Labelled ^{15}NO study on N_2 and N_2O formation over Pt-Ba/Al$_2$O$_3$ LNT catalysts

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1 **Abstract**

2 Mechanistic aspects involved in the formation of N_2 and of N_2O during the reduction of NO, stored nitrates

3 and stored nitrates in the presence of NO are investigated in this work by means of isotopic labeling

4 experiments over a model $PtBa/Al_2O_3$ NSR catalyst. The reduction of gaseous labeled NO with unlabelled

5 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

6 possible isotopes are observed, whereas only labeled molecules have been detected in the case of N_2O.

7 Hence the formation of nitrous oxide involves undissociated NO molecules, whereas that of N_2 can be

8 explained on the basis of the statistical coupling on Pt of ^{15}N- and ^{14}N-adatoms. However, due to a slight

9 excess of the mixed $^{15}N^{14}N$ isotope, a SCR-like pathway likely operates as well.

10 The reduction of the stored labelled nitrates is very selective to N_2 and all isotopes are observed, confirming

11 the occurrence of the recombination pathway. However also in this case a SCR-like pathway likely occurs

12 and this explain the abundance of the $^{14}N^{15}N$ species. When the reduction of the stored nitrates is carried out

13 in the presence of NO, NO is preferentially reduced pointing out the higher reactivity of gaseous NO if

14 compared to the nitrates.

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1 **Introduction**

2 The reduction of NO_x emissions from diesel- and lean burn gasoline-powered vehicles is deeply investigated

3 nowadays in view of the next coming strict regulations which limit the emissions of these pollutants. In fact

4 the Euro VI rules which will be applied starting from 2014 require a drastic reduction of NO_x from the actual

5 value of 0.18 g/km down to 0.08 g/km. To date, the available technologies for the control of NO_x emissions

6 are the urea-SCR technique and the NO_x Storage Reduction (NSR) or Lean NO_x Trap (LNT) system[1,2,3,4,5,6];

7 hybrid LNT/SCR systems have also been studied[7].

8 While the SCR technology requires an external reductant like NH_3 (or an ammonia-precursor like urea),

9 LNTs make use of unburned hydrocarbons or other reductants already present in the exhausts. In fact these

10 catalytic systems work under cycling condition, alternating a long lean phase of about 60–90 s during which

11 NO_x are stored on the catalyst, with a short rich phase of few seconds where the exhaust is deliberately

12 made rich to reduce the trapped NO_x. N_2 is the desired reduction product, but other by-products may be

13 formed (NO, N_2O, NH_3). The NSR catalyst formulations generally consist in a high surface area carrier

14 supporting precious metals (usually Pt, Rh) and NO_x storage components like Ba or K [8,9].

15 Mechanistic aspects of the reduction of NO_x stored over NSR catalytic systems have been investigated by

16 several groups[10,11,12,13,14]. It has been shown that the reduction of stored nitrates proceeds via a Pt-catalyzed

17 route which does not required the thermal desorption of stored NO_x and where the NO_x ad-species are

18 reduced/decomposed at the Pt sites leading to the formation of the reduction products. When H_2 is used as

19 reducing agent, it has also pointed out that N_2 formation occurs through a two-steps in series molecular

20 pathway involving the fast reaction of nitrates with hydrogen to give ammonia, followed by the slower

21 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

22 H_2 towards nitrates and to the integral nature of the trap, an hydrogen front develops in the trap travelling

23 along the axis. Ammonia formed upon reduction of the stored NO_x reacts with NO_x stored downstream the H_2

24 front to give nitrogen. Based on these findings, N_2 is thought to be formed upon reaction of ammonia with the

25 stored NO_x.

26 In this paper mechanistic aspects involved in the reaction of ammonia with the stored NOx have been

27 addressed. In particular, in a recent study from our group mechanistic aspects involved in the formation of N_2

28 and N_2O during the regeneration of NSR catalysts have been analyzed by the use of labeled ^{15}NO[17]. It has

29 been found that nitrogen formation can be explained by the statistical coupling of ^{15}N- and ^{14}N-adatoms

1   originated upon NH_3 and $^{15}NO_x$ decomposition on Pt; however the occurrence of a SCR-like pathway,

2   involving the formation and decomposition of a NH_x-^{15}NO intermediate, has also been suggested.

3   Based on these preliminary findings, in this study we extent such preliminary indications and address new

4   aspects like the presence of NO during the regeneration of the catalysts, as also investigated by Pereda-

5   Ayo et al.[18]. For this purpose, isotopic labeling experiments have been carried out using unlabeled NH_3 and

6   ^{15}NO as sources for unlabeled and labeled N-species, respectively. The reactivity of ammonia with stored

7     $^{15}NO_x$, gaseous ^{15}NO and stored $^{15}NO_x$ in the presence of gaseous NO has been investigated with the aim to

8   better clarify mechanistic aspects of the pathways involved in the formation of N_2 during regeneration of NSR

9   catalysts.

10

11   **Materials and Methods**

12   **Catalysts preparation and characterization –** An homemade Pt-Ba/Al_2O_3 (1/20/100 w/w) catalyst has been

13   prepared by incipient wetness impregnation of a commercial alumina sample (Versal 250 from UOP)

14   calcined at 700°C with aqueous solution of dinitro-diammine platinum (Strem Chemicals, 5% Pt in

15   ammonium hydroxide) and subsequently with a solution of Ba acetate (Aldrich, 99%), in line with recipes of

16   Toyota patents[19]. Further details on the catalyst preparation and characterization can be found elsewhere [17].

17   **Catalytic tests -** Catalytic tests have been performed in a quartz tube micro-reactor (7 mm I.D.) loaded with

18   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

19   experiments. The reactor outlet was analyzed by a mass spectrometer (Thermostar 200, Pfeiffer), an UV-

20   NO_x analyzer (LIMAS 11HW, ABB) and a micro-gas chromatograph (Agilent 3000A)[17,**Errore. Il segnalibro non è**

21   **definito.**20].

22   Prior to the catalytic activity runs, the catalyst sample has been conditioned by performing a few

23   storage/regeneration cycles at 350°C (using H_2 as a reductant) until a reproducible behavior was obtained.

24   After catalyst conditioning, Temperature Programmed Reaction (TPR) of NH_3 + ^{15}NO, and Temperature

25   Programmed Surface Reaction (TPSR) of labeled nitrates with NH_3 or NH_3 + ^{14}NO have been performed. In

26   a typical TPR experiment, a flow of 1000 ppm ^{15}NO and 1000 ppm NH_3 in He has been fed to the reactor at

27   40°C and then the temperature has been linearly increased to 400°C at a rate of 10°C/min.

28   In the case of TPSR experiments, labeled nitrates have been adsorbed on the catalyst surface at 350°C by

29   feeding ^{15}NO (1000 ppm) + 3% v/v O_2 in He. This procedure leads to the formation of nitrate species[21,22,23].

1   After the storage a He purge at the same temperature has been carried out to desorb weakly adsorbed NO_x

2   species, then the catalyst has been cooled down to 40°C under He flow. The reduction was eventually

3   carried out by admitting NH_3 (1000 ppm), in the absence or in the presence of NO (1000 ppm) in He and

4   heating the catalyst to 400°C.

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

6

7   **Results and discussion**

8   *Adsorption of Nitrates and reduction with H_2*

9   As preliminary experiments, the adsorption/reduction with H_2 of both unlabeled and labeled NO has been

10   investigated. Aim of these runs were to point out the reactivity of labeled/unlabeled stored NO_x species in the

11   reduction with H_2. Accordingly NO_x have been stored on the Pt-Ba/Al_2O_3 catalyst at 350°C starting from both

12   unlabeled and labeled NO and the stored species have been reduced with H_2. Figures 1 show the result

13   obtained in a typical storage/reduction cycle carried out with ^{15}NO, being the results of storage/reduction

14   cycle carried out with unlabeled NO already published in previous work[10,23].

15   In the case of NO_x storage from labeled ^{15}NO (Figure 1), an initial complete ^{15}NO uptake is observed,

16   followed by ^{15}NO and $^{15}NO_2$ evolution. On the basis of previous FTIR studies on the unlabeled NO_x

17   adsorption accomplished under both *in situ* and *operando* conditions[22,23], nitrate ad-species are formed at

18   this temperature. The reduction of the stored $^{15}NO_x$ with H_2 (right panel of Figure 1) leads to the initial

19   evolution of $^{15}N_2$, followed by labeled ammonia. This is expected according to the H_2 front model discussed

20   above, with nitrogen originating upon reaction of ammonia with NO_x stored downstream the H_2 front[12,15,16].

21   These results match those obtained in the case of NO/O_2, as expected, with the evolution of the unlabeled

22   species instead of that of labeled molecules. Notably, the runs with labeled molecules also served for the

23   calibration of labeled N_2 and NH_3 under the hypothesis that identical concentrations have been obtained in

24   the two experiments.
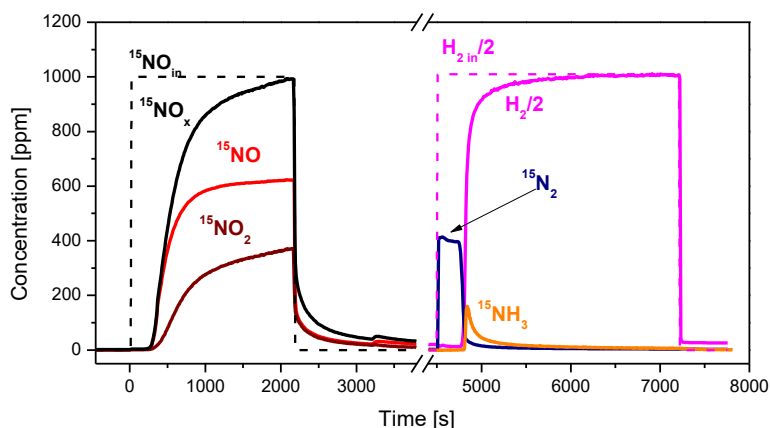
Fig.1 Adsorption of labeled ^{15}NO 350°C by imposing a rectangular step feed of ^{15}NO (1000 ppm) in flowing He + 3% v/v O_2 on Pt-Ba/Al$_2$O$_3$ catalyst

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 Figures 2 A and 2 B (NH$_3$-TPR and NH$_3$-TPSR, respectively).

During the NH$_3$-TPR (Fig. 2A), a desorption of ammonia is observed at the beginning of the heating ramp. 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$_2$O, ^{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 with the complete consumption of NO, is in line with the stoichiometry of the following reaction:

$$6\ NO + 4\ NH_3 \rightarrow 5\ N_2 + 6\ H_2O \qquad\qquad (1)$$
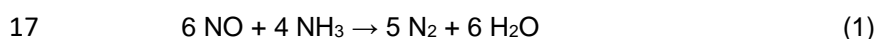
Accordingly these results indicate that the reaction is poorly selective to N$_2$ at low temperatures, in the presence of gaseous NO; above the temperature at which complete NO consumption is observed (160 °C) the reaction becomes very selective to N$_2$. Concerning the isotopic distribution, only labeled nitrous oxide molecules have been observed (i.e. both single- ^{15}NNO and double-labeled ^{15}N$_2$O), whereas all N$_2$ isotopes have been detected with abundance of the single labeled ^{15}N^{14}N species.

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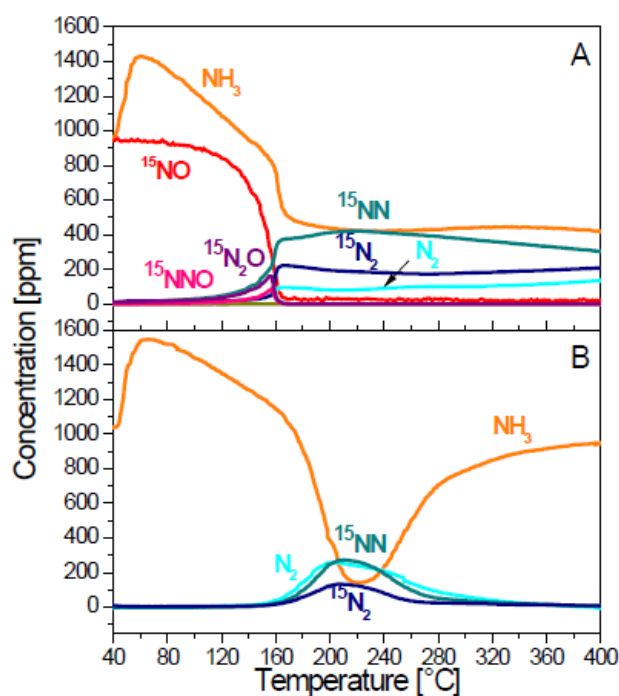
Fig.2 - (A) TPR run with NH_3 (1000 ppm) and [15]NO (1000 ppm) in He from 40 to 400°C, 10°C/min; (B) TPSR run with NH_3 (1000ppm) from 40 to 400°C, 10°C/min, after [15]NO_x adsorption at 350°C of 1000 ppm [15]NO + O_2 3% v/v in He, over Pt-Ba/Al_2O_3 catalyst

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 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):

$$3\ Ba(NO_3)_2 + 10\ NH_3 \rightarrow 8\ N_2 + 3\ BaO + 15\ H_2O \qquad (2)$$
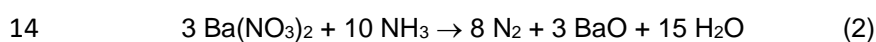
in line with the presence of nitrates on the catalyst surface. Concerning the isotopic distribution, all nitrogen

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 -TPSR runs points out the different onset temperature of the

gaseous 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°C vs 100°C), indicating the higher reactivity

1   of gaseous NO with respect to the adsorbed NOx species. Also, the reduction of the stored nitrates is very

2   selective to N_2.

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4   ***Reactivity of stored ^{15}nitrates in the presence of NO***

5   The reactivity of the stored nitrates with NH_3 in the presence of gas-phase NO has also been investigated. In

6   this case nitrates have been stored onto the catalyst surface starting from labeled ^{15}NO and a NH_3-TPSR

7   experiment has been carried out in the presence NO in the gas phase. The results are shown in Figure 3 B

8   where they are compared to a similar experiment carried out in the absence of adsorbed nitrates (Figure 3 A,

9   NH_3-TPR).

10   The run carried out in the absence of adsorbed nitrates (Figure 3 A) parallel the analogous experiment

11   carried out with labeled NO and displayed in Figure 2 A, confirming that the reactivity of unlabeled and

12   labeled NO is the same. In fact the reaction between NH_3 and NO is seen above 100°C with formation of

13   N_2O and of N_2; above 170°C where complete consumption of NO is observed, a drop in the concentration of

14   N_2O is observed and the reaction is completely selective to N_2. The consumption of ammonia is not complete

15   due to the excess of inlet ammonia concentration with respect to the stoichiometry of reaction (1).

16   In the case of NH_3+NO-TPSR (Figure 3 B), the desorption of ammonia is observed at first, and then it is

17   consumed along with gaseous NO. Formation of reaction products is monitored starting from 120°C with

18   evolution of unlabeled molecules only, i.e. $^{14}N_2O$ and $^{14}N_2$. This indicates that at low temperatures only

19   gaseous NO is involved in the reaction with NH_3. Near 180°C the concentration of gaseous ^{14}NO and $^{14}N_2O$

20   drops to zero, the concentration of unlabeled N_2 further increases and simultaneously the production of

21   single and double labeled N_2 (i.e. $^{14}N^{15}N$ and $^{15}N_2$) is observed. No significant formation of either single

22   labeled $^{14}N^{15}$NO or double labeled $^{15}N_2O$ is detected.

23   Notably, at temperature higher than 375°C, the concentration of labeled N_2 isotopes drop to zero and NH_3

24   evolution is observed. Since the stored nitrates are the only source of labeled ^{15}N atoms, this indicates that

25   above 375°C the surface has been cleaned from the nitrates and the reaction involves gaseous NO only.

26   Comparing the NH_3+NO-TPSR run (Figure 3B) with the NH_3-TPSR (Figure 2B) it clearly appears that the

27   formation of N_2O is related to the presence of gaseous NO, since no N_2O is observed in the reduction of the

28   stored nitrates in the absence of gaseous NO. The results also confirm the lower reactivity of the stored

29   nitrates if compared to gas-phase NO. Notably, the reactivity of NH_3 with gaseous NO seems to be slightly

30   inhibited by the presence of the stored nitrates. In fact, the reaction onset of the NH_3 + NO reaction is seen

1 near 100°C in the absence of stored nitrates (Figure 3 A), and near 120°C in the presence of the surface

2 nitrates (Figure 3B).
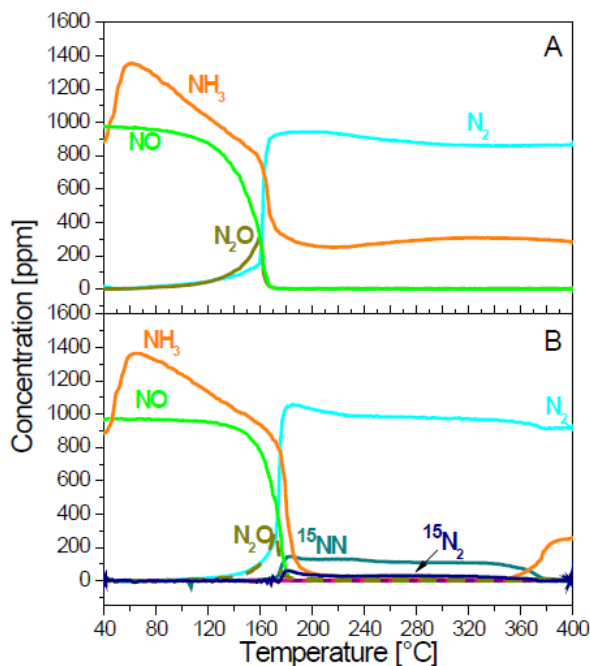
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4 Fig.3 - (A) TPR run with NH_3 (1000 ppm) and NO (1000 ppm) in He from 40 to 400°C, 10°C/min; (B) TPSR run with NH_3
5 (1000ppm) + NO (1000ppm) from 40 to 400°C, 10°C/min, after $^{15}NO_x$ adsorption at 350°C of 1000 ppm ^{15}NO + O_2 3%
6 v/v in He, over Pt-Ba/Al_2O_3 catalyst

7

Pathways for N_2 and N_2O formation

9 The results of NH_3-TPR and –TPSR reported above point out that nitrates stored onto the Pt-Ba/Al_2O_3 LNT

10 catalyst are selectively reduced by NH_3 to N_2, whereas the presence of gas-phase NO leads to a significant

11 formation of N_2O at low temperature. However when NO is fully consumed, the reaction becomes very

12 selective to N_2. Gas-phase NO is also slightly more reactive than the stored nitrates, as pointed out by the

13 comparison of the temperature onset for the NH_3-TPR and –TPSR reaction (100-120 °C vs. 160 °C).

14 Concerning N_2 formation, the evolution of all types of nitrogen isotopes (the single labeled $^{15}N^{14}N$ species,

15 and the double labeled $^{15}N_2$ and $^{14}N_2$ molecules) has been observed in the experiments with labeled NO or

16 labeled nitrates. This clearly points out the occurrence, in the formation of nitrogen, of self-coupling reactions

17 of unlabeled and labeled N-species, and from the coupling of labeled and unlabeled species as well. On the

18 other hand, labeled N_2O molecules have been detected when labeled NO is used, and unlabeled N_2O

19 starting from ^{14}NO. This clearly indicates that gaseous NO is involved in N_2O formation.

20 A schematic pathway for the formation of nitrogen and nitrous oxide during the reduction by NH_3 of gaseous

21 ^{15}NO and labeled nitrates adsorbed over Pt-Ba/Al_2O_3 is displayed in Figure 4. In the presence of ammonia at

1   sufficiently high temperatures, the Pt sites become reduced and this is the driving force for the onset of the

2   reduction process of gaseous ^{15}NO and/or of the stored ^{15}NO$_x$. Figure 4 depicts NO$_x$ species located on Ba

3   sites near Pt, but the same figure applies for NO$_x$ stored on Ba sites far away from Pt when the migration

4   (surface diffusion) of the stored ^{15}NO$_x$ towards the reduced Pt sites is considered[24]. The ^{15}NO$_x$ species are

5   hence decomposed at the reduced Pt sites with formation of a pool of O- and ^{15}N-adatoms. These latter

6   react with N-adspecies derived from NH$_3$ decomposition onto the Pt sites, eventually leading to the formation

7   of the various N$_2$ isotopes [6,11,25,26,27,28,29] whose abundance is expected to be determined by the surface

8   concentration on ^{14}N- and ^{15}N-adatoms (statistical recombination).
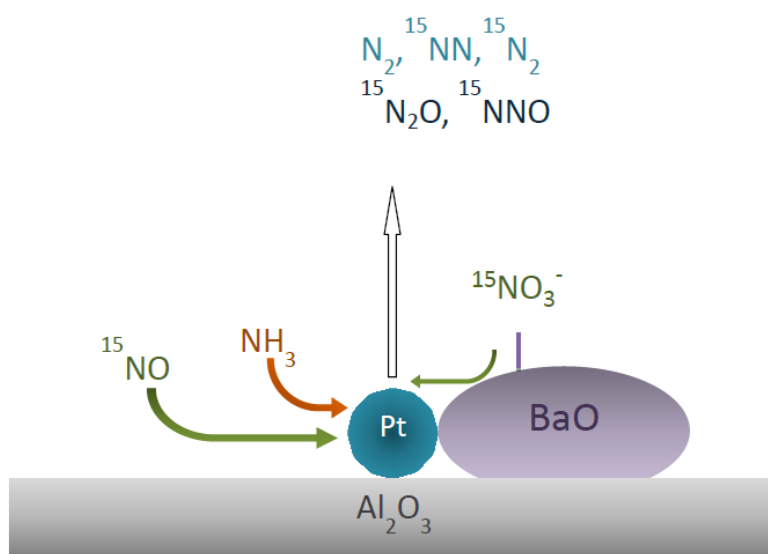
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10   Fig.7 Reaction pathway for ^{15}NO$_x$ reduction over Pt–Ba/Al$_2$O$_3$ catalyst

11

12   As a matter of facts, in the reduction of gas-phase ^{15}NO with NH$_3$ in the absence of oxygen (Figure 2 A),

13   where the reaction proceeds according to the stoichiometry of reaction (1), the expected statistical nitrogen

14   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

15   reasonably close to the measured average N$_2$ isotope distribution of the run in Figure 2 A at temperatures

16   above 180°C (^{14}N^{15}N/ ^{15}N$_2$/^{14}N$_2$ ≈ 57/29/14), although a slight excess of the single labeled isotope is

17   observed. In fact N$_2$ formation might involve a different pathway as well, i.e. the coupling of NO- and NH$_3$-

18   derived intermediates (SCR pathway), as suggested by Kondratenko and Baerns[25], and leading to the

19   selective formation of the single labeled nitrogen molecule (^{15}NN). The presence of significant amounts of

20   both the double labeled and of the unlabeled N$_2$ isotopes and the observation that the observed isotopic

1   distribution is reasonably close to that expected from the statistical recombination clearly rules out the SCR

2   pathway as unique route for N_2 formation, although its contribution is also likely.

3   Similar conclusion can also be derived for the reduction of the stored labeled nitrates (NH_3-TPSR), Figure 3

4   B. Also in this case the formation of only the mixed $^{14}N^{15}N$ species is not possible in view of the

5   stoichiometric ratio between the ^{14}N- and ^{15}N-containing reactants (reaction (2)), and the formation of the

6   double labeled $^{14}N_2$ isotope is expected. As a matter of fact, the NH_3-TPSR of nitrates (Figure 2 B) has led to

7   the formation of all the possible N_2 isotopes, with an average $^{14}N^{15}N/^{14}N/^{15}N_2$ isotopic distributions near

8   37/44/19. The presence of the double labeled N_2 isotope points out to the occurrence of a self-coupling

9   reaction of NO_x-derived intermediates, again ruling out the occurrence of a SCR pathway as unique pathway

10   for N_2 formation. However, as pointed out in a previous work[17], the reduction of nitrites (instead of nitrates)

11   gives initially the selective formation of the mixed $^{15}N^{14}N$ isotope, in line with the occurrence of a SCR-like

12   pathway. Hence, also in the case of nitrates the occurrence of a SCR-like pathways is also likely in

13   explaining the abundance of the $^{14}N^{15}N$ species.

14   The results obtained in the reduction of both the stored nitrates and NO (Figure 3 B) pointed out the greater

15   reactivity of gaseous NO if compared to stored NO_x. Apparently, stored nitrates are reduced by ammonia left

16   from the reaction with NO (the inlet NH_3 concentration exceeds the stoichiometry of reaction (1)) and the

17   relative concentrations of the ^{15}NN and $^{15}N_2$ isotopes resemble those observed in the absence of NO (Figure

18   2B), with ^{15}NN prevailing over $^{15}N_2$ (the high unlabeled N_2 concentration comes from the NH_3 + NO reaction).

19   Hence nitrogen formation upon reduction of the stored NO_x is apparently not altered by the concomitant

20   reduction of gas-phase unlabeled NO.

21   Concerning the formation of N_2O, negligible amounts of nitrous oxide have been observed during the TPSR

22   with adsorbed nitrates (Figure 2 B), whereas relevant quantities of N_2O have been detected in the runs in the

23   presence of NO (Figures 2 A and 3). The data converge in indicating that N_2O formation involve the

24   presence of gaseous NO: in the NH_3 +^{15}NO reaction, the formation of only labeled N_2O molecules has been

25   observed, whereas in the NH_3 + NO reaction in the presence of labeled stored nitrates no formation of

26   labeled N_2O has been observed. This is in line with literature proposals[,30] indicating that nitrous oxide

27   formation involves either the coupling of two adsorbed NO molecules or the recombination of an adsorbed

28   NO molecule with an adsorbed NH_x fragment.

29   Notably, nitrous oxide formation is strongly affected by temperature: in fact above 180 °C N_2O formation

30   becomes negligible. It is suggested that at high temperatures NO dissociation is favored since Pt is kept in a

1 reduced state by ammonia, and this prevents N_2O formation due to the lack of molecularly adsorbed NO

2 species. However, the possibility that N_2O is decomposed to N_2 and O_2 over reduced Pt sites is also likely,

3 as suggested by Cant et al.[31] . This route may contribute only to the formation of labelled N_2 molecules in the

4 experiment of Figure 2 A and of unlabeled N_2 in Figure 3 B in view of the fact that N_2O reduction does not

5 involve the cleavage of the N-N bond[31].

6

7 **Conclusions.**

8 In this paper mechanistic aspects involved in the formation of N_2 and N_2O during the reduction with ammonia

9 of gaseous NO and of NO_x stored over a model $Pt-Ba/Al_2O_3$ NSR catalyst have been investigated by means

10 of isotopic labeling experiments.

11 The reduction of gaseous labeled NO with unlabelled NH_3 leads to the formation of N_2O at low temperature

12 (below 180°C), and of N_2 at high temperature. The presence of all possible isotopes has been observed in

13 the case of N_2 ($^{15}N_2$, $^{14}N_2$ and the mixed $^{15}N^{14}N$ molecule), whereas only labeled molecules have been

14 detected in the case of N_2O. Based on the chemistry for the NO and NH_3 reaction on Pt-based catalysts, it

15 has been suggested that nitrous oxide formation involves either the coupling of two adsorbed NO molecules

16 or the recombination of an adsorbed NO molecule with an adsorbed NH_x fragment. On the other hand, the

17 observed N_2 product distribution can be explained on the basis of the statistical coupling of ^{15}N- and ^{14}N-

18 adatoms originated upon NH_3 and NO_x decomposition on Pt. However, the slight excess of the mixed $^{15}N^{14}N$

19 molecule suggests that SCR-like pathway operates as well in the reduction process. Indeed, in the case of

20 NH_3-SCR reaction, it has been shown that the reaction between unlabeled ammonia ($^{14}NH_3$) and labeled NO

21 (^{15}NO) leads to the selective formation of the single-labeled nitrogen molecule ($^{15}N^{14}N$)[17], indicating that one

22 N-atom comes from ammonia and the other from NO, as in the present case.

23 As opposite to the NH_3 + NO reaction, the reduction of the stored labelled nitrates with unlabelled NH_3 leads

24 to the selective formation of N_2, and again the presence of all possible isotopes has been observed. The

25 observed product distribution can be explained on the basis of the statistical coupling of ^{15}N- and ^{14}N-

26 adatoms originated upon NH_3 and NO_x decomposition on Pt, but the occurrence of a SCR pathway is also

27 likely.

28 Finally, the absence of N_2O in this case points out the lack of any significant NO release at low temperatures:

29 in fact when the reduction of the labeled stored NO_x is carried out in the presence of unlabeled gaseous NO,

1   unlabeled N_2O formation is greatly enhanced. Besides, gaseous NO shows a higher reactivity if compared to

2   the stored NO_x in the reduction with ammonia.

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