

# Effect of the addition of Na to Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for the reduction of NO by C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> under lean-burn conditions

P. Vernoux,\* A.-Y. Leinekugel-Le-Cocq, and F. Gaillard

Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634 CNRS-Université Claude Bernard Lyon 1, 69622 Villeurbanne cedex, France

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## Abstract

A series of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts promoted by various concentrations of Na were prepared and tested for the SCR of NO by propene and propane under lean-burn conditions. The addition of Na markedly modifies the Pt catalytic behaviors. Under a C<sub>3</sub>H<sub>8</sub>/NO/O<sub>2</sub> atmosphere, the presence of Na leads to a drastic decrease of the C<sub>3</sub>H<sub>8</sub> and NO conversions. In contrast, under C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>, Na promotion improves the Pt catalytic performance. For high Na loadings (5 wt%), we observed an enhancement of the selectivity to N<sub>2</sub> and a widening of the operating temperature window. The promotional phenomena observed have been explained in terms of modification of the adsorption strengths of the various reactants on the metal surface. The Na effects should be to strengthen the Pt–electron-acceptor (O and NO) bonds and to weaken the Pt–electron-donor (C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>) bonds. The opposite effects observed by using propane or propene have been attributed to their different mechanisms of adsorption on Pt.

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**Keywords:** Selective catalytic reduction; SCR; NOx; Propene; Propane; Platinum; Sodium; Lean-burn conditions

## 1. Introduction

The pollution coming from automotive traffic is an increasing problem, especially in urban areas. Intensive research on the posttreatment of the exhaust gas led to the development of the three-way catalytic converters (TWC) which are simultaneously able to reduce NOx (NO and NO<sub>2</sub>) into nitrogen and to oxidize carbon monoxide and unburned hydrocarbons. These catalytic systems are efficient in the case of engines that are operated with a fuel/air ratio close to the stoichiometry, as the conventional gasoline ones. However, under lean-burn conditions such as encountered with diesel and lean-burn gasoline engines, TWC are ineffective to reduce NOx into nitrogen. Future legislations, such as EURO 4 standards in Europe, which will be active from 2005, make necessary the posttreatment of the Diesel exhaust gas. Then, the development of an effective solution for NOx removal under excess oxygen conditions is vital to the future of Diesel cars, the use of which is ever in-

creasing in Europe. Selective catalytic reduction (SCR) of NOx by hydrocarbon under lean-burn conditions has been the subject of intensive research effort since it was demonstrated that hydrocarbons could be used as reducing agents. Among many investigated catalyst formulations, supported platinum-based catalysts have shown the highest activities for NOx removal in real Diesel exhaust gas. Furthermore, this metal is active at low temperatures (between 200 °C and 350 °C) corresponding to that of a Diesel engine working in an urban cycle. Supported platinum catalysts are resistant to poisoning by steam or SO<sub>2</sub> present in the exhaust stream and exhibit a good thermal stability. However, these catalysts have two limitations, high selectivity to N<sub>2</sub>O and a narrow temperature window of activity. The development of the selective NOx reduction by hydrocarbons is hindered by the production of N<sub>2</sub>O because it is a powerful greenhouse gas, 200 times the worth of CO<sub>2</sub>. Much work tried to improve the selectivity to N<sub>2</sub> of platinum by varying the nature of the support [1], the platinum dispersion [1], and the preparation method [2] or by using various hydrocarbons [3]. Up to the present time, there is no practical effective solution.

Some interesting results have been obtained by adding alkalis to platinum supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Most of these studies have been carried with low concentrations of oxygen,

\* Corresponding author. LACE, UMR 5634 CNRS, Université Claude Bernard Lyon 1, Bat. Raulin/1, 43 Blvd du 11 Novembre 1918, 69622 Villeurbanne cedex, France

E-mail address: [philippe.vernoux@univ-lyon1.fr](mailto:philippe.vernoux@univ-lyon1.fr) (P. Vernoux).

near to the stoichiometry [4], or in the absence of oxygen [5,6]. Konsolakis et al. [4] have shown that the catalytic activity and selectivity of alumina-supported catalysts for the reduction of NO by propene are strongly promoted by alkali metals. At the stoichiometry, the addition of Na significantly increases the selectivity to N<sub>2</sub>. The influence of sodium on the catalytic properties of Pd and Rh for the NO reduction by propene near the stoichiometry has also been demonstrated. The addition of Na to Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts operated under simulated TWC conditions has a beneficial effect on both NO conversion and selectivity to N<sub>2</sub> [7]. When using Rh as a catalyst, doping by sodium promotes the NO reduction by C<sub>3</sub>H<sub>6</sub> in the absence of oxygen [8] and inhibits it in the presence of oxygen, under TWC conditions [9]. The Na-induced effect is explained in terms of variation of the electronic density of the metal and consequently of the adsorption strengths of the various reactants onto its surface. Under lean-burn conditions, Tanaka et al. [10] have shown that the addition of small amounts of Na (0.1 wt%) does not change the catalytic properties of Pt-supported SiO<sub>2</sub> catalysts. Burch et al. [11] have shown that the addition of K, Cs, and Ba to Pt/Al<sub>2</sub>O<sub>3</sub> catalysts does not improve the catalytic performance as the selectivity to N<sub>2</sub>, even it reduces the NOx conversion. Recently, Burch and Coleman [12] have investigated the reduction of NO by H<sub>2</sub> under lean-burn conditions. They found that the addition of low loadings of sodium (0.27–1 wt%) to Pt/Al<sub>2</sub>O<sub>3</sub> catalysts increases the NO conversion whereas large quantities of alkalis (5–10 wt%) decreases it. At low temperatures (90–150 °C), the selectivity to N<sub>2</sub> does not vary with the addition of sodium while at higher temperatures, it decreases. These studies seem to indicate that the dissociation of NO is not enhanced under lean-burn conditions to the same extent as was found by Konsolakis et al. [4] at the stoichiometry point.

The effect of the interaction between alkalis and metals on the catalytic properties has also been investigated by using the electrochemical promotion (EP). In this concept, the metallic catalyst is deposited, as a thin porous layer, onto a dense substrate of solid electrolyte which is a sodium conductor, as  $\beta'$ -alumina or NASICON (NA Super Ionic Conductor). By polarizing the metal/solid electrolyte interface with respect to a reference electrode, Na<sup>+</sup> ions are pumped from the electrolyte to the surface of the catalyst. EP provides an in situ control of the promoter concentration at the surface of the working metal catalyst by varying the applied potential. Thus, one may control reversibly metal coverage by alkali ions. Furthermore, the total amount of sodium, which is pumped out from the electrolyte structure, interacts with the catalyst. On the contrary, in the case of highly dispersed metal catalysts on an oxide support such as alumina or silica, a large part of chemically added sodium is in contact with the support only and not to the catalytically active phase. Yentekakis et al. [13] have studied the EP by Na of the Pt-catalyzed reduction of NO by propene in the absence of oxygen. Their results are in good agreement with those obtained with a chemical Na doping of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

catalysts [5]. Indeed, pumping sodium from the electrolyte to the Pt surface causes a drastic increase of the NO conversion and the selectivity to N<sub>2</sub>. At high loadings of Na, the system exhibits poisoning. We have recently shown [14] that electrochemical promotion can strongly enhance the catalytic activity and the selectivity to N<sub>2</sub> of Pt interfaced with NASICON for the NO reduction by propene under lean-burn conditions. NASICON, i.e., Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub>, presents a high conductivity by Na<sup>+</sup> ions even at low temperatures.

The aim of the present paper is to elucidate the influence of a chemical addition of sodium to Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for the SCR of NO by hydrocarbons under lean-burn conditions. Our objective is to correlate the promoting effect on the selectivity to N<sub>2</sub> and on NO reduction induced via electrochemical promotion [14] to a chemical Na doping of a supported Pt/alumina catalyst. Alumina is a good candidate as a support because of its thermal stability and high surface area. We have selected two hydrocarbons, propane and propene, which are major constituents of the hydrocarbon components of automotive exhaust. Furthermore, these two reductants, despite similar steric factors, exhibit quite different behaviors according to their strength of adsorption on platinum. Indeed, several studies [4,15–17] have shown that alkenes adsorb strongly and compete with oxygen, whereas alkanes adsorb weakly and therefore without any significant adsorption competition with oxygen. Propene adsorbs strongly on platinum because of the interaction of its  $\pi$ -orbitals with Pt d-bands [18]. Several studies have shown that  $\pi$ -bonded olefins are the central species in the mechanism of catalytic hydrogenation reactions [19,20]. For propane oxidation, the limiting step would be the cleavage of a primary C–H bond [21]. The greater reactivity of alkanes on the more open (1 × 2) reconstructions of Pt (110) compared to the closed-packed (111) surfaces of these metals is believed to result from the presence of a higher concentration of sites on (110) surfaces which promote alkane dissociation. Other reactions involving alkane reactants, including hydrogenolysis [22,23], are also reported to be structure sensitive.

This study reports the catalytic behaviors of sodium-doped Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for the NO reduction under lean-burn conditions. Catalytic performances of various catalysts were compared according to the Na loadings and the nature of the hydrocarbon, propane, or propene. Temperature-programmed desorption (TPD) measurements were carried out in order to determine the influence of the Na content on the oxygen reactivity with Pt.

## 2. Experimental

### 2.1. Preparation of the catalysts

Catalysts were prepared from a commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Rhodia-SPH569) containing traces of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Four catalysts, containing different loadings of sodium, have been

synthesized by the impregnation method, as follows. The support,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was suspended in aqueous solutions containing various appropriate concentrations of NaOH (Pro-labo, 99% purity). Water was removed under reduced pressure at 60 °C. After drying overnight in air at 120 °C and crushing, the resulting powder was impregnated with a solution of PtCl<sub>4</sub> (Alfa Aesar, 99.9% purity) in order to yield 0.9 wt% Pt metal loading. Water was removed as in the first step. Then, the powdered catalyst was dried overnight at 120 °C, crushed, and calcinated under flowing oxygen (10 L h<sup>-1</sup>) at 500 °C for 2 h in order to perform precursor decomposition. After cooling and purging under nitrogen, the catalyst was reduced under flowing hydrogen (10 L h<sup>-1</sup>) at 300 °C for 2 h. The BET surface of the samples was measured by N<sub>2</sub> adsorption at 77 K and found to be 135 m<sup>2</sup> g<sup>-1</sup> which is the area of the support. Chemical analysis of Pt and Na was performed by ICP. Chlorine was analyzed by ion-capture chromatography. The percentage of accessible metallic fraction (AMF) was determined by H<sub>2</sub>–O<sub>2</sub> titration.

### 2.2. Temperature-programmed desorption of oxygen

TPD experiments after adsorption of oxygen were performed with fresh catalysts in order to determine the influence of the Na addition on the Pt–O bond strength. About 100 mg of each sample was placed on a quartz wool bed in a U-shaped quartz reactor, positioned vertically in a programmable tube furnace. The catalyst was pretreated at 500 °C for 1 h under He in order to clean its surface. Then, it was reduced under H<sub>2</sub> at 300 °C for 1 h. After purging under He, the oxygen adsorption occurred at 300 °C for 1 h under pure oxygen atmosphere. Then, the sample was cooled at 25 °C under the same atmosphere. After purging under He for 15 min, the TPD was performed under He flow (1.75 L h<sup>-1</sup>) with a temperature ramp of 20 °C min<sup>-1</sup> up to 850 °C. TPD was monitored by a VG Gaslab 300 quadrupole mass spectrometer. Signals at  $m/e = 16, 18, 28, 32, 35, 36,$  and  $44$  amu corresponding to O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, N<sub>2</sub><sup>+</sup> or CO<sup>+</sup>, O<sub>2</sub><sup>+</sup>, Cl<sup>+</sup>, HCl<sup>+</sup>, and CO<sub>2</sub><sup>+</sup> ions, respectively, were recorded. Blank experiments with the support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by itself and doped with Na (5 wt%) were performed and we did not observe any oxygen or chlorine desorption. After calibration, we estimated the amount of oxygen desorbed per gram of catalyst.

### 2.3. Catalytic activity measurements

Catalytic testing was performed at atmospheric atmosphere in a conventional U-shaped fixed-bed quartz reactor. The catalyst sample (about 200 mg) was placed onto a fritted quartz and a K-type thermocouple was located near the catalytic bed. The reaction gases were mixtures of NO (Air Liquide, 7970 ± 160 ppm NO in He), O<sub>2</sub> (Air Liquide, 99.99% purity), C<sub>3</sub>H<sub>6</sub> (Messer, 7780 ± 230 ppm C<sub>3</sub>H<sub>6</sub> in He), or C<sub>3</sub>H<sub>8</sub> (Air Products, 8000 ± 80 ppm C<sub>3</sub>H<sub>8</sub> in He) and helium (Air liquide, 99.999% purity) which

was used as the vector gas. The gas composition was controlled by mass-flow controllers (Brooks, with accuracies better than 1%). In the following, the gas composition will be expressed in parts per million or percentage. The reactive mixture is a simulated diesel exhaust gas containing HC/NO/O<sub>2</sub>: 2000 ppm/2000 ppm/5%, with HC = C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>. The overall gas-flow rate was kept with He constant at 10 L h<sup>-1</sup> (±0.1 L h<sup>-1</sup>). The corresponding space velocity is 20,000 h<sup>-1</sup>. The reactants and products were analyzed by a NO<sub>x</sub> (NO and NO<sub>2</sub>) analyser (Cosma, Topaze 3000) and an on-line microgas chromatograph (Varian CP2003). Before these analyses, the water produced by the catalytic reactions was trapped by an electrogas cooler (M&C Products, ECP1000-G). The microchromatograph was composed of two modules, each one equipped with a thermal conductivity microdetector. The first module enabled the separation of CO<sub>2</sub>, N<sub>2</sub>O, and the hydrocarbon (C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>) by using a Poraplot U column (10 m length and 0.32 mm in internal diameter) heated at 60 °C. The second one was equipped with a molecular sieve heated at 90 °C (10 m length and 0.32 mm in internal diameter) preceded by a back-flush column. This module analyzed O<sub>2</sub>, N<sub>2</sub>, and CO. The overall duration of one analysis was only 110 s.

Carbon and nitrogen mass balances were found to be within 2%. Blank experiments have shown that the fritted quartz was catalytically inert up to 600 °C. We have also investigated the catalytic performances of the bare support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Catalytic performances were studied as follows:

- in situ reduction by H<sub>2</sub> at 300 °C for 1 h,
- cooling from 300 to 200 °C under a flow of helium,
- introduction of the reactive mixture at 200 °C,
- heating from 200 to 500 °C at 1 °C min<sup>-1</sup>,
- plateau at 500 °C for 10 h,
- cooling from 500 to 200 °C at 1 °C min<sup>-1</sup>.

The catalytic activities presented in this study correspond to those recorded during the decrease of temperature. Carbon monoxide was not detected, according to our lower detection limit, about 10 ppm. Then, we did not take into account the reactions of partial oxidation of the hydrocarbons into CO, those of reforming of the hydrocarbons with steam produced by the combustion, the water–gas shift reaction, and the oxidation of CO into CO<sub>2</sub>.

We calculated the production of N<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, which was defined as the percentage of NO converted to these products. The selectivity to N<sub>2</sub> represented the amount of the production of N<sub>2</sub> compared to that of N<sub>2</sub>O. In order to compare the catalytic behaviors of the various catalysts, we used these following parameters:

- $T_{50}$ , which corresponds to 50% conversion of the hydrocarbon,
- $T_{N_2}$ ,  $T_{N_2O}$ , and  $T_{NO_2}$  which are representative of the temperature at optimal conversion of N<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, respectively.

### 3. Results

#### 3.1. Catalyst characterization

Table 1 summarizes the data of the different catalysts. The Na loading varies from 0 wt% (sample Pt) to 0.12 wt% (PtNa0.12), 1 wt% (PtNa1), and 5 wt% (PtNa5). The chlorine analyses showed that the residual chlorine was almost unaffected by the initial pretreatment successively under O<sub>2</sub> and H<sub>2</sub> since the theoretical initial chlorine is 0.8 wt%. The chemical addition of Na decreases the Pt dispersion (Table 1) by decreasing the number of exchange sites during the procedure of Pt impregnation.

The variations of signals at  $m/e = 32$  and 36, representative of O<sub>2</sub> and HCl, respectively, versus temperature are plotted in Fig. 1. The catalyst Pt, which does not contain Na, presents a symmetrical peak of oxygen desorption centered at 658 °C (Fig. 1). The amount of oxygen desorbed corresponds to the AMF determined by H<sub>2</sub>–O<sub>2</sub> titration (Table 1). With the sample PtNa0.12, the oxygen desorption peak, which is less important due to a lower Pt dispersion, presents a maximum at 666 °C. With catalysts PtNa1 and PtNa5, we observed two oxygen desorption peaks. The first one, starting around 400 °C, was very broad. The second peak took place at higher temperatures corresponding

Table 1  
Properties of the 0.9 wt% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

Catalysts	Na loading (wt%)	Cl loading (wt%)	AMF (%) fresh catalysts	AMF (%) after pretreatment <sup>a</sup>
Pt	0	0.72	60	20
PtNa0.12	0.12	0.75	36	23
PtNa1	1	0.7	25	9
PtNa5	5	0.7	20	6.5

<sup>a</sup> After the pretreatment at 500 °C for 10 h under the reactive mixture.

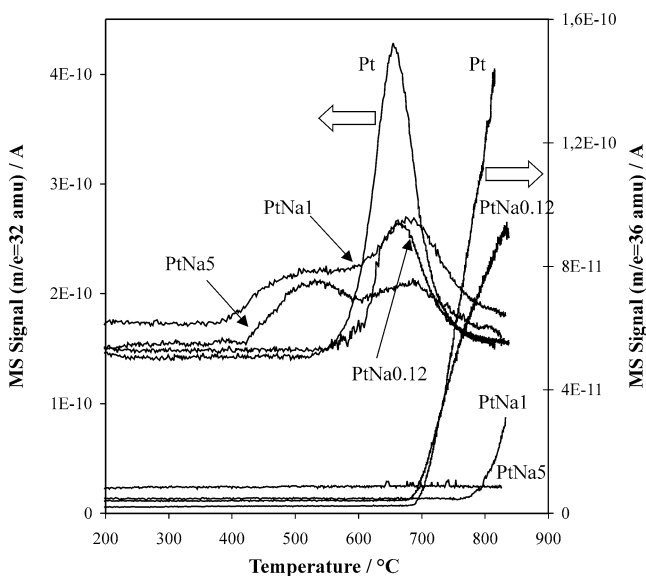


Fig. 1. Profiles corresponding to O<sub>2</sub><sup>+</sup> ion (at 32 amu) and HCl<sup>+</sup> (at 36 amu) detections during TPD of the catalysts, Pt, PtNa0.12, PtNa1, and PtNa5.

Table 2  
 $T_m$  and  $T_{50}$  values obtained with the Pt(Na)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

Catalysts	Na loadings (wt%)	$T_m$ (%)	$T_{50}$ (°C) (C <sub>3</sub> H <sub>8</sub> /NO/O <sub>2</sub> )	$T_{50}$ (°C) (C <sub>3</sub> H <sub>6</sub> /NO/O <sub>2</sub> )
Pt	0	658	338	268
PtNa0.12	0.12	666	327	248
PtNa1	1	679	454	238
PtNa5	5	689	529	229

$T_m$ , temperature for the top of the oxygen desorption peak.  $T_{50}$ , temperature for 50% hydrocarbon (propane or propene) conversion.

to those observed with Pt and PtNa0.12. The total amount of oxygen desorbed calculated from these TPD measurements corresponds to high Pt dispersion, higher than 80% for PtNa1 and close to 50% for PtNa5. These values are higher than those measured by H<sub>2</sub>–O<sub>2</sub> titration (Table 1). This indicates that the first oxygen evolution peak, recorded at low temperature, is not representative of oxygen adsorbed on Pt. Our assumption is that this oxygen could arise from the decomposition of a sodium peroxide (Na<sub>2</sub>O<sub>2</sub>). Indeed, the temperature of decomposition of this compound into oxygen and Na<sub>2</sub>O, i.e., 460 °C, corresponds to that of the oxygen desorption peak. By using the support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> doped with 5 wt% Na, we did not observe any oxygen desorption peak during TPD measurements. This could indicate that the presence of Pt is necessary to produce Na<sub>2</sub>O<sub>2</sub>. The role of Pt would be to adsorb oxygen which can spillover onto the Na-doped alumina support and then react with Na.

Table 2 summarizes the temperature,  $T_m$ , corresponding to the maximum of the oxygen desorption peak, related to the Pt–O chemical bond. The value of  $T_m$  increases when Na loading increases in the catalyst. One can suggest that this modification of  $T_m$  could be attributed to the variation of the platinum particle size which also increases with the Na amount in the catalyst (Table 1). However, several studies [24,25] have observed that the O<sub>2</sub> desorption temperature was higher on the small Pt particles relative to the large Pt particles. In addition, Briot et al. [26] have seen, by microcalorimetric measurements, a decrease in the heat of oxygen chemisorption when the platinum particle size increased. Consequently, the increase of  $T_m$  with the Na loading cannot be related to the increase of Pt particle size but to the promoting effect of Na. This clearly demonstrates that Pt particles are in interaction with Na and that this interaction strengthens the Pt–O chemical bond.

TPD measurements also show an emission of chlorine, as HCl, which is detected from 685 °C for the sample Pt. This confirms that chlorine which is coming from the platinum precursor has not been entirely eliminated during the pretreatment of the sample. Furthermore, a very high temperature is necessary to remove it under He. The poisoning of the catalysts by chlorine will be discussed during the next section on the catalytic activity measurements. An interesting point is that, when the Na loading is high, the temperature of HCl evolution significantly increases. For PtNa5, we did not detect HCl below 850 °C. This retention of the residual

chlorine by the catalyst has already been observed by Yentekakis et al. [30] by doping Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with Ba (15.2 wt%). The authors proposed the formation of a BaCl<sub>2</sub> phase which presents a good chemical stability. In our case, the presence of NaCl as a distinct phase at high Na loadings is probable. Yentekakis et al. [5] have already observed the presence of this compound with a Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst doped with 4.18 wt% Na.

### 3.2. Catalytic activity measurements under C<sub>3</sub>H<sub>8</sub>/NO/O<sub>2</sub> atmosphere

Despite the oxygen pretreatment at 500 °C and the in situ reduction, the performances of the fresh catalysts were not stable and improved with time on stream. We observed a hysteresis loop in a subsequent temperature increase–decrease cycle. This activation under the reactive mixture has already been reported in the literature. It has been linked to the elimination of chlorine coming from the platinum precursor [27–30]. Several studies [29,31] have demonstrated that the residual chlorine can be slowly removed under a reactive mixture. In addition, previous works have shown that the presence of water vapor accelerates the loss of chlorine from the catalyst surface [32,33]. Consequently after a pretreatment under a reactive mixture, the catalytic activity becomes similar to that of platinum-based catalysts prepared from a chlorine-free precursor. However, the presence of chlorine is not the only explanation for the activation of the catalytic performance under a reactive mixture because this phenomenon has already been observed with chlorine-free Pt-based catalysts [34,35]. Another possible origin is the Pt sintering under a reactive mixture. Denton et al. have shown [1] that the greater the decrease in dispersion, the greater the activation. This has been observed when platinum is supported on silica, but with alumina the effect is less significant [36,37].

In order to eliminate the residual chlorine and to stabilize the Pt dispersion, all the samples were pretreated under the reactive mixture at 500 °C for 10 h. Then, the catalytic performances were stable and we did not observe hysteresis any more between the increase and the decrease of temperature. We have observed a decrease of the Pt dispersion, after the pretreatment at 500 °C for 10 h under the reactive mixture (Table 1). The values of the Pt dispersion were the same ones as the catalyst pretreated under C<sub>3</sub>H<sub>8</sub>/NO/O<sub>2</sub> or C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>.

For the sample Pt, significant C<sub>3</sub>H<sub>8</sub> conversion starts at about 250 °C and becomes complete from 500 °C (Fig. 2). The oxidation of NO into NO<sub>2</sub> occurs at low temperatures and the associated conversion passes through a maximum at 289 °C, with a NO conversion into NO<sub>2</sub> of 47% (Fig. 3). Nitrogen dioxide is the main product since the conversions of NO into N<sub>2</sub> and N<sub>2</sub>O remain low (Fig. 4). The maximum NO conversion into N<sub>2</sub>O was only 5.3% and occurred at 360 °C while that of NO into N<sub>2</sub> was 2.6% at 395 °C. These catalytic behaviors are in good agreement with those de-

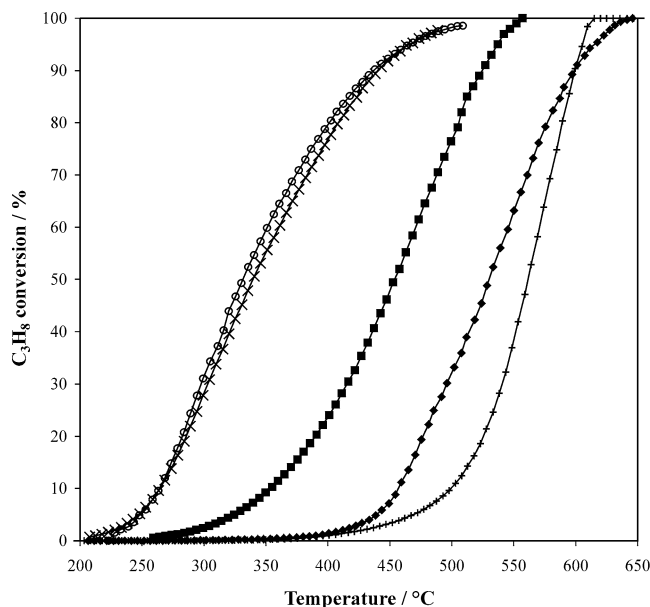


Fig. 2. Conversions of C<sub>3</sub>H<sub>8</sub> into CO<sub>2</sub> as a function of temperature for catalysts Pt (×), PtNa0.12 (○), PtNa1 (■), PtNa5 (◆), and Al<sub>2</sub>O<sub>3</sub> (+). Reactive mixture: C<sub>3</sub>H<sub>8</sub>/NO/O<sub>2</sub>.

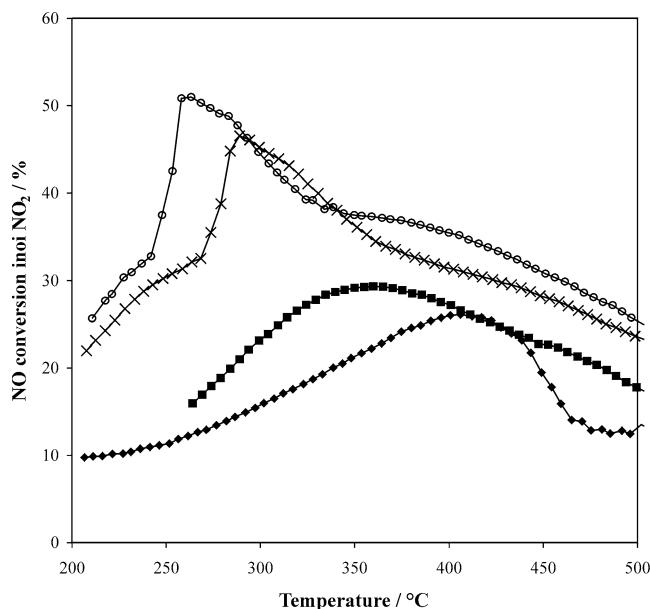


Fig. 3. Conversions of NO into NO<sub>2</sub> as a function of temperature for catalysts Pt (×), PtNa0.12 (○), PtNa1 (■), and PtNa5 (◆).

scribed in the literature [38,39]. The addition of moderate amounts of Na, as for catalyst PtNa0.12, slightly promotes the catalytic activity (Table 2). The promotional effect is particularly marked for the NO oxidation into NO<sub>2</sub> since the conversion maximum occurs at a lower temperature, 263 °C instead of 289 °C with Pt, and is slightly higher. However, when the Na loading increases, the catalytic activity drastically decreases. The *T*<sub>50</sub> value for propane conversion increases from 338 °C for Pt to 454 °C for PtNa1 and 529 °C for PtNa5. The catalytic performance of the sample PtNa5

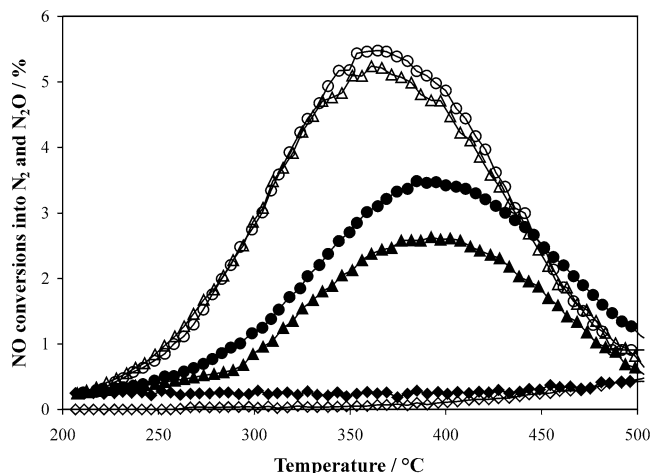


Fig. 4. Conversions of NO into N<sub>2</sub>O and N<sub>2</sub> as a function of temperature for catalysts Pt (Δ,▲), PtNa0.12 (○,●), and PtNa5 (◇,◆). Reactive mixture: C<sub>3</sub>H<sub>8</sub>/NO/O<sub>2</sub>.

Table 3

$T_{N_2}$ ,  $T_{N_2O}$ , and  $T_{NO_2}$  values and associated maximum NO conversion into N<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub> obtained with the Pt(Na)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts under C<sub>3</sub>H<sub>8</sub>/NO/O<sub>2</sub>

Catalysts	$T_{N_2}$ /conversion (%)	$T_{N_2O}$ /conversion (%)	$T_{NO_2}$ /conversion (%)
Pt	395/2.6	360/5.3	289/47
PtNa0.12	391/3.5	364/5.5	263/51.5
PtNa1	–	–	362/29.5
PtNa5	–	–	409/25

$T_{N_2}$ , temperature for the maximum NO conversion into N<sub>2</sub>.  $T_{N_2O}$ , temperature for the maximum NO conversion into N<sub>2</sub>O.  $T_{NO_2}$ , temperature for the maximum NO conversion into NO<sub>2</sub>.

for the C<sub>3</sub>H<sub>8</sub> combustion is comparable to that of the support itself (Fig. 2) whereas the Pt dispersion is 20% (Table 1). In the same way, the NO oxidation is considerably inhibited by the presence of Na (Table 3). The maximum NO conversion into NO<sub>2</sub> is divided by a factor 2 with an addition of 5 wt% of Na (PtNa5) and it is reached at a temperature 120 °C higher than that measured with Pt. Let us note that, whatever the catalyst, the maximum NO conversion into NO<sub>2</sub> always takes place before that the propane conversion becomes significant. With PtNa1 and PtNa5 samples, the conversion of NO into N<sub>2</sub> and N<sub>2</sub>O is negligible below 500 °C. Then, the values of the selectivity to N<sub>2</sub> are not significant.

### 3.3. Catalytic activity measurements under a C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub> atmosphere

The catalytic performances of the four samples are presented on Figs. 5–9. The catalytic behavior of Pt is similar to that reported in the literature for Pt-based catalysts [1,3]. The propene oxidation (Fig. 5) is strongly temperature dependent and is complete from 285 °C. The production of N<sub>2</sub> passes through a maximum of 19.6% at 270 °C (Fig. 6), temperature that corresponds to the 50% conversion of propene, while that of N<sub>2</sub>O reaches 33% at 287 °C (Fig. 7), temper-

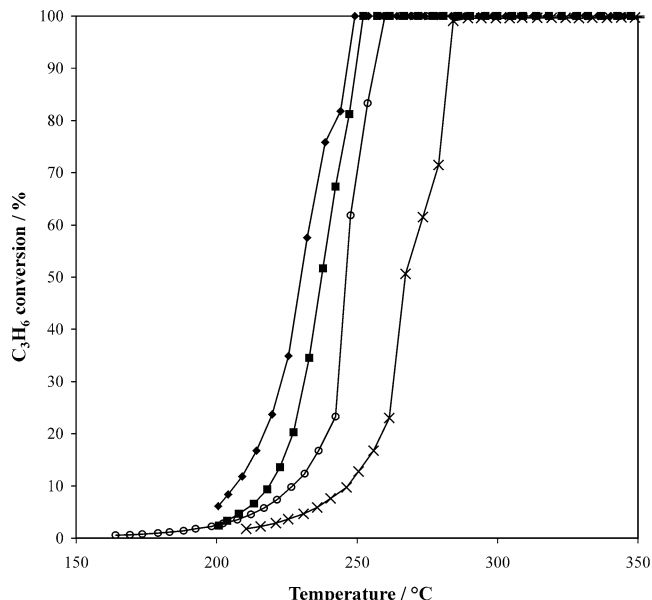


Fig. 5. Conversions of C<sub>3</sub>H<sub>6</sub> into CO<sub>2</sub> as a function of temperature for catalysts Pt (x), PtNa0.12 (○), PtNa1 (■), and PtNa5 (◆). Reactive mixture: C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>.

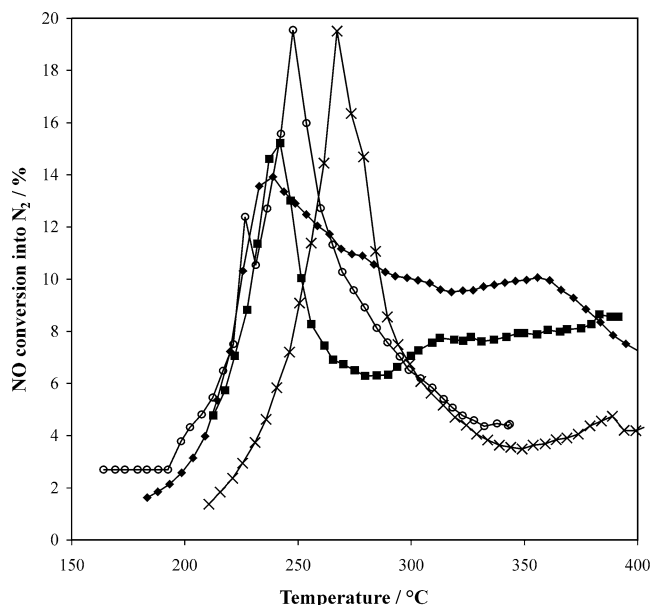


Fig. 6. Conversions of NO into N<sub>2</sub> as a function of temperature for catalysts Pt (x), PtNa0.12 (○), PtNa1 (■), and PtNa5 (◆). Reactive mixture: C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>.

ature at which the propene conversion becomes total. The operating temperature window, defined as the full width at half-maximum (FWHM) of the peak corresponding to NO conversion into N<sub>2</sub>, can be estimated to 34 °C in the range 260–294 °C. The production of NO<sub>2</sub> starts at 285 °C when the propene conversion is complete (Fig. 8). With propene as a reducing agent, the main reaction is the oxidation of propene. At temperatures sufficiently low to avoid the complete oxidation of C<sub>3</sub>H<sub>6</sub> into CO<sub>2</sub>, the NO reduction by propene can take place. At low C<sub>3</sub>H<sub>6</sub> conversions, the major

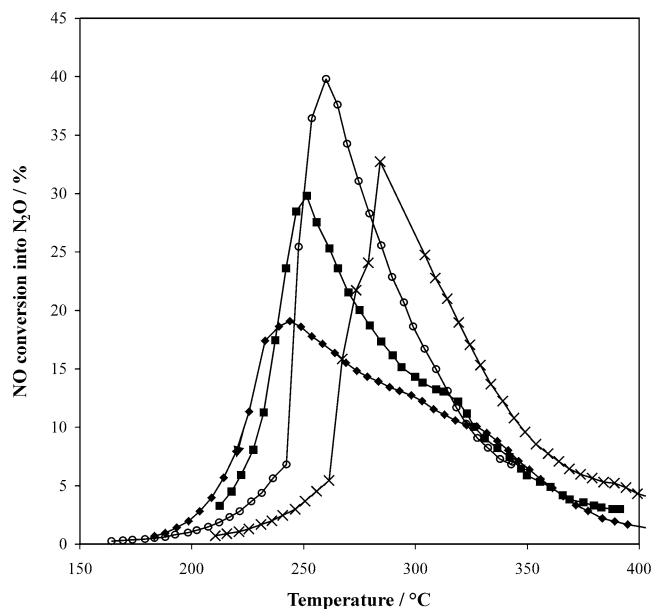


Fig. 7. Conversions of NO into N<sub>2</sub>O as a function of temperature for catalysts Pt (x), PtNa0.12 (O), PtNa1 (■), and PtNa5 (◆). Reactive mixture: C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>.

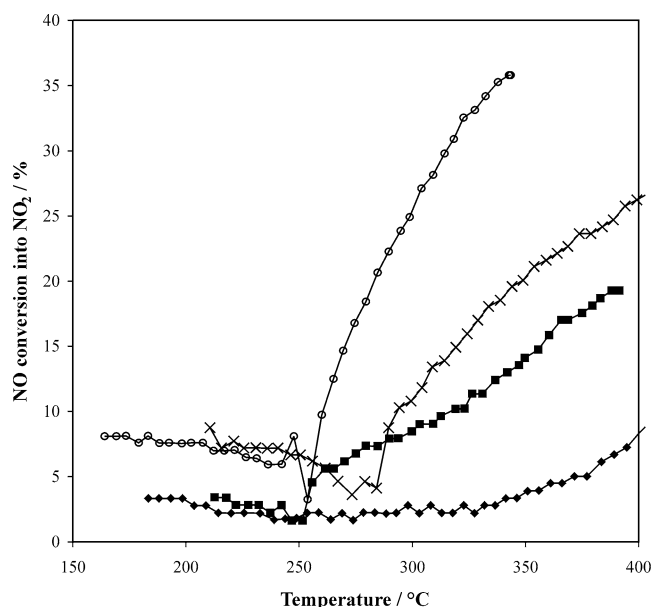


Fig. 8. Conversions of NO into NO<sub>2</sub> as a function of temperature for catalysts Pt (x), PtNa0.12 (O), PtNa1 (■), and PtNa5 (◆). Reactive mixture: C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>.

product is N<sub>2</sub> (Fig. 9). As soon as the temperature exceeds  $T_{50}$ , NO is mainly reduced into N<sub>2</sub>O.

The C<sub>3</sub>H<sub>6</sub> conversion is improved by the addition of Na (Fig. 5). The value of  $T_{50}$  linearly decreases with the Na loading (Table 2). Despite a lower Pt dispersion, the catalyst PtNa5 exhibits a complete propene conversion from 249 °C instead of 285 °C with Pt. The NO conversion into N<sub>2</sub> is shifted toward lower temperatures with the presence of Na (Fig. 6 and Table 4). The same trend is observed for the NO conversion into N<sub>2</sub>O (Fig. 7 and Table 4). With the sample

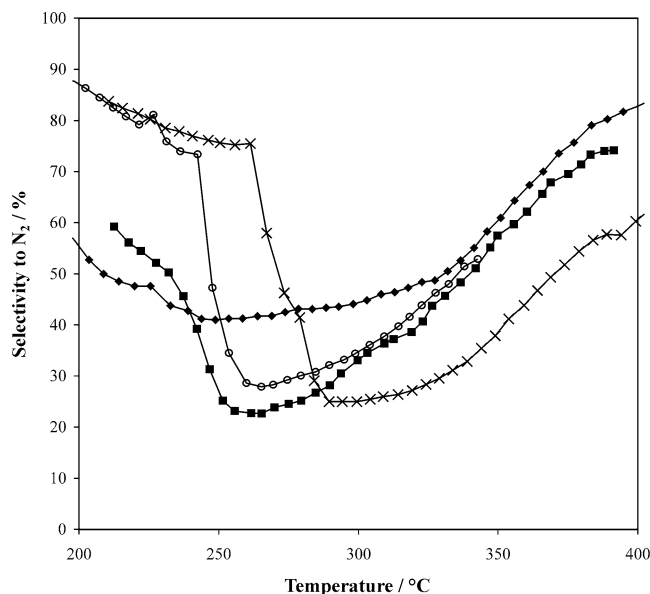


Fig. 9. Variation of the N<sub>2</sub> selectivity as a function of temperature for catalysts Pt (x), PtNa0.12 (O), PtNa1 (■), and PtNa5 (◆). Reactive mixture: C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub>.

PtNa0.12, the maximum NO conversion into N<sub>2</sub> does not vary, whereas it slightly decreases for higher Na loadings. We estimated the turnover frequency (TOF) of NO consumption at the temperature corresponding to the maximal overall NO conversion (Table 4). The TOF values were calculated by using the dispersion of catalysts which have been pretreated under reactive mixtures at 500 °C for 10 h. The addition of Na increases TOF of NO which passes through a maximum for 1 wt% Na (Table 4). For high Na loadings, the FWHM significantly increases. Let us note that the maximum NO conversions into N<sub>2</sub> observed with catalysts PtNa1 and PtNa5 take place at temperatures that do not correspond to the  $T_{50}$  values (Tables 2 and 4). With the sample PtNa0.12, the N<sub>2</sub>O and NO<sub>2</sub> productions are promoted (Figs. 7 and 8). On the contrary, the presence of a higher Na loading inhibits the conversion of NO into NO<sub>2</sub>. Optimum performance is observed for catalyst PtNa5, characterized by  $T_{50} = 229$  °C (39 °C lower than for the unpromoted catalyst Pt),  $T_{N_2} = 240$  °C (30 °C lower than Pt),  $T_{N_2O} = 244$  °C (43 °C lower than Pt), and a very low conversion to NO<sub>2</sub> in the temperature domain 200–400 °C. Furthermore, the sample PtNa5 presents two interesting properties:

- its operating temperature window is very wide; i.e., the N<sub>2</sub> production continues even after the complete oxidation of propene (Fig. 6). The NO conversion into N<sub>2</sub> is significant until 400 °C while that of N<sub>2</sub>O is higher than 10% until 325 °C;
- the selectivity to N<sub>2</sub> is higher than that of the unpromoted catalyst (Fig. 9). In the temperature range 250–325 °C, the C<sub>3</sub>H<sub>6</sub> conversion is complete. The NOx conversion gradually decreases from 30 to 20% with a selectivity to N<sub>2</sub> that increases from 41 to 51%.

Table 4

$T_{N_2}$ ,  $T_{N_2O}$  values and associated maximum NO conversion into  $N_2$ , and  $N_2O$  obtained with the Pt(Na)/ $\gamma$ - $Al_2O_3$  catalysts under  $C_3H_6/NO/O_2$

Catalysts	$T_{N_2}$ /conversion (%)	$T_{N_2O}$ /conversion (%)	TOF NO ( $10^{-2} s^{-1}$ ) at temperature of optimal NO conversion
Pt	270/19.6	287/33	14.7
PtNa0.12	250/19.6	262/40	15.7
PtNa1	243/15.2	250/29.5	34.7
PtNa5	240/14	244/19.5	30.8

$T_{N_2}$ , temperature for the maximum NO conversion into  $N_2$ .  $T_{N_2O}$ , temperature for the maximum NO conversion into  $N_2O$ .

The minimum value of the selectivity to  $N_2$  decreases for the sample PtNa0.12 which contains the lowest amount of Na. On the contrary, it increases with higher concentrations of Na from 1 wt%. These results clearly demonstrate that the SCR of NO by propene on Pt/ $\gamma$ - $Al_2O_3$  catalysts can be promoted by the addition of Na, even under lean-burn conditions. The operating temperature window of platinum can be drastically expanded and the selectivity to  $N_2$  increases.

## 4. Discussion

### 4.1. General

The aim of this work was to demonstrate if Na doping may influence the performance of Pt/ $Al_2O_3$  in NOx SCR under lean-burn conditions. Such an effect was detected and it is markedly different according to the nature of the hydrocarbon. By using propane as a reducing agent, the principal effects of Na are

- a slight enhancement of Pt activity, essentially for the oxidation of NO to  $NO_2$  for low Na amounts,
- an important decrease of the catalytic performances, at higher Na loadings (1–5 wt%).

When using propene,

- the presence of Na promotes the propene oxidation. The value of  $T_{50}$  decreases with the Na loading,
- the optimal NO conversions to  $N_2$  and  $N_2O$  are shifted toward lower temperatures according to the Na loading,
- the TOF of NO increases with Na loading and passes through a maximum for 1 wt% Na,
- the  $N_2O$  and  $NO_2$  productions are promoted for low amounts of Na (0.12 wt%) and inhibited for higher loadings,
- the selectivity to  $N_2$  slightly decreases for low Na concentration (0.12 wt%),
- for the sample PtNa5, which contains the highest concentration of Na (5 wt%), we observed an enhancement of the selectivity to  $N_2$  and also a widening of the operating temperature window.

The Na effects are spectacular and more marked for propane than for propene. For instance, when adding 5 wt% Na, the value of  $T_{50}$  increases by 191 °C with propane and decreases by 39 °C with propene. These opposite behaviors may not be attributed to a modification of Pt dispersion induced by the presence of Na since it is the same for both hydrocarbons. Consequently, we may attribute the considerable modification of the Pt catalytic properties to a chemical promotion of Pt by Na. The Na effects on the surface chemistry of Pt have already been observed, under TWC conditions, by Konsolakis et al. [4] for the NO reduction by propene. Their results are in good agreement with ours since they show that the presence of Na promotes the activity ( $C_3H_6$  and NO conversions) and the selectivity to  $N_2$ . However, under lean-burn conditions, Burch and Watling [11] have shown that the addition of K (2.42 wt%), Cs (7.25 wt%) and Ba (7.93 wt%) to Pt/ $Al_2O_3$  catalyst (1 wt% of Pt) does not improve the catalytic performance of Pt. By adding 2.42 wt% K, they observed an increase of the FWHM associated with a temperature of the maximum NOx conversion slightly shifted to lower temperatures (from 275 °C for the unpromoted catalyst to 265 °C), and a selectivity to  $N_2$  which was not modified. This is what we observed with 1 wt% Na. However, the authors have seen that the maximum NOx conversion decreased from 53 to 35%. This discrepancy may be due to differences in the Pt dispersion of the samples or because the space velocity used in this work ( $20,000 h^{-1}$ ) was much less than one used in Ref. [11] ( $87,000 h^{-1}$ ).

### 4.2. Origins of the chemical promotion of Na

The chemical promotion of Na to Pt suggests that Na is in interaction with Pt particles. Postreaction spectroscopic data, reported in the literature [13,40], indicate that Na is present at the catalyst surface in the form of chemical compounds such as  $Na_2CO_3$  or  $NaNO_3$ . One can think that NaCl might also be formed with the residual chlorine originating from the platinum precursor. This could explain why we observed, by TPD, a retention of chlorine when the Na loading is high. Our TPD measurements have demonstrated that Pt particles are in interaction with Na since the temperature of the oxygen desorption peak, which is related to the Pt–O chemical bond, increases when Na loading increases. These observations prove that the presence of Na, in interaction with Pt, strengthens the Pt–O chemical bond. Therefore, we may rationalize the promotional phenomena observed in terms of modification of the adsorption strengths of the various reactants on the metal surface. The ability of Na to enhance the NO adsorption on Pt has been demonstrated by Harkness et al. [41] by using NO TPD measurements. Furthermore, several studies have shown that the addition of Na promotes the NO dissociation [4,13]. According to Lang et al. [42], the Na effect should be due to an electrostatic field induced by the alkali cation. Taking into account that Na is present on the catalyst in the form of a chemical compound, this assumption supposes that the counteranion, such as  $NO_3^-$  or



$\text{CO}_3^{2-}$ , should exert a negligible opposite effect to cation. Konsolakis et al. [4] suggest that the electrostatic field due to the anion is low mainly due to its larger size compared to the cation. Recently, Yentekakis et al. [30] have clearly shown that the positive effect of Ba added to Pt/alumina catalysts, on the NO reduction by propene, overwhelms the negative effect of chlorine coming from the platinum precursor. We also observed in this present study, under  $\text{C}_3\text{H}_6/\text{NO}/\text{O}_2$  atmosphere, a promotional effect induced by the addition of Na despite the possible presence of NaCl on the catalyst. Konsolakis et al. [4] have exposed a similar beneficial effect of Na under TWC conditions by using  $\text{H}_2\text{PtCl}_6$  as a platinum precursor. Therefore one can conclude that, with the chemical promotion by  $\text{Na}^+$ , the nature of the counteranions seems not to be important.

Again referring to Lang et al. [42], the electrostatic field induced by  $\text{Na}^+$  should shift the  $\pi^*$ -orbital energy of a NO molecule adsorbed in the vicinity of an alkali ion below the Pt Fermi level. Then, valence electrons from the metal can populate the NO  $\pi^*$ -orbital energy, resulting in weakening of the N–O bond and a strengthening of the Pt–N bond. In a general way, the electrostatic field induced by the positive charge of sodium ions promotes the adsorption of electron acceptors such as NO and  $\text{O}_2$  and inhibits the adsorption of electron donors such as propene. Therefore, we can consider these modifications of the strength of the chemical bonds between Pt and the different adsorbates in order to elucidate the Na effect on the Pt catalytic performances. The opposite behaviors between propane and propene, depending on their strength of adsorption on Pt, induce different coverages of adsorbates on a Pt surface. This could explain that the addition of Na leads to opposite effects according to the hydrocarbon considered.

Under a  $\text{C}_3\text{H}_6/\text{NO}/\text{O}_2$  atmosphere, Burch and Watling [43] suggested that the Pt surface is predominately covered by carbonaceous species while the oxygen coverage is negligible. In contrast, under a  $\text{C}_3\text{H}_8/\text{NO}/\text{O}_2$  reactive mixture, the oxygen coverage on a Pt surface would be high [39]. Burch and co-workers [39,44] and Inaba et al. [45] have proposed that the mechanism of the NO<sub>x</sub> reduction on Pt/ $\text{Al}_2\text{O}_3$  catalysts is different according to the nature of the hydrocarbon. By using propene, NO<sub>x</sub> reduction only occurs on the Pt surface while, with propane, the reaction appears to occur via the formation of a surface nitrate species on the alumina support that activates the reductant.

When using propane as a reducing agent, our catalytic results confirm that the NO oxidation reaction is predominant since the propane conversion is low before the maximum conversion of NO into  $\text{NO}_2$ . The addition of Na strengthens the Pt–O bond, as confirmed by TPD measurements. One can think that this increase of the oxygen coverage saturates the Pt surface in oxygen and then inhibits the adsorption of  $\text{C}_3\text{H}_8$  and NO. This leads to a significant drop of the  $\text{C}_3\text{H}_8$  and NO conversions, as experimentally observed. Macleod et al. [9] proposed the same interpretation concerning the detrimental effect induced by Na addition with Rh-supported

alumina catalysts for the NO reduction by propene under TWC conditions. Contrary to the case of Pt, propene is not strongly adsorbed on Rh. Then, the authors suggest that an excessive promotion of oxygen adsorption due to the presence of Na inhibits the propene adsorption and oxidation. We have shown that the NO conversion to  $\text{NO}_2$  also decreases with the Na loadings. This could indicate that the strengthening of the Pt–O bond is much more pronounced than that of the Pt–NO bond because O is a much stronger electron acceptor than NO. Then, the NO coverage decreases leading to the drop of the NO conversion. At low loadings of Na (0.12 wt%), we observed a slight promotion of NO oxidation to  $\text{NO}_2$ . Let us note that we observed the same promotion by using propene with 0.12 wt% Na. One can suppose that the origin of this moderate activation could arise from a slightly higher Pt dispersion (Table 1). Indeed, we observed that the Pt dispersion of this sample decreases less than that of the catalyst which does not contain Na, during the pretreatment. Konsolakis et al. [4] have found similar results with their samples containing low loadings of Na.

Under a  $\text{C}_3\text{H}_6/\text{NO}/\text{O}_2$  atmosphere, the Pt surface is predominantly covered by carbonaceous species while the oxygen coverage is negligible. Therefore, the weakening of the Pt– $\text{C}_3\text{H}_6$  bond induced by Na addition should lead to an increase of O and NO coverages on Pt. This considerably promotes the catalytic behavior of Pt. The beneficial effect is much more pronounced for the  $\text{C}_3\text{H}_6$  combustion. This could be due to the fact that the oxygen coverage is much more increased than that of NO, because as already noted above, O is a much stronger electron acceptor than NO. For the highest Na concentration (5 wt%), the NO dissociation is favored by the presence of Na since we observed an increase of the selectivity to  $\text{N}_2$ . This confirms that the Na loading must be sufficiently important in order to promote the Pt catalytic behavior. This could explain why Tanaka et al. [10] observed that small amounts of Na (0.1 wt%) do not change the catalytic properties of Pt-supported silica catalysts. An interesting point is the widening of the operating temperature window observed with 5 wt% Na. Indeed, in the temperature range 250–325 °C when the propene conversion is total, the conversions of NO into  $\text{N}_2\text{O}$  and essentially into  $\text{N}_2$  remain significant whereas that into  $\text{NO}_2$  becomes negligible. This could indicate that a new mechanism occurs when the quantity of Na becomes important on the catalyst surface. This is also confirmed by the fact that the maximum NO conversions into  $\text{N}_2$  observed with catalysts PtNa1 and PtNa5 take place at temperatures that do not correspond to the  $T_{50}$  values. One can suggest that  $\text{NO}_2$  is trapped by the excess of Na present at the surface of alumina, in the form of sodium nitrates, and then is reduced by propene into  $\text{N}_2$  and  $\text{N}_2\text{O}$ .

#### 4.3. Correlation with electrochemical promotion using $\text{Na}^+$ -conducting solid electrolytes

One may correlate the assumption on the role of the  $\text{Na}^+$  electrostatic field with studies undertaken in electro-

chemical promotion with Na<sup>+</sup>-conducting solid electrolytes such as NASICON or  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>. We have recently observed [14] that the application of negative overpotentials through a Pt/NASICON interface significantly improves the Pt catalytic performances in the same oxygen-rich C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub> atmosphere used in this present study. Applying negative potentials to a Pt film on NASICON leads to a spillover of Na<sup>+</sup> ions from the electrolyte onto the Pt surface. At 295 °C, we have seen that the application of –100 mV leads to the enhancement of NO and C<sub>3</sub>H<sub>6</sub> conversions while the selectivity to N<sub>2</sub> increased from 41 to 61%. This promoting effect is quite similar to that observed in this study with 5 wt% Na. Therefore, the two ways of Na providing to Pt (electrochemically or chemically) lead to similar improvements of the Pt catalytic performances. Then, we may be certain that, in the present case, the promotion is mainly due to the effect of Na<sup>+</sup> on the platinum particles, rather than on the support. The comparison between the electrochemical and chemical Na addition suggests that the interactions between Pt and electrochemically supplied Na are many more than those with chemically added Na. Indeed, in this study the molar ratio of Pt to Na is 1:50 despite 100:1 in Ref. [14]. We tried to explain the observed electrochemically promotional effects [14] on the basis of the variation of the work function (WF) of Pt according to the rules proposed by Vayenas et al. [46,47]. These authors established that a change in the overpotential  $\Delta V_{WR}$  between the catalyst-electrode such as Pt and a solid electrolyte modifies the work function  $e\Phi$  of the gas-exposed surface of the porous catalyst-electrode film according to

$$\Delta(e\Phi) = e\Delta V_{WR}. \quad (1)$$

The variation of the Pt WF alters the strength of the chemical bonds between the metal and the adsorbates. The consequence of applying a negative overpotential, then supplying Na<sup>+</sup> to Pt, is to weaken the Pt chemical bonds with electron-donor adsorbates, such as C<sub>3</sub>H<sub>6</sub> and to strengthen those with electron-acceptor ones, such as O<sub>2</sub> and NO. According to the classification of C. Vayenas et al. [48], propane is also considered as an electron-donor, then the strength of the Pt–C<sub>3</sub>H<sub>8</sub> bond is supposed to decrease in the presence of Na. Therefore, whatever the mode of Na addition (electrochemical or chemical), the tentative interpretation of the Na effects operates in the same direction, namely a strengthening of the Pt–O and Pt–NO bonds and a weakening of the Pt–HC (HC = C<sub>3</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>) bonds.

## 5. Conclusions

The activity and nitrogen selectivity of platinum-supported alumina catalysts for the NO reduction by hydrocarbons under lean-burn conditions can be significantly modified by the addition of Na. The effect of the latter on the catalytic properties is markedly different according to the nature of the hydrocarbon. By using propane as a reducing

agent, the addition of Na is detrimental, leading to a drastic decrease of the C<sub>3</sub>H<sub>8</sub> and NO conversions. In contrast, with propene, Na promotion improves the activity of Pt. For high concentration of Na (5 wt%), we observed an enhancement of the selectivity to N<sub>2</sub> and also a widening of the operating temperature window. The Na effects on activity and selectivity of Pt have been correlated to modifications of the strength of the chemical bonds between Pt and the different adsorbates. The opposite effects observed by using propane or propene have been attributed to their different mechanisms of adsorption on Pt.

Similarities exist between the catalytic performances of an electrochemically promoted Pt film deposited on a NASICON electrolyte [14] and a powdered Pt-supported alumina promoted by chemical additions of Na. Whatever the mode of the Na addition (electrochemical or chemical), the interpretations of the Na effects operate in the same direction, namely a strengthening of the Pt–electron-acceptor (O and NO) bonds and a weakening of the Pt–electron-donor (C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>) bonds.

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