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## **Understanding the role of C<sub>3</sub>H<sub>6</sub>, CO and H<sub>2</sub> on efficiency and selectivity of NO<sub>x</sub> Storage Reduction (NSR) process.**

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### **Abstract**

The NO<sub>x</sub> storage reduction (NSR) process is commonly envisaged for the NO<sub>x</sub> treatment of exhaust gas from lean-burn engine vehicles. NO<sub>x</sub> are firstly stored on the catalyst, which is periodically submitted to a reducing mixture for few seconds in order to reduce the stored NO<sub>x</sub> into N<sub>2</sub>. The on-board reducer is coming from the gasoline/Diesel fuel and, in fact, the NSR catalyst is submitted to a mixture of hydrocarbons, CO and H<sub>2</sub> with various compositions depending on the lean/rich step. In this study, the influence of each reducer (C<sub>3</sub>H<sub>6</sub>, CO and H<sub>2</sub>) is evaluated separately, with a special consideration to the N<sub>2</sub>O selectivity. It is demonstrated that the N<sub>2</sub>O can be emitted during both lean and rich periods, with varying ratio depending on the considered reducer and the temperature of gas. For instance, at 300°C, a high N<sub>2</sub>O selectivity is observed when C<sub>3</sub>H<sub>6</sub> is used, and near half of the N<sub>2</sub>O emission occurs during the storage phase in lean condition.

Keywords: NO<sub>x</sub>, storage, reduction, NSR, selectivity, N<sub>2</sub>O, ammonia, NH<sub>3</sub>.

## 1. Introduction

One possible way to reduce NO<sub>x</sub> emissions from diesel and lean-burn engines is the use of a NO<sub>x</sub> storage reduction (NSR) catalyst [1]. 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 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 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> production during the NSR process must obviously be proscribed.

Both NH<sub>3</sub> and N<sub>2</sub>O can be observed during the NO<sub>x</sub> reduction [2,3,4,5,6,7]. Ammonia formation is favored when H<sub>2</sub> is used as reducer [8,9] whereas N<sub>2</sub>O is obtained with CO as reducer [4,10]. In fact, the on-board reducer is coming from the gasoline/Diesel fuel and, the NSR catalyst is finally submitted to a mixture of hydrocarbons, CO and H<sub>2</sub> with various compositions.

The objective of this work is to study the influence of the reducer on the selectivity of the NO<sub>x</sub> reduction during the NSR process, with a special consideration to the N<sub>2</sub>O selectivity. The examined reducers are C<sub>3</sub>H<sub>6</sub>, CO and H<sub>2</sub>. They were added separately in the rich pulses, as well as during the lean periods, in order to obtain a representative automotive exhaust gas. In this study, the catalyst was made of platinum (2.12%) supported over a ceria-zirconia based oxide, with the aim to evaluate a rhodium free catalyst.

## 2. Experimental part

### 2.1 Catalyst preparation

The support used in this work is a ceria-zirconia based oxide provided by Rhodia. It would be denoted CZ in this study. Platinum (2.12wt%) was impregnated at pH=10 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 500°C for 4h under synthetic air in order to stabilize Pt before the final hydrothermal treatment at 700°C for 25h (synthetic air and 10% H<sub>2</sub>O). The obtained catalyst is noted Pt/CZ and exhibits BET specific surface area of 82 m<sup>2</sup>g<sup>-1</sup>.

### 2.2. Specific surface measurement

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.

### 2.3. XRD analysis

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.

### 2.4. Hydrogen chemisorption

Metal accessibility was determined on Pt/CZ catalyst with a Micromeritics AutoChem II instrument. Typically, 200 mg of sample were reduced in hydrogen flowing ( $30 \text{ mL min}^{-1}$ ) at 400°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  $\text{HC} = \text{HC1} - \text{HC2}$ .

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

Before measurements, the catalyst (70mg) was firstly pretreated in situ for 15 min at 500°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°C with the same mixture. The catalyst was then submitted to 4%  $\text{CO}$ , 1.33%  $\text{H}_2$ , 10%  $\text{H}_2\text{O}$ , 10%  $\text{CO}_2$  and  $\text{N}_2$  for 15min and cool down to 200°C under the same mixture. After a purge under  $\text{N}_2$ , the sample was then submitted to 500ppm  $\text{NO}$ , 10%  $\text{O}_2$ , 10%  $\text{H}_2\text{O}$ , 10%  $\text{CO}_2$  and  $\text{N}_2$  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  $20 \text{ L.h}^{-1}$ . The gas flow was introduced using mass-flow controllers, except for  $\text{H}_2\text{O}$  which was introduced using a saturator. Gas analysis ( $\text{NO}$ ,  $\text{NO}_2$ ) 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,  $99.2 \text{ }\mu\text{mol NO}_x$  per gram of catalyst were injected in 60s. The NO<sub>x</sub> storage fraction is then defined as follows:

$$\text{NO}_x \text{ storage fraction (\%)} = 100 \times \text{NO}_x \text{ stored } (\mu\text{mol/g}) / 99.2$$

In addition, the platinum oxidation activity was estimated as the  $\text{NO}_2/\text{NO}_x$  ratio (%) at

saturation (usually after about 900s).

## 2.6. NOx conversion in cycling conditions

Before measurement, 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 NOx 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. NOx 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 a simplified gas mixture, *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 reducer/oxidant ratio as used with the complete gas mixture (Table 1). The reductant/oxidant ratio is calculated using equation (1), and corresponds to 0.017 and 3.35 for the lean and the rich gas mixture, respectively.

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

**Table 1:** rich and lean gas compositions used for the NOx conversion test (60s lean/4s rich). Total flow rate: 20L h<sup>-1</sup> (SV= 200.000 h<sup>-1</sup>). The redox ratio is constant at 0.017 at 3.35 in lean and rich gas mixture, respectively.

Gas		Reducer			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	10	10	balance
		ppm	ppm	ppm	ppm	%			
	<i>Rich</i>	9000	4	1.33	100	2	%	%	
		ppm	%	%	ppm	%			
Only C <sub>3</sub> H <sub>6</sub> as reducer	<i>Lean</i>	374	-	-	500	10	10	10	balance
		ppm			ppm	%			
	<i>Rich</i>	1.49	-	-	100	2	%	%	
		%			ppm	%			
Only CO as reducer	<i>Lean</i>	-	3300	-	500	10	10	10	balance
			ppm		ppm	%			
	<i>Rich</i>	-	13.4	-	100	2	%	%	
			%		ppm	%			
Only H <sub>2</sub> as reducer	<i>Lean</i>	-	-	3300	500	10	10	10	balance
				ppm	ppm	%			
	<i>Rich</i>	-	-	13.4	100	2	%	%	
				%	ppm	%			

## 2.7. Selective catalytic reduction (SCR) tests

The SCR experiments were performed with various lean conditions as 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 and discussion

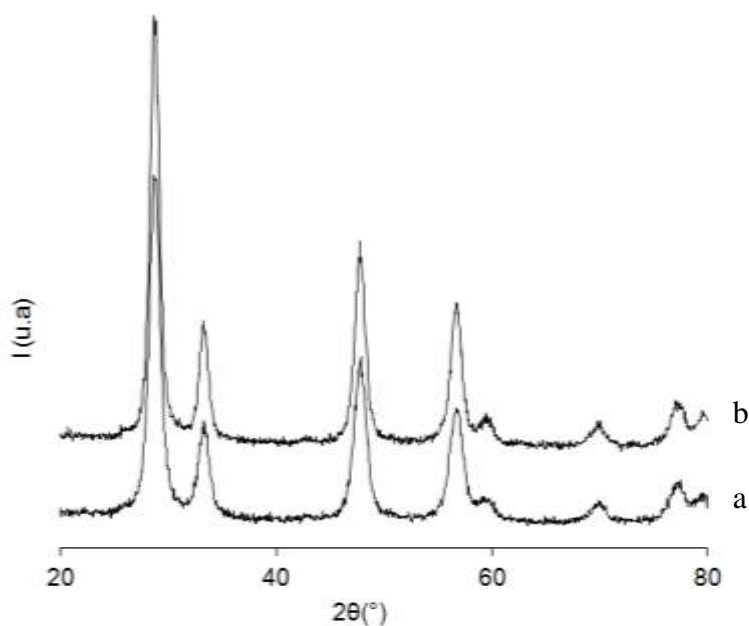
### 3.1. Chemical surface properties

The chemical surface properties of catalysts were characterized using XRD analysis, BET surface area, H<sub>2</sub>-chemisorption and H<sub>2</sub>-TPR.

XRD patterns of the CZ support and the Pt-impregnated catalyst are reported in Figure 1.

XRD phase analysis of CZ mixed oxide shows the presence of only single phase solid solutions with a ceria cubic fluorite-like structure. In accordance with Damyanova and coll. [11], the main XRD peaks of mixed ceria-zirconia oxide are detected at  $2\theta = 28.8, 47.7$  and  $56.5^\circ$ . The average particle size deduced from the Scherrer equation is between 7.5 and 7.9 nm, in agreement with ceria-zirconia oxides with similar specific surface areas [12].

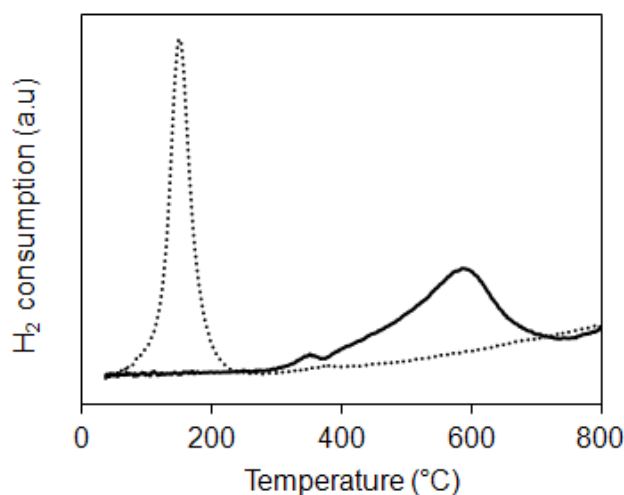
The Pt impregnation step usually leads to barium leaching when BaO/Al<sub>2</sub>O<sub>3</sub> supports are used. XRD experiments show that BaCO<sub>3</sub> and especially BaAl<sub>2</sub>O<sub>4</sub> are significantly affected in aqueous media [9,13]. On the contrary, no change is observed by XRD analysis with the Pt/CZ catalyst, and no other diffraction peaks assigned to platinum or other compound is detected.



**Figure 1:** X ray diffractograms of CZ (a) and Pt/CZ (b) catalysts.

**Table 2:** Specific surface area, Pt dispersion and hydrogen consumption measured from TPR experiments (25-800°C temperature range) for CZ and Pt/CZ catalysts after hydrothermal treatment at 700°C.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	D (%)	$\text{H}_2$ consumption (TPR) ( $\mu\text{mol H}_2/\text{g}_{\text{cata.}}$ )
CZ	116	-	858
Pt/CZ	82	16%	938



**Figure 2:**  $\text{H}_2$ -TPR profiles of CZ (full line) and Pt/CZ (dotted line) samples.

Table 2 shows the BET surface area of the samples before and after the platinum impregnation step, and the platinum dispersion which was obtained by hydrogen chemisorption. Before platinum impregnation, the ceria-zirconia-based support exhibited a specific surface area of 116  $\text{m}^2/\text{g}$ . A drop of  $S_{\text{BET}}$  close to 30% is observed after Pt impregnation. From the hydrogen chemisorption measurement, the platinum dispersion is appraised to 16%, which corresponds to particle size of 6.2 nm.

Figure 2 displays the  $\text{H}_2$  temperature programmed reduction (TPR) profiles for CZ and Pt/CZ samples. Concerning the support without metal, maximum hydrogen consumption is observed close to 600°C, with a shoulder at much lower temperature (380°C). The reducibility behaviors of ceria and ceria-zirconia mixed oxides have been extensively studied in the literature. As described by Yao et al. [14], the reduction of pure ceria typically occurs in two steps: bulk reduction occurs above 800-900°C, while surface shell reduction step takes place at lower temperature (400–550°C). With the incorporation of zirconia, a part of the bulk reduction occurs with the surface reduction step [15]. Depending on the Zr loading and the specific surface area, the reduction process of  $\text{CeO}_2\text{-ZrO}_2$  mixed oxides split into two features, namely a low temperature step reduction (400–600°C), and a higher temperature peak, around 900°C [16].

After platinum addition, a main reduction peak is observed at around 150°C. It corresponds to the platinum reduction, but mainly to the easily reducible Ce<sup>IV</sup> reduction in Ce<sup>III</sup>. In fact, addition of 2.12% of platinum facilitates the “surface” reduction step. However, the H<sub>2</sub> consumption in the 25-800°C temperature range is not really affected by the platinum addition (table 2).

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

The NO<sub>x</sub> storage capacities were measured at 200, 300 and 400°C in lean mixture containing H<sub>2</sub>O and CO<sub>2</sub>. The fractions of storage for 60s are reported in Table 3, as well as the NO<sub>2</sub>/NO<sub>x</sub> ratio calculated at saturation.

The NO<sub>x</sub> storage capacity is rather limited, less than half of the introduced NO<sub>x</sub> for the first 60s are trapped (41-48%), with a maximum storage rate 300°C. In the same time, the NO oxidation rate, estimated by the NO<sub>2</sub>/NO<sub>x</sub> ratio after saturation, also exhibits a maximum at 300°C, at 64%. It decreases to 54% at 400°C but it corresponds to the thermodynamic limitation at this temperature. These relatively high NO<sub>2</sub>/NO<sub>x</sub> ratios indicate that the storage may be limited by a lack of basic sites able to store NO<sub>x</sub>. Note that this catalyst is strongly dependant of a reducing pretreatment applied in this study before the NO<sub>x</sub> storage measurements. If the sample is not firstly submitted to a reducing atmosphere, the NO oxidation rate is strongly lower, especially at 200°C, as already reported for ceria-zirconia oxides [15]. However, it was also showed that this low NO oxidation rate is partially compensated by the participation of the oxygen from the support in order to store NO<sub>x</sub>.

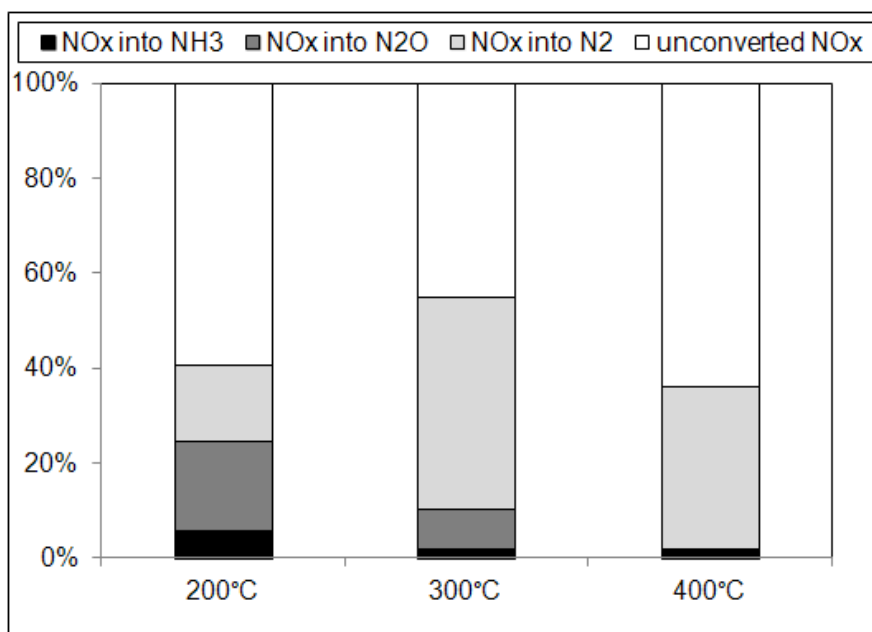
**Table 3:** Pt/CZ catalyst: percentage of stored NO<sub>x</sub> for 60s (NO<sub>x</sub> storage fraction; inlet: 500ppm NO, 10% O<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> and N<sub>2</sub>, 200mL/min) and NO<sub>2</sub>/NO<sub>x</sub> ratio after saturation.

Temperature test	200°C	300°C	400°C
NO <sub>x</sub> storage fraction (%)	41	48	45
NO <sub>2</sub> /NO <sub>x</sub> (%)	41	64	54

### 3.3. NSR efficiency

In the literature, the NO<sub>x</sub> storage-reduction efficiency is often discussed toward model Pt/BaAl catalysts, or with simplified gas mixture. The particularity of this work is that reducers are also present in the lean mixture, as well as oxidant in the rich mixture (Table 1), awarding to this study applied conditions very close to the automotive exhaust gas.





**Figure 3:** Pt/CZ catalyst (70mg): NOx storage/reduction efficiency test at 200, 300 and 400°C with C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub> reducers.

Results at 200°C, 300°C and 400°C (Figure 3) show that the NOx conversion depends on the temperature, with a maximum efficiency obtained at 300°C. These results are consistent with the NOx storage fraction for 60s (Table 3), which reveals a higher amount of stored NOx at this temperature. NOx storage fraction and corresponding NOx reduction rate are rather close, contrary to previous results obtained with less complex mixtures, for which the NOx storage fraction was higher than the NOx reduction rate [9]. However, reactions involved in the NSR process with more complete mixtures are more complex than only storage during lean period and then reduction in rich condition. This point is discussed in section 3.5. Anyway, the observed NOx conversion is not selective into nitrogen, with significant emissions of NH<sub>3</sub> and especially N<sub>2</sub>O. These by-products yields decrease with temperature. In fact, the lower N<sub>2</sub> selectivity is always obtained at 200°C. Ammonia is supposed to be easily oxidized into N<sub>2</sub>, or it can be used for the NOx reduction in a second catalytic bed [17]. Finally, except for the higher temperature (i.e 400°C), the main problematic by-product detected from this experiments remains N<sub>2</sub>O, which is a powerful greenhouse gas (300 times more potent than CO<sub>2</sub>).

In the next part of this work, the NOx storage-reduction efficiency was firstly focused at 300°C, with a special attention in the nature of reducers which should favor the N<sub>2</sub>O emission.

### 3.4. Influence of reducer toward N<sub>2</sub>O emission

In this section, the efficiency and the selectivity of the NSR catalyst was investigated using only one reducer (the same) in both lean and rich gas mixtures. For all the experiments, the

reducer/oxidant ratio was kept constant and corresponds to 0.017 and 3.35 for lean and rich mixture, respectively. The concentration of each reducer ( $C_3H_6$ , CO or  $H_2$ ) was adjusted consequently, as reported in Table 1. Results are presented in Figure 4.

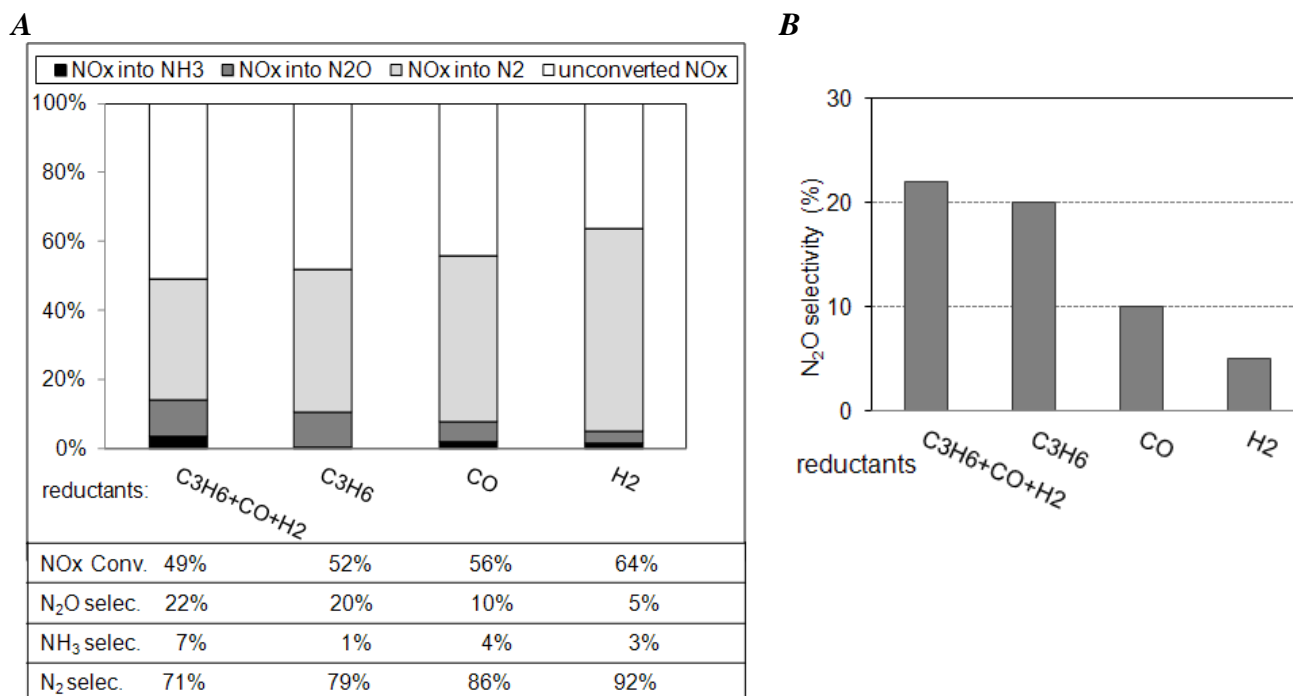


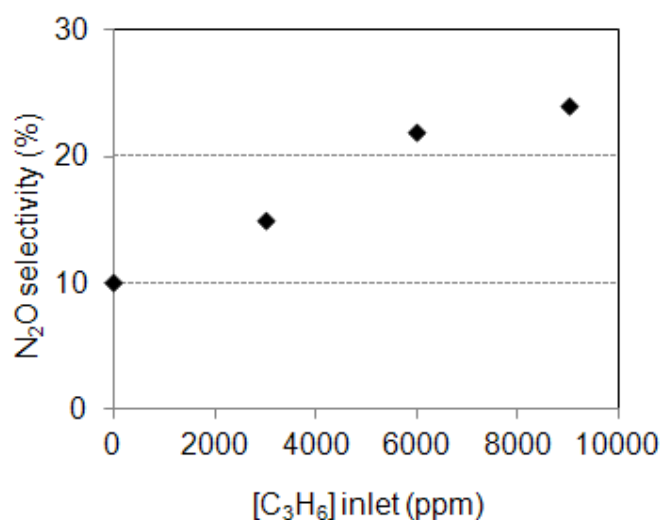
Figure 4: Pt/CZ catalyst (70mg): NO<sub>x</sub> removal efficiency (A) and N<sub>2</sub>O selectivity (B) obtained at 300°C depending on the introduced reducer(s) (same in both lean and rich gas mixture).

As presented previously in Figure 3, with the whole of reducers ( $C_3H_6+CO+H_2$ ), the NO<sub>x</sub> conversion at 300°C is close to 50%, with a high N<sub>2</sub>O selectivity (22%). Ammonia is also detected (7% of selectivity). When only propylene is used as reducer (1.49 % and 374 ppm in rich and lean periods, respectively), the NO<sub>x</sub> conversion remains nearly constant (Figure 4A), as well as the N<sub>2</sub>O selectivity. On the contrary, NH<sub>3</sub> selectivity dramatically drops to 1%. The ammonia selectivity reaches 4% and 3% with carbon monoxide or hydrogen as single reducer, respectively. In fact, the formation of ammonia is related to the presence of H<sub>2</sub>, which is also detected when CO is the only reducer. It was attributed to the water gas shift (WGS) reaction  $CO + H_2O \rightleftharpoons CO_2 + H_2$ . Then, pulses of H<sub>2</sub> are detected during the CO rich pulses, corresponding to an average H<sub>2</sub> concentration of 2.37% during the rich pulses. Note that the reverse WGS also occurs when only H<sub>2</sub> is introduced as reducer, leading to significant CO formation (average CO concentration: 202ppm, with maximum of 503ppm during the rich pulses). Finally, even if only H<sub>2</sub> or CO is introduced, both H<sub>2</sub> and CO are detected at 300°C. In

addition, thermodynamic calculations were performed at 300°C for WGS reaction equilibrium. Considering 10% H<sub>2</sub>O, 10% CO<sub>2</sub>, 2% O<sub>2</sub> and 13.4% CO as initial mixture, the thermodynamic equilibrium leads to concentrations of 1.7% CO and 7.7% H<sub>2</sub>. With H<sub>2</sub> as reducer (13.4%), CO and H<sub>2</sub> concentrations at equilibrium (300°C) are 0.15% and 9.25%, respectively. However, the NO<sub>x</sub> conversion grows when CO and especially H<sub>2</sub> are used as reducer (Figure 4A).

In addition to the WGS equilibrium, which influences the real reducing mixture, the steam reforming of C<sub>3</sub>H<sub>6</sub> also occurs, but only from 300°C. Indeed, using only C<sub>3</sub>H<sub>6</sub> as reducer, emissions of CH<sub>4</sub>, CO and H<sub>2</sub> are detected during the rich pulses. At 300°C, taking into account the whole lean/rich cycles, the average concentrations for CH<sub>4</sub>, CO and H<sub>2</sub> are 97ppm, 136ppm and 1.5%, respectively. Using the C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub> mixture, the mean CH<sub>4</sub> concentration reaches 66 ppm. Over emissions of CO and H<sub>2</sub> are also detected, but they are not evaluable since both reducers are introduced in the inlet mixture, and they are supposed to be reactive. Finally, whatever the introduced reducer, CO and H<sub>2</sub> are always detected at 300°C. This can explain the possible formation of ammonia when only C<sub>3</sub>H<sub>6</sub> is introduced as reducer.

The Figure 4B reports the N<sub>2</sub>O selectivity function of the nature of the reducer used for the NO<sub>x</sub> reduction in cycling condition. It appears that N<sub>2</sub>O is detected whatever the nature of reducer. However, the main compound responsible for the N<sub>2</sub>O emission is clearly propylene. The N<sub>2</sub>O selectivity reaches 20%, compared with 10% and 5% with CO and H<sub>2</sub>, respectively. Indeed, the N<sub>2</sub>O selectivity was evaluated in regard of the propylene concentration in the rich pulses (Figure 5). For these experiments, the amount of reducer in the rich gas mixture is balanced with hydrogen in order to keep the reducer/oxidant ratio constant. The lean period is composed of only propylene (374ppm), in order to have similar reducer in both mixtures. Figure 5 shows that N<sub>2</sub>O emission is clearly related with the propylene concentration in the rich pulses. However, when the rich gas composition does not contain propylene but hydrogen alone, the N<sub>2</sub>O selectivity is still quite high, with about 10%. It is higher than the 5% previously observed when hydrogen is the only introduced reducer both in lean and rich mixtures (Figure 4). Similar experiments were thus performed without any reducers in the lean pulses. In this case, results presented in Table 4 show that the N<sub>2</sub>O emission in the global NSR cycles dramatically decreases from 10% to 4%. It strongly suggests that NO<sub>x</sub> reduction also occurs during the lean period, leading to N<sub>2</sub>O formation.



**Figure 5:** Pt/CZ catalyst : N<sub>2</sub>O selectivity in function of propylene concentration in the rich pulses at 300°C. The reducer/oxidant ratio was kept constant using H<sub>2</sub>.

**Table 4:** NO<sub>x</sub> storage-reduction efficiency and selectivity over Pt/CZ using only H<sub>2</sub> in the rich pulses: test with or without C<sub>3</sub>H<sub>6</sub> in lean mixture.

Introduced reducer	Rich (4s)	13% H <sub>2</sub> (%)	
	Lean (60s)	300ppm C <sub>3</sub> H <sub>6</sub>	/
NSR efficiency	Selec. N <sub>2</sub> O (%)	10	4
	NO <sub>x</sub> conv. (%)	75	

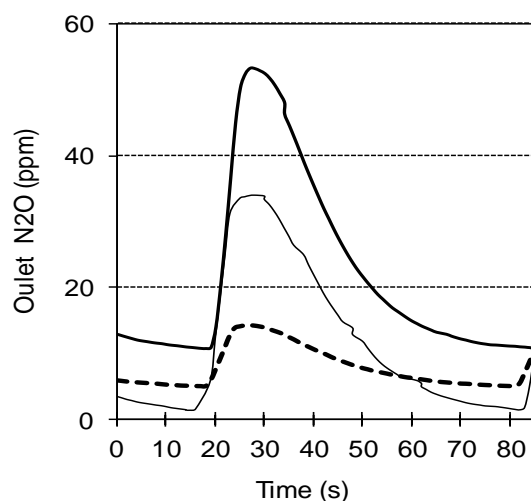
### 3.5. Discussion

Results presented previously indicate that N<sub>2</sub>O is also produced during the lean period. In the NSR process, the NO<sub>x</sub> storage phase has been studied extensively in the literature. But, as far as we know, the NO<sub>x</sub> reduction activity of NSR sample during the lean storage phase is not described. Some nitrous oxide formation recorded during NSR cycles experiments are detailed in Figure 6. Based on these results, the distribution of N<sub>2</sub>O formation during each gas mixture, namely lean and rich, has been evaluated at 300°C and reported in Table 5. Different behaviors are observed in function of reducer. When propylene is used as reducer, the N<sub>2</sub>O selectivity in NSR cycles reaches 20% at 300°C (Figure 4B) and it appears that around half of N<sub>2</sub>O is produced during the lean mixture (Table 5). Similar ratio is observed with H<sub>2</sub> but the nitrous oxide selectivity during NSR cycles is only about 5% (Figure 4B). On the contrary, 90% of the N<sub>2</sub>O emission occurs during the rich pulses when carbon monoxide is the used as reducer (global N<sub>2</sub>O selectivity at around 10%).

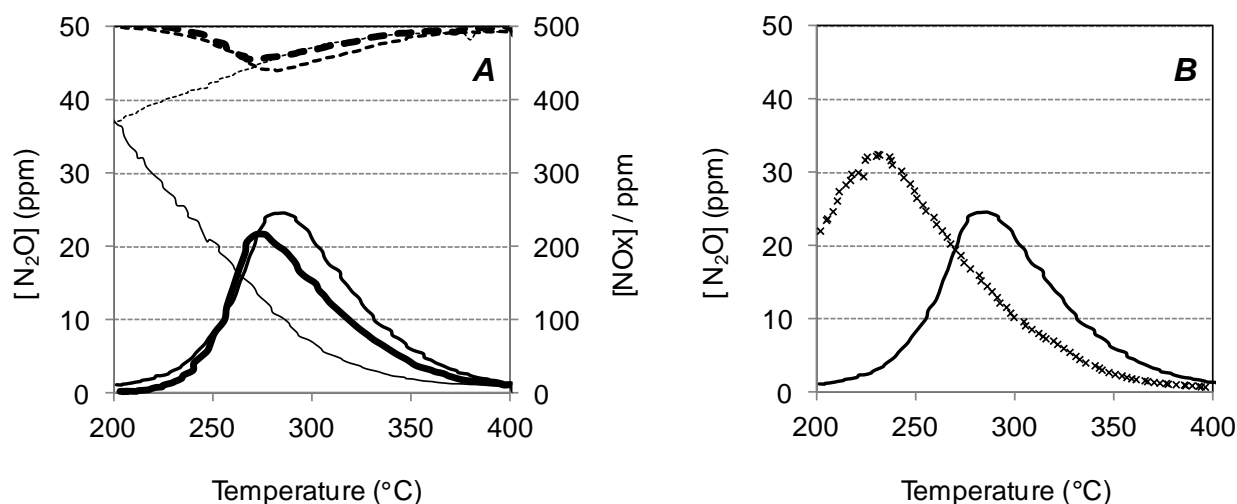
Finally, it appears that an important amount of N<sub>2</sub>O can be produced during the lean phase, depending on the nature of the reducer. To our knowledge, these observations are never discussed in the literature. In fact, usually, no reducers are present during the NO<sub>x</sub> storage phase.

**Table 5:** Pt/CZ catalyst: distribution of N<sub>2</sub>O emission between lean and rich mixtures during the NSR cycles.

	200°C		300°C	
	Lean	Rich	Lean	Rich
C <sub>3</sub> H <sub>6</sub>	78%	22%	45%	55%
CO	13%	87%	10%	90%
H <sub>2</sub>	78%	22%	60%	40%



**Figure 6:** Pt/CZ catalyst: N<sub>2</sub>O profiles recorded during NSR cycles at 300°C with C<sub>3</sub>H<sub>6</sub> (—) or CO (---) or H<sub>2</sub> (....) as reducer.



**Figure 7:** NO<sub>x</sub> reduction in lean mixture depending on the used reducer

(A) NO<sub>x</sub> conversion (dotted line) and N<sub>2</sub>O emission (full line) for:

(—, ---): (500ppm NO + 10% O<sub>2</sub>) + (300 ppm C<sub>3</sub>H<sub>6</sub> + 500ppm CO + 167ppm H<sub>2</sub>)

(—, .....): (500ppm NO + 10% O<sub>2</sub>) + (3300 ppm H<sub>2</sub>)

(—, .....): (500ppm NO + 10% O<sub>2</sub>) + (374 ppm C<sub>3</sub>H<sub>6</sub>)

(B) N<sub>2</sub>O emission using (500ppm NO + 10% O<sub>2</sub>) + (374 ppm C<sub>3</sub>H<sub>6</sub>) mixture

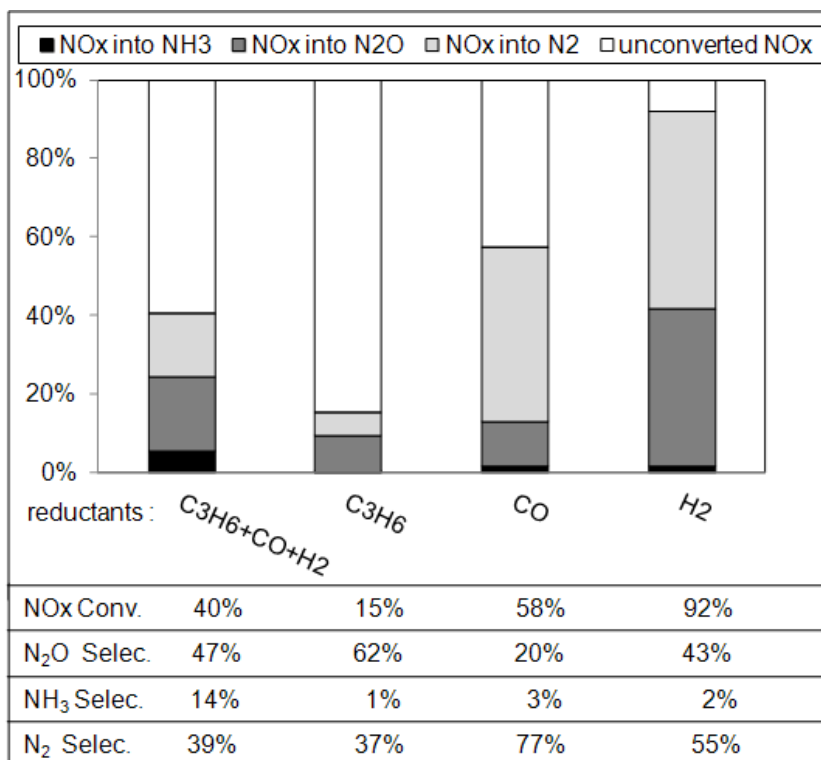
(—): fresh catalyst

(×××): catalyst previously tested in NSR cycled conditions at 400°C

In order to obtain more information concerning the NO<sub>x</sub> conversion and the N<sub>2</sub>O formation during the lean phase, Pt/CZ catalyst was tested using a selective catalytic reduction (SCR) type test. Experiments were performed using the same gas mixture than the lean gas compositions of the NSR test as reported in Table 1 (mixture of reducers, or each reducer separately). Firstly, near no NO<sub>x</sub> reduction is observed with CO as reducer, with a maximum of 2~3 ppm of N<sub>2</sub>O emitted (results not shown), in accordance with Figure 6 and Table 5 which indicate nearly no N<sub>2</sub>O emission during the lean periods with this reducer. Results obtained with other reducers are reported in Figure 7A and show that the NO<sub>x</sub> conversion in excess of oxygen can be effective but depends on the temperature as well as the nature of reducer. With the whole reducers (C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub>), the NO<sub>x</sub> conversion reaches about 10% at 270°C, corresponding to a maximum N<sub>2</sub>O emission of 22ppm (bold line, Figure 7A). Interestingly, when propylene is used as single reducer, results are very similar. The maximum NO<sub>x</sub> conversion (about 12%) is then obtained at 283°C, and 24 ppm of N<sub>2</sub>O are emitted. These results are in accordance with the literature. For instance, Kotsifa et al. [18], have investigated the selective catalytic reduction of NO by propylene over platinum catalysts supported on various metal oxide supports (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>...). Authors concluded that the catalytic performance of catalyst may be improved by proper selection of the support. With alumina, N<sub>2</sub> and N<sub>2</sub>O yields pass through maxima at 270°C. Activities of Pt/CeO<sub>2</sub> catalysts are qualitatively similar to that supported on alumina, especially for the T<sub>max</sub> conversion (i.e 270°C).

NO<sub>x</sub> conversion is likewise effective with H<sub>2</sub> as reducer, but mainly at lower temperature. In fact, maximum NO<sub>x</sub> conversion is obtained at 200°C (27%), with the formation of about 37ppm of N<sub>2</sub>O. Then, both NO<sub>x</sub> conversion and N<sub>2</sub>O concentration significantly decrease with temperature. Finally, note that ammonia emission is never observed in lean condition.

To conclude, the N<sub>2</sub>O formation in lean condition strongly depends on the nature of the reducer but also of the temperature. The SCR test shows that Pt/CZ catalyst is not efficient to reduce NO<sub>x</sub> by CO in excess of O<sub>2</sub>. In fact, the observed N<sub>2</sub>O selectivity is essentially due to the rich pulses, in accordance with results reported in Table 5. However, H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> exhibit very different behaviors depending on the temperature. Concerning C<sub>3</sub>H<sub>6</sub>, no N<sub>2</sub>O emission is observed at 200°C and 400°C, and a maximum is observed at about 283°C. On the contrary, hydrogen favors the nitrous oxide emission for the lower temperatures. These behaviors suggest different impact of each reducer on the N<sub>2</sub>O selectivity at 200°C. Then, the influence of the nature of the reducer(s) was also studied at 200°C.



**Figure 8:** Pt/CZ catalyst (70mg): NO<sub>x</sub> removal efficiency obtained at 200°C depending on the introduced reducer(s) (same in both lean and rich gas mixtures).

Figure 8 reports the NO<sub>x</sub> efficiency, as well as the selectivity in nitrogen containing products at 200°C, depending of the introduced reducer(s) for NSR experiments. It clearly appears that the higher NO<sub>x</sub> conversion, associated to the higher N<sub>2</sub>O emission, is observed with hydrogen. The global NO<sub>x</sub> conversion is thus about 92%, and the corresponding selectivity into N<sub>2</sub>O reaches 43%. As reported previously, the nitrous oxide formation is not only due to the NO<sub>x</sub> reduction which occurs during rich pulses. The distribution of N<sub>2</sub>O formation in each periods (*i.e.* lean and rich) is reported and Table 5. It confirms that the nitrous oxide formation is enhanced in the lean period with hydrogen at 200°C, according with light-off curves reported in Figure 7.

As expected, using only CO as reducer, the lean periods do not significantly participate to the N<sub>2</sub>O emission. When only C<sub>3</sub>H<sub>6</sub> is used, the NO<sub>x</sub> reduction rate is low at 200°C, but the N<sub>2</sub>O selectivity is rather high. Quantification of the N<sub>2</sub>O emission during the rich and lean periods (Table 5) shows that a large amount of the N<sub>2</sub>O occurs during the lean phases, in opposition with the SCR profile reported in Figure 7. Actually, the catalyst behavior at 200°C is strongly dependant of the previous redox treatment, as previously mentioned in section 3.2 about the NO<sub>x</sub> storage measurement. In fact, Pt/CZ is not active at 200°C in the NSR test if this

measurement is carried out after the *in situ* pretreatment at 500°C for 15 min under the lean mixture (Table 1). On the contrary, NO<sub>x</sub> reduction activity is observed at 200°C if the catalyst is previously evaluated under redox cycles at 300 or 400°C. In parallel, SCR test in lean mixture over Pt/CZ catalyst previously submit to NSR tests at 400°C leads to a significant NO<sub>x</sub> reduction activity at 200°C (Figure 7B). The measured N<sub>2</sub>O concentration at 200°C is then consistent with that observed during the lean periods of the NSR test.

However, in opposition with results obtained at 300°C for which similar activities are obtained using C<sub>3</sub>H<sub>6</sub> or mixture of C<sub>3</sub>H<sub>6</sub>+CO+H<sub>2</sub> (Figure 4A), results of NSR cycles reported in Figure 8 at 200°C with the whole reducers indicates that the influence of C<sub>3</sub>H<sub>6</sub> is rather nil. It indicates that the adsorption competition between the three reducers strongly varies with the temperature. Propylene is the main active NO<sub>x</sub> reducer at 300°C, whereas behavior at 200°C suggests the participation of the three reducers.

Finally, whatever the temperature (200 or 300°C), it is confirmed that the formation of N<sub>2</sub>O is enhanced by the presence of reducer during the lean periods, due to the NO<sub>x</sub> reduction activity in excess of oxygen. It depends of both on the temperature test and the nature of the reducer.

#### 4. Conclusion

This study puts in evidence the possible problem of N<sub>2</sub>O emission during the NSR process. In fact, the production of N<sub>2</sub>O during the NSR cycles is function of both the used reducer(s) and the temperature test. Particularly, it appears in this study that presence of reducer in the lean gas mixture can lead to a competition between the NO<sub>x</sub> storage and the NO<sub>x</sub> reduction in excess of oxygen. Depending on temperature and reducer, near half of N<sub>2</sub>O can be produce during the lean periods, in accordance with results obtained during specific catalytic tests to study the NO<sub>x</sub> reduction in excess of O<sub>2</sub> (SCR type tests). At 300°C, the responsible for the N<sub>2</sub>O emission are  $CO \geq C_3H_6 > H_2$  for the rich periods, and  $C_3H_6 > H_2 > CO (\approx 0)$  for the lean periods. The influence of the nature of the reducer is different at 200°C:  $CO > H_2 \geq C_3H_6$  for the rich periods, and  $H_2 > CO \geq C_3H_6 (\approx 0)$  for the lean periods. However, the catalytic behavior at 200°C of the Pt/CZ material strongly depends on the atmosphere pretreatment.

Finally, the nitrous oxide production at 200°C is mainly favored by hydrogen, whereas the most part the N<sub>2</sub>O emission at 300°C is attributed to propylene. These results point out the influence of complex gas mixtures on the catalytic behaviors.



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