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## The chemistry of DeNO<sub>x</sub> reactions over Pt/Al<sub>2</sub>O<sub>3</sub>: The oxime route to N<sub>2</sub> or N<sub>2</sub>O

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### Abstract

The reactivity of 12 nitrogen compounds with different organic functions (nitro, nitrite, nitrate, oxime, isocyanate, amide, amine, nitrile) was investigated over a 1% Pt/ $\delta$ -Al<sub>2</sub>O<sub>3</sub> catalyst (mean metal particle size, 20 nm) in oxygen excess conditions (5% O<sub>2</sub> + 5% H<sub>2</sub>O). Two series of experiments, at temperatures ranging from 150 to 500°C, were carried out: (i) decomposition of the N compounds without any addition of NO and (ii) reduction of NO by these compounds. The results were compared with the catalytic behavior of the Pt catalyst in NO reduction by propene. Some of the N compounds as well as oxygenated products were identified by GC-MS in the NO + C<sub>3</sub>H<sub>6</sub> reaction. The nitrogen organic intermediates could be classified into two groups: (i) class 1 compounds, which react with NO at relatively high temperatures (300°C) with a high selectivity to N<sub>2</sub> (nitro, nitrite, nitrate, nitrile), and (ii) class 2 compounds, which reduce NO in the same temperature range as propene (200–225°C) with a selectivity of  $\approx$ 50% close to that of NO reduction by propene (oximes, amides, amines, and, to a lesser extent, isocyanate). A mechanism is proposed in which oxime species play a key role in NO reduction. N<sub>2</sub>O would be produced mainly by a Nef reaction (leading to ketones and N<sub>2</sub>O), whereas N<sub>2</sub> would be formed by successive steps starting with a Beckmann rearrangement of oxime species, with the byproducts of the N<sub>2</sub> formation being acids, alcohols, and nitrate and nitrite species.

**Keywords:** DeNO<sub>x</sub> catalysis over Pt; Organic nitrogen compounds in NO SCR; Oximes in DeNO<sub>x</sub> reaction; Reaction intermediates in catalytic NO reduction

## 1. Introduction

Automotive traffic constitutes one of the major sources of atmospheric NO<sub>x</sub> emissions (NO + NO<sub>2</sub>). Although NO<sub>x</sub> abatement has been technically solved for stroke spark-ignition engine by using three-way catalysts, the problem of meeting future regulations in 2008–2009 remains pending for lean-burn and diesel engines, due to the high O<sub>2</sub> content in the exhaust gases of these vehicles. NO<sub>x</sub> storage is certainly the most advanced technology for meeting the future regulations for light vehicles. In the 1990s, intensive studies were carried out to develop a technology based on the selective catalytic reduction (SCR) of NO by hydrocarbons. Numerous classes of catalysts (e.g., noble metals, nonnoble metals, oxides, zeolites) were investigated. Despite very interesting results obtained with each class of catalysts (very good activity or selectivity to N<sub>2</sub> at low or high temperatures), none of these studies have succeeded in finding a catalytic system sufficiently active, selective, and stable over the wide temperature range required for vehicles in real working conditions [1]. Nevertheless, due to the complexity of the NO<sub>x</sub> storage technology, SCR of NO<sub>x</sub> by hydrocarbons has not been completely abandoned, and increased knowledge of the mechanism of this reaction remains of the utmost importance.

The different mechanisms proposed in the 1990s were roughly classified as “dissociative” and “reduction” mechanisms [2,3]. The “dissociative” mechanism was proposed by Burch et al. for the reduction of NO by propene over noble metal catalysts, essentially Pt [1,4,5]. The reaction starts with a dissociative adsorption of NO yielding N and O species. The molecule of propene or hydrocarbons fragments issued from its adsorption on Pt surfaces react with O species to give CO<sub>x</sub> and H<sub>2</sub>O, whereas N may recombine into N<sub>2</sub> or react with a nondissociated NO molecule to give N<sub>2</sub>O. A more complex mechanism, involving a cooperative effect between the support and the metal, was proposed by Burch et al. to explain NO reduction by propane, which is much less reactive than propene in NO<sub>x</sub> SCR [6]. The reaction starts by an oxidation of NO into NO<sub>2</sub>, which would migrate onto the support to react with C<sub>3</sub>H<sub>7</sub> fragments issued from the dehydrogenative adsorption of propane. In the reaction scheme proposed by Burch et al., this final step leads to N<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub>, and H<sub>2</sub>O, but the intimate mechanism of the surface reaction is not described. The “dissociative” mechanism can account for most kinetic observations; it can be anticipated that, in the absence of any sites other than metal ones, this mechanism is the only one that works on noble metal catalysts. Similar reaction schemes were proposed for NO<sub>x</sub> SCR by hydrocarbons over Pt/SiO<sub>2</sub> catalysts [7]. When the metal is not fully

reduced, an “associative” mechanism can occur:  $M^{n+}$  ionic species can adsorb NO as dimer, dinitrosyl, or hyponitrite, which further decompose to  $N_2O$  or to N- and O-atoms [8].

Within the second type of mechanism,  $NO_x$  reduction starts with a reaction between NO or  $NO_2$  and the hydrocarbon to give a series of organic intermediates before ending to  $N_2$  or  $N_2O$ . To simplify, we can call these surface organic intermediate (SOI) mechanisms. Most of these mechanistic studies were supported by in situ FTIR identification of reaction intermediates adsorbed on the working catalyst. Four main classes of organic intermediates were detected:

- Isocyanates ( $R-NCO$ ).
- Nitriles ( $R-CN$ ) or isonitriles ( $R-NC$ ).
- Nitro ( $R-NO_2$ ), nitrito ( $R-ONO$ ), or nitrate ( $R-ONO_2$ ) compounds.
- Oximes ( $R-CH=NOH$ ), amines ( $R-NH_2$ ), or ammonia.

A close examination of the mechanistic proposals shows that these organic intermediates in  $NO_x$  reduction to  $N_2$  or  $N_2O$  are largely interdependent.

Detailed investigations centered on the identification and reactivity of isocyanate species were carried out over  $Al_2O_3$  and  $Cu/Al_2O_3$  [9–11]  $Rh/Al_2O_3$  [12],  $Ag/Al_2O_3$  [13],  $PtO_x$  [14],  $Ga_2O_3-Al_2O_3$  [15],  $Pt/Al_2O_3$  of an MCM-41 type structure [16], or  $Pt-Ba-Al_2O_3$  [17]. The transformation of isocyanate intermediates into  $N_2 + N_2O$  was ascertained by injecting isocyanate compounds as reducers into the  $NO + O_2$  mixture [18,19]. Among all of the possible reactions leading to isocyanates species, the most likely ones within the framework of SCR by HC are the reduction of nitro compounds, the oxidation of isonitriles, and the Hofmann rearrangement of alkylamides [20]. The chemical species that can be involved in the reduction of  $R-NO_2$  to  $R-N=C=O$  are CO,  $CH_x$  species issued from the decomposition of propylene, or a redox couple of the catalyst (probable with Cu, less probable with  $Pt/Al_2O_3$ ). Detection of isocyanate species requires a dry medium. Small amounts of  $H_2O$  are sufficient for their hydrolysis into amines. Nitrile or isonitriles have been detected over  $Cu/MFI$  [21–23],  $Cu/ZrO_2$  [24],  $Rh/Al_2O_3$  [25], and  $Pt/SiO_2$  [26], sometimes together with isocyanates [27,28]. Nitriles or isonitriles can be formed by oxime dehydration, reduction of nitro compounds (in parallel with isocyanates), or olefin ammoxidation [29]. Nitriles have essentially been observed in dry medium. In the presence of  $H_2O$ , they are hydrolyzed into amides.

Nitro, nitrito, or nitrate surface species are formed on Pt/SiO<sub>2</sub> [30], Pt/Al<sub>2</sub>O<sub>3</sub> [31], Cu-ZSM5 [32–34], Ce-ZSM5 [35, 36], and Ag catalysts [37,38]. Nitro, nitrito, and nitrate species can be formed by reaction of NO<sub>2</sub> (or adsorbed nitrates) on an alkane. With olefins, nitrosoalkenes can be formed and can isomerize into oximes or oxidize into nitro, nitrito, and nitrate species. The reactivity of nitro compounds as NO reducers over Pd/Al<sub>2</sub>O<sub>3</sub> was investigated by Oulad Haj et al. [39]. Gorce et al. [40] and Thomas et al. [41] stressed the role of the R–NO<sub>x</sub> nitrogen organic intermediates, but did not precisely describe their nature. According to these authors, R–NO<sub>x</sub> intermediates may be transformed into oxygenates, especially on CeZrO<sub>x</sub> catalysts.

Adsorbed amines or –NH species were sometimes detected together with nitriles or isocyanates [42]. Oximes were never observed on catalysts under SCR conditions, probably because they are highly reactive. Beutel et al. used acetone oxime to show that its reaction with NO and O<sub>2</sub> led mainly to <sup>15</sup>N<sup>14</sup>NO and <sup>15</sup>N<sup>14</sup>N. A similar isotopic study based on NMR detection of adsorbed species was performed by Wu and Larsen [43], who confirmed the main results of Beutel et al. They also showed that N<sub>2</sub>O was formed by reaction of adsorbed acetone oxime with nondissociated NO. Chen et al. [44] and Cant et al. [45,46] extended the work of Beutel et al. to other possible intermediates, including amines, nitriles, isocyanates, and nitroalkanes; however, most of these studies were carried out in closed or closed-loop reactors connected to FTIR, MS or NMR apparatus, that is, far from the usual conditions for SCR reactions. Finally, isocyanates and other organic species are suspected to be the precursors of carbonaceous deposits, which could be the reducer species, especially at high temperatures (typically above 300°C) [47,48].

The purpose of the present study was to investigate the reactivity of possible intermediates under conditions very close to those of DeNO<sub>x</sub> reactions. Major products (CO, CO<sub>2</sub>, NO<sub>x</sub>, N<sub>2</sub>O) were analyzed by GC and specific analyzers, whereas organic intermediates were analyzed by GC-MS. The study was conducted according to the following strategy: (i) identification of possible intermediates in the minor organic products of the NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> + H<sub>2</sub>O reactions, (ii) selection of the most probable intermediates X on the basis of the literature and of the known reactions that could occur on the catalyst; and (iii) reaction of X with O<sub>2</sub> + H<sub>2</sub>O or with NO + O<sub>2</sub> + H<sub>2</sub>O. As we show, oxidized compounds (not containing nitrogen) are formed: alcohols, aldehydes, ketones, and acids. The possible mechanisms in which propene is transformed into

oxygenates, more efficient NO reducers [49], are not examined here. The present investigation is restricted to SOI mechanisms via nitrogen intermediates.

## 2. Experimental

### 2.1. Apparatus and reaction conditions

The reaction was carried out in a flow reactor at a space velocity of 14,000 h<sup>-1</sup>. The gas composition was typically NO, 800–1000 ppm; reducer, 167–500 ppm; O<sub>2</sub>, 5%; and H<sub>2</sub>O, 5% diluted in He. The reducer-to-NO ratio 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 standard experiments with 800 ppm NO and 500 ppm propene.

The catalyst was initially heated in 5% O<sub>2</sub> + 5% H<sub>2</sub>O at 150°C (starting temperature) before admission of the complete reaction gas mixture. The temperature was then increased by steps of 25 or 50°C at a rate of 10°C min<sup>-1</sup> from 150 to 700°C. The catalyst performance was evaluated at each temperature after stabilization for 40 min. 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 be analyzed only by GC (Porapak Q column) in the upper range of concentration (200–400 ppm), and [N<sub>2</sub>] was most often obtained by the 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 selectivity,  $S_Z$ , of a product Z is defined as follows:

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

where n is the number of nitrogen atoms in the molecule of Z. A similar definition can be given for  $X_{CO_2}$ , with a 100% yield obtained for complete oxidation of the reducer into  $CO_2$ .

Organic intermediates were identified and analyzed by GC-MS in specific experiments following a procedure previously developed for similar analyses in DeNOx reaction over Cu/ZSM-5 [48], Pt/Al<sub>2</sub>O<sub>3</sub> [50], and Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts [51]. The gases issued from the reactor at a given temperature were trapped at -196°C for 1–4 h. Once closed, the trap was slowly heated by 70–80°C before being injected into the GC-MS apparatus. The gases were injected on-column (AT1 or GCQ Alltech; temperature programmed from 35 to 240°C at a rate of 5°C min<sup>-1</sup>). The peaks were detected and mass analyzed on a Finnigan Incos 500 quadrupole. Identification was made by comparison with a library of about 40,000 spectra and checked against pure compounds when available.

Table 1: Nitrogen-containing compounds tested as potential intermediates in the DeNOx reaction. Temperature of the saturator and corresponding concentration in the inlet gases

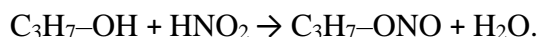
| Nitrogen compound       | T <sub>sat</sub> (°C) | Concentration (ppm) |
|-------------------------|-----------------------|---------------------|
| 1-Nitropropane          | -25                   | 460                 |
| 2-Nitropropane          | -25                   | 650                 |
| 2-Methyl-2-nitropropane | 5                     | 510                 |
| Propylnitrite           | -75                   | 450                 |
| Propylnitrate           | 34                    | 450                 |
| Ethanal oxime           | IW <sup>a</sup>       | 500                 |
| Acetone oxime           | IW <sup>a</sup>       | 1000                |
| Propanamide             | IW <sup>a</sup>       | 690                 |
| Urea                    | IW <sup>a</sup>       | 780                 |
| Ethyl isocyanate        | -63                   | 570                 |
| n-Propylamine           | IW <sup>a</sup>       | 1050                |
| Propane nitrile         | -50                   | 525                 |

<sup>a</sup> IW: dissolved and injected with water.

## 2.2. Catalyst and reagents

A 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> sample was prepared by impregnation of a  $\delta$ -alumina (SCS79 provided by Rhodia; 80 m<sup>2</sup> g<sup>-1</sup>; main impurities: Na, 590 ppm; Ca, 490 ppm; Fe, 315 ppm; S, 400 ppm) with an aqueous solution of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>. Before impregnation, the support was crushed and sieved to 0.1–0.3 mm. The Pt solution was evaporated to dryness, and the catalyst was dried at 120°C, calcined for 4 h at 700°C in air, and reduced for 3 h in H<sub>2</sub> at 450°C. The Pt dispersion (H<sub>2</sub> chemisorption, XRD, and TEM) was then 5% (Pt particle size of 15–25 nm). This low dispersion allowed maintenance of high catalyst stability whatever the reaction conditions and the reagent processed.

The standard reducer was propene at 500 ppm, with which preliminary experiments were carried out to evaluate the catalyst performance in DeNO<sub>x</sub> and to identify and analyze the different classes of minor organic intermediates. The nitrogencontaining compounds tested as potential intermediates in the DeNO<sub>x</sub> reaction are listed in Table 1. Most compounds were injected into the inlet gases (with 5% O<sub>2</sub> and 5% H<sub>2</sub>O) via a saturator held at a specific temperature, yielding about 500 ppm the nitrogen compound (Table 1). Some compounds were dissolved in H<sub>2</sub>O and injected together with water. All of these compounds were commercially available except propylnitrite, which was synthesized by reaction of propan-1-ol with sodium nitrite in sulfuric acid at 0°C, according to the following reaction:



The organic phase was washed with sodium carbonate and dried over sodium sulfate. The product was 97% pure (GC-MS, NMR, IR) with a yield of 90%.

## 2.3. Specific experiments with nitrogen compounds

Two series of experiments were carried out with the nitrogen compounds (NC) listed in Table 1:

- NC decomposition. The nitrogen compounds (concentrations given in Table 1) were injected in a stream of 5% O<sub>2</sub> + 5% H<sub>2</sub>O + He (10 L h<sup>-1</sup>) at 150°C. The temperature was increased in steps of 25 or 50°C. Gas-phase analyses (NO, NO<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub>, HC) were carried out after stabilization of the conversion at each temperature, which allowed us to calculate the conversion of NC into NO<sub>x</sub>: X<sub>NO<sub>x</sub></sub>, the conversion of NC into N<sub>2</sub>O: X<sub>N<sub>2</sub>O</sub>, and the conversion of NC into CO<sub>2</sub>: X<sub>CO<sub>2</sub></sub>. Some results for 1-nitropropane and acetone oxime are reported in Table 2.



Table 2: Decomposition of 1-nitropropane and acetone oxime in a stream of 5% O<sub>2</sub> + 5% H<sub>2</sub>O in helium. Conversions (%) of the nitrogen compounds into NO, N<sub>2</sub>O and CO<sub>2</sub>

| T (°C) | 1-nitropropane  |                             |                             | Acetone oxime   |                             |                             |
|--------|-----------------|-----------------------------|-----------------------------|-----------------|-----------------------------|-----------------------------|
|        | X <sub>NO</sub> | X <sub>N<sub>2</sub>O</sub> | X <sub>CO<sub>2</sub></sub> | X <sub>NO</sub> | X <sub>N<sub>2</sub>O</sub> | X <sub>CO<sub>2</sub></sub> |
| 150    | 58              | 10                          | 19                          | 24              | 17                          | 5                           |
| 200    | 56              | 12                          | 55                          | 20              | 48                          | 12                          |
| 225    | 50              | 13                          | 75                          | 9               | 75                          | 100                         |
| 250    | 45              | 17                          | 96                          | 22              | 54                          | 100                         |
| 300    | 60              | 22                          | 100                         | 40              | 19                          | 100                         |
| 350    | 61              | 10                          | 100                         | 46              | 17                          | 100                         |

• NO reduction by NC. The nitrogen compounds were injected in a stream of 800 ppm NO+5% O<sub>2</sub> +5% H<sub>2</sub>O+He at 200–350°C, chosen to have a high (or total) conversion of HC into CO<sub>2</sub>. Because nitrogen atoms in oximes and urea are extremely reactive, NO reduction by these compounds could be carried out at low temperature (200°C). The reactions were carried out in three steps: (i) NC was first introduced alone into the stream of O<sub>2</sub> + H<sub>2</sub>O + He, with concentrations of NO<sub>x</sub>, N<sub>2</sub>O, and CO<sub>2</sub> at T°C of C<sub>NO<sub>x</sub></sub>, C<sub>N<sub>2</sub>O</sub>, and C<sub>CO<sub>2</sub></sub>, respectively; (ii) 800 ppm NO was then added to the feed, and new outlet concentrations, C\*<sub>NO<sub>x</sub></sub>, C\*<sub>N<sub>2</sub>O</sub>, and C\*<sub>CO<sub>2</sub></sub>, were recorded; and (iii) NO injection was stopped to check that C\* outlet concentrations came back to C values. If no NO reduction occurred, then its theoretical outlet concentration would be NO<sub>x</sub> th = 800 + C<sub>NO<sub>x</sub></sub>. The amount of NO<sub>x</sub> reduced by NC is Q<sub>NO<sub>x</sub></sub> = 800 + C<sub>NO<sub>x</sub></sub> - C\*<sub>NO<sub>x</sub></sub> which corresponds to a percentage of NO<sub>x</sub> reduction of

$$\Delta X_{\text{NO}_x} = 100 \times \frac{Q_{\text{NO}_x}}{800} = 100 - \frac{C_{\text{NO}_x}^* - C_{\text{NO}_x}}{8} \quad (4)$$

The reaction chart for 1-nitropropane at 300°C (Fig. 1) shows that the amount of NO<sub>x</sub> produced in 1-nitropropane at 300°C is C<sub>NO<sub>x</sub></sub> = 130 ppm (28.5% nitropropane conversion into NO<sub>x</sub>). The amount of NO<sub>x</sub> remaining in gas phase after NO admission (800 ppm) is C\*<sub>NO<sub>x</sub></sub> =

680 ppm, whereas the theoretical amount should be 930 ppm. The amount of NO<sub>x</sub> reduced is then Q<sub>NO<sub>x</sub></sub> = 250 ppm, which corresponds to a percentage reduction of 32%.

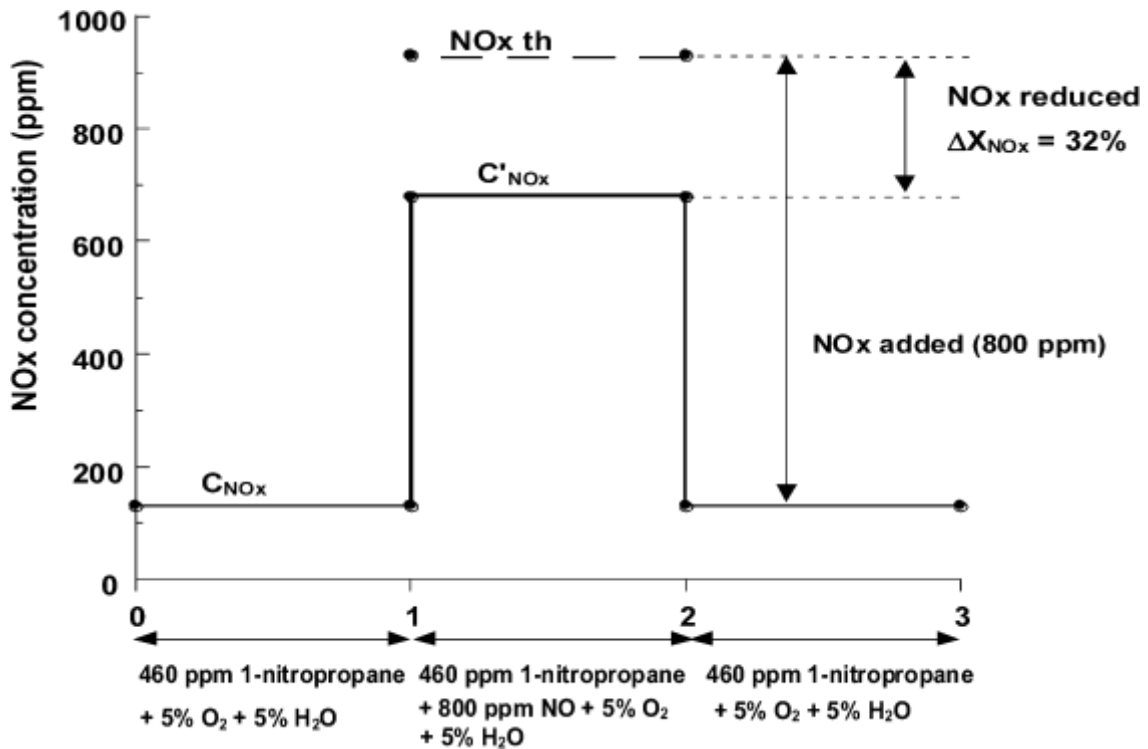
By analogy, ΔX<sub>N<sub>2</sub>O</sub> is defined as the conversion of NO+NC into N<sub>2</sub>O in step (ii),

$$\Delta X_{N_2O} = 100 \times \frac{C_{N_2O}^*}{[NO]_i + [NC]_i} \quad (5)$$

whereas ΔX<sub>CO<sub>2</sub></sub> is the conversion of NC into CO<sub>2</sub> in step (ii),

$$\Delta X_{CO_2} = 100 \times \frac{C_{CO_2}^*}{n[NC]_i} \quad (6)$$

where *n* is the number of carbon atoms in the NC molecule.



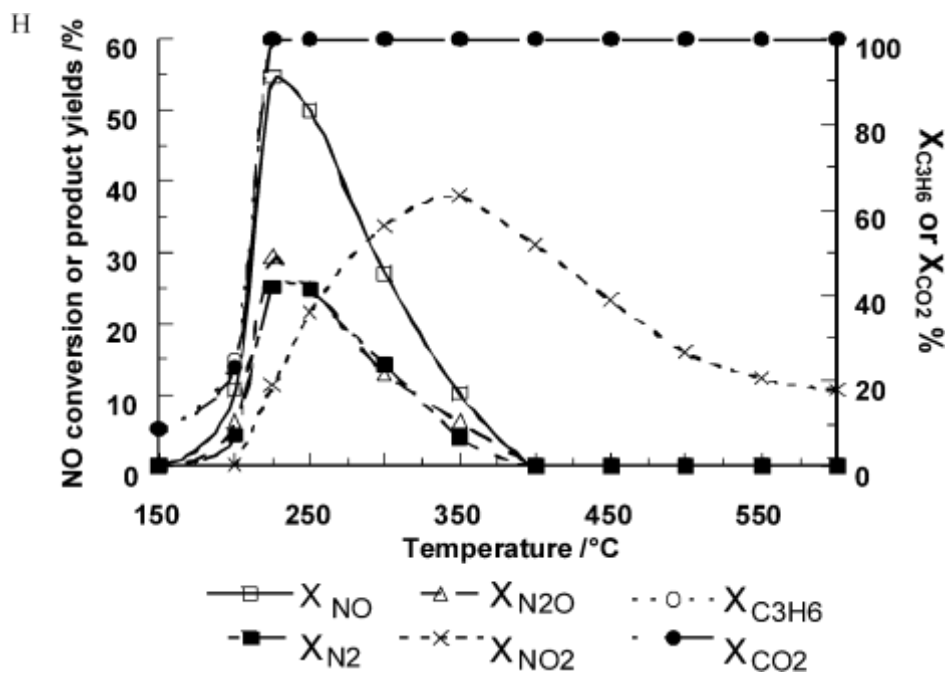
**Fig. 1.** Reaction chart between NO and 1-nitropropane (300°C). Phase 0–1: 1-nitropropane decomposition; phase 1–2: reduction of NO by 1-nitropropane; phase 2–3: again, 1-nitropropane decomposition

### 3. Results and discussion

#### 3.1. NO reduction by propene: identification of the minor products of reaction

Preliminary experiments carried out in the absence of reducer (800 ppm NO + 5% O<sub>2</sub> + 5% H<sub>2</sub>O, balance in He) showed that NO conversion started at 200°C, reached a maximum at 250–300°C (12.5% conversion), and decreased down to zero at 400°C. NO oxidation to NO<sub>2</sub> followed a similar profile with a maximum conversion (55%) at 250–300°C. Above 300°C, the NO<sub>2</sub> decreased and followed the thermodynamic tendency.

The reaction with propene was carried out in the 150–600°C temperature range. The support alone exhibited negligible activity below 450°C. A maximum NO<sub>x</sub> conversion of 17% was observed at 550°C, with 11% leading to N<sub>2</sub>O and 6% to N<sub>2</sub>. Fig. 2 shows the results obtained at R = 1.9 (800 ppm NO and 500 ppm C<sub>3</sub>H<sub>6</sub>) over Pt/Al<sub>2</sub>O<sub>3</sub>.



**Fig. 2.** NO reduction by propene in O<sub>2</sub> excess over Pt/Al<sub>2</sub>O<sub>3</sub> (800 ppm NO; 500 ppm C<sub>3</sub>H<sub>6</sub>; 5% O<sub>2</sub> and 5% H<sub>2</sub>O; space velocity: 14,000 h<sup>-1</sup>).

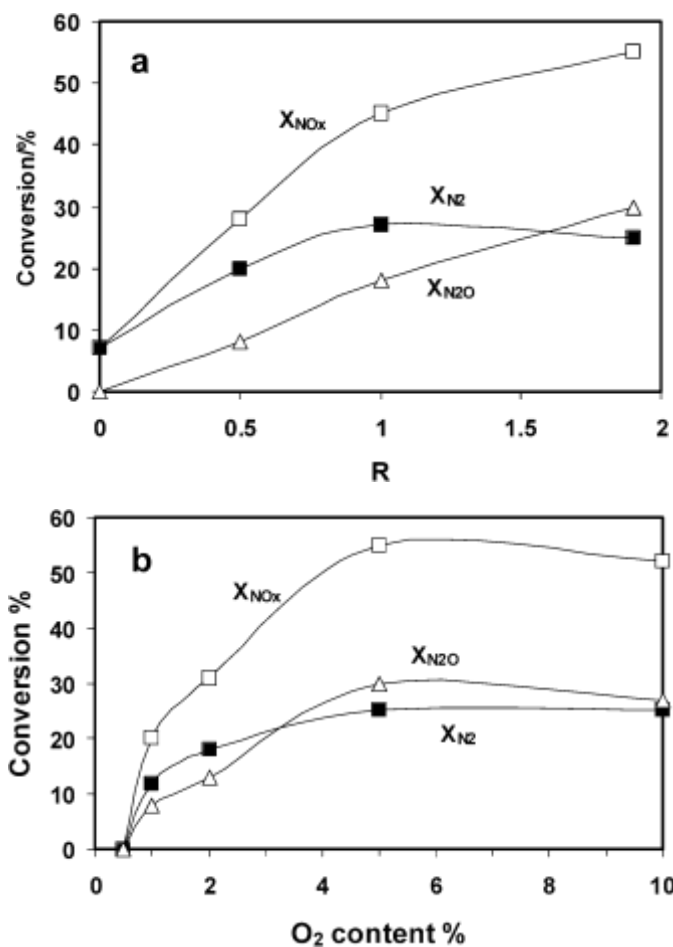
A sharp maximum of NO<sub>x</sub> conversion can be seen at around 225°C, with very close selectivities to N<sub>2</sub> and N<sub>2</sub>O. Within the pool of NO<sub>x</sub> (NO + NO<sub>2</sub>), the transformation of NO by oxidation into NO<sub>2</sub> was greatest at 350°C. Other experiments were carried out at R = 1 (1000 ppm NO and 333 ppm propene) and at R = 0.5 (1000 ppm NO and 167 ppm propene). The main characteristics of the reaction are as follows:

- Whatever the value of R, a maximum NO<sub>x</sub> conversion was always observed at 225°C. The conversion increased but the selectivity to N<sub>2</sub> decreased with R (Fig. 3a).
- The maximum NO<sub>x</sub> conversion coincided with achievement of complete combustion of propene. The carbon conversion to CO<sub>2</sub> was always very close to the propene conversion, demonstrating that the selectivity to CO was negligible.

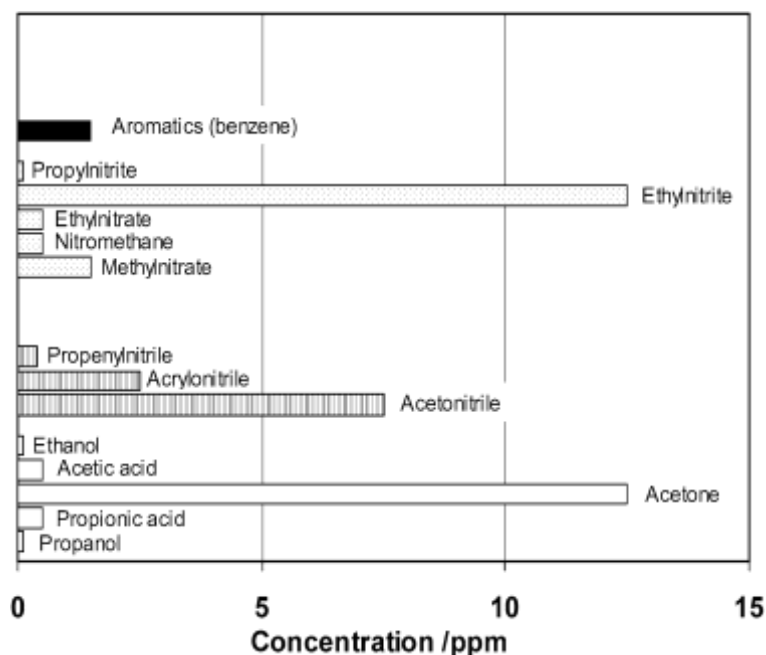
The reaction cannot occur in the absence of O<sub>2</sub>; if the water content was maintained constant (5%), the conversion was virtually nil for 0.5% O<sub>2</sub> (Fig. 3b). It passed through a maximum for 5% O<sub>2</sub> and slowly decreased between 5% and 10% O<sub>2</sub>. This is a very crucial point demonstrating that oxygen is necessary for the formation and/or decomposition of the reaction intermediates.

The minor products of reaction were identified and analyzed by GC-MS (Fig. 4). They were typically formed in minute amounts (ppm or sub-ppm). Their abundance decreased with increasing temperature, with maximum amounts compounds (about 40 ppm) obtained at 200°C. The products can be classified according to their relative abundance as follows:

- C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> (O-compounds): acetone >> acids >> alcohols.
- C<sub>x</sub>H<sub>y</sub>N<sub>t</sub> (N-compounds): acetonitrile > other nitriles.
- C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>t</sub> (O,N-compounds): alkylnitrites > alkylnitrates > nitro.
- C<sub>x</sub>H<sub>y</sub> (HC): aromatics (mainly benzene).



**Fig. 3.** (a) NO reduction by propene in the presence of 5% O<sub>2</sub> and 5% H<sub>2</sub>O at 225°C over Pt/Al<sub>2</sub>O<sub>3</sub>. Change with R of the total conversion ( $X_{NOx}$ ) and of the conversion of NOx to N<sub>2</sub> and to N<sub>2</sub>O. The values at R=0 correspond to the NO decomposition reaction (no propene added). (b) Effect of the O<sub>2</sub> content on NO reduction by propene at 225°C (500 ppm NO + 800 ppm C<sub>3</sub>H<sub>6</sub> + 5% H<sub>2</sub>O).

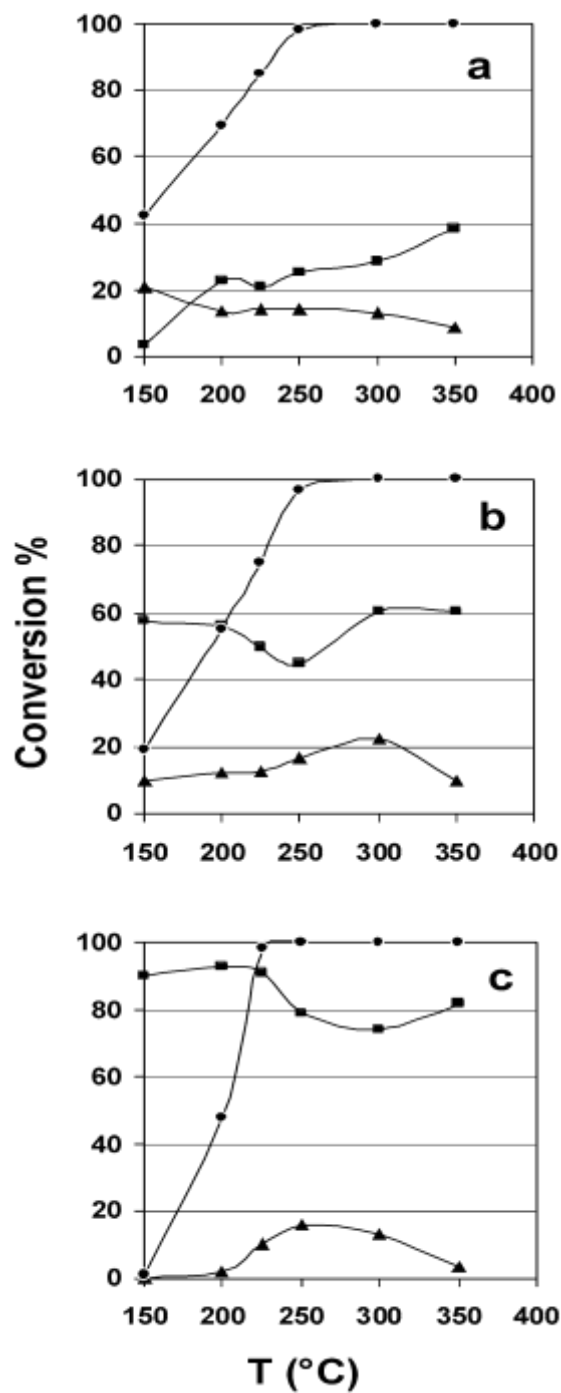


**Fig. 4.** Minor organic compounds formed in the NO reduction by propene at 200°C over Pt/Al<sub>2</sub>O<sub>3</sub> (800 ppm NO + 500 ppm C<sub>3</sub>H<sub>6</sub> + 5% O<sub>2</sub> + 5% H<sub>2</sub>O).

White bars: O-compounds; hatched bars: N-compounds; gray bars: N,O-compounds; black bar: aromatics hydrocarbons.

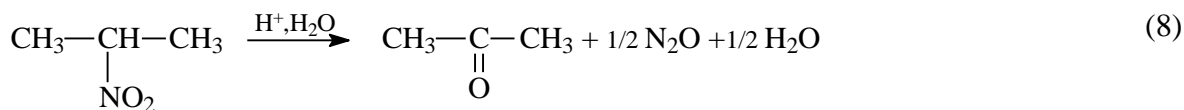
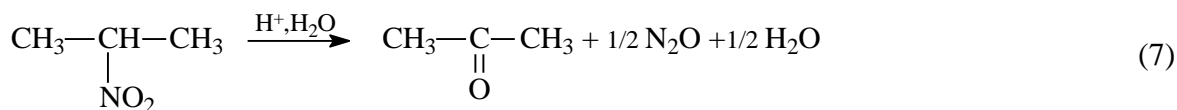
### 3.2. Reactivity of nitroalkanes, alkylnitrite, and alkylnitrate

The decomposition of selected nitroalkanes into NO<sub>x</sub>, N<sub>2</sub>O, and CO<sub>2</sub> is represented in Fig. 5. The hydrocarbon structure and the position of the nitro group in the molecule are predominant factors in its reactivity. The n-alkane skeleton is significantly easier to oxidize into CO<sub>2</sub> in the initial temperature range (150–200°C). The reverse situation can be observed for the C–NO<sub>2</sub> bond cleavage; 2-methyl-2-nitropropane loses its nitro group at very low temperature and leads to NO<sub>x</sub> and N<sub>2</sub>O exclusively. Above 250°C, the entire carbonaceous skeleton is oxidized into CO<sub>2</sub>; the nitro group is then transformed into NO<sub>x</sub>, N<sub>2</sub>O, and, most likely, N<sub>2</sub>. Fig. 5 shows that the sum NO<sub>x</sub> + N<sub>2</sub>O is particularly low with 1-nitropropane, indicative of a high selectivity to N<sub>2</sub> (66% for 1-nitropropane instead of 39% for 2-nitropropane and only 5% for 2-methyl-2nitropropane). The same tendency was observed by Oulad Haj et al. over Pd/Al<sub>2</sub>O<sub>3</sub> [39].

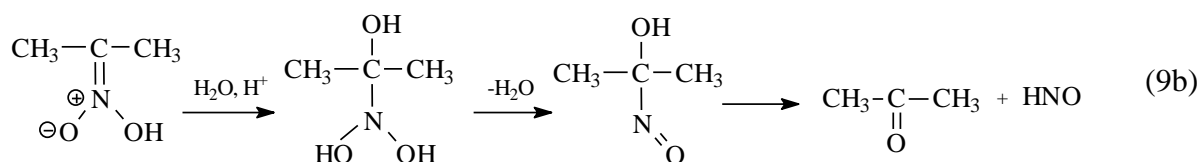
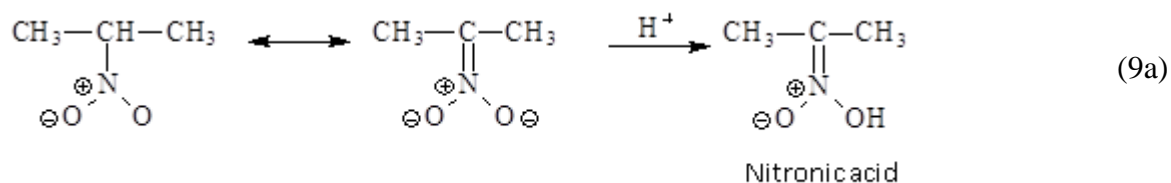


**Fig. 5.** Decomposition of different nitroalkanes over Pt/Al<sub>2</sub>O<sub>3</sub> in O<sub>2</sub> (5%) + H<sub>2</sub>O (5%): (a) 1-nitropropane, (b) 2-nitropropane, (c) 2-methyl-2-nitropropane; conversions to NO<sub>x</sub> (squares), N<sub>2</sub>O (triangles), and CO<sub>2</sub> (circles).

The formation of N<sub>2</sub>O can be explained by the protonassisted hydrolysis of nitro compounds into aldehydes (or ketones) and N<sub>2</sub>O (reaction known as Nef reaction [20,52]):



The first step of reaction (8) would be a proton-assisted isomerization of the conjugate base of 2-nitropropane into nitronic acid (Eq. (9a)), which in turn hydrolyses into acetone and HNO (Eq. (9b)). Nitrous oxide results from the dismutation of HNO (reaction (10)):



This mechanism implies H atom abstraction in  $\alpha$  of the nitro group and cannot occur with NO<sub>2</sub> bonded to a tertiary carbon. It is the reason why 2-methyl-2-nitropropane does not produce N<sub>2</sub>O in the 150–200°C range (Fig. 5). The Nef reaction occurs in competition with the reverse reaction of nitration, which leads to NO<sub>x</sub> and CO<sub>2</sub> after cleavage of the C–NO<sub>2</sub> bond. Although the differences in the C–N bond energy are relatively small (250 kJ mol<sup>-1</sup> in 1-nitropropane, 247 kJ mol<sup>-1</sup> in 2-nitropropane, and 245 kJ mol<sup>-1</sup> in 2-methyl-2-nitropropane), there is good correlation between these bond energies and the NO<sub>x</sub> formation in nitro compound decomposition; 2-methyl-2-nitropropane, which cannot give N<sub>2</sub>O via the Nef reaction and has the lowest C–N bond energy, decomposes mainly into NO<sub>x</sub> (75–90%; see Fig. 5c). Because



oximes may lead to nitronic acid (see Section 3.3), these nitrogen compounds are also likely intermediates to ketones and N<sub>2</sub>O via the Nef reaction.

Decomposition products of propylnitrite and propylnitrate between 150 and 350°C are shown in Fig. 6. The two molecules have a similar behavior, essentially giving NO<sub>x</sub> by rupture of the R–O–NO (nitrite) or of the R–O–NO<sub>2</sub> bond (nitrate). Practically no N<sub>2</sub>O is formed by the decomposition of propylnitrite and propylnitrate. This behavior is likely due to the low dissociation energy of the O–NO bond (168 kJ mol<sup>-1</sup>), which favors alcohol formation by the following reaction:

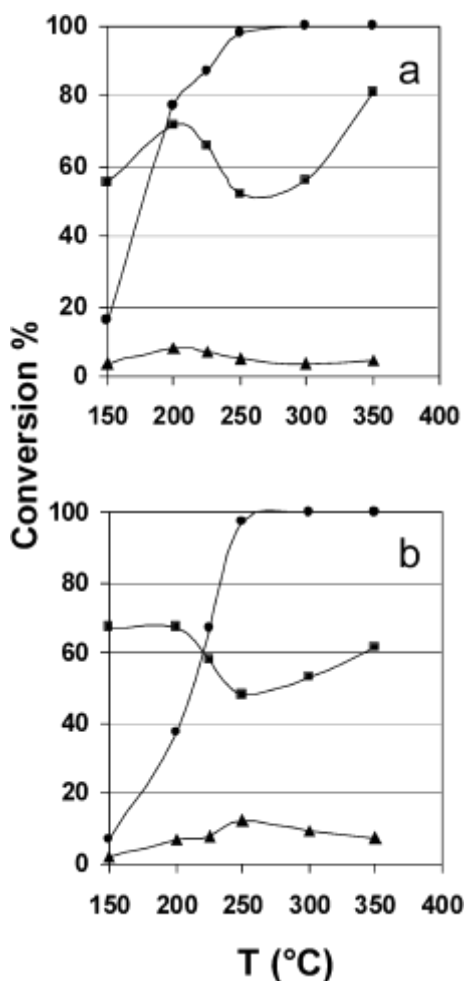


Fig. 6. Decomposition of propylnitrite (a) and propylnitrate (b) over Pt/Al<sub>2</sub>O<sub>3</sub> in O<sub>2</sub> (5%) + H<sub>2</sub>O (5%). Same symbols as in Fig. 5.

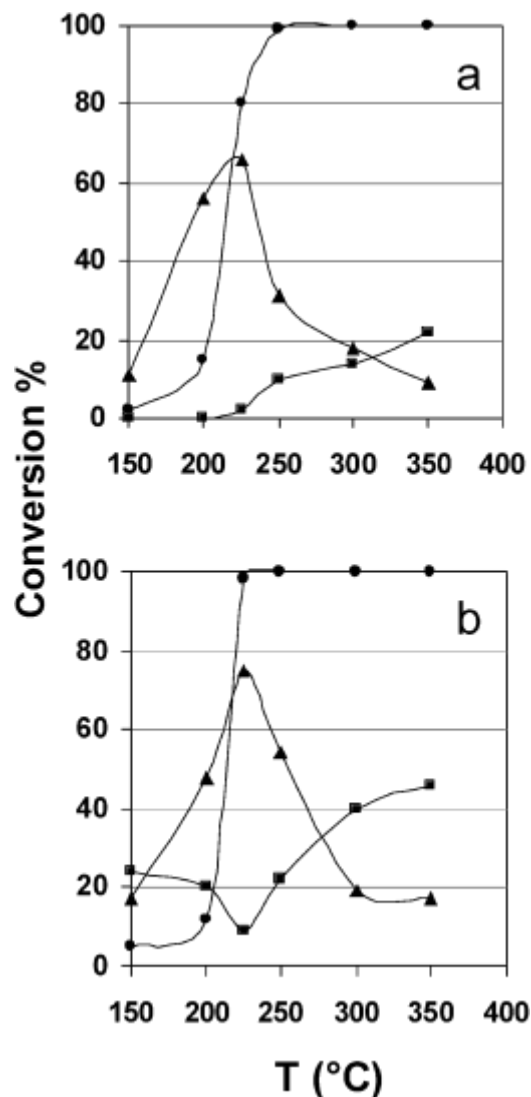
NO reduction by NC (NC = nitroalkanes, propyl nitrite, and propyl nitrate) was investigated by adding 800 ppm NO into the gas mixture NC + H<sub>2</sub>O + He (see Section 2.3). The results are reported in Table 3. Among the nitroalkanes, the compound with the nitro group borne by a secondary carbon (2-nitropropane) was the most reactive, allowing a 79% reduction of the NO added to the reactant flow.

Table 3: NO reduction by nitrogen-containing compounds (NC). The decomposition of the nitrogen compounds is evaluated in a first step in a mixture NC + 5% O<sub>2</sub> + 5% H<sub>2</sub>O + He. Then the NO reduction assisted by NC is determined by adding 800 ppm NO in the previous mixture. See details in Section 2.3

| N-compound              | T°C | $\Delta X_{\text{NO}_x}$ %<br>(Eq. 4) | $\Delta X_{\text{N}_2\text{O}}$ %<br>(Eq. 5) | $\Delta X_{\text{CO}_2}$ %<br>(Eq. 6) |
|-------------------------|-----|---------------------------------------|--|---------------------------------------|
| 1-nitropropane          | 300 | 32                                    | 12   | 100                                   |
| 2-nitropropane          | 300 | 79                                    | 10   | 100                                   |
| 2-methyl-2-nitropropane | 300 | 49                                    | 8  | 100                                   |
| Propyl nitrite          | 300 | 43                                    | 5  | 100                                   |
| Propyl nitrate          | 300 | 39                                    | 9  | 95                                    |
| Ethanal oxime           | 200 | 40                                    | 51   | 75                                    |
| Acetone oxime           | 200 | 77                                    | 65   | 45                                    |
| Propanamide             | 200 | 66                                    | 54   | 100                                   |
| Urea                    | 200 | 100                                   | 74   | 70                                    |
| Ethyl isocyanate        | 250 | 51                                    | 37   | 85                                    |
| n-propylamine           | 225 | 85                                    | 49   | 100                                   |
| Propanenitrile          | 300 | 32                                    | 8  | 100                                   |

### 3.3. Reactivity of oximes

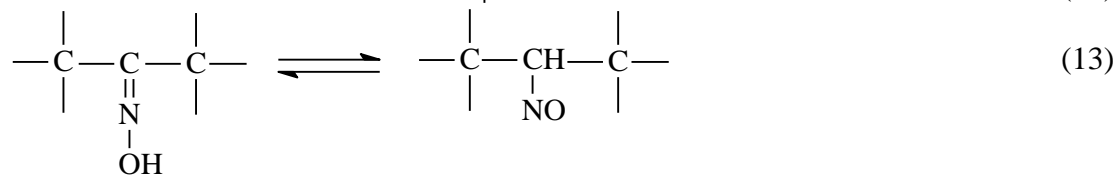
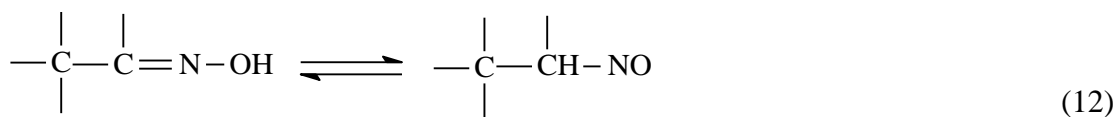
Two oximes were investigated: ethanal oxime and acetone oxime. Their decomposition products between 150 and 350°C are shown in Fig. 7.



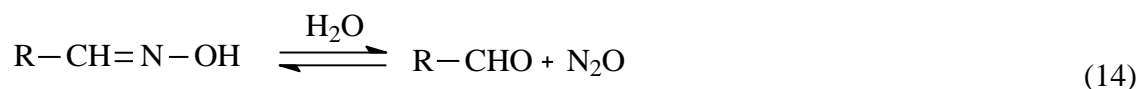
**Fig. 7.** Decomposition of ethanal oxime (a) and acetone oxime (b) over Pt/Al<sub>2</sub>O<sub>3</sub> in O<sub>2</sub> (5%) + H<sub>2</sub>O (5%). Same symbols as in Fig. 5.

In contrast with nitroalkanes, alkylnitrites, and alkylnitrates, the main reaction was the formation of N<sub>2</sub>O with a maximum between 60 and 80% at 225°C. At this temperature, ethanal oxime did not form any NO<sub>x</sub>; the only decomposition products were N<sub>2</sub>O and N<sub>2</sub>.

Oximes are tautomer forms of nitroso compounds:



Assuming that oxidation of nitroso into nitro compounds is fast, oxime decomposition should resemble that of nitroalkanes. As a result, the highest NO<sub>x</sub> production can be observed with acetone oxime giving rise to the most branched nitro compounds, in agreement with the results of Fig. 5. Nevertheless, the formation of nitrous oxide is specific to oxime hydrolysis, a probable route of oxime transformation:



The same reaction can occur by mild oxidation of oximes into nitronic acid further transformed into ketones (or aldehydes) and N<sub>2</sub>O as in the Nef reaction (Eq. (9)) [53]. Oxime hydrolysis leads to acetone and ethanal, which behave similarly to NO reducer (15% NO conversion at 200°C [54]). Consequently, the difference in behavior between the two oximes cannot be ascribed to the ketone or aldehyde formed in oxime hydrolysis. In contrast, ethanal oxime can undergo a dehydration reaction into nitrile:



Because the nitrile compound is strongly adsorbed via the C≡N triple bond, it could act as a poison of the catalyst.

Another important route of oxime transformation is the Beckmann rearrangement either into N-alkylformamides and amines or into amides. The selectivity of the rearrangement depends on the size of the migrating group. This route of oxime transformation will be further discussed as a possible route for N<sub>2</sub> formation.

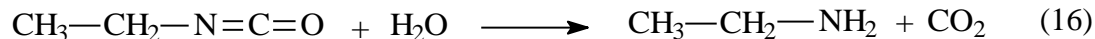
NO reduction by oximes was carried out at 200°C by adding 800 ppm NO in the same reactant feed streams (including O<sub>2</sub> and water) as those used for oxime decomposition. The results, presented in Table 3, show that oximes and specially acetone oxime were very good NO reducers; a 77% conversion was reached with acetone oxime despite the low temperature of reaction. However, the reduction led to a rather high selectivity in N<sub>2</sub>O while the oxime was far from being totally oxidized. To follow the possible intermediates of reaction, a GC-MS study of the products formed in NO reduction by oximes was carried out. Besides the gases (NO<sub>x</sub>, N<sub>2</sub>O, N<sub>2</sub>, and CO<sub>2</sub>), acetone was the main product of the reaction of acetone oxime/NO/O<sub>2</sub>/H<sub>2</sub>O over Pt/Al<sub>2</sub>O<sub>3</sub> at 200°C, while significant amounts of CH<sub>3</sub>-CN and ethanal were detected in the

products of ethanal oxime/NO/O<sub>2</sub>/H<sub>2</sub>O reaction. These results are in good agreement with the sequence of reactions (12)–(15) proposed above.

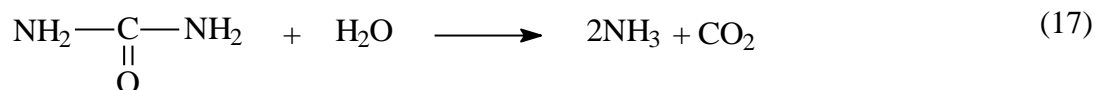
### 3.4. Reactivity of amides and isocyanates

The decomposition reactions of three compounds—propanamide, urea, and ethyl isocyanate—were investigated. Product distributions between 150 and 350°C are shown in Fig. 8. The formation of CO<sub>2</sub> predominated at low temperature in the decomposition of urea and ethyl isocyanate. This CO<sub>2</sub> formation was due not to total oxidation of the organic carbon, but most likely to hydrolysis reactions that can occur in milder conditions:

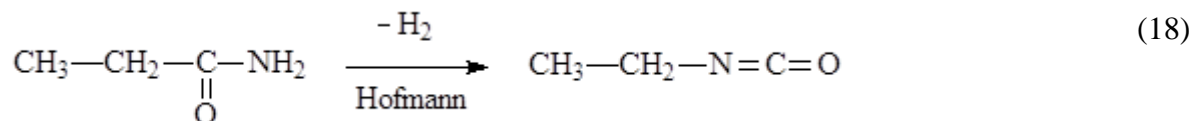
For ethyl isocyanate:



and for urea:



Direct hydrolysis is not possible with propanamide. However, Hofmann rearrangement of this amide (Eq. (18)) may lead to ethyl isocyanate, the hydrolysis of which (Eq. (16)) produces ethyl amine and CO<sub>2</sub>:



There was a strong temperature effect on the nitrogen oxidation in amides and isocyanate. Whereas N<sub>2</sub>O was formed at low temperatures, with a maximum around 250°C, NO<sub>x</sub> appeared only above 250°C. Nitrogen monoxide or dioxide were most likely formed at low temperatures but rapidly reduced by ammonia or amines remaining in the medium. As soon as ammonia and amine oxidation predominated (above 250°C), NO<sub>x</sub> no longer could be reduced because of the disappearance of potential reducers.

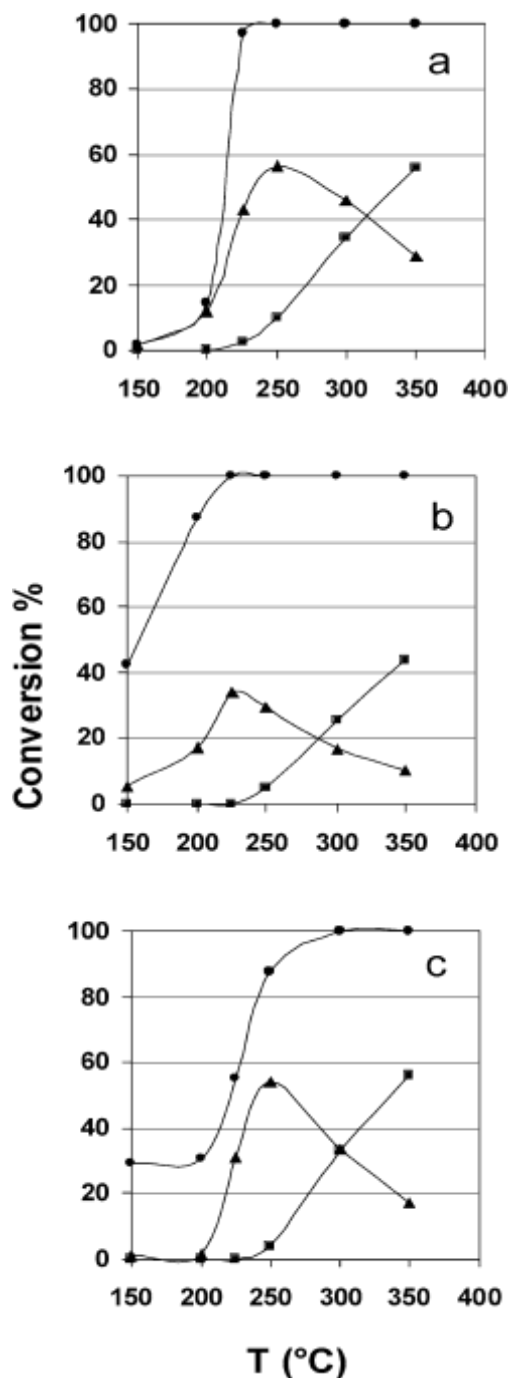


Fig. 8. Decomposition of propanamide (a), urea (b), and ethyl isocyanate (c) over Pt/Al<sub>2</sub>O<sub>3</sub> in O<sub>2</sub> (5%) + H<sub>2</sub>O (5%). Same symbols as in Fig. 5.

The results of NO reduction by amides and isocyanates (800 ppm NO added) are reported in Table 3. Propanamide and, to a lesser extent, ethyl isocyanate were very good reducers at low temperature, with DeNO<sub>x</sub> activity approaching that of acetone oxime. As expected, urea was

by far the most active reducer, because it allowed a total transformation of NO at 200°C. Two reactions leading to N<sub>2</sub> or N<sub>2</sub>O could occur with ammonia produced by urea hydrolysis. In the presence of O<sub>2</sub>, the stoichiometry between NH<sub>3</sub> and NO may fluctuate, with the likely reactions

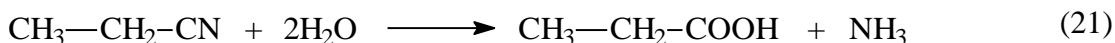


However, all of the organic reducers gave high amounts of N<sub>2</sub>O over Pt/Al<sub>2</sub>O<sub>3</sub>. It is noteworthy that the central carbon of urea was not totally oxidized at 200°C, which would prove that urea hydrolysis was not complete. Because this reaction yielded 2 mol of ammonia per mol of urea, ammonia could be in excess in the medium, which may explain why NO reduction was total whereas urea hydrolysis was not.

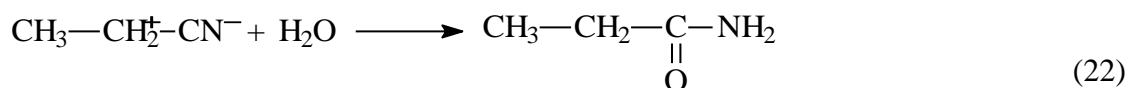
### 3.5. Reactivity of amines and nitriles

Two molecules representative of this class of compounds were studied: n-propylamine and propane nitrile. Their reactivity in the presence of O<sub>2</sub> and water is shown in Fig. 9. As for oximes and amides, virtually no NO<sub>x</sub> was produced below 250°C. Remarkably, the selectivity pattern between 150 and 350°C was quite similar for propanamide (Fig. 8a) and n-propylamine (Fig. 9a), strengthening the reaction scheme proposed for amide: Hofmann rearrangement into isocyanates (Eq. (18)), followed by hydrolysis into amines (Eq. (16)).

The fast degradation of the nitriles between 150 and 200°C could come from their hydrolysis into acids and ammonia:



Propanoic acid was rapidly oxidized into CO<sub>2</sub> and H<sub>2</sub>O at 150°C, and the presence of ammonia explains why NO<sub>x</sub> could not be detected while N<sub>2</sub>O was formed. Nitrile hydrolysis may also give amides:



which also may explain the formation of N<sub>2</sub>O.

NO reduction by propanamide and propane nitrile was investigated by adding 800 ppm NO to the NC + O<sub>2</sub> + H<sub>2</sub>O mixture. The results (last lines of Table 3) show that propanamine and

propanamide exhibited practically the same behavior in NO reduction, with very high reactivity but also noticeable selectivity in N<sub>2</sub>O (around 50%). In contrast, the nitrile was much less reactive, although with better selectivity to N<sub>2</sub> (>90%).

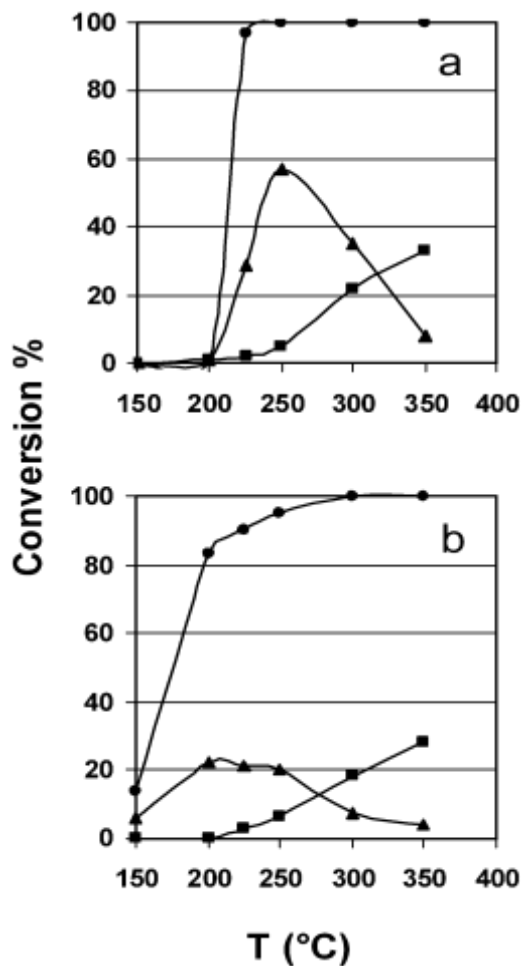


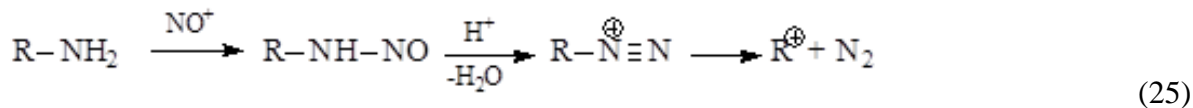
Fig. 9. Decomposition of n-propylamine (a) and propane nitrile (b) over Pt/Al<sub>2</sub>O<sub>3</sub> in O<sub>2</sub> (5%) + H<sub>2</sub>O (5%). Same symbols as in Fig. 5.

### 3.6. Proposal of a route to N<sub>2</sub> and N<sub>2</sub>O via oxime intermediates

This study has investigated the decomposition of nitrogen-containing intermediates and explored their potential impact in NO reduction. Two classes of compounds can be distinguished: (i) those like nitroalkanes, alkylnitrate, and alkylnitrite, which decompose and reduce NO at relatively high temperature, typically 300°C (class 1), and (ii) those like oximes,

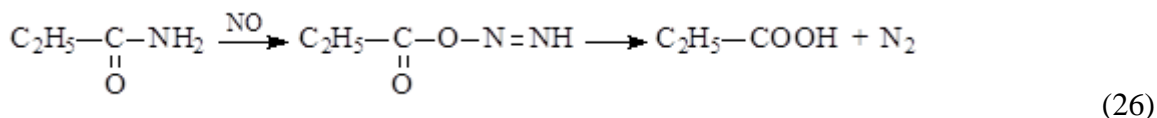






The carbocation may react with water to form alcohols or with nitrous or nitric acids to form alkylnitrites or alkylnitrates, which were detected in significant amounts in the NO reduction by propylene (Fig. 4).

The reaction of NO on amides gives an imine, which further decomposes into a carboxylic acid and N<sub>2</sub>:



Applied to acetone oxime, the Beckmann rearrangement would produce acetic acid and methyl amine. This amine can lead to N<sub>2</sub> (Eq. (25)) or to HCN (also detected in the products of NO reduction).

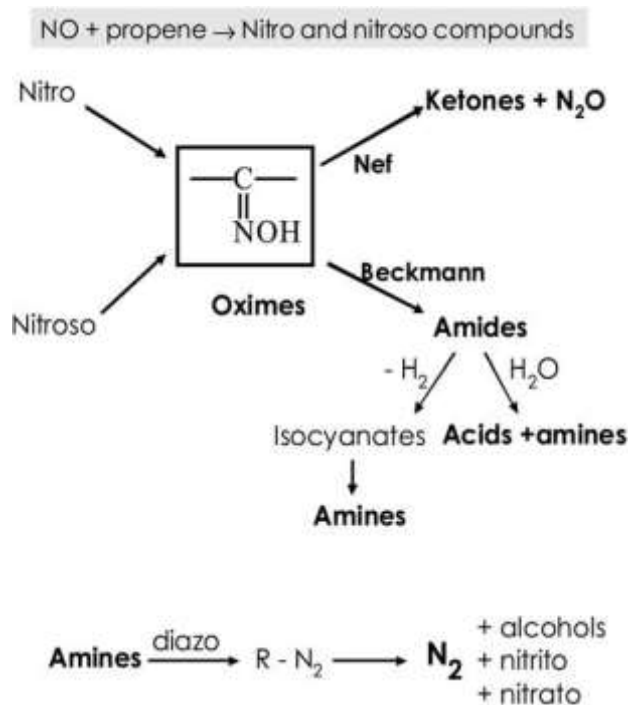


Fig. 10. Reaction scheme proposed for the NO reduction by propene via the oxime route at the maximum NO<sub>x</sub> conversion over Pt/Al<sub>2</sub>O<sub>3</sub> (200–250°C). The selectivity to N<sub>2</sub>O and N<sub>2</sub> is governed by the reaction selectivity of oximes (Nef reaction or Beckmann rearrangement).

## 4. Conclusion

Two classes of nitrogen-containing organic intermediates have been defined:

- Class 1: nitro compounds, alkylnitrites, and alkylnitrates, which may participate in NO reduction at relatively high temperatures (300°C) with a good selectivity to N<sub>2</sub>.
- Class 2: oximes, amides, amines, and, to a lesser extent, isocyanates, much more reactive but reducing NO to N<sub>2</sub>O and N<sub>2</sub> (with selectivity of about 50% each).

Class 2 intermediates are most probably involved in NO reduction by propene; their reactivity and selectivity are close to those of propene in the temperature window in which NOx conversion is maximal.

Oxime species should play a key role in NOx reduction by alkenes via two major reactions: the Nef reaction to ketones (or aldehydes) and N<sub>2</sub>O, and the Beckmann rearrangement to amides or amines, further transformed into alcohols, acids, and N<sub>2</sub>. The proposed reaction scheme involving all of these intermediates is summarized in Fig. 10. As demonstrated in this paper, most of these intermediates are themselves able to reduce NO.

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