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Labeled ^{15}NO Study on N_2 and N_2O Formation Over Pt–Ba/Al$_2$O$_3$ NSR Catalysts

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Abstract Mechanistic aspects involved in the formation of N_2 and of N_2O during the reduction of NO, stored nitrites and stored nitrates in the presence of NO are investigated in this work by means of isotopic labeling experiments over a model PtBa/Al$_2$O$_3$ NSR catalyst. The reduction of gaseous labeled NO with unlabelled NH$_3$ leads to the formation of N_2O at low temperature (below 180 °C), and of N_2 at high temperature. All N_2 possible isotopes are observed, whereas only labeled molecules have been detected in the case of N_2O. Hence the formation of nitrous oxide involves undissociated NO molecules, whereas that of N_2 can be explained on the basis of the statistical coupling of ^{15}N- and ^{14}N-adatoms on Pt. However, due to a slight excess of the mixed $^{15}N^{14}N$ isotope, a SCR-like pathway likely operates as well. The reduction of the stored labelled nitrates is very selective to N_2 and all isotopes are observed, confirming the occurrence of the recombination pathway. However also in this case a SCR-like pathway likely occurs and this explains the abundance of the $^{14}N^{15}N$ species. When the reduction of the stored nitrates is carried out in the presence of NO, this species is preferentially reduced pointing out the higher reactivity of gaseous NO if compared to the nitrates.

Keywords Isotopic labeling experiments · PtBa/Al$_2$O$_3$ NSR catalysts · NO$_x$ storage-reduction · Reduction of nitrates

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1 Introduction

The reduction of NO$_x$ emissions from diesel- and lean burn gasoline-powered vehicles is deeply investigated nowadays in view of the upcoming strict regulations which limit the emissions of these pollutants. In fact the Euro VI rules which will be applied starting from 2014 require a drastic reduction of NO$_x$ from the actual value of 0.18 down to 0.08 g/km. To date, the available technologies for the control of NO$_x$ emissions are the urea-SCR technique and the NO$_x$ Storage Reduction (NSR) or Lean NO$_x$ Trap (LNT) system [1–6]; hybrid LNT/SCR systems have also been studied [7].

While the SCR technology requires an external reductant like NH$_3$ (or an ammonia-precursor like urea), NSR make use of unburned hydrocarbons or other reductants already present in the exhausts. In fact these catalytic systems work under cycling condition, alternating a long lean phase of about 60–90 s during which NO$_x$ are stored on the catalyst, with a short rich phase of few seconds where the exhaust is deliberately made rich to reduce the trapped NO$_x$. N_2 is the desired reduction product, but other by-products may be formed (NO, N_2O, NH$_3$). The NSR catalyst formulations generally consist in a high surface area carrier supporting precious metals (usually Pt, Rh) and NO$_x$ storage components like Ba or K [8, 9].

Mechanistic aspects of the reduction of NO$_x$ stored over NSR catalytic systems have been investigated by several groups [10–14]. It has been shown that the reduction of stored nitrates proceeds via a Pt-catalyzed route which does not required the thermal desorption of stored NO$_x$ and where the NO$_x$ ad-species are reduced/decomposed at the Pt sites leading to the formation of the reduction products. When H$_2$ is used as reducing agent, it has also pointed out that N_2 formation occurs through a two-steps in series

molecular pathway involving the fast reaction of nitrates with hydrogen to give ammonia, followed by the slower reaction of the formed NH_3 with residual stored nitrates to give N_2 [12, 13, 15, 16]. In fact, due to the high reactivity of H_2 towards nitrates and to the integral nature of the trap, an hydrogen front develops in the trap travelling along the axis. Ammonia formed upon reduction of the stored NO_x reacts with NO_x stored downstream the H_2 front to give nitrogen. Based on these findings, N_2 is thought to be formed upon reaction of ammonia with the stored NO_x.

In this paper mechanistic aspects involved in the reaction of ammonia with the stored NOx have been addressed. In particular, in a recent study from our group mechanistic aspects involved in the formation of N_2 and N_2O during the regeneration of NSR catalysts have been analyzed by the use of labeled ^{15}NO [17]. It has been found that nitrogen formation can be explained by the statistical coupling of ^{15}N- and ^{14}N-adatoms originated upon NH_3 and $^{15}NO_x$ decomposition on Pt; however the occurrence of a SCR-like pathway, involving the formation and decomposition of a NH_x–^{15}NO intermediate, has also been suggested.

Based on these preliminary findings, in this study we extent such preliminary indications and address new aspects like the presence of NO during the regeneration of the catalysts, as also investigated by Pereda-Ayo et al. [18]. For this purpose, isotopic labeling experiments have been carried out using unlabeled NH_3 and ^{15}NO as sources for unlabeled and labeled N-species, respectively. The reactivity of ammonia with stored $^{15}NO_x$, gaseous ^{15}NO and stored $^{15}NO_x$ in the presence of gaseous NO has been investigated with the aim to better clarify mechanistic aspects of the pathways involved in the formation of N_2 during regeneration of NSR catalysts.

2 Materials and Methods

2.1 Catalyst Preparation and Characterization

An homemade Pt–Ba/Al_2O_3 (1/20/100 w/w) catalyst has been prepared by incipient wetness impregnation of a commercial alumina sample (Versal 250 from UOP calcined at 700 °C) with aqueous solution of dinitro-diammine platinum (Strem Chemicals, 5 % Pt in ammonium hydroxide) and subsequently with a solution of Ba acetate (Aldrich, 99 %), in line with recipes of Toyota patents [19]. Further details on the catalyst preparation and characterization can be found elsewhere [17].

2.2 Catalytic Tests

Catalytic tests have been performed in a quartz tube micro-reactor (7 mm I.D.) loaded with 60 mg of catalyst powder

(70–100 μm). A total flow of 100 cm^3/min (at 1 atm and 0 °C) has been used in the experiments. The reactor outlet was analyzed by a mass spectrometer (Thermostar 200, Pfeiffer), an UV–NO_x analyzer (LIMAS 11HW, ABB) and a micro-gas chromatograph (Agilent 3000A) [17], [20].

Prior to the catalytic activity runs, the catalyst sample has been conditioned by performing a few storage/regeneration cycles at 350 °C (using H_2 as a reductant) until a reproducible behavior was obtained.

After catalyst conditioning, Temperature Programmed Reaction (TPR) of NH_3 + ^{15}NO, and Temperature Programmed Surface Reaction (TPSR) of labeled nitrates with NH_3 or NH_3 + ^{14}NO have been performed. In a typical TPR experiment, a flow of $\sim$1,000 ppm ^{15}NO and $\sim$1,000 ppm NH_3 in He has been fed to the reactor at 40 °C and then the temperature has been linearly increased to 400 °C at a rate of 10 °C/min.

In the case of TPSR experiments, labeled nitrates have been adsorbed on the catalyst surface at 350 °C by feeding ^{15}NO ($\sim$1,000 ppm) + 3 % v/v O_2 in He. This procedure leads to the formation of nitrate species [21–23]. After the storage, a He purge at the same temperature has been carried out to desorb weakly adsorbed NO_x species, then the catalyst has been cooled down to 40 °C under He flow. The reduction was eventually carried out by admitting NH_3 ($\sim$1,000 ppm), in the absence or in the presence of NO (1,000 ppm) in He and heating the catalyst to 400 °C.

Details about the procedure adopted for the quantification of the reaction products can be found elsewhere [17].

3 Results and Discussion

3.1 Adsorption of Nitrates and Reduction with H_2

As preliminary experiments, the adsorption/reduction with H_2 of both unlabeled and labeled NO has been investigated. Aim of these runs were to point out the reactivity of labeled/unlabeled stored NO_x species in the reduction with H_2. Accordingly NO_x have been stored on the Pt–Ba/Al_2O_3 catalyst at 350 °C starting from both unlabeled and labeled NO and the stored species have been reduced with H_2. Figure 1 shows the results obtained in a typical storage/ reduction cycle carried out with ^{15}NO, being the results of storage/reduction cycle carried out with unlabeled NO already published in previous work [10, 23].

In the case of NO_x storage from labeled ^{15}NO (Fig. 1), an initial complete ^{15}NO uptake is observed, followed by ^{15}NO and $^{15}NO_2$ evolution. After about 2000s, steady state conditions have been roughly achieved and the NO_x outlet concentration approximates the inlet value. On the basis of previous FTIR studies on the unlabeled NO_x adsorption accomplished under both in situ and *operando* conditions

Fig. 1 Adsorption of labeled ^{15}NO at 350 °C by imposing a rectangular step feed of ^{15}NO (1,000 ppm) in flowing He + 3 % v/v O_2(*left panel*); isothermal reduction of stored $^{15}NO_x$ by imposing a rectangular step feed of H_2 (2,000 ppm) in flowing He on Pt–Ba/Al$_2$O$_3$ catalyst (*right panel*)
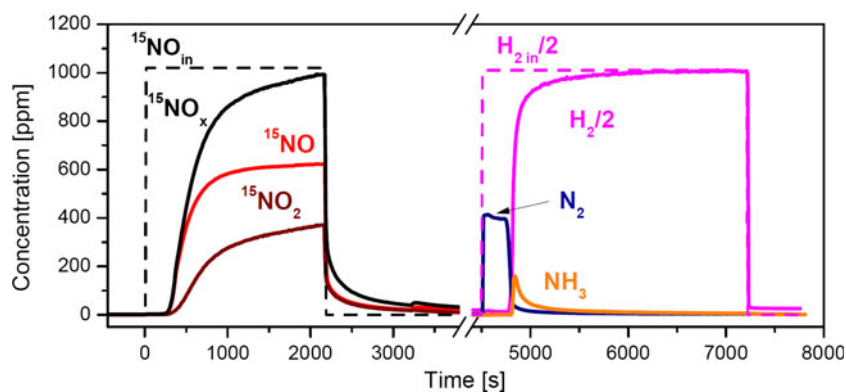
[22, 23], nitrate ad-species are formed at this temperature. The reduction of the stored $^{15}NO_x$ with H_2 (right panel of Fig. 1) leads to the initial evolution of $^{15}N_2$, followed by labeled ammonia. This is expected according to the H_2 front model discussed above, with nitrogen originating upon reaction of ammonia with NO_x stored downstream the H_2 front [12, 15, 16]. The total amounts of N_2 and NH_3 produced agree with the amount of stored NO_x, and the N-balance close within 5–10 %.

These results match those obtained in the case of NO/O_2, as expected, with the evolution of the unlabeled species instead of that of labeled molecules. Notably, the runs with labeled molecules also served for the calibration of labeled N_2 and NH_3 under the hypothesis that identical concentrations have been obtained in the two experiments.

3.2 Reactivity of NH$_3$ with Gaseous ^{15}NO and Labeled Nitrates

In order to compare the reactivity of ammonia with gaseous ^{15}NO and with labeled nitrates ad-species, NH$_3$-TPR and NH$_3$-TPSR have been carried out and results are shown in Fig. 2a, b (NH$_3$-TPR and NH$_3$-TPSR, respectively).

During the (NH$_3$ + NO TPR) (Fig. 2a), a desorption of ammonia is observed at the beginning of the heating ramp. Indeed ammonia is fed at 50 °C where it is able to weakly adsorb onto the catalytic surface. After reaching steady-state concentration values, the temperature is increased and this causes the instantaneous desorption of ammonia. Then, the NH$_3$ concentration decreases due to the reaction with gaseous ^{15}NO. The onset temperature of the reaction is near 100–120 °C, as pointed out by the evolution of the reaction products and by the consumption of NO. The formation of only labeled species like $^{15}N_2O$, $^{15}N^{14}N$ and minor amounts of $^{15}N^{14}NO$ are initially observed. Near 160 °C, in correspondence with the complete consumption of NO, a drop in the concentration of nitrous oxides is observed and the reaction is very selective towards N$_2$. The concentration of ammonia is near 400 ppm and, together
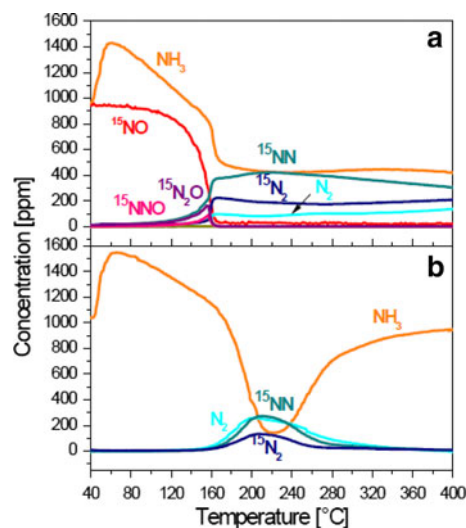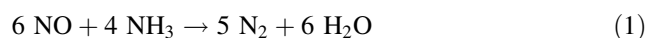

Fig. 2 a TPR run with NH$_3$ (1,000 ppm) and ^{15}NO (1,000 ppm) in He from 40 to 400 °C, 10 °C/min; **b** TPSR run with NH$_3$ (1,000 ppm) from 40 to 400 °C, 10 °C/min, after $^{15}NO_x$ adsorption at 350 °C of 1,000 ppm ^{15}NO + O_2 3 % v/v in He, over Pt–Ba/Al$_2$O$_3$ catalyst

with the complete consumption of NO, is in line with the stoichiometry of the following reaction:

$$6\ NO + 4\ NH_3 \rightarrow 5\ N_2 + 6\ H_2O \qquad (1)$$

Accordingly these results indicate that the reaction is poorly selective to N$_2$ at low temperatures, in the presence of gaseous NO; above the temperature at which complete NO consumption is observed (160 °C) the reaction becomes very selective to N$_2$. Concerning the isotopic distribution, only labeled nitrous oxide molecules have been observed (i.e. both single- ^{15}NNO and double-labeled $^{15}N_2O$), whereas all N$_2$ isotopes have been detected with abundance of the single labeled $^{15}N^{14}N$ species.

Figure 2b shows the results obtained when ammonia is contacted with stored NO$_x$ instead of gaseous NO (NH$_3$-TPSR). Labeled nitrates have been stored onto the catalyst surface in this case. As already discussed in a previous work [17], after an initial desorption ammonia consumption is

observed accompanied by the evolution of N_2. The onset of the reaction can be set slightly above 150 °C where N_2 evolution is seen. Notably, no N_2O formation is observed in this case; accordingly, in line with previous literature reports, the reduction of nitrates with ammonia is very selective towards N_2 [12, 13, 15, 16].

The consumption of ammonia (0.6 mmol/g_{cat}) and the formation of N_2 (0.5 mmol/g_{cat}) roughly obey to the stoichiometry of reaction (2):

$$3\ Ba(NO_3)_2 + 10\ NH_3 \rightarrow 8\ N_2 + 3\ BaO + 15\ H_2O \quad (2)$$
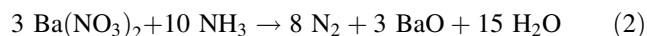
in line with the presence of nitrates on the catalyst surface. Concerning the isotopic distribution, all nitrogen isotopes have been observed, with overall abundance of the unlabeled $^{14}N_2$ and the single labeled $^{15}N^{14}N$ (respectively 44 and 37 %).

The comparison between the NH_3-TPR and NH_3-TPSR runs points out the different onset temperature of the gaseous NO and stored NO_x. In fact the reaction between ammonia and the stored nitrates starts at higher temperature if compared to the reaction with gas-phase NO (150 vs 100 °C), indicating the higher reactivity of gaseous NO with respect to the adsorbed NO_x species. Also, the reduction of the stored nitrates is very selective to N_2.

3.3 Reactivity of Stored ^{15}Nitrates in the Presence of NO

The reactivity of the stored nitrates with NH_3 in the presence of gas-phase NO has also been investigated. In this case nitrates have been stored onto the catalyst surface starting from labeled ^{15}NO and a NH_3-TPSR experiment has been carried out in the presence of NO in the gas phase. The results are shown in Fig. 3b where they are compared to a similar experiment carried out in the absence of adsorbed nitrates (Fig. 3a, NH_3-TPR).

The run carried out in the absence of adsorbed nitrates (Fig. 3a) parallels the analogous experiment carried out with labeled NO and displayed in Fig. 2a, confirming that the reactivity of unlabeled and labeled NO is the same. In fact the reaction between NH_3 and NO is seen above 100 °C with formation of N_2O, of N_2 and of water (not shown in the figure, but displaying a behavior which is specular to that of consumed NH_3). Above 170 °C, where complete consumption of NO is observed, a drop in the concentration of N_2O is observed and the reaction is completely selective to N_2. The consumption of ammonia is not complete due to the excess of inlet ammonia concentration with respect to the stoichiometry of reaction (1).

In the case of (NH_3 + NO)-TPSR (Fig. 3b), the desorption of ammonia is observed at first, and then it is consumed along with gaseous NO. Formation of reaction products is monitored starting from 120 °C with evolution of unlabeled
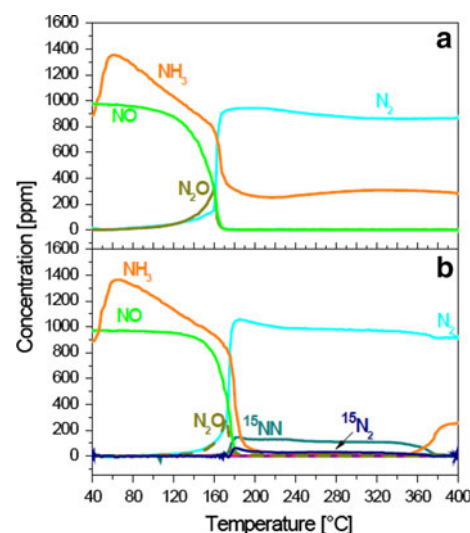

Fig. 3 a TPR run with NH_3 (1,000 ppm) and NO (1,000 ppm) in He from 40 to 400 °C, 10 °C/min; **b** TPSR run with NH_3 (1,000 ppm) + NO (1,000 ppm) from 40 to 400 °C, 10 °C/min, after $^{15}NO_x$ adsorption at 350 °C of 1,000 ppm ^{15}NO + O_2 3 % v/v in He, over Pt–Ba/Al$_2$O$_3$ catalyst

molecules only, i.e. $^{14}N_2O$ and $^{14}N_2$. This indicates that at low temperatures only gaseous NO is involved in the reaction with NH_3. Near 180 °C the concentration of gaseous ^{14}NO and $^{14}N_2O$ drops to zero, the concentration of unlabeled N_2 further increases and simultaneously the production of single and double labeled N_2 (i.e. $^{14}N^{15}N$ and $^{15}N_2$) is observed. No significant formation of either single labeled $^{14}N^{15}NO$ or double labeled $^{15}N_2O$ is detected.

Notably, at temperature higher than 375 °C, the concentration of labeled N_2 isotopes drops to zero and NH_3 evolution is observed. Since the stored nitrates are the only source of labeled ^{15}N atoms, this indicates that above 375 °C the surface has been cleaned from the nitrates and the reaction involves gaseous NO only.

Comparing the (NH_3 + NO)-TPSR run (Fig. 3b) with the NH_3-TPSR (Fig. 2b) it clearly appears that the formation of N_2O is related to the presence of gaseous NO, since no N_2O is observed in the reduction of the stored nitrates in the absence of gaseous NO. The results also confirm the lower reactivity of the stored nitrates if compared to gas-phase NO. Notably, the reactivity of NH_3 with gaseous NO seems to be slightly inhibited by the presence of the stored nitrates. In fact, the reaction onset of the NH_3 + NO reaction is seen near 100 °C in the absence of stored nitrates (Fig. 3a), and near 120 °C in the presence of the surface nitrates (Fig. 3b).

4 Pathways for N_2 and N_2O Formation

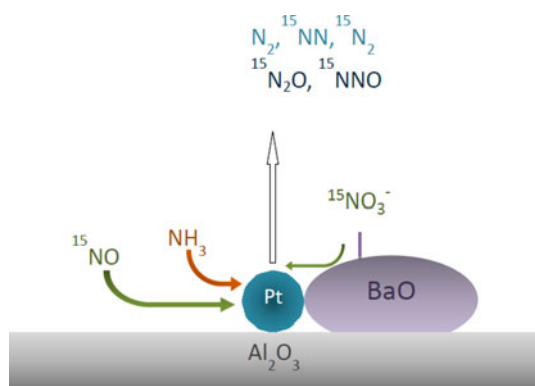The results of NH_3-TPR and NH_3-TPSR reported above point out that nitrates stored onto the Pt–Ba/Al$_2$O$_3$ NSR

Fig. 4 Reaction pathway for $^{15}NO_x$ reduction over Pt–Ba/Al$_2$O$_3$ catalyst

catalyst are selectively reduced by NH$_3$ to N$_2$, whereas the presence of gas-phase NO leads to a significant formation of N$_2$O at low temperature. However when NO is fully consumed, the reaction becomes very selective to N$_2$. Gas-phase NO is also slightly more reactive than the stored nitrates, as pointed out by the comparison of the temperature onset for the NH$_3$-TPR and NH$_3$-TPSR reactions (100–120 °C vs. 160 °C).

Concerning N$_2$ formation, the evolution of all types of nitrogen isotopes (the single labeled $^{15}N^{14}N$ species, the double labeled $^{15}N_2$ and unlabeled $^{14}N_2$ molecules) has been observed in the experiments with labeled NO or labeled nitrates. This clearly points out the occurrence, in the formation of nitrogen, of self-coupling reactions of unlabeled and labeled N-species, and from the coupling of labeled and unlabeled species as well. On the other hand, only labeled N$_2$O molecules have been detected when labeled NO is used, and only unlabeled N$_2$O starting from ^{14}NO. This clearly indicates that gaseous NO is involved in N$_2$O formation.

A schematic pathway for the formation of nitrogen and nitrous oxide during the reduction by NH$_3$ of gaseous ^{15}NO and labeled nitrates adsorbed over Pt–Ba/Al$_2$O$_3$ is displayed in Fig. 4. In the presence of ammonia at sufficiently high temperatures, the Pt sites become reduced and this is the driving force for the onset of the reduction process of gaseous ^{15}NO and/or of the stored $^{15}NO_x$. Figure 4 depicts NO$_x$ species located on Ba sites near Pt, but the same figure applies for NO$_x$ stored on Ba sites far away from Pt when the migration (surface diffusion) of the stored $^{15}NO_x$ towards the reduced Pt sites is considered [24]. The $^{15}NO_x$ species are hence decomposed at the reduced Pt sites with formation of a pool of O- and ^{15}N-adatoms. These latter react with N-adspecies derived from NH$_3$ decomposition onto the Pt sites, eventually leading to the formation of the various N$_2$ isotopes [6, 11, 25–29], whose abundance is expected to be determined by the surface concentration on ^{14}N- and ^{15}N-adatoms (statistical recombination).

As a matter of fact, in the reduction of gas-phase ^{15}NO with NH$_3$ in the absence of oxygen (Fig. 2a), where the reaction proceeds according to the stoichiometry of reaction (1), the expected statistical nitrogen isotope distribution based on the stoichiometry of the reaction is $^{14}N^{15}N/^{15}N_2/^{14}N_2 = 48/36/16$, which is reasonably close to the measured average N$_2$ isotope distribution of the run in Fig. 2a at temperatures above 180 °C ($^{14}N^{15}N/^{15}N_2/^{14}N_2 \approx 57/29/14$), although a slight excess of the single labeled isotope is observed. In fact N$_2$ formation might involve a different pathway as well, i.e. the coupling of NO- and NH$_3$-derived intermediates (SCR pathway), as suggested by Kondratenko and Baerns[25], and leading to the selective formation of the single labeled nitrogen molecule (^{15}NN). The presence of significant amounts of both the double labeled and of the unlabeled N$_2$ isotopes and the observation that the observed isotopic distribution is reasonably close to that expected from the statistical recombination clearly rules out the SCR pathway as unique route for N$_2$ formation, although its contribution is also likely.

Similar conclusion can also be derived for the reduction of the stored labeled nitrates (NH$_3$-TPSR), Fig. 3b. Also in this case the formation of only the mixed $^{14}N^{15}N$ species is not possible in view of the stoichiometric ratio between the ^{14}N- and ^{15}N-containing reactants (reaction (2)), and the formation of the double labeled $^{14}N_2$ isotope is expected. As a matter of fact, the NH$_3$-TPSR of nitrates (Fig. 2b) has led to the formation of all the possible N$_2$ isotopes, with an average $^{14}N^{15}N/^{14}N/^{15}N_2$ isotopic distributions near 37/44/19. The presence of the double labeled N$_2$ isotope points out to the occurrence of a self-coupling reaction of NO$_x$-derived intermediates, again ruling out the occurrence of a SCR pathway as unique pathway for N$_2$ formation. However, as pointed out in a previous work [17], the reduction of nitrites (instead of nitrates) gives initially the selective formation of the mixed $^{15}N^{14}N$ isotope, in line with the occurrence of a SCR-like pathway.

The results obtained in the reduction of both the stored nitrates and NO (Fig. 3b) pointed out the greater reactivity of gaseous NO if compared to stored NO$_x$. Apparently, stored nitrates are reduced by ammonia left from the reaction with NO (the inlet NH$_3$ concentration exceeds the stoichiometry of reaction (1)) and the relative concentrations of the ^{15}NN and $^{15}N_2$ isotopes resemble those observed in the absence of NO (Fig. 2b), with ^{15}NN prevailing over $^{15}N_2$ (the high unlabeled N$_2$ concentration comes from the NH$_3$ + NO reaction). Hence nitrogen formation upon reduction of the stored NO$_x$ is apparently not altered by the concomitant reduction of gas-phase unlabeled NO.

Concerning the formation of N$_2$O, negligible amounts of nitrous oxide have been observed during the TPSR with

adsorbed nitrates (Fig. 2b), whereas relevant quantities of N_2O have been detected in the runs in the presence of NO (Figs. 2a and 3). The data converge in indicating that N_2O formation involves the presence of gaseous NO: in the $NH_3 + {}^{15}NO$ reaction, the formation of only labeled N_2O molecules has been observed, whereas in the $NH_3 + NO$ reaction in the presence of labeled stored nitrates only unlabeled N_2O has been observed. This is in line with literature proposals [30], indicating that nitrous oxide formation involves either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH_x fragment.

Notably, nitrous oxide formation is strongly affected by temperature: in fact above 180 °C N_2O formation becomes negligible. It is suggested that at high temperatures NO dissociation is favored since Pt is kept in a reduced state by ammonia, and this prevents N_2O formation due to the lack of molecularly adsorbed NO species. However, the possibility that N_2O is decomposed to N_2 and O_2 over reduced Pt sites is also likely, as suggested by Cant et al. [31]. This route may contribute only to the formation of labelled N_2 molecules in the experiment of Fig. 2a and of unlabeled N_2 in Fig. 3b in view of the fact that N_2O reduction does not involve the cleavage of the N–N bond [31].

5 Conclusions

In this paper mechanistic aspects involved in the formation of N_2 and N_2O during the reduction with ammonia of gaseous NO and of NO_x stored over a model Pt–Ba/Al$_2$O$_3$ NSR catalyst have been investigated by means of isotopic labeling experiments.

The reduction of gaseous labeled NO with unlabelled NH_3 leads to the formation of N_2O at low temperature (below 180 °C), and of N_2 at high temperature. The products distribution and the relative isotopic aboundance suggested that: (i) N_2O formation involves either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH_x fragment; (ii) N_2 formation can be explained on the basis of the statistical coupling of ${}^{15}N$- and ${}^{14}N$-adatoms originated upon NH_3 and NO_x decomposition on Pt and likely by the occurrence of an SCR-like pathway.

On the other hand the reduction of the stored labelled nitrates with unlabeled NH_3 is very selective to N_2; formation of all possible N_2 isotopes is observed and this can be explained on the basis of the statistical coupling of ${}^{15}N$- and ${}^{14}N$-adatoms, although the occurrence of a SCR pathway is also likely. Notably, the absence of N_2O formation during nitrates reduction points out the lack of any significant NO release at low temperatures: in fact when the reduction of the labeled stored NO_x is carried out in the

presence of unlabeled gaseous NO, unlabeled N_2O formation is greatly enhanced. Besides, gaseous NO shows a higher reactivity if compared to the stored NO_x in the reduction with ammonia.

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