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**NO reduction by hydrocarbons and oxygenated compounds in O<sub>2</sub> excess over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. A comparative study of the efficiency of different reducers (hydrocarbons and oxygenated compounds).**

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**Abstract:**

A 1% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by wet impregnation of a  $\delta$ -alumina with an aqueous solution of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>. Metal particle sizes were centered around 20 nm. Twenty-seven reducers (12 hydrocarbons and 15 oxygenated compounds) were tested in NO reduction in O<sub>2</sub> excess while keeping the same experimental conditions (inlet gas: 5% O<sub>2</sub> and 5% H<sub>2</sub>O; space velocity: 14100 h<sup>-1</sup>; same temperature program from 150 to 600°C). To compare the reducers between them, two criteria were used: (i) the catalyst behavior at the maximum NO<sub>x</sub> conversion, and (ii) the efficiencies in NO<sub>x</sub> conversion and N<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub> production taking into account the temperature integrated performances of the reducers between 150 and 600°C. Among the hydrocarbons tested, cyclic C<sub>6</sub> compounds show the highest efficiency in NO<sub>x</sub> conversion while, among the oxygenated compounds, diols and particularly butane-diols are the most efficient reducers. However, the selectivity to N<sub>2</sub> is extremely dependent on the structure of the molecule. For instance, cyclohexadiene is very selective to N<sub>2</sub> while aromatics are not. Moreover, the position of the two OH groups in diols can largely control the selectivity: butane-1,3-diol is very selective to N<sub>2</sub> while butane-1,4-diol produces a great amount of N<sub>2</sub>O. The best ten reducers in terms of NO<sub>x</sub> reduction efficiency are: cyclohexadiene, 292 > butane-1,4-diol, 234 > benzene, 221 > butane-1,3-diol, 212 > cyclohexene, 209 > propane-1,3-diol, 161 > propene, 153  $\approx$  propan-1-ol, 149 > ethanol, 124 > propanoic acid, 114. If these data are coupled with a criterion of selectivity, cyclohexadiene, butane-1,3-diol, propan-1-ol, propanoic acid and to a lesser extent ethanol would be the best candidates for the selective NO<sub>x</sub> reduction.

*Key-words:* catalytic NO reduction, Pt/alumina catalyst, hydrocarbons, C<sub>6</sub> hydrocarbons, cyclohexadiene, aromatics, oxygenated compounds, diols, butane-1,3-diol, alcohols, aldehydes, ketones, carboxylic acids.

## Introduction

Surface transportation is a source of huge emissions of pollutants, CO, HC and NO<sub>x</sub> which are now treated in catalytic converters placed in the exhaust line of cars and trucks. Though converters based on three-way catalysts appear as a mature technology for gasoline engine at the stoichiometry, NO<sub>x</sub> abatement in Diesel engines and gasoline lean-burn engines is a challenge for Catalysis since NO<sub>x</sub> should be globally reduced in a large O<sub>2</sub> excess. The catalytic reduction of NO<sub>x</sub> in O<sub>2</sub> excess has largely been investigated in the 90's [1]. Since mid-90's, the passive DeNO<sub>x</sub> catalysis using reducers normally present in the exhaust gas has been replaced by active DeNO<sub>x</sub> systems like those based on the NO<sub>x</sub>-trap concept [2,3,4], and more generally cyclic addition of reducers not normally present in the exhaust gas. These technologies are more efficient than those based on passive DeNO<sub>x</sub> catalysis. However, whatever the technology employed, both car and catalyst makers need more information on the reducer efficiency for the conception of modern converters.

Numerous reducers have been investigated: hydrocarbons [5,6,7,8,9,10,11,12,13], oxygenated compounds (mainly alcohols, more rarely aldehydes, ketones, ethers,...) [13,14,15] and nitrogen containing compounds (ammonia, urea, nitrocompounds,...) [15,16,17,18,19]. Nevertheless, most studies were carried out on very different catalysts so that the comparison between reducer efficiencies in such conditions is difficult. Although recent studies have shown that silver catalysts could have promising properties in selective NO<sub>x</sub> reduction by heavy HC in the presence of hydrogen [1,20], Pt remains a reference catalyst having a broad spectrum of potential applications with very different reducers. The objective of this work was to acquire data on a large number of reducers (i) by using the same Pt catalyst throughout the study and (ii) while performing the DeNO<sub>x</sub> reaction under similar conditions with an excess of O<sub>2</sub> and in the presence of water. Some of the reducers investigated in this study are present in the Diesel exhaust gases, specially ethylene, propene and aromatics (HC), ketones, aldehydes and carboxylic acids (oxygenates) [21,22].

## 1. Experimental

The catalyst used throughout this study was a 1 wt-%Pt/Al<sub>2</sub>O<sub>3</sub> prepared by impregnation of a  $\delta$ -alumina (Rhône-Poulenc SCS79; 80 m<sup>2</sup> g<sup>-1</sup> ; main impurities in ppm : Na, 590 ; Ca, 490 ; Fe, 315 and S, 400) with an aqueous solution of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>. Prior to impregnation, the support was crushed and sieved to 0.1-0.3 mm. The suspension was evaporated to dryness and

the catalyst was dried at 120°C, calcined for 4h at 700°C in air and reduced for 3h in H<sub>2</sub> at 450°C. The Pt dispersion measured by H<sub>2</sub> chemisorption, DRX and TEM was close to 5 %. This low dispersion allowed to maintain a high catalyst stability whatever the reaction conditions and the reagent processed.

The reaction was carried out in the following conditions: gas hourly space velocity: 14100 h<sup>-1</sup>, 300-800 ppm NO, 120-600 ppm reducer, 5%O<sub>2</sub>, 5%H<sub>2</sub>O. The reducer to NO ratio ("richness") can be characterized by the ratio R defined as follows:

$$R = \frac{P_{\text{red}}}{P_{\text{NO}}} \times n_C \quad (1)$$

where  $n_C$  is the number of atoms of carbon in the molecule of reducer. For instance,  $R = 1.9$  for experiments with 800 ppm NO and 500 ppm propene.

The catalyst was initially heated at 150°C (starting temperature) before admission of the reaction gas mixture. The temperature was then increased by steps of 25 or 50°C at 10°C min<sup>-1</sup> from 150°C to 600°C. The catalyst performances were evaluated at each temperature after stabilization for 40 minutes. This was sufficient to reach a stable conversion. Moreover, when the reaction was carried out at decreasing temperatures from 600 down to 150°C gave, the same curves "conversion vs T°C were obtained". At the reactor outlet, the gases were dried by water elimination on a permeation membrane. Nitrogen oxides were analyzed by means of specific analyzers: chemiluminescence for NO and NO<sub>2</sub> (Cosma Topaze 2020) and IR for N<sub>2</sub>O (Cosma Beryl 100). Dinitrogen could only be analysed in the upper range of concentration (200-400ppm) and [N<sub>2</sub>] was most often obtained by difference from the N-balance. Carbon oxides (TCD) and organics (FID) were analyzed by GC.

The conversion  $X_{\text{NOx}}$  (%) is calculated from the disappearance of the NOx (NO+NO<sub>2</sub>):

$$X_{\text{NOx}} = \frac{[\text{NOx}]_i - [\text{NOx}]_T}{[\text{NOx}]_i} \times 100 \quad (2)$$

where  $[\text{NOx}]_i$  and  $[\text{NOx}]_T$  are the inlet NOx concentration and the outlet NOx concentration at T°C, respectively. The yield  $X_Z$  (%) and the selectivity  $S_Z$  (%) of a product Z is defined as follows:

$$X_Z = \frac{n ([Z]_T - [Z]_i)}{[\text{NOx}]_i} \times 100 \text{ and } S_Z = \frac{n ([Z]_T - [Z]_i)}{[\text{NOx}]_i - [\text{NOx}]_T} \times 100 \quad (3)$$

where n is the number of nitrogen atoms in the molecule of Z. According to the definitions of Eq. (3),  $X_{\text{NOx}} = X_{\text{N}_2} + X_{\text{N}_2\text{O}}$  and  $S_{\text{N}_2} + S_{\text{N}_2\text{O}} = 100\%$ , while  $X_{\text{NO}_2}$  may be higher than  $X_{\text{NOx}}$ . An example is given below for the NOx reduction by ethane in the presence of 5% O<sub>2</sub> and 5% H<sub>2</sub>O. For  $[\text{NO}]_i = 420$  ppm NO and  $[\text{red}] = 400$  ppm ( $R = 1.9$ ), the outlet concentrations at 225°C

and 14100 h<sup>-1</sup> are: [NO] = 165 ppm, [NO<sub>2</sub>] = 169 ppm, [N<sub>2</sub>O] = 1.0 ppm and [CO<sub>2</sub>] = 36 ppm. The calculated conversions are then: X<sub>NOx</sub> = 20.3%, X<sub>N<sub>2</sub></sub> = 19.8%, X<sub>N<sub>2</sub>O</sub> = 0.5% and X<sub>NO<sub>2</sub></sub> = 40.3%.

A similar definition can be given for X<sub>CO<sub>2</sub></sub>, a 100% yield being obtained for a complete oxidation of the reducer into CO<sub>2</sub>:

$$X_{CO_2} = \frac{[red]_i - [red]_T}{n_C [red]_i} \quad (4)$$

[red]<sub>i</sub> and [red]<sub>T</sub> being the inlet and the outlet HC concentrations at T°C and n<sub>C</sub> is the number of C atoms in the reducer molecule.

## 2. Results and discussion

### 2.1 Hydrocarbons

The same temperature program having being applied for every reducer, a comparative evaluation of the reducer efficiency can be given by the temperature integrated conversion, i.e. the sum of the conversions at 150, 200, 225, 250, 300 and so on by step of 50°C up to 600°C.

$$\sum X_{NOX} = \sum_{T=150}^{600^\circ C} X_{NOX} \text{ and } \sum X_Z = \sum_{T=150}^{600^\circ C} X_Z \quad (5)$$

An example corresponding to the NO reduction by ethane is given in Table 1.

**Table 1:** NO reduction by ethane in the 200-400°C range of temperature. Inlet composition: 420 ppm NO + 400 ppm C<sub>2</sub>H<sub>6</sub> + 5% O<sub>2</sub> + 5% H<sub>2</sub>O diluted in He (R = 1.9). Space velocity: 14100 h<sup>-1</sup>.

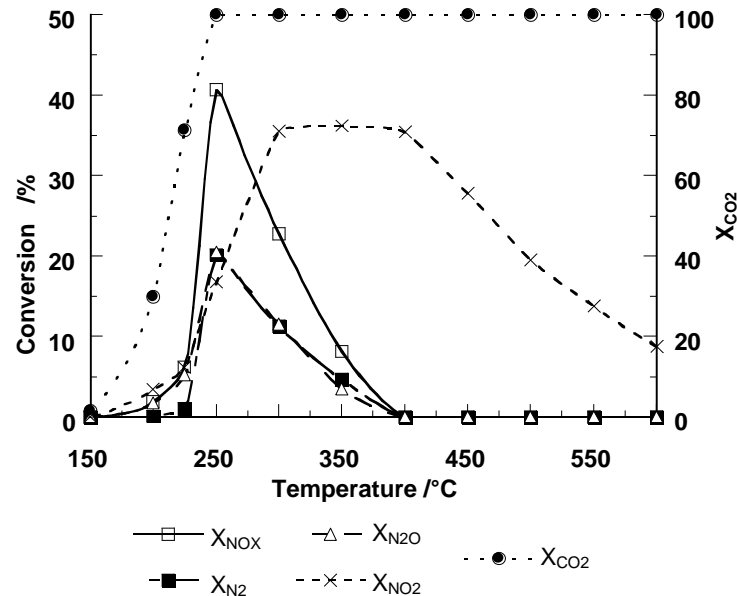
T °C	X <sub>NO<sub>x</sub></sub> %	X <sub>N<sub>2</sub></sub> %	X <sub>N<sub>2</sub>O</sub> %	X <sub>NO<sub>2</sub></sub> %	X <sub>red</sub> %	X <sub>CO<sub>2</sub></sub> %	S <sub>N<sub>2</sub></sub> %	S <sub>N<sub>2</sub>O</sub> %
200	21.8	21.3	0.5	25.8	4.2	4.0	98	2
225	20.3	19.8	0.5	40.3	9.8	4.5	98	2
250	16.8	16.3	0.5	49.3	10.7	5.7	97	3
300	6.8	6.3	0.5	52.0	13.7	7.6	93	7
350	1.3	0.8	0.5	47.5	21.8	19.1	60	40
400	0	0	0	34.8	45.2	41.0		
Efficiency	Σ= 67	Σ= 65	Σ= 3	Σ= 329				

The temperature range in the Table is limited to 200-400°C, the NO reduction being nil at 150°C, at 400°C and above. This illustrates the classical behaviour of Pt catalysts in NO reduction by HC with a maximal conversion around 200-250°C and an irremediable decrease of activity at higher temperatures. The catalyst efficiencies are given in the last line of Table 1. Except for NO<sub>2</sub> (whose formation goes on above 400°C), catalyst efficiencies in NO<sub>x</sub>, N<sub>2</sub> and N<sub>2</sub>O conversion are the same in the 150-600°C range as in the 200-400°C range.

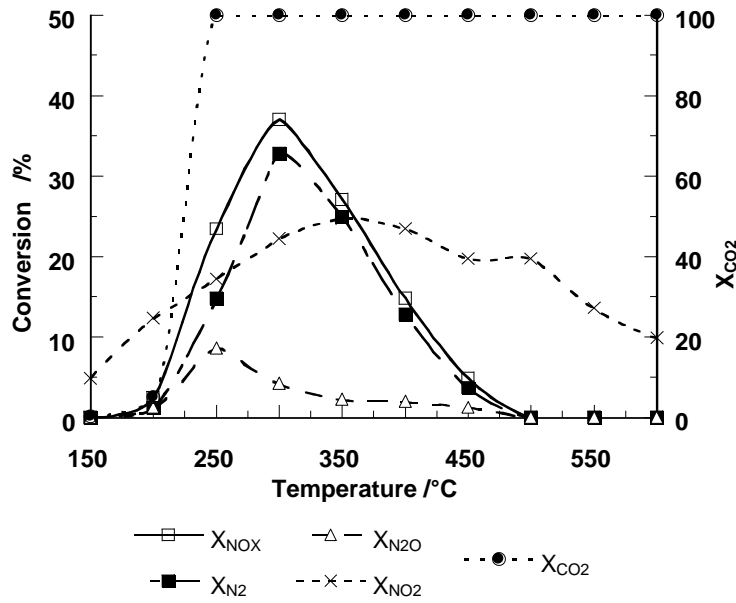
Other parameters are considered for evaluating the catalyst performances with a given reducer:

- the maximum NO<sub>x</sub> conversion,  $X_{\text{NO}_x \text{ max}}$ , and the temperature,  $T_{\text{max}}$ , at which this  $X_{\text{NO}_x \text{ max}}$  is reached,
- the width at half height of NO<sub>x</sub> conversion. This is the temperature range in which a significant NO<sub>x</sub> conversion (at least  $X_{\text{NO}_x \text{ max}}/2$ ) is maintained.
- The temperature  $T_{50}$  of half conversion and the lowest temperature  $T_{100}$  of full conversion of the reducer.

This is illustrated in Fig. 1 for NO reduction by n-hexane and in Fig. 2 for NO reduction by cyclohexane.



**Fig. 1:** NO reduction by n-hexane. Inlet gas composition: 800 ppm NO + 450 ppm C<sub>6</sub>H<sub>14</sub> + 5% O<sub>2</sub> + 5% H<sub>2</sub>O in He (R = 3.3). Space velocity: 14100 h<sup>-1</sup>.

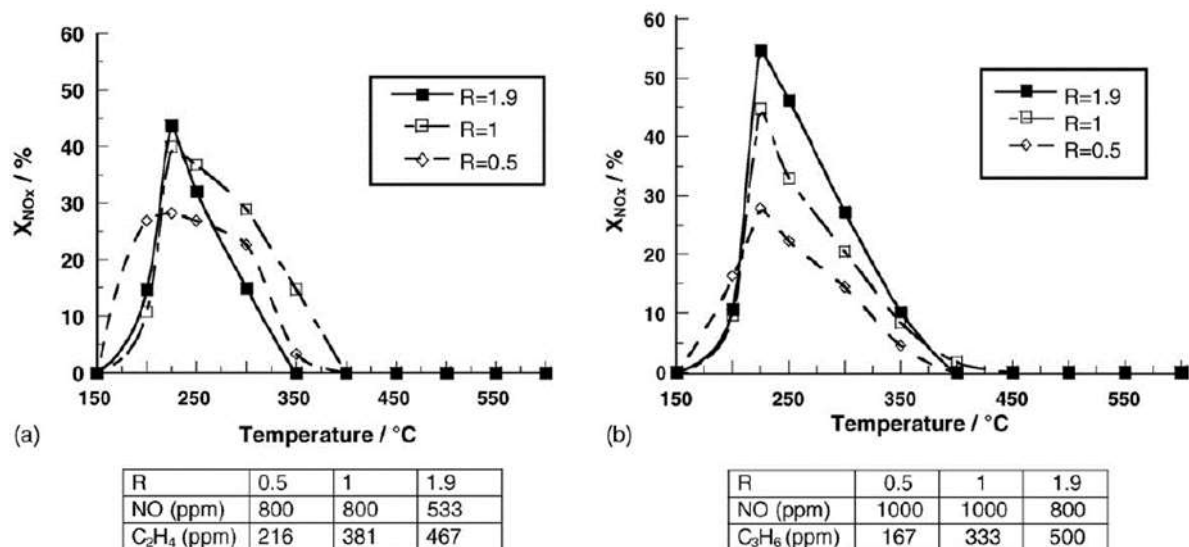


**Fig. 2:** NO reduction by cyclohexane. Inlet gas composition: 800 ppm NO + 440 ppm C<sub>6</sub>H<sub>12</sub> + 5% O<sub>2</sub> + 5% H<sub>2</sub>O in He (R = 3.4). Space velocity: 14100 h<sup>-1</sup>.

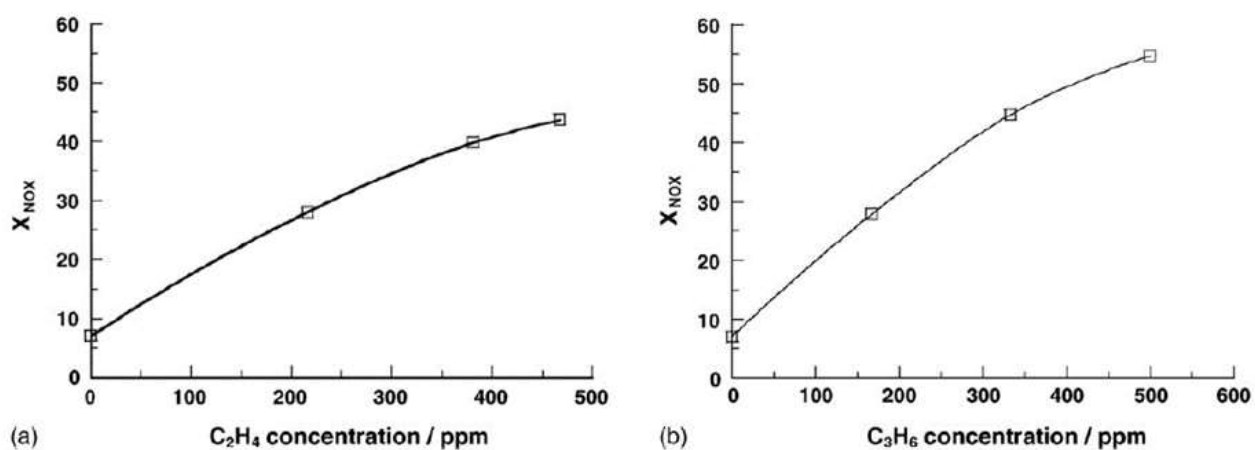
The maximum NO<sub>x</sub> conversion  $X_{\text{NO}_x \text{ max}}$  in the reduction by n-hexane is 40% reached at 250°C (Fig. 1) while it is of 37% at 300°C in the reduction by cyclohexane (Fig. 2). Although very close  $X_{\text{NO}_x \text{ max}}$  are obtained with both C<sub>6</sub> compounds,  $X_{\text{NO}_x}$  profiles are quite different with a relatively narrow peak for n-hexane (width at 20% conversion: 75°C) and a rather broad peak for cyclohexane (width at 18.5% conversion: 130°C).

Before comparing the different reducers, the impact of several reaction parameters were investigated. Fig. 3 shows the effect of the R ratio on the NO<sub>x</sub> conversion profile for ethene (Fig. 3a) and propene (Fig. 3b).

As expected, an increase of the richness R improves the NO<sub>x</sub> conversion. Nevertheless, no significant change in the width of the NO<sub>x</sub> conversion peak with propene can be observed. As  $X_{\text{NO}_x \text{ max}}$  is observed at temperature where the reducer is fully oxidized (see for instance Fig 1 and 2), this means that NO<sub>x</sub> are reduced in the very first part of the catalytic bed with hydrocarbon adsorbed species or with organic intermediates issued from the partial oxidation of the reducer. These intermediates (CH<sub>x</sub> or CH<sub>x</sub>O<sub>y</sub>) should survive, even at high temperature, over a large distance in the catalytic bed. The change of  $X_{\text{NO}_x}$  with the reducer concentration (ethene and propene) is shown in Fig. 4.

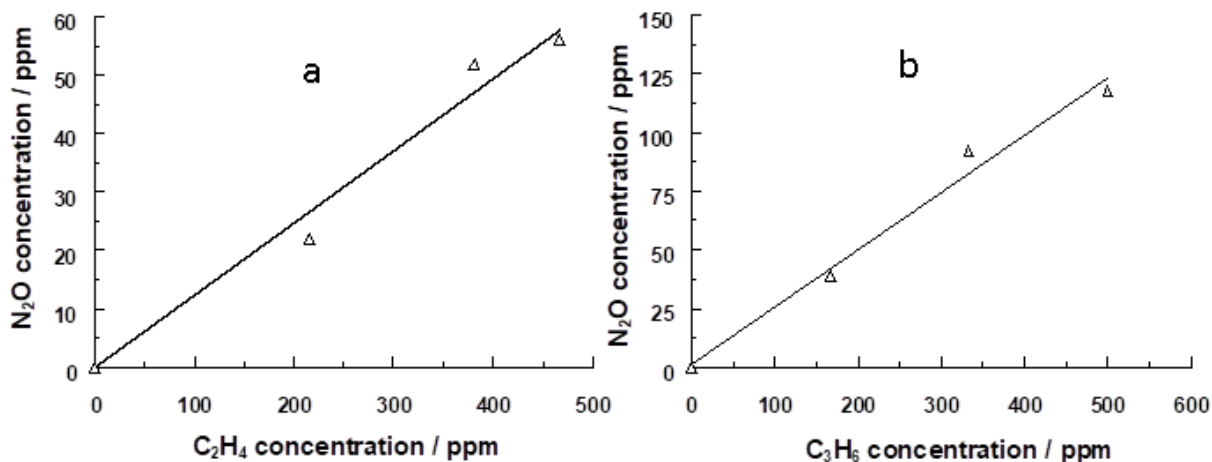


**Fig. 3:** Effect of the richness  $R$  (see Eq. 1) on the NO<sub>x</sub> conversion profile with ethene (a) and with propene (b) as reducers. NO and HC composition are given in the tables inserted below the figures. Other gases: 5% O<sub>2</sub> and 5% H<sub>2</sub>O in He. Space velocity: 14100 h<sup>-1</sup>.



**Fig. 4:** Effect of the reducer concentration on the NO<sub>x</sub> conversion: a) ethene; b) propene. Reactions conditions are given in Fig. 3.



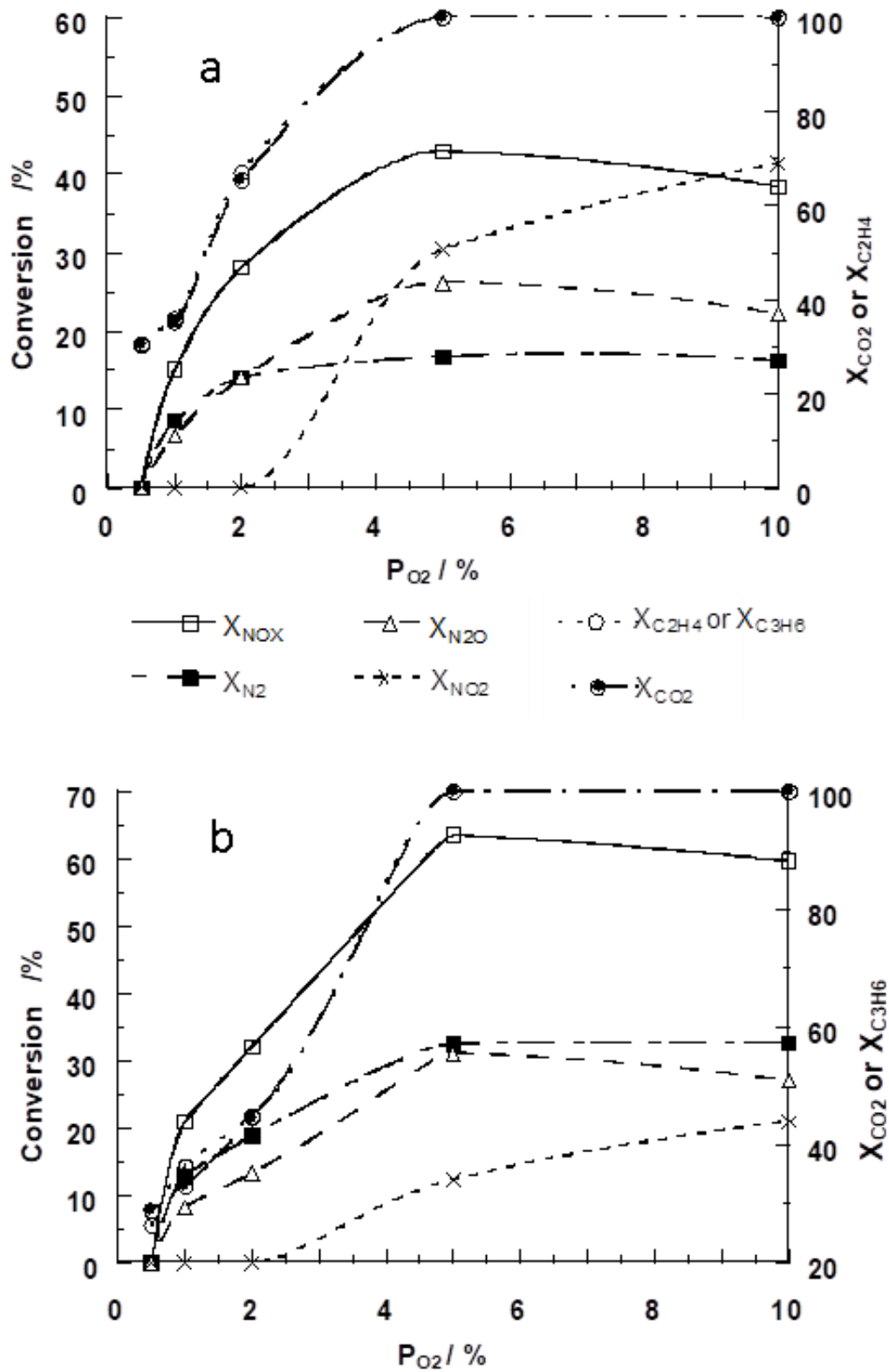


**Fig. 5:** Effect of the reducer concentration on the  $N_2O$  formation at 225°C: a) ethene; b) propene. Reactions conditions are given in Fig. 3.

A continuous increase of  $X_{NOx}$  with  $P_{C_2H_4}$  and  $P_{C_3H_6}$  can be observed. Worthy of note also is the small  $NOx$  conversion in absence of reducer which could originate from homogeneous radical reactions or from  $NO_2$  adsorption (or more likely,  $NO_2$ -water co-adsorption) on the apparatus walls or in the analyzers. The formation of  $N_2O$  depends linearly on the reducer concentration (Fig. 5).





Moreover, there is no  $N_2O$  formed in the absence of reducer, which proves that the small  $NOx$  abatement observed at zero concentration in reducer is probably not a  $NOx$  reduction. The effect of the oxygen concentration was also investigated (Fig. 6).

The results confirm the prominent role of  $O_2$  in  $NOx$  reduction with virtually no  $NOx$  conversion when  $O_2$  is absent. There is a parallelism between the  $NOx$  reduction and the HC oxidation.  $X_{NOx}$  reaches its maximum when the hydrocarbon becomes fully oxidized. Within the concentration range used for most hydrocarbons, this maximum of  $NOx$  conversion can be observed at 5%  $O_2$ , which justifies the  $O_2$  concentration adopted for a general comparison of the different reducers. The data for the 12 hydrocarbons tested in  $NOx$  reduction are reported in Table 2.



**Fig. 6:** Effect of the oxygen concentration on the performance of the 1% Pt/Al<sub>2</sub>O<sub>3</sub> in NO<sub>x</sub> reduction by ethene (a) or propene (b) at 225°C. R = 1.9. Other conditions as in Fig. 3.

**Table 2:** Summary table of the performances of 12 hydrocarbons in NO<sub>x</sub> reduction over the 1%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Reducer	R	X <sub>NO<sub>x</sub> max</sub> % T (°C)	Width at half conversion X <sub>NO<sub>x</sub> max</sub> /2 (°C)	T <sub>50</sub> (°C)	T <sub>100</sub> (°C)	Efficiency (Temperature integrated conversion)			
						ΣX <sub>NO<sub>x</sub></sub>	ΣX <sub>N<sub>2</sub></sub>	ΣX <sub>N<sub>2</sub>O</sub>	ΣX <sub>N<sub>2</sub>O<sub>2</sub></sub>
CH <sub>4</sub>	2.2	29 (225)	105	550	650	80	75	5	294
C <sub>2</sub> H <sub>4</sub>	1.9	42 (225)	75	200	225	105	42	63	216
C <sub>2</sub> H <sub>2</sub>	1.9	42 (250)	90	225	250	92	56	36	206
C <sub>2</sub> H <sub>6</sub>	1.9	22 (200)	115	410	550	67	64	3	328
C <sub>3</sub> H <sub>6</sub>	1.9	55 (225)	90	210	225	153	73	80	198
C <sub>3</sub> H <sub>4</sub>	1.3	31 (250)	90	225	250	75	47	28	157
C <sub>3</sub> H <sub>8</sub>	2.5	13 (200)	55	365	500	18	17	1	263
C <sub>6</sub> H <sub>14</sub>	3.3	40 (250)	75	210	250	84	39	45	203
 C <sub>6</sub> H <sub>12</sub>	3.4	37 (300)	130	225	250	110	90	20	168
 C <sub>6</sub> H <sub>6</sub>	3.8	65 (200)	125	165	200	221	90	131	203
 C <sub>6</sub> H <sub>8</sub>	5.2	70 (200)	160	165	200	292	219	73	181
 C <sub>6</sub> H <sub>10</sub>	5.2	70 (250)	125	220	250	209	119	90	183

From these results, the following rules can be drawn:

- light alkanes are poor NO<sub>x</sub> reducers but they are very selective in N<sub>2</sub>. Methane is surprisingly rather active compared to ethane and propane probably because it is difficult to oxidize so that it can be active over a relatively large window of temperature. The behaviour of light alkanes contrasts with that of C<sub>6</sub> saturated hydrocarbons (n-hexane and cyclohexane) slightly more active but also much less selective into N<sub>2</sub>. A good compromise occurs with cyclohexane rather active and not too selective in N<sub>2</sub>O.
- light alkenes are better reducers than are alkanes in the order C<sub>3</sub>H<sub>6</sub> > C<sub>2</sub>H<sub>4</sub> > C<sub>2</sub>H<sub>6</sub> >> C<sub>3</sub>H<sub>8</sub>. A similar ranking was observed over Cu-MFI catalysts by the group of Iwamoto [23] and by Gaudin et al. [24] while Maunula et al. reported the same activity for ethene and propene over In catalysts [25]. However, unsaturated C<sub>6</sub> hydrocarbons are by far much more active with cyclohexadiene being the best reducer of the twelve hydrocarbons tested. The

- selectivity to N<sub>2</sub>O remains generally high specially with propene and benzene. Compared to its high activity, cyclohexadiene shows an interestingly low selectivity to N<sub>2</sub>O.
- c- the relatively high activity of aromatic hydrocarbon coupled with a poor selectivity to N<sub>2</sub> has already been reported by Bourges et al. in NO<sub>x</sub> reduction by toluene in a gas mixture containing water [26]. On the contrary, Burch and Ottery did not observe the same tendency in NO<sub>x</sub> reduction by benzene in the absence of water. As already suggested by one of us [27], H<sub>2</sub>O could play a decisive role in N<sub>2</sub>O formation via the Neff reaction [28].
  - d- although they are fully oxidized at very low temperature, cyclic C<sub>6</sub> compounds maintain a significant NO<sub>x</sub> activity over a large temperature range. This can be explained by the formation of organic intermediates, partially oxygenated, present over a long distance in the catalyst bed, even when the initial hydrocarbon is almost totally oxidized.
  - e- the rate of NO<sub>2</sub> formation is the highest with alkanes and apparently decreases with the degree of insaturation and when the number of carbon in the molecule increases. There is certainly a competition between the reducer and NO at the Pt surface, thus inhibiting the NO oxidation reaction when the hydrocarbon is too strongly adsorbed.

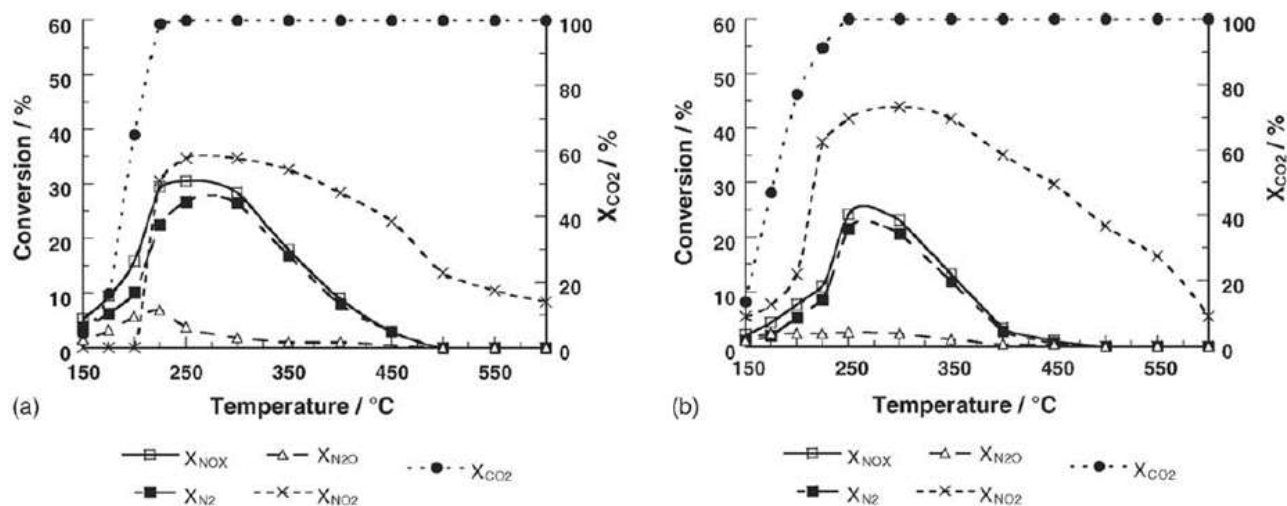
## 2.2 Oxygenated compounds

This study was performed with alcohols (methanol, ethanol, propan-1-ol, propan-2-ol), diols (propane diols and butane diols), aldehydes (ethanal, propanal), ketone (propanone), C<sub>3</sub> carboxylic acids. It was completed with propene oxide and tetrahydrofurane (THF) which may be formed intermediary in the transformation of diols. The reaction was carried out in the following conditions: 800 ppm NO, 500 ppm reducer (except ethanal, 310 ppm and THF 300 ppm), 5% O<sub>2</sub>, 5% H<sub>2</sub>O in He, 14100 h<sup>-1</sup>. The temperature programme was the same as in NO<sub>x</sub> reduction by hydrocarbons. To take into account the presence of O atoms in the reducer molecule, the definition of R (Eq. 1) was modified as follow:

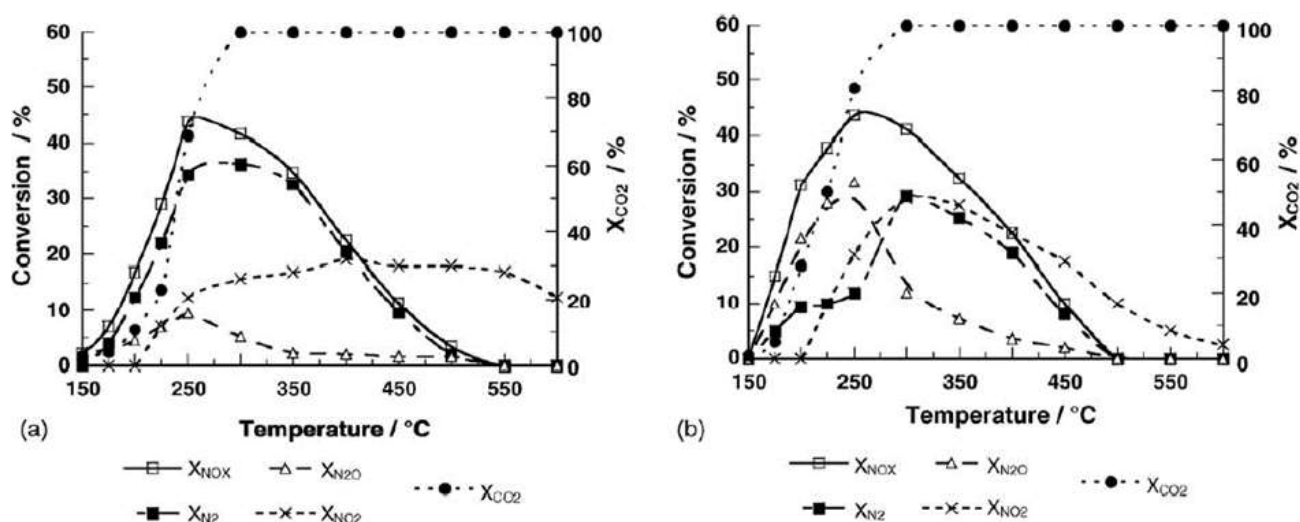
$$R = \frac{P_{\text{red}}}{P_{\text{NO}}} \times \left( n_{\text{C}} - \frac{n_{\text{O}}}{2} \right) \quad (6)$$

where  $n_{\text{C}}$  and  $n_{\text{O}}$  are the numbers of C and O atoms in the molecule.

Compared to hydrocarbons, one of the most interesting feature of the alcohols is their good selectivity to N<sub>2</sub> in NO<sub>x</sub> reduction. This is illustrated in Fig. 7a (propan-1-ol) and 7b (propan-2-ol) where it can be seen that the N<sub>2</sub>O production is remarkably low, particularly with the secondary alcohol.



**Fig. 7:** NO reduction by propan-1-ol (a) and propan-2-ol (b) over 1% Pt/Al<sub>2</sub>O<sub>3</sub>. Inlet gas: 800 ppm NO, 500 ppm alcohol, 5% O<sub>2</sub>, 5% H<sub>2</sub>O in He. Space velocity: 14100 h<sup>-1</sup>.

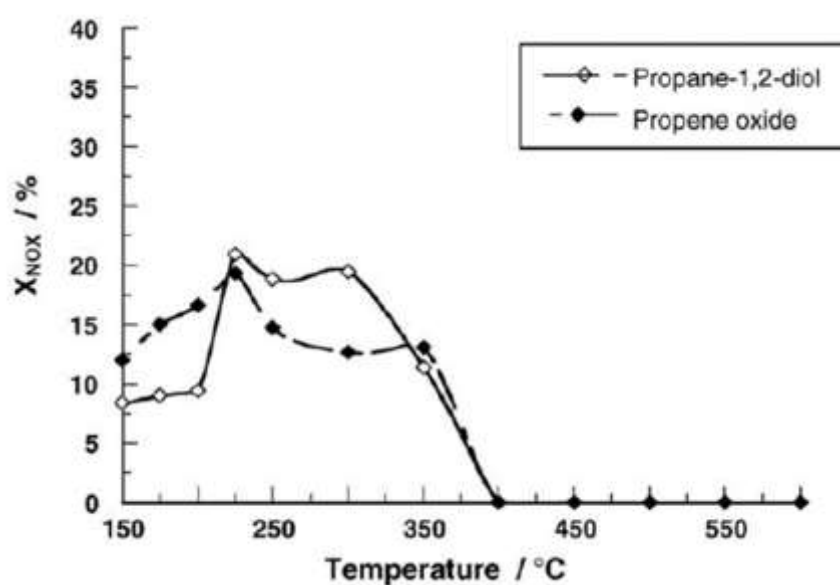


**Fig. 8:** NO reduction by butane-1,3-diol (a) and butane-1,4-diol (b) over 1% Pt/Al<sub>2</sub>O<sub>3</sub>. Inlet gas: 800 ppm NO, 500 ppm diol, 5% O<sub>2</sub>, 5% H<sub>2</sub>O in He. Space velocity: 14100 h<sup>-1</sup>.

This feature cannot be extrapolated to all the diols as shown on Fig. 8a (butane-1,3-diol) and Fig. 8b (butane-1,4-diol).

Though butane-1,3-diol produces little N<sub>2</sub>O (and resembles alcohols), butane-1,4, diol leads to a great amount of N<sub>2</sub>O which makes this diol comparable to most of the hydrocarbons. With this diol, nitrogen production is shifted to higher temperatures so that the selectivity to N<sub>2</sub>O is very high in the 200-250°C range of temperature.

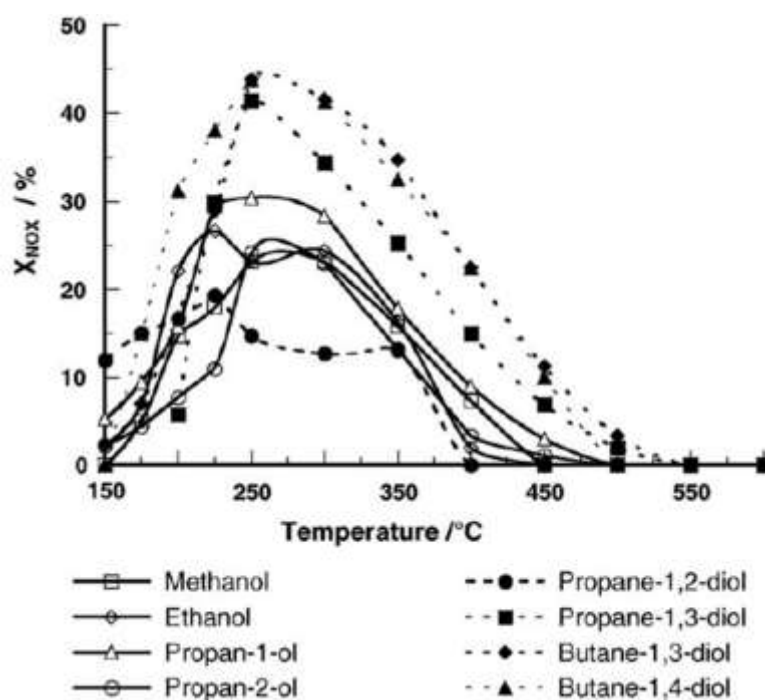
When the two OH are in adjacent position as in propane-1,2-diol, the NO reduction is limited to less than 20%. This diol can lead to propene oxide by internal dehydration. Interestingly, there is a close parallelism between the behaviour of the two reducers (Fig. 9).



**Fig. 9:** Comparison of the NOx conversion profile with propane-1,2-diol and propene oxide.

A similar result was obtained with butane-1,4-diol which can be cyclized into THF by internal dehydration. Both reducers (diol and furane) gives very close NO<sub>x</sub> conversion profiles at low temperature (<250°C). Above 250°C, the diol is more active than THF which does no longer seem to be an intermediate in the transformation of butane-1,4-diol. A comparison of the NO<sub>x</sub> conversion profiles between the different alcohols and diols is given on Fig. 10.

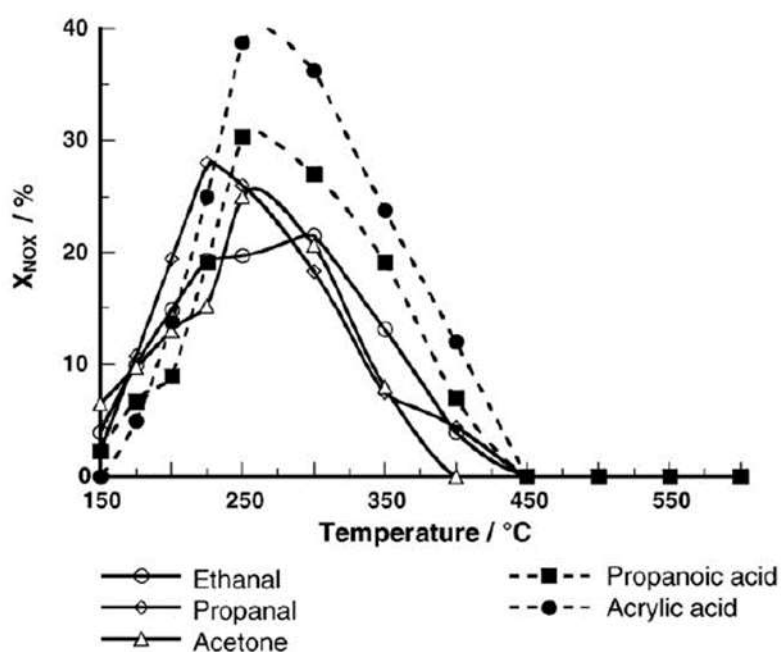
The reducers can be ranked in the following order: butane-1,3-diol  $\approx$  butane-1,4-diol > propane-1,3-diol > propan-1-ol > ethanol > methanol > propan-2-ol > propane-1,2-diol with maximum NO<sub>x</sub> conversion ranging between 20 and 44%.



**Fig. 10:** NO<sub>x</sub> conversion profiles obtained with alcohols and diols over the 1%PtAl<sub>2</sub>O<sub>3</sub> catalyst. Inlet gas: 800ppm NO, 500 ppm reducer, 5% O<sub>2</sub>, 5% H<sub>2</sub>O in He. Space velocity: 14100 h<sup>-1</sup>.

Five carbonyl and carboxylic compounds were finally investigated over the 1%Pt catalyst. As a rule, these reducers are very, sometimes fairly, selective to  $N_2$  and show a behaviour close to that of alcohols. Their  $NO_x$  conversion profiles are compared in Fig. 11.

Carboxylic acids are more active than carbonyl compounds, the order of  $X_{NO_x}$  efficiency being: acrylic acid > propanoic acid > propanal > ethanal > acetone.



**Fig. 11:**  $NO_x$  conversion profiles obtained with carbonyl and carboxyl compounds over the 1%PtAl<sub>2</sub>O<sub>3</sub> catalyst. Inlet gas: 800ppm NO, 500 ppm reducer, 5% O<sub>2</sub>, 5% H<sub>2</sub>O in He. Space velocity: 14100 h<sup>-1</sup>.



The performances of the 15 oxygenated compounds tested in NO<sub>x</sub> reduction are summarised in Table 3.

**Table 3:** Summary table of the performances of 15 oxygenated compounds in NO<sub>x</sub> reduction over the 1%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Reducer	R	X <sub>NO<sub>x</sub> max</sub> % T(°C)	Width at X <sub>NO<sub>x</sub> max</sub> /2 °C	T <sub>50</sub> °C	T <sub>100</sub> °C	Efficiency (Temperature integrated conversion)			
						ΣX <sub>NO<sub>x</sub></sub>	ΣX <sub>N<sub>2</sub></sub>	ΣX <sub>N<sub>2</sub>O</sub>	ΣX <sub>NO<sub>2</sub></sub>
Methanol	0,5	23 (250)	180	<150	<150	107	99	8	353
Ethanol	1,3	27 (225)	150	220	250	124	91	36	271
Propan-1-ol	1,9	31 (250)	145	185	225	149	124	25	217
Propan-2-ol	1,9	24 (250)	100	180	250	91	75	16	300
Propane-1,2-diol	1,9	10 (225)	200	-	-	88	52	36	299
Propane-1,3-diol	1,9	41 (250)	145	210	250	161	115	46	206
Butane-1,3-diol	2,5	44 (250)	210	240	300	212	174	38	136
Butane-,1,4-diol	2,5	44 (250)	223	225	300	234	118	116	114
Ethanal	0,9	21,5 (300)	185	200	300	96	84	12	275
Propanal	1,7	28 (225)	130	170	225	106	65	41	257
Acetone	1,7	25 (250)	125	185	230	88	76	12	295
Propanoic acid	1,7	30 (250)	160	210	225	114	100	14	191
Acrylic acid	1,7	39 (250)	160	220	250	149	95	54	194
Propene oxide	1,9	21 (225)	140	-	-	89	64	25	236
THF	1,5	36 (200)	75	170	200	100	47	53	216

From these data, some conclusions can be drawn:

- a- primary alcohols are relatively good NO<sub>x</sub> reducers. Among the C1-C3 alcohols tested, methanol shows the better selectivity to N<sub>2</sub>. Secondary alcohols would be less active than the corresponding primary alcohols.
- b- diols and specially butane-diols are very active in NO<sub>x</sub> reduction. However, the selectivity to N<sub>2</sub> depends strongly on the relative position of the two OH groups: though butane-1,3-diol has both a high activity and a good selectivity to N<sub>2</sub>, butane-1,4-diol is active but produces a great amount of N<sub>2</sub>O.

- c- aldehydes are slightly less active than the corresponding primary alcohols. On the contrary, carboxylic acids are rather more active.
- d- NO oxidation into NO<sub>2</sub> seems to be correlated with the adsorption strength of the reducer: those molecules which are subject to strong adsorption decrease the NO oxidation properties of Pt.

### 3. Conclusions

The objective of this work was to compare a series of reducers in NO<sub>x</sub> conversion on the same 1%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and under similar conditions (space velocity, gas composition including O<sub>2</sub> and H<sub>2</sub>O, temperature program from 150 to 600°C). Instead of the maximum NO<sub>x</sub> conversion, a criterion based on the performance of the reducer over the entire range of temperature (NO<sub>x</sub> conversion and product formation efficiencies) was preferred to compare the reducers. If one combines the NO<sub>x</sub> conversion and the selectivity to N<sub>2</sub>, cyclohexadiene, butane-1,3-diol, propan-1-ol, propanoic acid and to a lesser extent ethanol are good candidates for the selective NO<sub>x</sub> reduction. Molecular structures, specially in diols, alcohols and C<sub>6</sub> hydrocarbons were proved to have a strong impact on both the NO<sub>x</sub> reduction and the selectivity to nitrogen.

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### References

- [1] R. Burch, J. P. Breen, F. C. Meunier, *Appl. Catal. B*, 39 (2002) 283.
- [2] L. Olsson, E. Fridell, M. Skoglundh, B. Andersson, *Catal. Today*, 73 (2002) 263.
- [3] P. Koči, M. Marek, M. Kubiček, T. Maunula, M. Härkönen, *Chem. Eng. J.*, 97 (2004) 131.
- [4] W. S. Epling, L. E. Campbell, A. Yezerets, N. W. Currier, J. E. Parks II, *Catal. Rev.-Sci. Eng.* 46 (2004) 163.
- [5] M. Konsolakis, I. V. Yentekakis, *J. Catal.*, 198 (2001) 142.
- [6] J. Shibata, K.-I. Shimizu, A. Satsuma, T. Hattori, *Appl. Catal. B*, 37 (2002) 197.
- [7] E. F. Iliopoulou, A. P. Evdou, A.A. Lemonidou, I. A. Vasalos, *Appl. Catal. A*, 274 (2004) 179.
- [8] K. Arve, F. Klingstedt, K. Eränen, J. Wärnä, L.-E. Lindfors, D. Yu. Murzin, *Chem. Eng. J.*, 107 (2005) 215.
- [9] I. Sobczak, M. Ziolek, M. Nowacka, *Microporous Mesoporous Mat.*, 78 (2005) 103.
- [10] S.-C. Chen, S. Kawi, *Appl. Catal. B*, 45 (2003) 63.
- [11] L. F. Cordoba, W. M. H. Sachtler, C. M. de Correa, *Appl. Catal. B*, 56 (2005) 269.
- [12] I. V. Yentekakis, V. Tellou, G. Botzolaki, I. A. Rapakousios, *Appl. Catal. B*, 56 (2005) 229.
- [13] T. Maunula, J. Ahola, H. Hamada, *Appl. Catal. B*, 26 (2000) 173.
- [14] D. Tran, C. L. Aardahl, K. G. Rappe, P. W. Park, C. L. Boyer, *Appl. Catal. B*, 48 (2004) 155.
- [15] K. O. Haj, S. Ziyade, M. Ziyad, F. Garin, *Appl. Catal. B*, 37 (2002) 49.

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- [16] N. W. Cant, A. D. Cowan, I. O. Y. Liu, A. Satsuma, *Catal. Today*, 5' (1999) 473.
- [17] N. W. Cant, I. O. Y. Liu, *Catal. Today*, 63 (2000) 133.
- [18] V. Zuzaniuk, F. C. Meunier, J. R. H. Ross, *J. Catal.*, 202 (2001) 340.
- [19] I. O. Y. Liu, N. W. Cant, *J. Catal.*, 230 (2005) 123.
- [20] K. Eränen, F. Klingstedt, K. Arve, L.-E. Lindfors, D. Yu. Murzin, *J. Catal.*, 227 (2004) 328.
- [21] D. Haupt, K. Nord, K.-E. Egeback, P. Ahlvik, *SAE Techn. Pap. Ser.* 011882 (2004)
- [22] K. Nord, Thesis, Luleå University (Sweden) 2005.
- [23] M. Konno, T. Chikahisa, T. Murayama, M. Iwamoto, *SAE Techn. Pap. Ser.*, 920091 (1992).
- [24] C. Gaudin, D. Duprez, G. Mabilon, M. Prigent, *J. Catal.*, 160 (1996) 10.
- [25] T. Maunula; Y. Kintaichi, M. Inaba, M. Haneda, K. Sato, H. Hamada, *Appl. Catal. B*, 15 (1998) 291.
- [26] P. Bourges, S. Lunati, G. Mabilon, (CaPoC 4, N. Kruse, A. Frennet, J. M. Bastin, Eds), *Stud. Surf. Sci. Catal.*, 116 (1998) 213.
- [27] E. Joubert, T. Bertin, J. C. Menezos, J. Barbier, *Appl. Catal. B*, 23 (1999) L83.
- [28] J. March, in *"Advanced Organic Chemistry"*, 4<sup>th</sup> Edition, Wiley Interscience Publ. (1992).