{C}$ , which is very close to the thermodynamic equilibrium.

Since the  $\text{NO}_x$  storage capacity for the first 60s almost corresponds to the  $\text{NO}_x$  storage rate (%), it appears that it is rather limited. This behavior is mainly attributed to the presence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the gas mixture [24]. Water affects the oxidation activity of the catalysts, leading to a decrease of NO oxidation activity of Pt, while  $\text{CO}_2$  competes with  $\text{NO}_x$  for the adsorption on the basic storage sites. The more the basic strength of the storage sites is high, the more the carbon dioxide competes [24].

Table 2:  $\text{NO}_x$  storage capacity ( $\mu\text{mol/g}$ ) for 60s ( $\text{NO}_x$  storage fraction; inlet: 500ppm NO, 10%  $\text{O}_2$ , 10%  $\text{H}_2\text{O}$ , 10%  $\text{CO}_2$  and  $\text{N}_2$ , 200mL/min) and  $\text{NO}_2/\text{NO}_x$  ratio after saturation for Pt-Ba/Al catalyst.

Temperature test	$200^\circ\text{C}$	$300^\circ\text{C}$	$400^\circ\text{C}$
$\text{NO}_x$ storage capacity ( $\mu\text{mol/g}$ )	9	22	46
$\text{NO}_2/\text{NO}_x$ (%)	14	57	60

### 3.2. NSR efficiency

Catalytic results of NSR experiments in cycling conditions are presented in Figure 1, for the full gas mixture depicted in Table 1, including reductants in both lean and rich mixtures. Such complex conditions are usually not applied in literature and infer some news results.

Firstly,  $\text{NO}_x$  conversions reported in Figure 1 are lower than corresponding  $\text{NO}_x$  storage capacity, indicating that the reduction of the stored  $\text{NO}_x$  is the limiting step, as already reported in previous work with simplified gas mixture and higher barium loading (1%Pt/20%BaO/ $\text{Al}_2\text{O}_3$  sample) [25]. As expected, Figure 1 shows that both  $\text{NO}_x$  conversion and selectivity depend on the temperature test. At  $200^\circ\text{C}$ , with the whole of reductants, the  $\text{NO}_x$  conversion is very low (4%). It increases to 37% at  $300^\circ\text{C}$  and reaches 39% at  $400^\circ\text{C}$ .

Concerning the selectivity, both  $\text{N}_2\text{O}$  and  $\text{NH}_3$  undesired by-products are emitted. The best  $\text{N}_2$  selectivity is obtained at  $200^\circ\text{C}$  (86%), but it is not very significant since the  $\text{NO}_x$  conversion is very low at this temperature. For higher temperatures and conversions, the  $\text{NH}_3$  selectivity increases from 32% at  $300^\circ\text{C}$  to 59% at  $400^\circ\text{C}$ . On the opposite,  $\text{N}_2\text{O}$  selectivity strongly decreases with the temperature, from 18% at  $300^\circ\text{C}$  to 2% at  $400^\circ\text{C}$ . Finally, the nitrogen

selectivity reaches only 50% at 300°C, and 39% at 400°C.

In the next part of this work, the NO<sub>x</sub> storage-reduction efficiency was evaluated depending on the nature of the reductant.

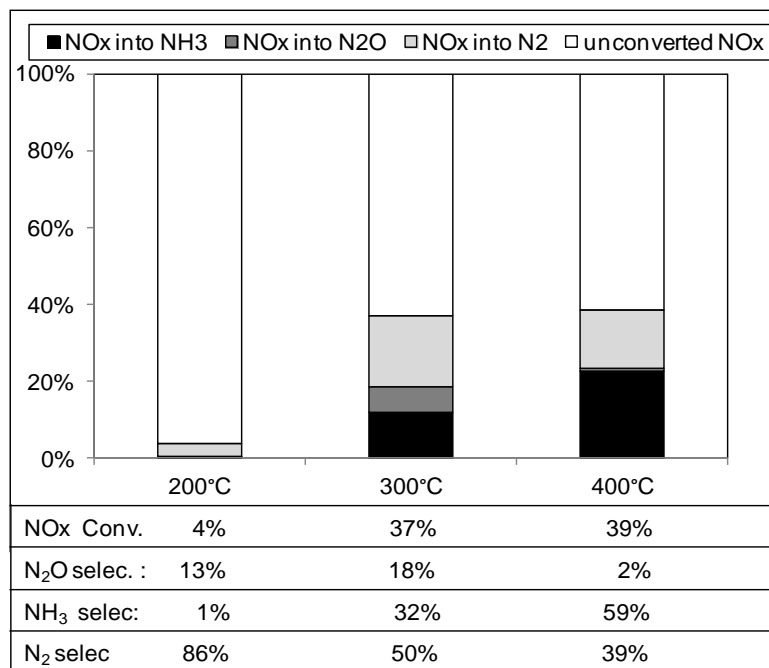


Figure 1. NO<sub>x</sub> storage/reduction efficiency test at 200, 300 and 400°C (full gas) over Pt-Ba/Al catalyst.

### 3.3. Influence of the nature of the reductant on the NO<sub>x</sub> conversion and selectivity

The effect of various reducing agent (H<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub>) on the efficiency and selectivity of NSR catalysts was already studied on platinum supported on alumina-based oxides [15,26,27], but usually with simplified mixtures. Using CO or C<sub>3</sub>H<sub>6</sub> as reducing agents, authors have reported that significant N<sub>2</sub>O emission occurs rather at low temperature (*i.e.* T ≤ 300°C). Lindholm et al. [28] have also reported that N<sub>2</sub>O formation can be observed with H<sub>2</sub>, depending on the hydrogen concentration: the higher is the H<sub>2</sub> concentration, the higher is the N<sub>2</sub>O formation.

In this part of the study, the NO<sub>x</sub> conversion and selectivity over the Pt-Ba/Al catalyst was investigated using only one reductant (the same) in both lean and rich gas mixtures, with compositions reported in Table 1. Results are presented in Figure 2. Results with the whole reductants (C<sub>3</sub>H<sub>6</sub> + CO + H<sub>2</sub>) were also reported for comparison.

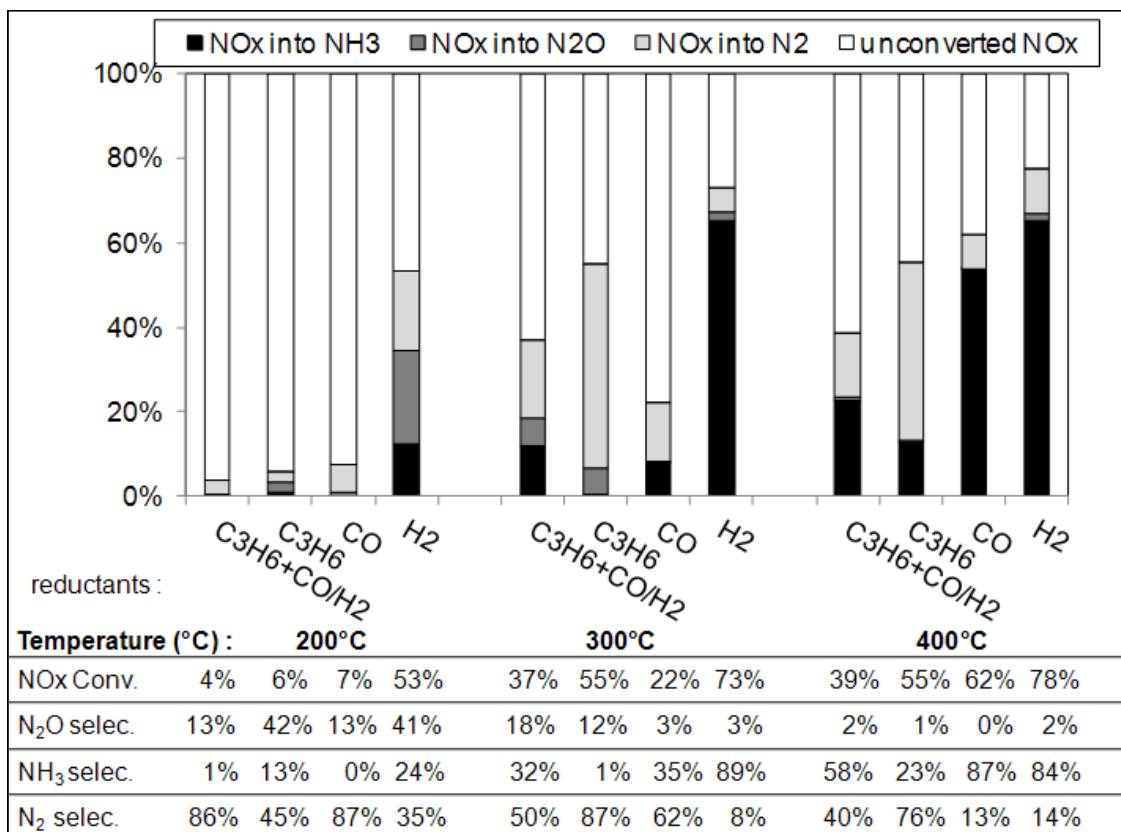


Figure 2. Effect of the nature of the reductant(s) (in both lean and rich gas mixture) on NOx storage/reduction efficiency and selectivity at 200°C, 300°C and 400°C over Pt-Ba/Al catalyst.

At 200°C, using only C<sub>3</sub>H<sub>6</sub> or CO as reductant, the NOx conversion remains low (< 7%), as with the mix of the three reductants. Compared with the full gas, the N<sub>2</sub>O selectivity is not affected using only CO, at 13%, but it significantly increases to 42% when only propylene is introduced. The NOx conversion strongly increases with H<sub>2</sub> as single reductant, up to 53%. These results illustrate the competitive adsorptions between each reductant when they are blended together at 200°C. With H<sub>2</sub>, the N<sub>2</sub>O selectivity reaches a value close to the one observed with C<sub>3</sub>H<sub>6</sub>, at 41%. In the same time, high ammonia yield is also observed at 24%. As a consequence, the nitrogen selectivity reaches only 35% at 200°C.

At 300°C, various results are also obtained depending on the nature of the reductant(s) (Figure 2). Compare with tests obtained with the “full gas” mixture, NOx conversion is enhanced with only C<sub>3</sub>H<sub>6</sub> or H<sub>2</sub>, at 55% and 73%, respectively. On the contrary, using CO as reductant leads to the lower NOx conversion at this temperature at only 22%. This result appears surprising since NSR experiments performed at 400°C show a higher NOx conversion with CO than with the “full gas” mixture. This point is discussed in section 3.4.

Selectivities also strongly differ. Using propylene as single reductant leads to a N<sub>2</sub>O selectivity of 12%, which it quite close to the one obtained with the mixture of the three reductants (18%).

On the contrary, low N<sub>2</sub>O selectivity is observed with CO or H<sub>2</sub> as reductant (3%).

Concerning ammonia, it is almost not emitted with propylene whereas the NH<sub>3</sub> selectivity reaches 89% with H<sub>2</sub>. Note that the presented result is obtained using a very high H<sub>2</sub> concentration in the rich pulses (13.4%), in order to respect the fixed reductant/oxidant ratio (Table 1). Then, this behavior is in accordance with literature which reports that NH<sub>3</sub> formation is favored in case of unconverted hydrogen [25]. With only CO, NH<sub>3</sub> selectivity is 35%, close to the one observed with the full gas, which is quite surprising. The ammonia formation mechanism was largely studied in the literature. Ammonia can be formed via the isocyanate route when CO is used as the main reductant, as reported in [29,30]. NH<sub>3</sub> can also be formed by the direct reaction of H<sub>2</sub> with NO<sub>x</sub> [31,32]. Besides, due to water gas shift equilibrium reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) H<sub>2</sub> can be produced even if only CO is introduced. This point is discussed in section 4.2.

Results obtained at 400°C show that the NO<sub>x</sub> conversions are quite similar to those measured at 300°C, except using only CO as previously mentioned. The N<sub>2</sub>O selectivity tends to be nil at this temperature. On the contrary, the ammonia selectivity becomes very high, at around 85% using H<sub>2</sub> or CO, and 58% with the complete reducing mixture. Propylene still allows the lower ammonia selectivity, at 23%.

To conclude, NO<sub>x</sub> conversion and N-compound selectivities depends on the temperature and reductants. At low temperature (200°C), H<sub>2</sub> is the only significantly effective reductant, but N<sub>2</sub>O is the main product. At 300°C, H<sub>2</sub> or C<sub>3</sub>H<sub>6</sub>, considered separately, enhance the NO<sub>x</sub> efficiency. Propylene leads to an important formation of N<sub>2</sub>O whereas H<sub>2</sub> strongly favors NH<sub>3</sub>. For higher temperature (400°C), N<sub>2</sub>O tends to be nil whatever the used reductant(s), but NH<sub>3</sub> becomes the main product, excepted with C<sub>3</sub>H<sub>6</sub> as reductant.

Considering that ammonia is an interesting NO<sub>x</sub> reductant, especially in lean atmosphere, N<sub>2</sub>O appears the more problematic by-product of the NO<sub>x</sub> reduction. The next parts of this work focus on the influence of the nature of the reductant agent on the N<sub>2</sub>O emission.

### 3.4. Influence of reductant(s) in the lean phases on the N<sub>2</sub>O formation

It is generally admitted that the N<sub>2</sub>O formation over precious metals comes from the recombination of atomic N (from the NO dissociative adsorption on metallic platinum sites) with adsorbed NO [33]. In NSR cycles, N<sub>2</sub>O was reported to be especially detected during the lean/rich switches, due to a lack in metal reduction [34]. Results reported above in this study show that the composition of the rich and lean gas mixtures dramatically modifies the catalytic results. Particularly, compared with simplified NSR experiments usually reported in literature

(i.e. without reductant(s) during the lean storage phases for instance), high  $N_2O$  selectivities are observed. Then, in order to evaluate the contribution of each lean and rich phase on the  $N_2O$  emission, operating conditions were modified.

### 3.4.1. Tests without reductants in the lean mixture

With the aim to obtain more information about the  $N_2O$  production, new catalytic tests were performed without reductants in the lean mixture (flow rate was kept constant by adding  $N_2$ ). The temperatures of 200 and 300°C were selected since no significant amount of  $N_2O$  is emitted at 400°C. The influence of the absence of reductant(s) in the lean mixtures is depicted in Figure 3.

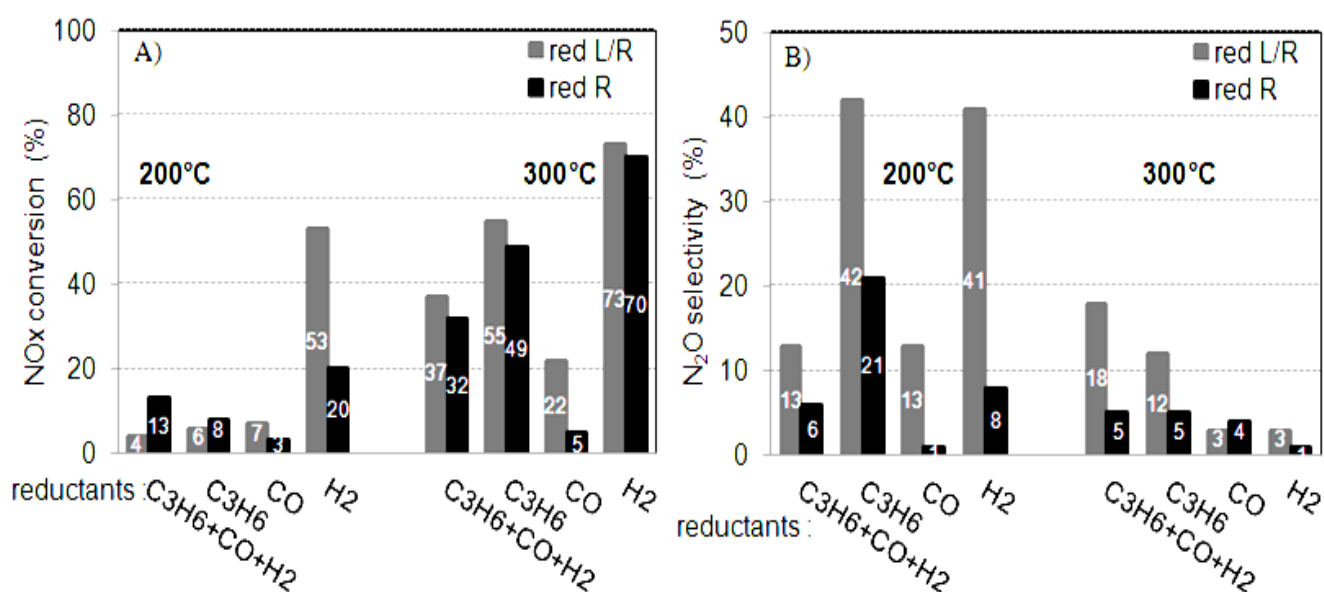


Figure 3. Influence of the absence of reductant(s) in the lean mixture at 200°C and 300°C over Pt-Ba/Al catalyst on (A) NOx conversion and (B)  $N_2O$  selectivity. Results in grey (red L/R) correspond to test with reductant(s) in both lean and rich mixtures; results in black (red R) correspond to test with reductant(s) only in rich mixtures.

Firstly, at 200°C, it appears from Figure 3A that the absence of reductant in the lean mixture leads to increase the NOx conversion for tests carried out with  $C_3H_6$  ( $C_3H_6+CO+H_2$  reducing mixture or  $C_3H_6$  alone). This improvement is particularly significant considering the mix of reductants ( $C_3H_6+CO+H_2$ ), the NOx conversion grows from 4% to 13% when reductants are removed from the lean mixture. This observation is attributed to an inhibiting effect of  $C_3H_6$  on the NO oxidation on platinum during the lean periods: using the full gas mixtures, only few ppm of  $NO_2$  are detected (all produced  $NO_2$  are trapped), whereas an average value of 145ppm  $NO_2$  is recorded when  $C_3H_6$  is removed from the lean mixture (recorded profiles not shown). Different results are obtained with CO or  $H_2$  as reductant since the NOx conversion decreases

of about 50% if CO or H<sub>2</sub> is removed from the lean mixture. These decreases are associated with remarkable drops in N<sub>2</sub>O selectivity (Figure 3B). It tends to be nil when CO is suppressed from the lean mixture, and a drop of about 80% is observed for hydrogen. Same trends are also observed from tests with propylene (C<sub>3</sub>H<sub>6</sub> alone or mixed with CO and H<sub>2</sub>), the N<sub>2</sub>O selectivity is divided by two.

At 300°C, as depicted above, higher NO<sub>x</sub> conversions are obtained compared to tests at 200°C. Tests carried out with C<sub>3</sub>H<sub>6</sub> (alone or mixed with CO and H<sub>2</sub>) show that the NO<sub>x</sub> conversion slightly decreases when reductant is removed from the lean mixture. In the same time, the N<sub>2</sub>O selectivity is strongly altered, by a factor 2.4 to 3.6. Same trends are observed considering H<sub>2</sub> as reductant, but, as already mentioned, the obtained N<sub>2</sub>O selectivity is low at this temperature. Results are more complex with CO. A decrease of 77% of the NO<sub>x</sub> conversion is observed when CO is removed from the lean mixture (Figure 3A). This surprising result is illustrated in Figure 4 by the NO<sub>x</sub> and CO concentration profiles recorded during the NSR experiments, with or without CO in the lean mixture. Note that the rich pulses appear longer than 4 seconds due to the gas dilution mainly due to the volume of the IR cell.

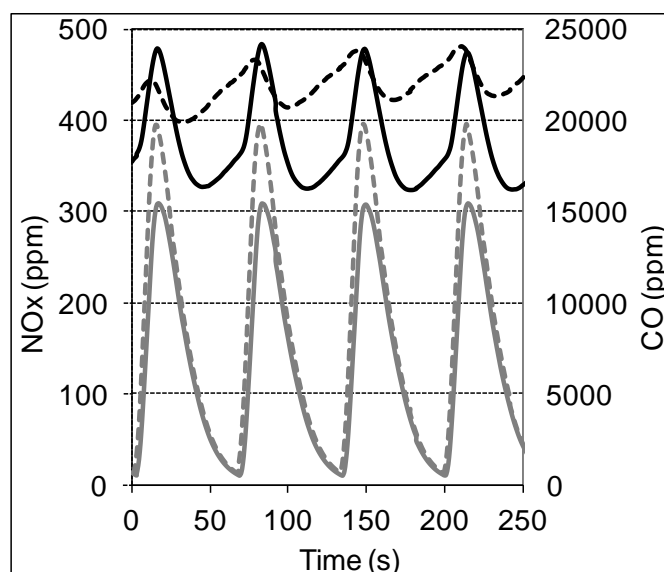


Figure 4. NSR cycles at 300°C over Pt-Ba/Al catalyst using CO as reductant: comparison of NO<sub>x</sub> (—,···) and CO (—,···) outlet profiles with (full lines) or without (dotted lines) CO in lean mixture.

It is observed that CO conversion is higher in the rich pulses when carbon monoxide is present in both lean and rich mixture (full line). On the opposite, similar CO concentration profiles are obtained during the lean periods even if CO is introduced in the lean mixture (same observed minima). This result indicates a total CO conversion in lean atmosphere. In parallel, NO<sub>x</sub> storage fraction is higher when CO is present in the lean period, but a strong increase in NO<sub>x</sub>

concentration is also observed when switching to rich atmosphere, indicating an important NO<sub>x</sub> desorption. In fact, it corresponds to NO emission (NO concentration profiles not shown). Then, it clearly appears that CO in lean mixture favors the NO<sub>x</sub> reduction during the rich pulses, while the N<sub>2</sub>O selectivity is not affected (Figure 3B). Furthermore, as presented in the next section, CO does not allow any significant NO<sub>x</sub> reduction in lean mixture (Figure 6D), but it is fully converted into CO<sub>2</sub>. In addition, it is assumed that the NO<sub>x</sub> reduction during the rich phases occurs over reduced metallic sites, which are needed to allow the NO<sub>x</sub> dissociative adsorption. As a consequence, we suppose that CO oxidation in the lean phase modifies the platinum redox state since CO removes the adsorbed oxygen atoms (Pt-O<sub>a</sub>) from the Pt particles to form CO<sub>2</sub>, leading to the regeneration of the metallic platinum sites [29]. It would lead to an easier platinum reduction at the beginning of the rich pulses. At 400°C, the catalyst reduction during the rich pulses is faster, the NO<sub>x</sub> conversion strongly increases (Figure 2) and there is no more influence of the presence of CO in the lean mixture (result not shown).

The N<sub>2</sub>O profiles recorded during the NSR cycles at 300°C are detailed in Figure 5 depending on the presence or absence of reductant in the lean mixture.

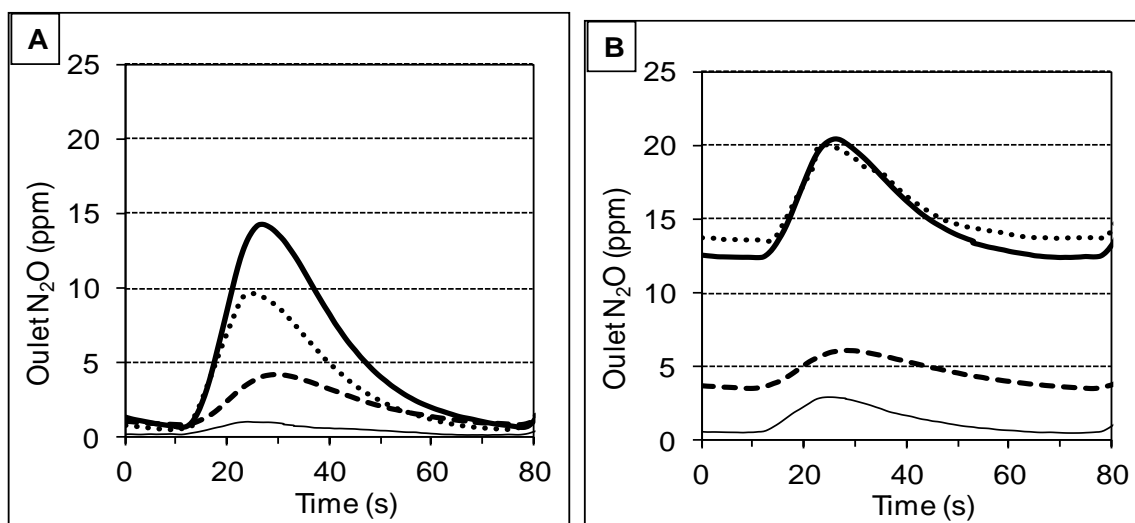


Figure 5. N<sub>2</sub>O profiles recorded during NSR cycles at 300°C over Pt-Ba/Al catalyst depending on the used reductant(s): C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub> (....); C<sub>3</sub>H<sub>6</sub> (—); CO (— —) or H<sub>2</sub> (— — —). Reductant(s) present in lean and rich mixtures (A) or only in the rich pulses (B).

As expected, Figure 5B shows that N<sub>2</sub>O is not produced during the lean periods if there is no reductant in the lean mixture. On the contrary, significant N<sub>2</sub>O concentrations are detected if reductants are added in the lean mixture (Figure 5A). In accordance with results reported in Figure 3B, it appears that N<sub>2</sub>O is largely detected during the lean phases when C<sub>3</sub>H<sub>6</sub> is used (alone or mixed with CO and H<sub>2</sub>). Few ppm of N<sub>2</sub>O are also detected using H<sub>2</sub>, whereas near no N<sub>2</sub>O emission is observed during the lean phases with CO as reductant.

### 3.4.2. Light-off tests in lean mixture

In order to have a better overview of the  $\text{N}_2\text{O}$  formation during the lean steps of the NSR process depending of the temperature, new experiments were performed in light-off mode with conditions corresponding to usual SCR experiments in lean condition, using the different lean mixtures reported in Table 1. Results reported in Figure 6 show the  $\text{NO}_x$  and  $\text{N}_2\text{O}$  concentrations profiles recorded in the 200-400°C temperature range.

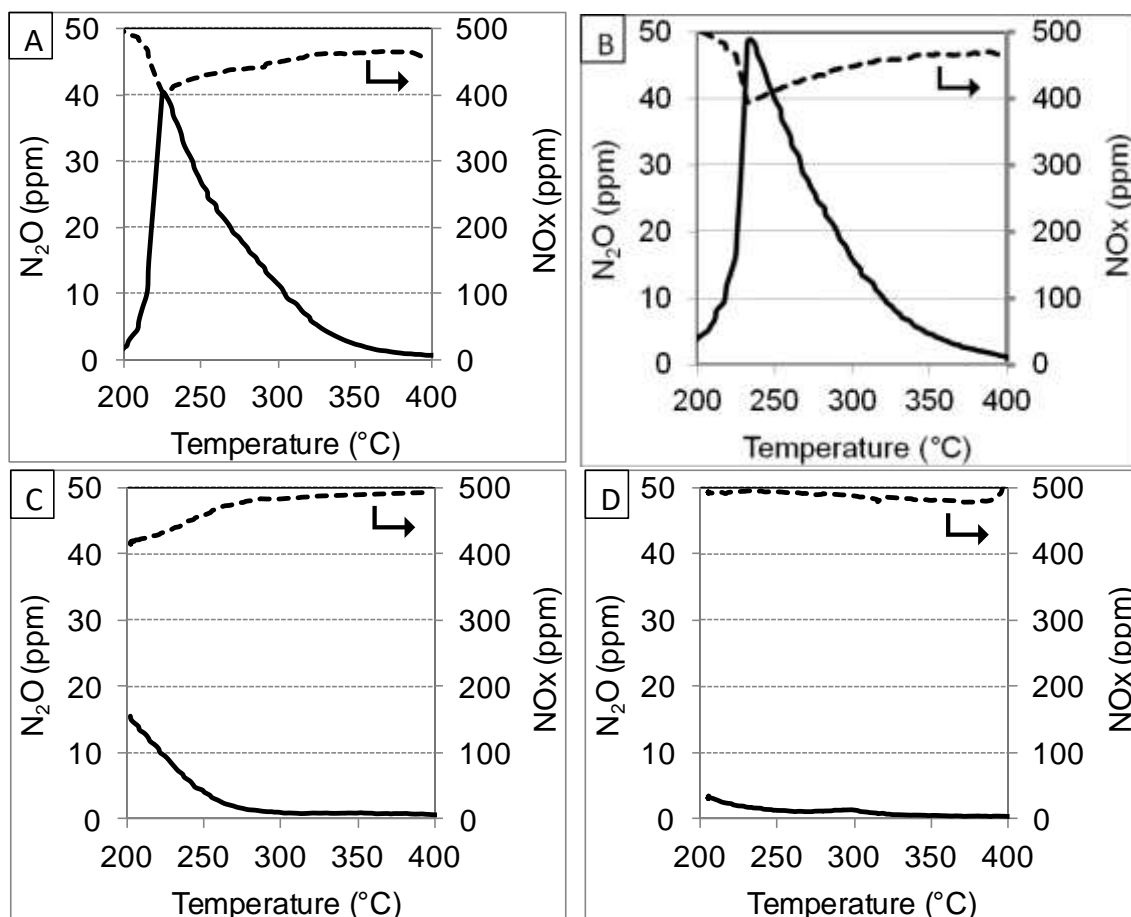


Figure 6. Catalytic tests over Pt-Ba/Al catalyst in lean mixture depending on the introduced reductant(s):  $\text{NO}_x$  concentration (dotted line) and  $\text{N}_2\text{O}$  concentration (full line).

(A): 500ppm NO + 10%  $\text{O}_2$  + (300 ppm  $\text{C}_3\text{H}_6$  + 500ppm CO + 167ppm  $\text{H}_2$ ).

(B): 500ppm NO + 10%  $\text{O}_2$  + (374 ppm  $\text{C}_3\text{H}_6$ ).

(C): 500ppm NO + 10%  $\text{O}_2$  + (3300 ppm  $\text{H}_2$ ).

(D): 500ppm NO + 10%  $\text{O}_2$  + (3300 ppm CO).

As previously suggested, near no NO<sub>x</sub> reduction is observed with CO as reductant (Figure 6D), with a maximum of 2~3 ppm of N<sub>2</sub>O emitted. Nevertheless, CO is fully oxidized into CO<sub>2</sub> in the whole 200-400°C temperature range. The NO<sub>x</sub> conversion in excess of oxygen can be effective with other reductants over Pt-Ba/Al, but it depends on the temperature and the nature of reductant. With the whole reductants (C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>, Figure 6A), the NO<sub>x</sub> conversion is low at 200°C, with 2 ppm of N<sub>2</sub>O emitted. The NO<sub>x</sub> conversion reaches a maximum of about 20% at 220°C, corresponding to a N<sub>2</sub>O emission of 40 ppm (black full line, Figure 6A). Increasing the temperature leads to the decrease of the NO<sub>x</sub> conversion to 10% at 300°C, with a corresponding N<sub>2</sub>O emission of 11 ppm. No more NO<sub>x</sub> conversion is observed at 400°C. Interestingly, similar profiles are obtained with propylene as single reductant (Figure 6B). The maximum NO<sub>x</sub> conversion (about 22%) is obtained at 230°C and 49 ppm of N<sub>2</sub>O are emitted. At 300°C, the N<sub>2</sub>O concentration reaches 13 ppm, and it tends to zero at 400°C. From these results it appears that N<sub>2</sub>O emission is enhanced with propylene as only reductant, but in order to keep the same oxidant/reductant ratio, a higher C<sub>3</sub>H<sub>6</sub> concentration was used compared to the full gas (Table 1). The obtained NO<sub>x</sub> profiles are consistent with those reported in literature for NO<sub>x</sub> SCR by hydrocarbons over platinum based catalysts [35-39], with maximum NO<sub>x</sub> conversion between 200 and 300°C and a high N<sub>2</sub>O selectivity at low temperature.

NO<sub>x</sub> conversion is also effective with H<sub>2</sub> as reductant, but mainly for lower temperatures (Figure 6C), in accordance with other reported studies over platinum based catalysts [40,41].

The maximum NO<sub>x</sub> conversion is obtained at 200°C (19%), with the formation of about 17 ppm of N<sub>2</sub>O. Then, both NO<sub>x</sub> conversion and N<sub>2</sub>O concentration significantly decrease with temperature, they are nil at 300°C. Finally, note that ammonia emission is never observed in lean condition.

Results reported in this section show good agreements between tests carried out in lean mixture (light-off test) and N<sub>2</sub>O values recorded at the end of the lean periods during the NSR tests at 200 and 300°C. Major difference is observed for tests performed with hydrogen at 300°C. There is no N<sub>2</sub>O emission detected when the test is carried out exclusively in lean mixture, whereas 3.4 ppm of H<sub>2</sub> are recorded at the end of the lean periods during the NSR tests. In order to clarify this point, tests with gas dilution after the reactor were performed to allow a faster purge of the IR cell. Obtained results were then consistent with those recorded at the end of the lean period, taking into accounts that the gas dilution (by a factor 5) induced also a loss of sensibility. To conclude about the N<sub>2</sub>O emission during the lean periods due to the presence of reductant(s), it appears that at 200°C, N<sub>2</sub>O emission is essentially favored when H<sub>2</sub> is used as only reductant. At higher temperature, N<sub>2</sub>O emission is mainly related to the presence of C<sub>3</sub>H<sub>6</sub>, with a

maximum N<sub>2</sub>O emission near 220-230°C. CO is nearly inactive toward NO<sub>x</sub> reduction in the whole studies temperature range.

### 3.5. Contribution each lean and rich phase on the N<sub>2</sub>O formation

Based on results reported in the previous section, the distribution of the N<sub>2</sub>O formation during each lean and rich phase of the NSR cycles has been evaluated. For the lean periods, we have selected the last N<sub>2</sub>O concentration recorded before the switch to the rich mixture. Integration of the N<sub>2</sub>O peak associated with the rich phase was used to obtain an average value for the length of the rich pulse (4s). Results are reported in Table 3, associated with the NO<sub>x</sub> conversion and the N<sub>2</sub>O selectivity.

Table 3: NO<sub>x</sub> conversion, N<sub>2</sub>O selectivity and N<sub>2</sub>O distribution between lean and rich mixtures of the NSR cycles (*and corresponding average of N<sub>2</sub>O concentration*) at 200°C and 300°C for Pt-Ba/Al and Pt/CZ catalysts.

		200°C				300°C			
		Cycled tests		N <sub>2</sub> O distribution		Cycled tests		N <sub>2</sub> O distribution	
		NO <sub>x</sub> Conv.	S <sub>(N<sub>2</sub>O)</sub>	lean	rich	NO <sub>x</sub> Conv.	S <sub>(N<sub>2</sub>O)</sub>	lean	rich
Pt-Ba/Al	C <sub>3</sub> H <sub>6</sub> +CO+H <sub>2</sub>	4%	13%	37%	63%	37%	18%	72%	28%
				<i>0.4ppm</i>	<i>0.8ppm</i>			<i>11.4ppm</i>	<i>4.4ppm</i>
	C <sub>3</sub> H <sub>6</sub>	6%	42%	78%	22%	55%	12%	71%	29%
				<i>4.6ppm</i>	<i>1.3ppm</i>			<i>11.2ppm</i>	<i>4.6ppm</i>
	CO	7%	13%	67%	33%	22%	3%	32%	68%
			<i>1.4ppm</i>	<i>0.7ppm</i>			<i>0.5ppm</i>	<i>1.1ppm</i>	
	H <sub>2</sub>	53%	41%	91%	9%	73%	3%	66%	34%
				<i>47.3ppm</i>	<i>4.7ppm</i>			<i>3.4ppm</i>	<i>1.8ppm</i>
Pt/CZ	C <sub>3</sub> H <sub>6</sub> +CO+H <sub>2</sub>	40%	47%	61%	39%	49%	22%	45%	55%
				<i>27.8ppm</i>	<i>17.8ppm</i>			<i>11.2ppm</i>	<i>14.4ppm</i>
	C <sub>3</sub> H <sub>6</sub>	15%	62%	78%	22%	52%	20%	45%	55%
				<i>17.2ppm</i>	<i>4.9ppm</i>			<i>11.3ppm</i>	<i>13.8ppm</i>
	CO	58%	20%	13%	87%	56%	10%	10%	90%
			<i>3.6ppm</i>	<i>24.5ppm</i>			<i>1.3ppm</i>	<i>12.2ppm</i>	
	H <sub>2</sub>	92%	43%	78%	22%	64%	5%	60%	40%
				<i>74.9ppm</i>	<i>21.1ppm</i>			<i>4.7ppm</i>	<i>3.1ppm</i>

At 200°C, the NO<sub>x</sub> conversions are too low to be discussed toward N<sub>2</sub>O distribution, except with H<sub>2</sub> as single reductant. In this case, NO<sub>x</sub> conversion and N<sub>2</sub>O selectivity reach 53% and 41%, respectively. Calculations from recorded N<sub>2</sub>O profile show that 91% of nitrous oxide is emitted during the lean period, due to the significant NO<sub>x</sub> reduction in excess of O<sub>2</sub> at low temperature (Figure 6C).

At 300°C, N<sub>2</sub>O yields of approximately 7% are obtained using the full gas mixture (C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>) or only propylene. Again, the major part (71-72%) of the N<sub>2</sub>O emission is

attributed to the lean phases. This is also the case using only H<sub>2</sub> as reductant (66%), but the N<sub>2</sub>O selectivity is then low, at 3%. Finally, only CO, which is not really active in NO<sub>x</sub> reduction in excess of oxygen over Pt-Ba/Al, leads a major contribution of the rich pulses on the N<sub>2</sub>O formation, but the global N<sub>2</sub>O concentration is recorded at a low level.

#### 4. Influence of the redox behavior of the support: Pt-Ba/Al versus Pt/CZ

In a previous work [21], with the same approach as described above, the NO<sub>x</sub> conversion and selectivity were discussed toward platinum supported over a ceria-zirconia based oxide catalyst (Pt/CZ), with a special attention to the N<sub>2</sub>O formation during the NSR process. Even if platinum loading, NO<sub>x</sub> storage component and specific surface area differ for both Pt-Ba/Al and Pt/CZ catalysts, the main difference between both catalysts is their respective redox properties. Barium-alumina supports exhibits no significant redox behavior, whereas Pt/CZ is reducible by a large extend. Comparison of the catalytic behaviors of these catalysts is depicted below.

##### 4.1. NO<sub>x</sub> conversion and NO<sub>x</sub> reduction selectivity in cycled condition

At 200°C, as previously described (Figure 2), the NO<sub>x</sub> conversion over Pt-Ba/Al catalyst is significantly effective only with H<sub>2</sub> as reductant. The NH<sub>3</sub> and N<sub>2</sub>O selectivity reach 24% and 41%, respectively, and more than 90% of the emitted N<sub>2</sub>O is produced during the rich pulses. Compared to Pt-Ba/Al, Pt/CZ catalyst is more active at this temperature, and significant NO<sub>x</sub> reductions are observed whatever the considered reductant (Table 3). Using H<sub>2</sub>, the NO<sub>x</sub> conversion reaches 92%. The ammonia selectivity is limited at 2% [21]. Interestingly, N<sub>2</sub>O selectivity (43%) and the N<sub>2</sub>O distribution (78% from the lean phases) are very similar than those calculated for Pt-Ba/Al. Other results obtained at 200°C over Pt/CZ with other reducing mixtures are discussed in [21]. However, note that the higher N<sub>2</sub>O selectivities (47-62%) are observed with C<sub>3</sub>H<sub>6</sub> (alone or mixed with CO and H<sub>2</sub>), with a main contribution of the lean periods (78% of the emitted N<sub>2</sub>O using C<sub>3</sub>H<sub>6</sub>, and 61% using C<sub>3</sub>H<sub>6</sub>+CO+ H<sub>2</sub>, Table 3). On the opposite, the N<sub>2</sub>O selectivity is limited at 20% using CO, and most of the N<sub>2</sub>O emission (87%) occurs during the rich pulses.

At 300°C, comparison of NO<sub>x</sub> conversion and selectivity over both Pt-Ba/Al and Pt/CZ is illustrated Figure 7, depending on the introduced reductant(s) in both lean and rich mixtures of the NSR test.

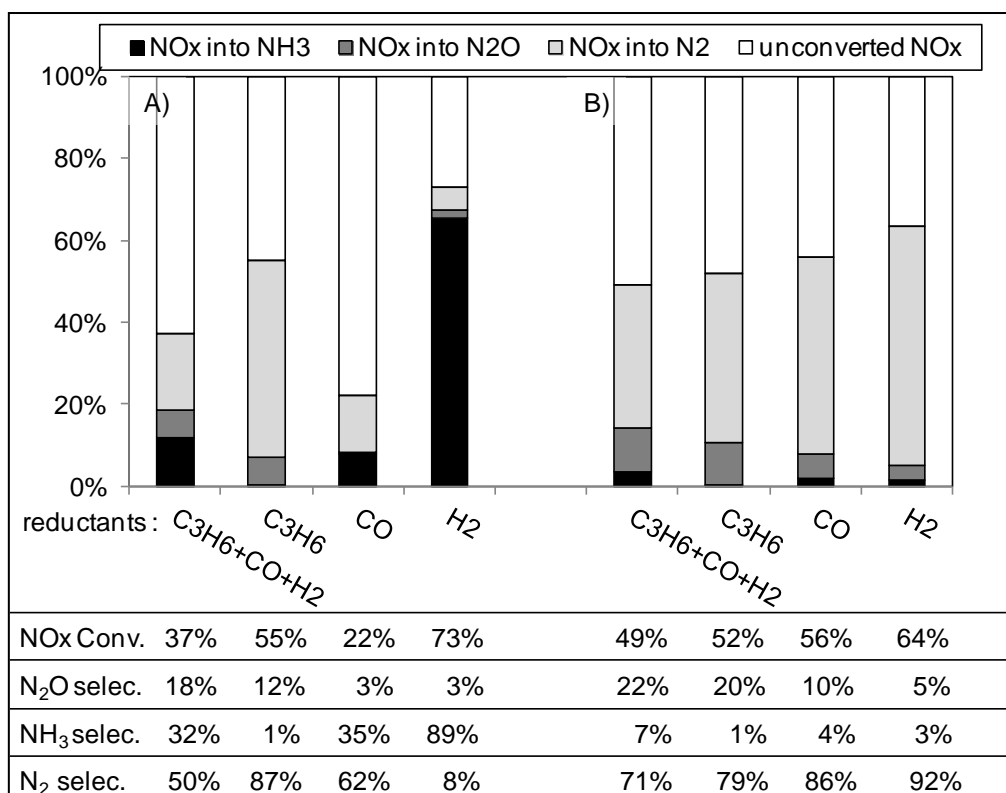


Figure 7. Comparative effect of the support on NO<sub>x</sub> conversion and N-compound selectivities at 300°C depending on the introduced reductant(s) over (A) Pt-Ba/Al and (B) Pt/CZ catalysts.

It clearly appears that the NO<sub>x</sub> conversion is more sensitive to the nature of the introduced reductant over Pt-Ba/Al than over Pt/CZ, with conversion ranges of 22-73% and 49-64%, respectively. Besides, Figure 7 also highlights a strong influence of the support composition on the ammonia selectivity at 300°C. It does not exceed 7% on Pt/CZ catalyst whatever the considered reductant(s), whereas NH<sub>3</sub> emissions can be very high on Pt-Ba/Al catalyst, especially using hydrogen as reductant (NH<sub>3</sub> yield = 65%, S<sub>NH<sub>3</sub></sub> = 89%). In fact, the selective NH<sub>3</sub> oxidation into N<sub>2</sub> was previously proposed for platinum supported over reducible oxide to explain the low ammonia emission in NSR test using H<sub>2</sub> as reductant [42]. Only the use of propylene as single reductant leads to similar NO<sub>x</sub> conversions (52-55%) and low ammonia selectivities (1%) for both catalysts. At 300°C. Figure 7 also shows that the global N<sub>2</sub>O selectivity is lower on Pt-Ba/Al than on Pt/CZ, whatever the reductant(s). However, the same evolutions are observed depending on the reducing agent. The higher N<sub>2</sub>O selectivities are obtained using the full reducing mixture (C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>) or only propylene, with values of 18% and 12% for the Pt-Ba/Al, versus 22% and 20% on Pt/CZ sample. The N<sub>2</sub>O selectivities drop to 3% with CO or H<sub>2</sub> as reductant using the Pt-Ba/Al catalyst, and to 10% and 5% with Pt/CZ, respectively. A detailed comparison of the N<sub>2</sub>O emissions during the lean and rich periods is reported in section 4.3

In order to understand these different behaviors in NO<sub>x</sub> conversion for Pt-Ba/Al and Pt/CZ, the possible transformation of the introduced reductant during the rich pulse was envisaged since the reaction mixture included 10 % H<sub>2</sub>O and 10 % CO<sub>2</sub>. Indeed, ceria based catalyst are known to enhance the water-gas-shift (WGS) reaction [43]. A comparison of the behaviors of both Pt-Ba/Al and Pt/CZ catalyst in reductant transformation is detailed thereafter in section 4.2.

#### 4.2 Reductants transformation during the rich pulses

The possible reductants transformation was examined by comparing the reductants profiles recorded in by-pass to profiles recorded during the tests. Note that this procedure does not allow to access to the real amount of transformed reductant since a part of reductants reacts during the test. For both the Pt-Ba/Al and Pt/CZ catalysts, the CO, H<sub>2</sub> or C<sub>3</sub>H<sub>6</sub> transformation in the rich pulses was examined at 200°C and 300°C and results are reported in Figures 8, 9 and 10, respectively.

When CO is the only reducing agent in the rich pulses, results presented in Figure 8 show that no H<sub>2</sub> emission is detected at 200°C with Pt/Ba-Al, whereas H<sub>2</sub> is emitted in high amount over Pt/CZ (maximum concentration: 1.78%). At 300°C, pulses of H<sub>2</sub> are then detected during the CO rich pulses over Pt/Ba-Al, with a maximum H<sub>2</sub> concentration recorded at 486ppm, while maxima of 2.37% are detected with Pt/CZ. These results demonstrate the higher activity of Pt/CZ catalysts for the water gas shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ).

With H<sub>2</sub> as reductant in the rich pulses, Figure 9 illustrates that significant CO emission is detected from 200°C, whatever the catalyst formulation. However, Pt/CZ sample clearly enhances the CO formation by the reverse water gas shift (RWGS) reaction ( $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ ). At 200°C, the maximum CO concentrations are 82 ppm and 325 ppm for Pt-Ba/Al and Pt/CZ catalyst, respectively. At 300°C, these concentrations increase to 229 ppm and 503 ppm, respectively. Then, even if only H<sub>2</sub> is introduced, both H<sub>2</sub> and CO are detected at 200°C and 300°C, but CO emission is higher on the catalyst supported over the reducible support.

Tests with C<sub>3</sub>H<sub>6</sub> as inlet reductant also show some possible transformation. Few ppm CO are detected at 200°C and 300°C over Pt-Ba/Al. Same results are obtained with Pt/CZ at 200°C, but more significant transformation is evidenced 300°C. Indeed, peaks of H<sub>2</sub>, CO and CH<sub>4</sub> are detected with maximum concentrations of 1.47 %, 435 ppm and 250 ppm, respectively (Figure 10). From these observations, it is assumed that steam reforming of C<sub>3</sub>H<sub>6</sub> occurs on Pt/CZ at 300°C.

Note that for Pt-Ba/Al, all these results are in perfect accordance with results previously established about the ammonia emission [25,44]. Using simplified gas mixtures (lean:

NO+O<sub>2</sub>+CO<sub>2</sub>+ H<sub>2</sub>O in N<sub>2</sub>; rich: H<sub>2</sub>+CO<sub>2</sub>+ H<sub>2</sub>O in N<sub>2</sub>), it was demonstrated that ammonia is detected in the outlet gas when hydrogen is not fully converted, indicating that the ammonia formation rate via the NO<sub>x</sub> reduction by H<sub>2</sub> is higher than the ammonia reaction rate with NO<sub>x</sub> to form N<sub>2</sub>. In this study, with Pt-Ba/Al, H<sub>2</sub> is detected in the outlet gas during the rich pulses at 300°C when H<sub>2</sub>, CO or C<sub>3</sub>H<sub>6</sub>+CO<sub>2</sub>+ H<sub>2</sub> are used as reductant(s), and ammonia is also detected (Figure 2). On the contrary, no hydrogen is detected using C<sub>3</sub>H<sub>6</sub> and the ammonia selectivity tends to be nil. At 400°C, H<sub>2</sub> is detected in the outlet gas during the rich pulses whatever the considered reducing mixture (results not shown), and the ammonia yield varies between 12% and 65% (Figure 2). As a reminder, the low ammonia selectivity with Pt/CZ is attributed to the ability of this catalyst to oxidize NH<sub>3</sub> into N<sub>2</sub>, in relation with its oxygen mobility.

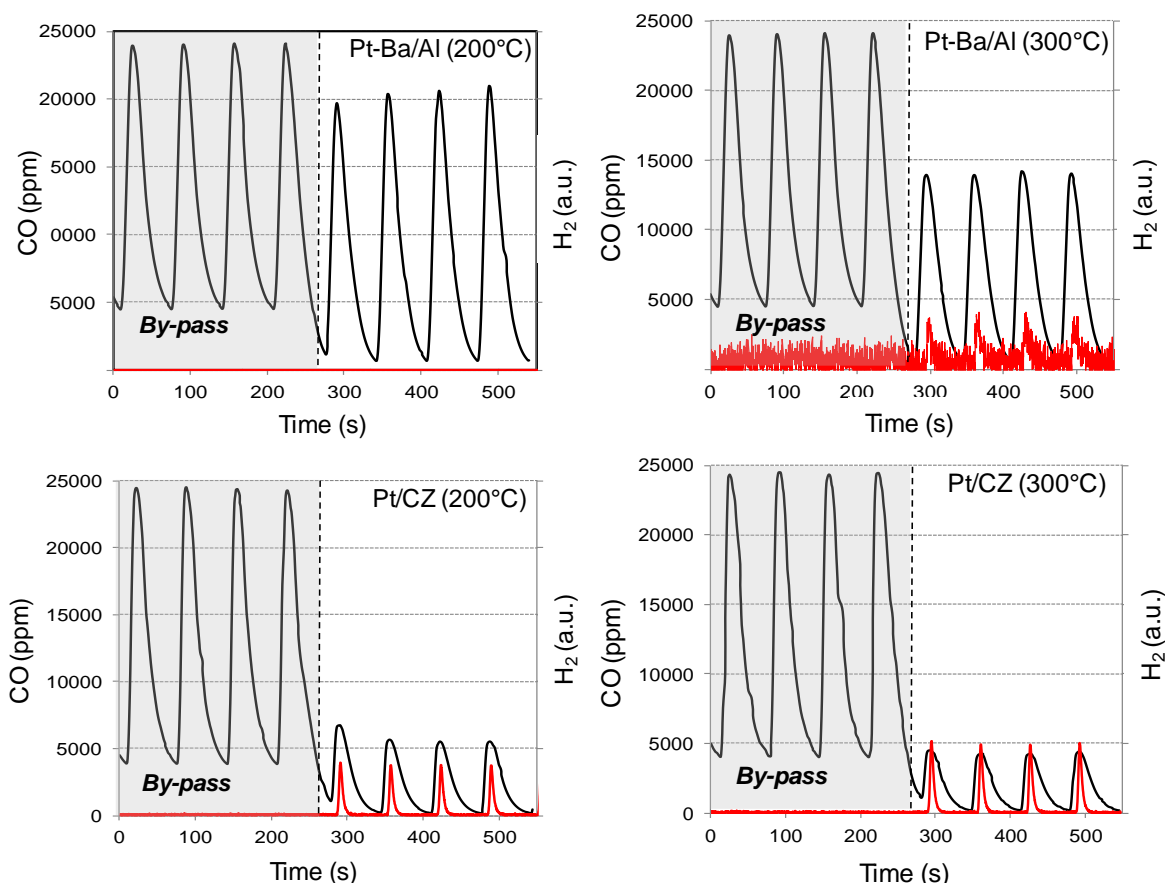


Figure 8. Evidence of water gas shift (WGS) activity during NSR cycles with CO as reductant. (—): CO; (—): H<sub>2</sub>.

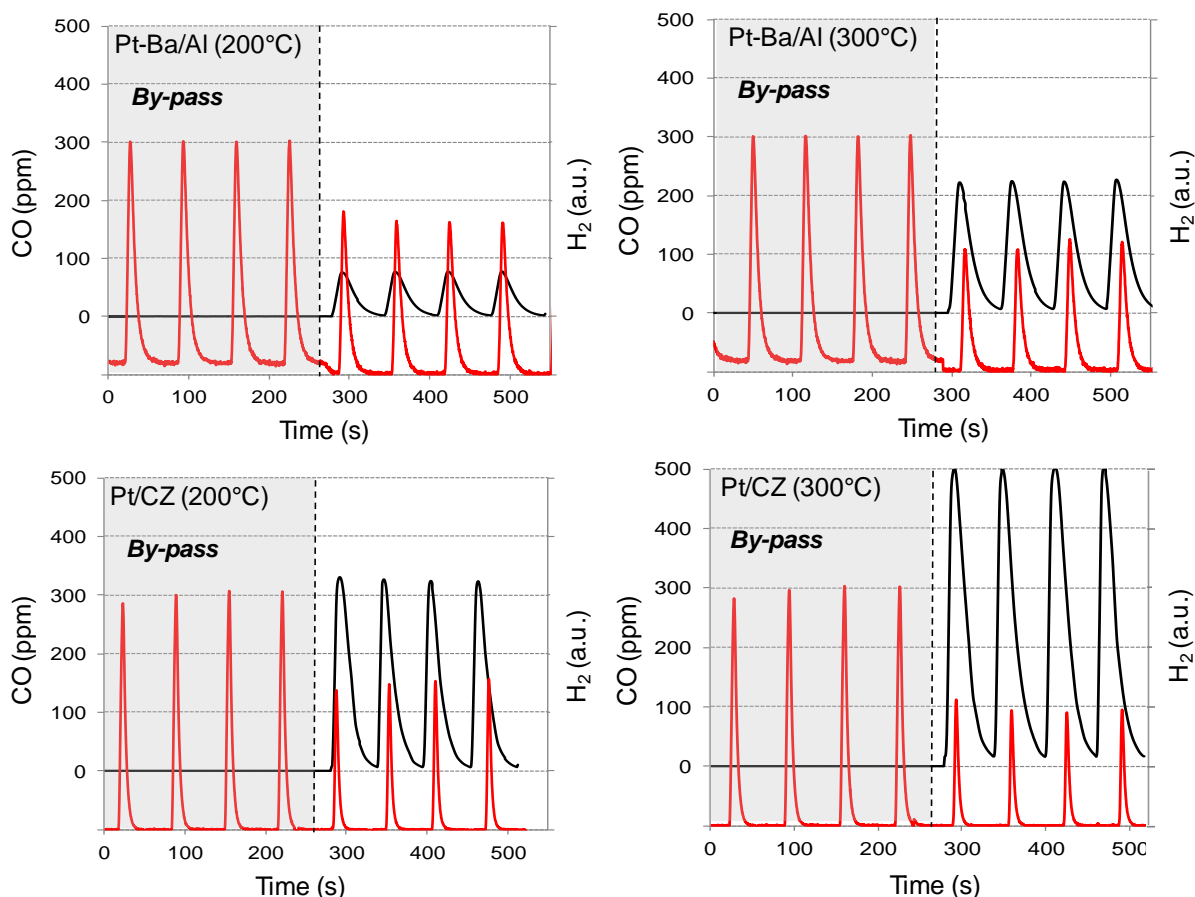


Figure 9. Evidence of reverse water gas shift (RWGS) activity during NSR cycles with  $H_2$  as reductant. (—): CO; (—):  $H_2$ .

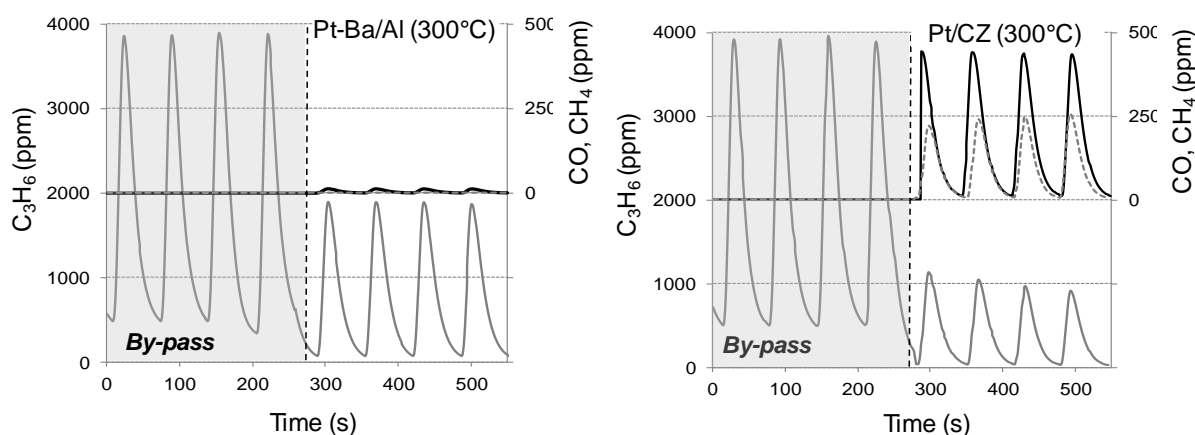


Figure 10.  $C_3H_6$  (—), CO (---) and  $CH_4$  (---) emission over Pt-Ba/Al and Pt/CZ catalysts at  $300^\circ C$  during NSR cycles with  $C_3H_6$  as reductant.

To conclude, the real reducing mixture at the catalyst surface during the rich excursions is strongly dependant on the transformation reactions of the introduced reductant(s), which are very sensitive to the support behaviors. At  $300^\circ C$ , WGS equilibrium and steam reforming are

favored over Pt/CZ. As a consequence, whatever the introduced reductant, the reducing mixture on the Pt/CZ catalyst is balanced, especially toward CO and H<sub>2</sub>. Then, the observed NO<sub>x</sub> conversions are relatively close and vary in a lower extent with Pt/CZ compared with Pt-Ba/Al.

#### 4.3 Comparison of Pt-Ba/Al and Pt/CZ toward N<sub>2</sub>O emissions

It was previously reported that the N<sub>2</sub>O formation is not only reliable to the excursions in rich atmosphere, but can also be largely produced during the lean periods, depending on reductant. Based on the recorded N<sub>2</sub>O profiles during the NSR tests, contributions of both lean and rich phases are detailed in Table 3. In addition to the global NO<sub>x</sub> conversion and N<sub>2</sub>O selectivity, the N<sub>2</sub>O distribution and average N<sub>2</sub>O concentrations are reported for both Pt-Ba/Al and Pt/CZ catalysts. The NO<sub>x</sub> conversions being rather limited at 200°C over Pt-Ba/Al, comparison of both catalysts is focused on tests performed at 300°C.

##### 4.3.1 N<sub>2</sub>O emission during the lean periods

At 300°C, Table 3 shows that the proportion of the N<sub>2</sub>O emitted during the lean periods is significantly higher over Pt-Ba/Al when the gas mixtures include C<sub>3</sub>H<sub>6</sub>, at 71-72% versus 45% for Pt/CZ. These differences are assigned to the higher global N<sub>2</sub>O selectivity of Pt/CZ material. Indeed, it is worth noting that the amounts of N<sub>2</sub>O emitted during the lean periods are very similar for both catalysts: near 11 ppm using the full gas mixture (C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>) or only propylene.

Using only H<sub>2</sub> as reductant, the major part of the N<sub>2</sub>O production occurs during the lean phases for both catalysts, at 66% and 60% for Pt-Ba/Al and Pt/CZ, respectively. Again, the amounts of N<sub>2</sub>O emitted during the lean atmosphere are very close whatever the support formulation, from 3.4 to 4.7 ppm (Table 3).

With CO as reductant, the N<sub>2</sub>O emission during the lean phases is practically nil for both catalysts, because there is no NO<sub>x</sub> reduction with CO in excess of O<sub>2</sub> (Figure 6D). In this case, the global N<sub>2</sub>O selectivity observed during NSR cycles depends mainly on the behavior of the catalyst in rich atmosphere. N<sub>2</sub>O production is enhanced during the rich pulses over Pt/CZ. This behavior is depicted in the section 4.3.2.

Whatever the chemical nature of considered reductant, and whatever the catalyst, these N<sub>2</sub>O concentrations are consistent with results obtained from light-off tests performed only in lean atmosphere, reported in [21] for Pt/CZ. Indeed, similar profiles were obtained with Pt-Ba/Al (Figure 6) depending on the used reductant(s). The main differences are observed at low temperature with mixtures containing C<sub>3</sub>H<sub>6</sub>: Pt/CZ is able to convert NO<sub>x</sub> at 200°C, almost

only into  $N_2O$ , whereas Pt-Ba/Al is inactive at this temperature. However, both catalysts exhibit close  $N_2O$  concentrations at 300°C, in accordance with  $N_2O$  concentration reported in Table 3 for the lean periods of the NSR test. In addition, with  $H_2$  as reductant, higher  $N_2O$  emissions are detected with Pt/CZ during the test in lean atmosphere. The  $N_2O$  concentration is two times higher at 200°C, and 7 ppm  $N_2O$  were still recorded at 300°C with Pt/CZ, whereas no more  $NO_x$  reduction is observed with Pt-Ba/Al (Figure 6). This result is also in accordance with data reported in Table 3 when only  $H_2$  is used: higher  $N_2O$  concentrations were recorded at 200°C and 300°C during the lean periods of the NSR tests with Pt/CZ, compared with Pt-Ba/Al.

To summarize, the amounts of nitrous oxides emitted at 300°C during the lean phases of the NSR test mainly depend on the considered reductant agent, with nearly no influence of the support composition. The variation of the  $N_2O$  distribution between both catalysts depends on reactions during the rich pulses, as described in the following part.

#### 4.3.2. $N_2O$ emission during rich pulses

In opposition with  $N_2O$  concentrations recorded during the lean periods of the NSR test,  $N_2O$  emissions during the rich pulses significantly vary depending on the catalyst. Whatever the reducing mixture,  $N_2O$  concentrations are higher on Pt/CZ than on Pt-Al/Ba (Table 3). With gas mixtures containing  $C_3H_6$  (alone or mixed with CO and  $H_2$ ), the  $N_2O$  concentration in the rich pulses is 3 times higher over Pt/CZ, at around 14 ppm versus 4.5 ppm with Pt-Ba/Al. Differences are even more important using CO, at 12.2 ppm and 1.1 ppm, respectively, but the  $NO_x$  conversion is significantly lower on Pt-Ba/Al. Finally, with hydrogen,  $N_2O$  concentration in the rich pulses is also higher over Pt/CZ.

Two main hypotheses can be proposed to explain these behaviors. As previously described in section 4.2, Pt/CZ catalyst strongly favors the transformation of the introduced reductants, leading to a balanced mixture, especially toward CO and  $H_2$ . This phenomenon could explain the very narrow  $N_2O$  concentrations recorded in the rich pulses over Pt/CZ for full gas,  $C_3H_6$  and CO as used reductant(s) at 12.2-14.4 ppm.  $N_2O$  concentration observed with  $H_2$  is lower, but the CO concentration recorded during the rich pulses was relatively low, at around 500 ppm. However, another phenomenon could participate to the higher  $N_2O$  concentration in the rich pulses over Pt/CZ. Indeed, the ceria based support exhibits a significant oxygen storage capacity [21], which should be associated with a high oxygen mobility (not measured). Taking into accounts that  $N_2O$  formation is due to a lack of reduced sites to favor the NO dissociative adsorption, the oxygen mobility of the CZ support may provide oxygen to platinum and favors the  $N_2O$  formation. During its own reduction, the support may act as an oxygen tank for

platinum. This hypothesis is in accordance with lower N<sub>2</sub>O selectivities with the increase of the rich/lean periods length [27], since the relative time in presence oxygen during the rich phases (from support or due to the mix of the rich and lean mixtures) is reduced.

To conclude, the comparison of catalyst formulation in regard to the N<sub>2</sub>O formation put in evidence that the amounts of nitrous oxide emitted at 300°C during the lean mixture are very close depending on the reductant agent studied. The variation of the N<sub>2</sub>O distribution between both catalysts mainly depends on reactions during the rich pulses. In this case, both the reductant transformations and the oxygen storage/mobility of the support are supposed to be involved.

## 5. Conclusion

The influence of the chemical nature of the reductant agent (C<sub>3</sub>H<sub>6</sub>, CO, H<sub>2</sub> or a mixture of them) was investigated on the NO<sub>x</sub> reduction behaviors of a model Pt-Ba/Al catalyst submitted to NSR cycles with complex gas mixtures, including reductant(s) during the lean phases. The influence of the redox properties of the support were studied by comparison with a platinum catalyst supported on reducible based oxide (Pt/CZ). It is established that the DeNO<sub>x</sub> efficiency and selectivity depend on (i) the temperature, (ii) the chemical nature of the inlet reductant and (iii) the ability of the catalyst to transform the reductant(s).

Generally, over Pt-Ba/Al, the NO<sub>x</sub> conversion increases in the 200-400°C temperature range, but the N<sub>2</sub> selectivity is rather poor due to N<sub>2</sub>O emissions at 200-300°C, and NH<sub>3</sub> emission which tends to increase with temperature.

More precisely, at 200°C, only the use of hydrogen alone allows a significant NO<sub>x</sub> conversion (at 53%), but with a high N<sub>2</sub>O selectivity (41%), which is mainly due to the lean DeNO<sub>x</sub> activity (for 91%). For comparison, Pt/CZ catalyst is more active at this temperature, with NO<sub>x</sub> conversions between 15% and 92% depending on the considered reductant(s), hydrogen still being the more efficient reductant. High N<sub>2</sub>O selectivities are also observed over Pt/CZ, especially in presence of propylene. Again, the major part of the N<sub>2</sub>O emission is attributable to the NO<sub>x</sub> reduction during the lean phases.

At 300°C, the NO<sub>x</sub> conversions vary between 22 and 73% over Pt-Ba/Al with the following order: H<sub>2</sub>>C<sub>3</sub>H<sub>6</sub>>C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>>CO. Significant N<sub>2</sub>O selectivities are associated with the presence of C<sub>3</sub>H<sub>6</sub> in the reaction mixture, with again a large contribution of the lean periods (70%). The NO<sub>x</sub> conversions are less dispersed over Pt/CZ (49-64%) depending on the used reductant(s). This behavior is attributed to reductants transformations during rich pulses over Pt/CZ. The water gas shift equilibrium and steam reforming reactions being (becomes ?)

enhanced on platinum supported over ceria-zirconia based oxide. The resulting gas mixture is then composed of a large amount of H<sub>2</sub> and CO for this catalyst, whatever the inlet gas composition. Concerning the N<sub>2</sub>O emissions, they are very similar during the lean periods for both catalysts, but higher N<sub>2</sub>O concentrations are recorded during the rich pulses over Pt/CZ. In fact; the significant contributions of the lean phases on the global N<sub>2</sub>O emissions are consistent with tests performed only in lean atmosphere in the 200-400°C temperature range. H<sub>2</sub> leads to N<sub>2</sub>O emission for the lowest temperature, C<sub>3</sub>H<sub>6</sub> exhibits a N<sub>2</sub>O peak near 220-230°C, and no N<sub>2</sub>O emission is observed with CO as reductant in the lean periods.

It was also confirmed in this study that ammonia formation during the rich pulses over Pt-Ba/Al is strongly favored in the presence of unconverted hydrogen, whatever its origin (introduced in the rich mixture or *in-situ* produced), while the catalyst supported over a ceria based support limits the ammonia emission.

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