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The chemistry of DeNOx reactions over Pt/Al_2O_3: The oxime route to N_2 or N_2O

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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/δ-Al_2O_3 catalyst (mean metal particle size, 20 nm) in oxygen excess conditions (5% O_2 + 5% H_2O). 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 $NO + C_3H_6$ 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_2 (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_2O would be produced mainly by a Nef reaction (leading to ketones and N_2O), whereas N_2 would be formed by successive steps starting with a Beckmann rearrangement of oxime species, with the byproducts of the N_2 formation being acids, alcohols, and nitrato and nitrito species.

Keywords: DeNOx catalysis over Pt; Organic nitrogen compounds in NO SCR; Oximes in DeNOx reaction; Reaction intermediates in catalytic NO reduction

1. Introduction

Automotive traffic constitutes one of the major sources of atmospheric NOx emissions ($NO + NO_2$). Although NOx 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_2 content in the exhaust gases of these vehicles. NOx 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_2 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 NOx storage technology, SCR of NOx 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

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its adsorption on Pt surfaces react with O species to give COx and H_2O, whereas N may recombine into N_2 or react with a nondissociated NO molecule to give N_2O. 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 NOx SCR [6]. The reaction starts by an oxidation of NO into NO_2, which would migrate onto the support to react with C_3H_7 fragments issued from the dehydrogenative adsorption of propane. In the reaction scheme proposed by Burch et al., this final step leads to N_2, N_2O, CO_2, and H_2O, 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 NOx SCR by hydrocarbons over Pt/SiO_2 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, NOx 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 nitrato ($R–ONO_2$) compounds.
- Oximes (R–CH=NOH), amines ($R–NH_2$), or ammonia.

A close examination of the mechanistic proposals shows that these organic intermediates in NOx 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], PtOx [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 nitrato surface species are formed on Pt/SiO_2 [30], Pt/Al_2O_3 [31], Cu-ZSM5 [32–34], Ce-ZSM5 [35,36], and Ag catalysts [37,38]. Nitro, nitrito, and nitrato species can be formed by reaction of NO_2 (or adsorbed nitrates) on an alkane. With olefins, nitrosoalkenes can be formed and can isomerize into oximes or oxidize into nitro, nitrito, and nitrato species. The reactivity of nitro compounds as NO reducers over Pd/Al_2O_3 was investigated by Oulad Haj et al. [39]. Gorce et al. [40] and Thomas et al. [41] stressed the role of the R–NOx nitrogen organic intermediates, but did not precisely describe their nature. According to these authors, R–NOx intermediates may be transformed into oxygenates, especially on CeZrOx 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_2 led mainly to $^{15}N^{14}NO$ and $^{15}N^{14}N$. 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_2O 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 DeNOx reactions. Major products (CO, CO_2, NOx, N_2O) 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 $NO + C_3H_6 + O_2 + H_2O$ 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 $O_2 + H_2O$ or with $NO + O_2 + H_2O$. 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^{-1}. The gas composition was typically NO, 800–1000 ppm; reducer, 167–500 ppm; O_2, 5%; and H_2O, 5% diluted in He. The reducer-to-NO ratio can be characterized by the ratio R, defined as follows:

$$R = \frac{P_{\mathrm{red}}}{P_{\mathrm{NO}}} \times n_{\mathrm{C}}, \quad (1)$$

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_2 + 5% H_2O 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^{-1} 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_2 (Cosma Topaze 2020) and IR for N_2O (Cosma Beryl 100). Dinitrogen could be analyzed only by GC (Porapak Q column) in the upper range of concentration (200–400 ppm), and $[N_2]$ was most often obtained by the difference from the N-balance. Carbon oxides (TCD) and organics (FID) were analyzed by GC.

The conversion, X_{NOx}, is calculated from the disappearance of the NOx (NO + NO_2),

$$X_{\mathrm{NOx}} = \frac{[\mathrm{NOx}]_{\mathrm{i}} - [\mathrm{NOx}]_{\mathrm{T}}}{[\mathrm{NOx}]_{\mathrm{i}}} \times 100, \quad (2)$$

where $[\mathrm{NOx}]_i$ and $[\mathrm{NOx}]_T$ 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:

$$X_{\mathrm{Z}} = \frac{n([\mathrm{Z}]_{\mathrm{T}} - [\mathrm{Z}]_{\mathrm{i}})}{[\mathrm{NOx}]_{\mathrm{i}}} \times 100 \quad \text{and}$$
$$S_{\mathrm{Z}} = \frac{n([\mathrm{Z}]_{\mathrm{T}} - [\mathrm{Z}]_{\mathrm{i}})}{[\mathrm{NOx}]_{\mathrm{i}} - [\mathrm{NOx}]_{\mathrm{T}}} \times 100, \quad (3)$$

where n is the number of nitrogen atoms in the molecule of Z. A similar definition can be given for $X_{\mathrm{CO_2}}$, 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_2O_3 [50], and Ga_2O_3/Al_2O_3 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^{-1}). 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_{sat} (°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[a]	500
Acetone oxime	IW[a]	1000
Propanamide	IW[a]	690
Urea	IW[a]	780
Ethyl isocyanate	−63	570
n-Propylamine	IW[a]	1050
Propane nitrile	−50	525

[a] IW: dissolved and injected with water.

2.2. Catalyst and reagents

A 1-wt% Pt/Al_2O_3 sample was prepared by impregnation of a δ-alumina (SCS79 provided by Rhodia; 80 $m^2\,g^{-1}$; main impurities: Na, 590 ppm; Ca, 490 ppm; Fe, 315 ppm; S, 400 ppm) with an aqueous solution of $Pt(NH_3)_2(NO_2)_2$. 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_2 at 450 °C. The Pt dispersion (H_2 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 DeNOx and to identify and analyze the different classes of minor organic intermediates. The nitrogen-containing compounds tested as potential intermediates in the DeNOx reaction are listed in Table 1. Most compounds were injected into the inlet gases (with 5% O_2 and 5% H_2O) via a saturator held at a specific temperature, yielding about 500 ppm the nitrogen compound (Table 1). Some compounds were dissolved in H_2O 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:

$$C_3H_7\text{–}OH + HNO_2 \rightarrow C_3H_7\text{–}ONO + H_2O.$$

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%

Table 2
Decomposition of 1-nitropropane and acetone oxime in a stream of 5% O_2 + 5% H_2O in helium. Conversions (%) of the nitrogen compounds into NO, N_2O and CO_2

T (°C)	1-Nitropropane			Acetone oxime		
	X_{NO}	X_{N_2O}	X_{CO_2}	X_{NO}	X_{N_2O}	X_{CO_2}
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

$O_2 + 5\%\ H_2O + He$ ($10\ L\,h^{-1}$) at 150 °C. The temperature was increased in steps of 25 or 50 °C. Gas-phase analyses (NO, NO_2, N_2O, CO_2, HC) were carried out after stabilization of the conversion at each temperature, which allowed us to calculate the conversion of NC into NOx: X_{NOx}, the conversion of NC into N_2O: X_{N_2O}, and the conversion of NC into CO_2: X_{CO_2}. Some results for 1-nitropropane and acetone oxime are reported in Table 2.

- NO reduction by NC. The nitrogen compounds were injected in a stream of 800 ppm $NO + 5\%\ O_2 + 5\%\ H_2O + He$ at 200–350 °C, chosen to have a high (or total) conversion of HC into CO_2. 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 $O_2 + H_2O + He$, with concentrations of NOx, N_2O, and CO_2 at T °C of C_{NOx}, C_{N_2O}, and C_{CO_2}, respectively; (ii) 800 ppm NO was then added to the feed, and new outlet concentrations, C^*_{NOx}, $C^*_{N_2O}$, and $C^*_{CO_2}$, 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

$$NOx\ th = 800 + C_{NOx}.$$

The amount of NOx reduced by NC is

$$Q_{NOx} = 800 + C_{NOx} - C^*_{NOx}$$

which corresponds to a percentage of NOx reduction of

$$\Delta X_{NOx} = 100 \times \frac{Q_{NOx}}{800} = 100 - \frac{C^*_{NOx} - C_{NOx}}{8}. \qquad (4)$$

The reaction chart for 1-nitropropane at 300 °C (Fig. 1) shows that the amount of NOx produced in 1-nitropropane at 300 °C is $C_{NOx} = 130$ ppm (28.5% nitropropane conversion into NOx). The amount of NOx remaining in gas phase after NO admission (800 ppm) is $C^*_{NOx} = 680$ ppm, whereas the theoretical amount should be 930 ppm. The amount of NOx reduced is then $Q_{NOx} = 250$ ppm, which corresponds to a percentage reduction of 32%.

By analogy, ΔX_{N_2O} is defined as the conversion of NO + NC into N_2O in step (ii),

$$\Delta X_{N_2O} = 100 \times \frac{2C^*_{N_2O}}{[NO]_i + [NC]_i}, \qquad (5)$$

whereas ΔX_{CO_2} is the conversion of NC into CO_2 in step (ii),

$$\Delta X_{CO_2} = 100 \times \frac{C^*_{CO_2}}{n[NC]_i}, \qquad (6)$$

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

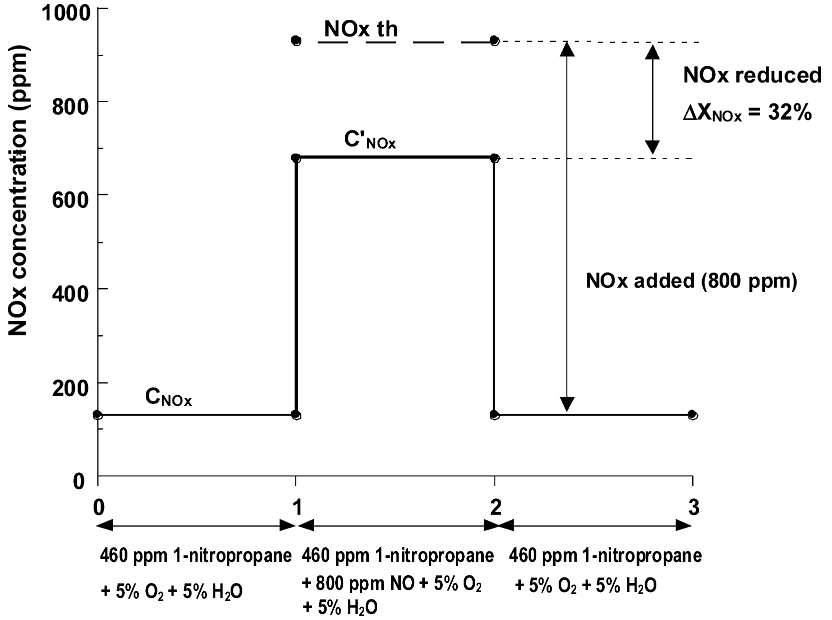


Fig. 1. Reaction chart between NO and 1-nitropropane (300 °C). Phase 0–1: 1-nitropropane decomposition; phase 1–2: reduction of NO by 1-nitropropane; phase 2–3: again, 1-nitropropane decomposition.

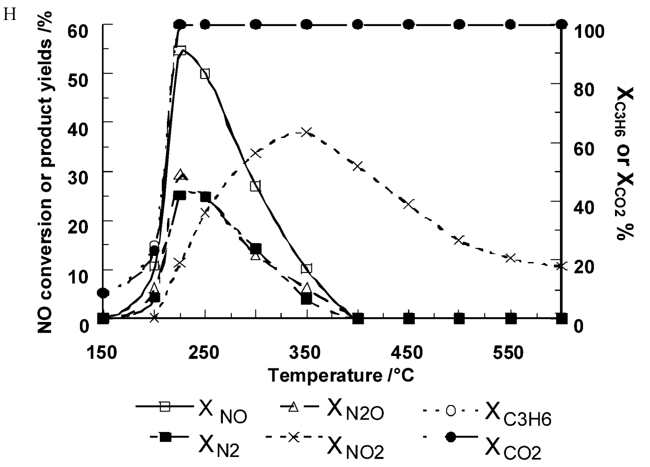


Fig. 2. NO reduction by propene in O_2 excess over Pt/Al_2O_3 (800 ppm NO; 500 ppm C_3H_6; 5% O_2 and 5% H_2O; space velocity: 14,000 h^{-1}).

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_2 + 5% H_2O, 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_2 followed a similar profile with a maximum conversion (55%) at 250–300 °C. Above 300 °C, the NO_2 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 NOx conversion of 17% was observed at 550 °C, with 11% leading to N_2O and 6% to N_2. Fig. 2 shows the results obtained at $R = 1.9$ (800 ppm NO and 500 ppm C_3H_6) over Pt/Al_2O_3. A sharp maximum of NOx conversion can be seen at around 225 °C, with very close selectivities to N_2 and N_2O. Within the pool of NOx (NO + NO_2), the transformation of NO by oxidation into NO_2 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 NOx conversion was always observed at 225 °C. The conversion increased but the selectivity to N_2 decreased with R (Fig. 3a).
- The maximum NOx conversion coincided with achievement of complete combustion of propene. The carbon conversion to CO_2 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_2; if the water content was maintained constant (5%), the conversion was virtually nil for 0.5% O_2 (Fig. 3b). It passed through a maximum for 5% O_2 and slowly decreased between 5% and 10% O_2. This is a very crucial point demonstrating that oxygen is necessary for the formation and/or decomposition of the reaction intermediates.

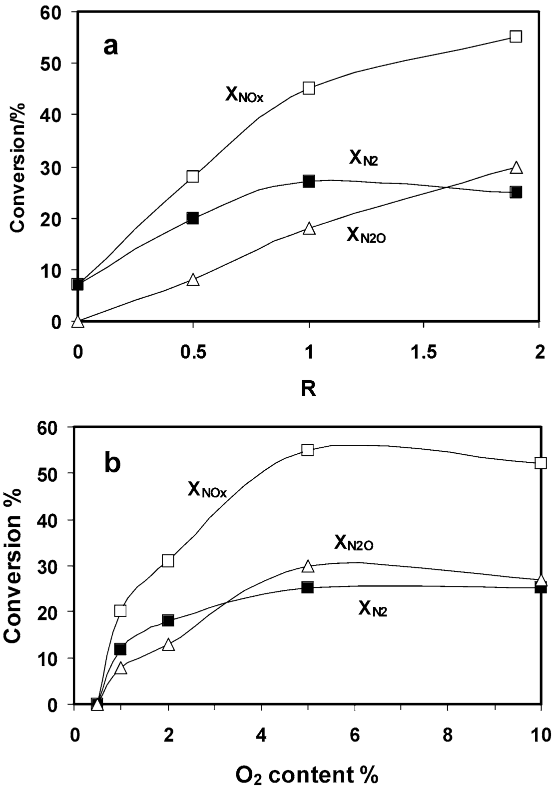


Fig. 3. (a) NO reduction by propene in the presence of 5% O_2 and 5% H_2O at 225 °C over Pt/Al_2O_3. Change with R of the total conversion (X_{NOx}) and of the conversion of NOx to N_2 and to N_2O. The values at $R = 0$ correspond to the NO decomposition reaction (no propene added). (b) Effect of the O_2 content on NO reduction by propene at 225 °C (500 ppm NO + 800 ppm C_3H_6 + 5% H_2O).

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:

- $C_xH_yO_z$ (O-compounds): acetone ≫ acids ≫ alcohols.
- $C_xH_yN_t$ (N-compounds): acetonitrile > other nitriles.
- $C_xH_yO_zN_t$ (O,N-compounds): alkylnitrites > alkylnitrates > nitro.
- C_xH_y (HC): aromatics (mainly benzene).

3.2. Reactivity of nitroalkanes, alkylnitrite, and alkylnitrate

The decomposition of selected nitroalkanes into NOx, N_2O, and CO_2 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_2 in the initial temperature range (150–200 °C). The reverse situation can be observed for the C–NO_2 bond cleavage; 2-methyl-2-nitropropane looses its

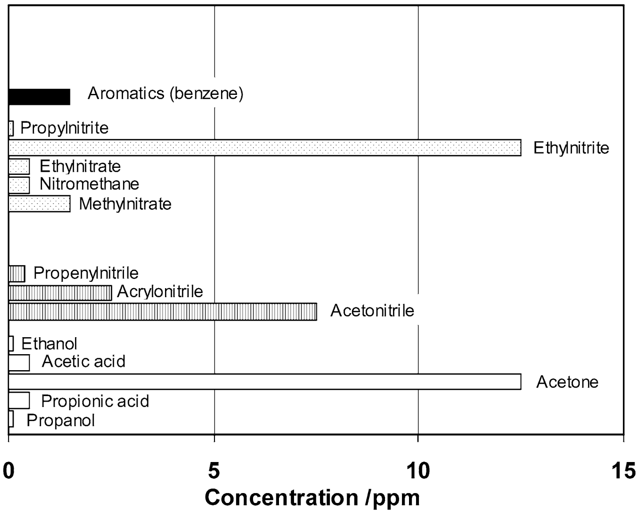
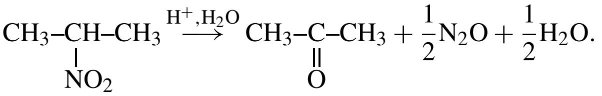


Fig. 4. Minor organic compounds formed in the NO reduction by propene at 200 °C over Pt/Al_2O_3 (800 ppm NO + 500 ppm C_3H_6 + 5% O_2 + 5% H_2O). White bars: O-compounds; hatched bars: N-compounds; gray bars: N,O-compounds; black bar: aromatics hydrocarbons.

nitro group at very low temperature and leads to NOx and N_2O exclusively. Above 250 °C, the entire carbonaceous skeleton is oxidized into CO_2; the nitro group is then transformed into NOx, N_2O, and, most likely, N_2. Fig. 5 shows that the sum NOx + N_2O is particularly low with 1-nitropropane, indicative of a high selectivity to N_2 (66% for 1-nitropropane instead of 39% for 2-nitropropane and only 5% for 2-methyl-2-nitropropane). The same tendency was observed by Oulad Haj et al. over Pd/Al_2O_3 [39].

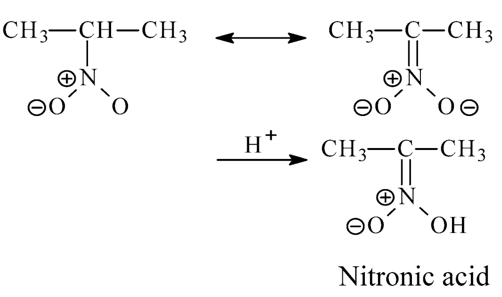
The formation of N_2O can be explained by the proton-assisted hydrolysis of nitro compounds into aldehydes (or ketones) and N_2O (reaction known as Nef reaction [20,52]):

$$R\text{–}CH_2\text{–}NO_2 \xrightarrow{H^+,H_2O} R\text{–}CHO + \frac{1}{2}N_2O + \frac{1}{2}H_2O, \quad (7)$$



$$\underset{\displaystyle NO_2}{CH_3\text{–}\underset{|}{CH}\text{–}CH_3} \xrightarrow{H^+,H_2O} CH_3\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}CH_3 + \frac{1}{2}N_2O + \frac{1}{2}H_2O. \quad (8)$$

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)):



(9a)

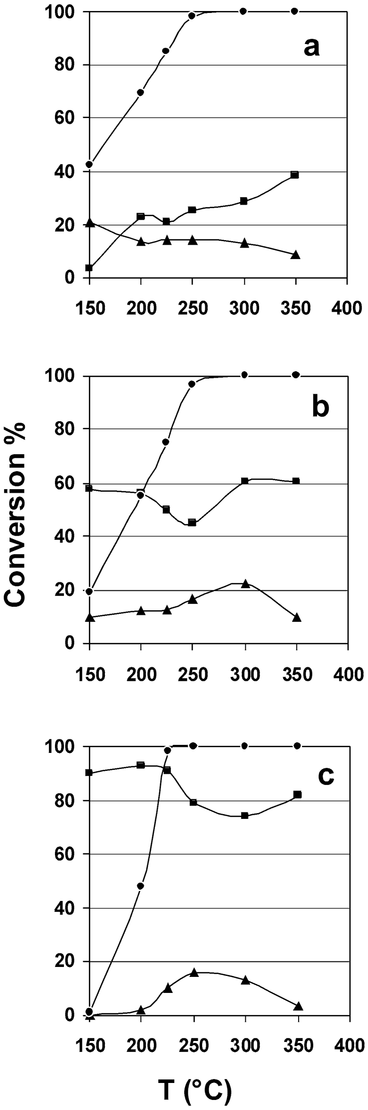
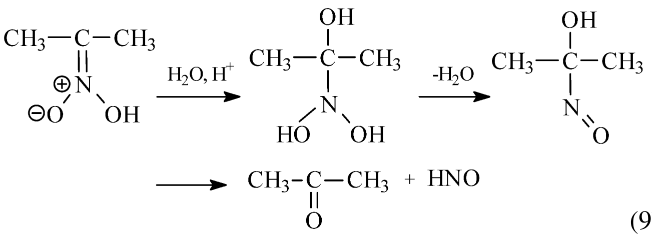


Fig. 5. Decomposition of different nitroalkanes over Pt/Al_2O_3 in O_2 (5%) + H_2O (5%): (a) 1-nitropropane, (b) 2-nitropropane, (c) 2-methyl-2-nitropropane; conversions to NOx (squares), N_2O (triangles), and CO_2 (circles).



(9b)

$$2HNO \longrightarrow N_2O + H_2O. \quad (10)$$

This mechanism implies H atom abstraction in α of the nitro group and cannot occur with NO_2 bonded to a tertiary carbon. It is the reason why 2-methyl-2-nitropropane does not produce N_2O in the 150–200 °C range (Fig. 5). The Nef reaction occurs in competition with the reverse reaction of nitration, which leads to NOx and CO_2 after cleavage of the C–NO_2 bond. Although the differences in the C–N bond energy are relatively small (250 kJ mol^{-1} in 1-nitropropane, 247 kJ mol^{-1} in

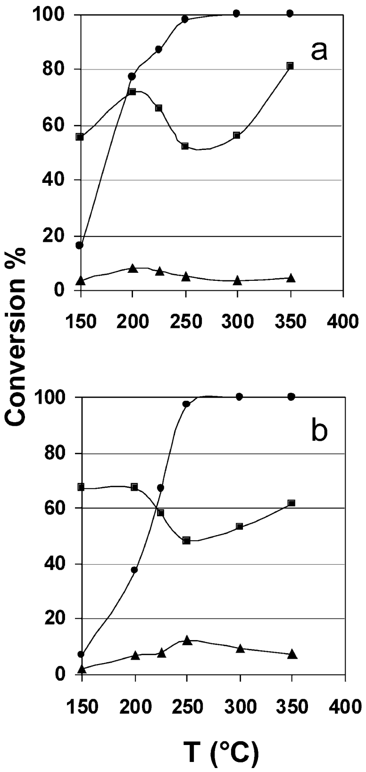


Fig. 6. Decomposition of propylnitrite (a) and propylnitrate (b) over Pt/Al_2O_3 in O_2 (5%) + H_2O (5%). Same symbols as in Fig. 5.

2-nitropropane, and 245 kJ mol^{-1} in 2-methyl-2-nitropropane), there is good correlation between these bond energies and the NOx formation in nitro compound decomposition; 2-methyl-2-nitropropane, which cannot give N_2O via the Nef reaction and has the lowest C–N bond energy, decomposes mainly into NOx (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_2O 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 NOx by rupture of the R–O–NO (nitrite) or of the R–O–NO_2 bond (nitrate). Practically no N_2O 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^{-1}), which favors alcohol formation by the following reaction:

$$\text{R–O–NO} + H_2O \longrightarrow \text{R–OH} + \text{HONO}. \tag{11}$$

NO reduction by NC (NC = nitroalkanes, propylnitrite, and propylnitrate) was investigated by adding 800 ppm NO into the gas mixture NC + H_2O + 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.

3.3. Reactivity of oximes

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_2 + 5% H_2O + 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)	ΔX_{NOx} (%) (Eq. (4))	ΔX_{N_2O} (%) (Eq. (5))	ΔX_{CO_2} (%) (Eq. (6))
1-Nitropropane	300	32	12	100
2-Nitropropane	300	79	10	100
2-Methyl-2-nitropropane	300	49	8	100
Propylnitrite	300	43	5	100
Propylnitrate	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
Propane nitrile	300	32	8	100

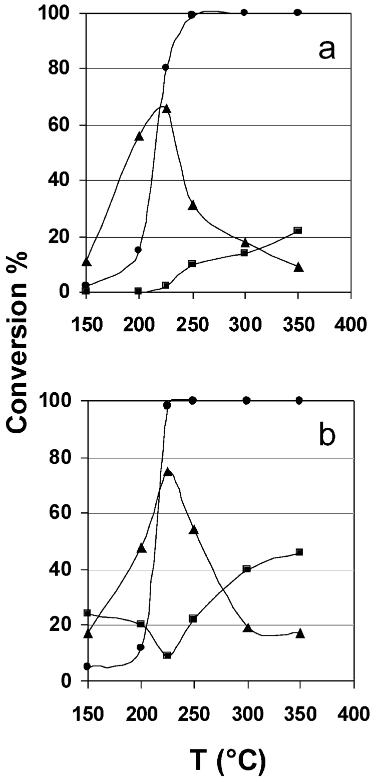
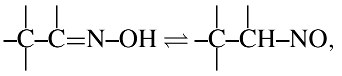


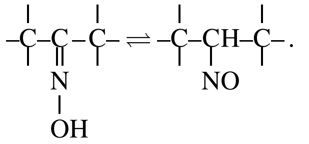
Fig. 7. Decomposition of ethanal oxime (a) and acetone oxime (b) over Pt/Al_2O_3 in O_2 (5%) + H_2O (5%). Same symbols as in Fig. 5.

Two oximes were investigated: ethanal oxime and acetone oxime. Their decomposition products between 150 and 350 °C are shown in Fig. 7. In contrast with nitroalkanes, alkylnitrites, and alkylnitrates, the main reaction was the formation of N_2O with a maximum between 60 and 80% at 225 °C. At this temperature, ethanal oxime did not form any NOx; the only decomposition products were N_2O and N_2.

Oximes are tautomer forms of nitroso compounds:



$$-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\text{N–OH} \rightleftharpoons -\overset{|}{\underset{|}{C}}-\overset{|}{C}\text{H–NO}, \tag{12}$$



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{\underset{OH}{|}}{\overset{\|}{N}}}{C}}-\overset{|}{\underset{|}{C}}- \rightleftharpoons -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{NO}{C}}H-\overset{|}{\underset{|}{C}}-. \qquad (13)$$

Assuming that oxidation of nitroso into nitro compounds is fast, oxime decomposition should resemble that of nitroalkanes. As a result, the highest NOx 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:

$$R–CH{=}N–OH \overset{H_2O}{\rightleftharpoons} R–CHO + N_2O. \qquad (14)$$

The same reaction can occur by mild oxidation of oximes into nitronic acid further transformed into ketones (or aldehydes) and N_2O 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:

$$CH_3–CH{=}N–OH \xrightarrow{-H_2O} CH_3–C{\equiv}N. \qquad (15)$$

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_2 formation.

NO reduction by oximes was carried out at 200 °C by adding 800 ppm NO in the same reactant feed streams (including O_2 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_2O 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 (NOx, N_2O, N_2, and CO_2), acetone was the main product of the reaction of acetone oxime/NO/O_2/H_2O over Pt/Al_2O_3 at 200 °C, while significant amounts of CH_3–CN and ethanal were detected in the products of ethanal oxime/NO/O_2/H_2O 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_2 predominated at low temperature in the decomposition of urea and ethyl isocyanate. This CO_2 formation was due not to total oxidation of the organic carbon, but most likely to hydrolysis reactions that can occur in milder conditions:

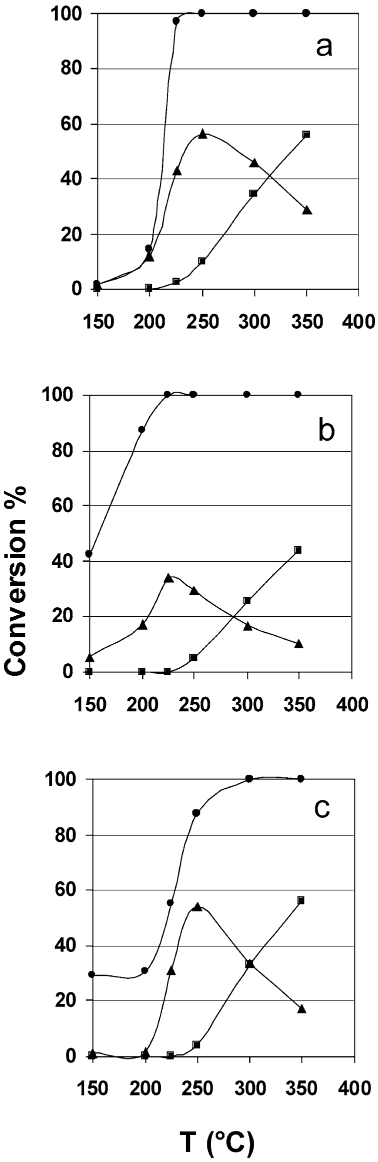
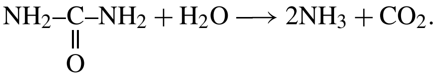


Fig. 8. Decomposition of propanamide (a), urea (b), and ethyl isocyanate (c) over Pt/Al_2O_3 in O_2 (5%) + H_2O (5%). Same symbols as in Fig. 5.

For ethyl isocyanate:

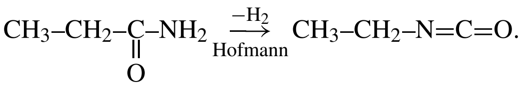
$$CH_3–CH_2–N{=}C{=}O + H_2O \longrightarrow CH_3–CH_2–NH_2 + CO_2, \qquad (16)$$

and for urea:



$$NH_2–\underset{\underset{O}{\|}}{C}–NH_2 + H_2O \longrightarrow 2NH_3 + CO_2. \qquad (17)$$

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_2:



$$CH_3–CH_2–\underset{\underset{O}{\|}}{C}–NH_2 \xrightarrow[\text{Hofmann}]{-H_2} CH_3–CH_2–N{=}C{=}O. \tag{18}$$

There was a strong temperature effect on the nitrogen oxidation in amides and isocyanate. Whereas N_2O was formed at low temperatures, with a maximum around 250 °C, NOx 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), NOx no longer could be reduced because of the disappearance of potential reducers.

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 DeNOx 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_2 or N_2O could occur with ammonia produced by urea hydrolysis. In the presence of O_2, the stoichiometry between NH_3 and NO may fluctuate, with the likely reactions

$$2NH_3 + 2NO + \frac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O \tag{19}$$

and

$$2NH_3 + 2NO + O_2 \rightarrow 2N_2O + 3H_2O. \tag{20}$$

However, all of the organic reducers gave high amounts of N_2O over Pt/Al_2O_3. 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.

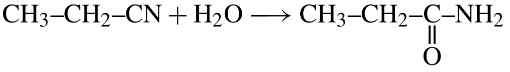
3.5. Reactivity of amines and nitriles

Two molecules representative of this class of compounds were studied: *n*-propylamine and propane nitrile. Their reactivity in the presence of O_2 and water is shown in Fig. 9. As for oximes and amides, virtually no NOx 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:

$$CH_3–CH_2–CN + 2H_2O \longrightarrow CH_3–CH_2–COOH + NH_3. \tag{21}$$

Propanoic acid was rapidly oxidized into CO_2 and H_2O at 150 °C, and the presence of ammonia explains why NOx could not be detected while N_2O was formed. Nitrile hydrolysis may also give amides:



$$CH_3–CH_2–CN + H_2O \longrightarrow CH_3–CH_2–\underset{\underset{O}{\|}}{C}–NH_2 \tag{22}$$

which also may explain the formation of N_2O.

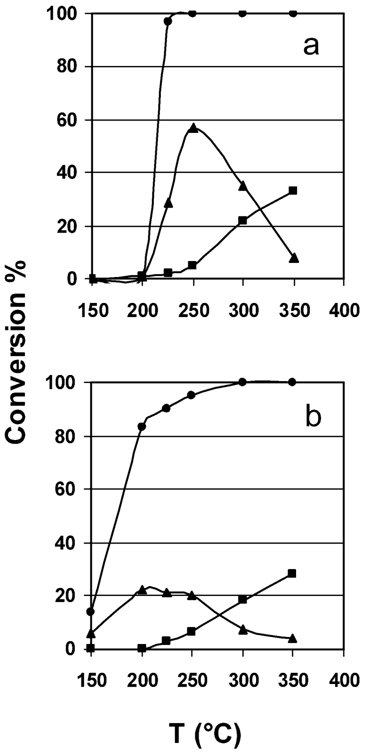


Fig. 9. Decomposition of *n*-propylamine (a) and propane nitrile (b) over Pt/Al_2O_3 in O_2 (5%) + H_2O (5%). Same symbols as in Fig. 5.

NO reduction by propanamide and propane nitrile was investigated by adding 800 ppm NO to the NC + O_2 + H_2O 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_2O (around 50%). In contrast, the nitrile was much less reactive, although with better selectivity to N_2 (>90%).

3.6. Proposal of a route to N_2 and N_2O 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, isocyanates, amides, and amines, which decompose and react with NO at temperatures below 250 °C (class 2). When they are able to react with NO, class 1 intermediates are much more selective to N_2 than are the class 2 nitrogen compounds. Another important difference is that class 1 molecules decompose in NOx as majority products in $O_2 + H_2O$ media.

Pt/Al_2O_3 is an active catalyst in NO reduction by propene with a maximum centered around 225–250 °C and presenting relatively poor selectivity to N_2 (≈50%). It is very likely that class 2 intermediates intervene mainly in the reduction steps at temperatures at which the catalyst has the highest activity. For that reason, the discussion here focuses on the specific role of these intermediates. Conversely, class 1 compounds could be important intermediates at high temperatures of reduction and also might intervene in selective routes to N_2.

The first step in the SOI mechanism is the reaction of NO or NO_2 with propene, giving nitroso or nitro compounds. Most likely, nitroso intermediates are formed with propene at low temperatures. The fact that the hydrocarbon is an alkene and that NO_2 is present mainly at high temperature (Fig. 2) supports this hypothesis. Because oximes are tautomeric forms of nitroso compounds (Eqs. (12) and (13)), they should play a decisive role in the SOI mechanism.

Oximes may undergo oxidative hydrolysis into ketones (or aldehydes) and N_2O (Eq. (14)), a reaction very similar to the Nef reaction on nitroalkanes (Eq. (9)). This is probably the main route to N_2O. Oximes may also undergo the Beckmann rearrangement. Two reactions can occur according to the size of the migrating group; for instance, with propanal oxime:

$$\begin{aligned}&\mathrm{CH_3{-}CH_2{-}CH{=}N{-}OH} \xrightarrow[-H_2O]{\text{Beckmann}} \underset{\text{(I)}}{\mathrm{CH_3{-}CH_2{-}NH{-}}}\underset{\mathrm{O}}{\overset{}{\underset{\|}{\mathrm{C}}}}\mathrm{{-}H}\\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow\\ &\mathrm{CH_3{-}CH_2{-}NH_2 + HCOOH} \xleftarrow{H_2O} \mathrm{CH_3{-}CH_2{-}NCO} \qquad (23)\end{aligned}$$

or

$$\mathrm{CH_3{-}CH_2{-}CH{=}N{-}OH} \xrightarrow[-H_2O]{\text{Beckmann}} \underset{\text{(II)}}{\mathrm{CH_3{-}CH_2{-}}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}NH_2}. \qquad (24)$$

The formation of N-ethylformamide (I, Eq. (23)) should dominate the Beckmann rearrangement of propanal oxime because the migrating group, $CH_3–CH_2$, is bigger than the H group involved in propanamide formation (II, Eq. (24)). In both cases, the Beckmann rearrangement of oximes leads to amines or amides that are potential intermediates in the reduction of NO to N_2 via N-nitrosation and formation of a diazonium salt [20, 44]:

$$\mathrm{R{-}NH_2} \xrightarrow{NO^+} \mathrm{R{-}NH{-}NO} \xrightarrow[-H_2O]{H^+} \mathrm{R{-}N^{\oplus}{\equiv}N} \longrightarrow \mathrm{R^{\oplus} + N_2}. \qquad (25)$$

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_2:

$$\begin{aligned}&\mathrm{C_2H_5{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}NH_2} \xrightarrow{NO} \mathrm{C_2H_5{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}O{-}N{=}NH}\\ &\qquad\qquad\longrightarrow \mathrm{C_2H_5{-}COOH + N_2}. \qquad (26)\end{aligned}$$

Applied to acetone oxime, the Beckmann rearrangement would produce acetic acid and methyl amine. This amine can lead to N_2 (Eq. (25)) or to HCN (also detected in the products of NO reduction).

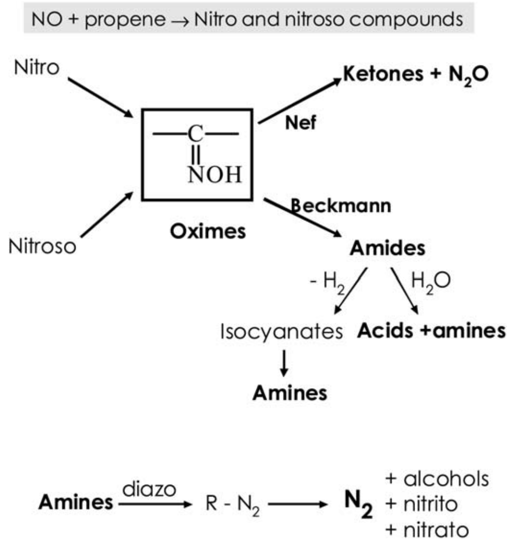


Fig. 10. Reaction scheme proposed for the NO reduction by propene via the oxime route at the maximum NOx conversion over Pt/Al_2O_3 (200–250 °C). The selectivity to N_2O and N_2 is governed by the reaction selectivity of oximes (Nef reaction or Beckmann rearrangement).

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_2.
- Class 2: oximes, amides, amines, and, to a lesser extent, isocyanates, much more reactive but reducing NO to N_2O and N_2 (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_2O, and the Beckmann rearrangement to amides or amines, further transformed into alcohols, acids, and N_2. 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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