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## Study of the remarkable reactivity of HNCO/urea with NO<sub>2</sub> in the NO<sub>x</sub> SCR by urea process over an oxide-based catalyst.

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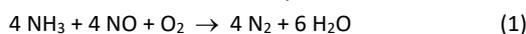
† Electronic supplementary information (ESI) available: Experimental set-up for catalytic tests (Urea-SCR and NH<sub>3</sub>-SCR). See DOI: 10.1039/c7cy00995j

An exceptional reactivity between NO<sub>2</sub> and probably HNCO was demonstrated over an oxide-based catalyst during NO<sub>2</sub>-SCR experiments with urea as injected reductant. This was observed when only NO<sub>2</sub> was used as NO<sub>x</sub>, but not with gaseous NH<sub>3</sub> as reductant. Roughly, one third the injected reductant reacted with NO<sub>2</sub> and two thirds appeared oxidized by O<sub>2</sub>, the main product being N<sub>2</sub>. 28 reactions may be involved in the observed results. A cooperative effect of NO<sub>2</sub> with O<sub>2</sub> was demonstrated and the observed global stoichiometry did not depend on the NO<sub>2</sub> concentration for (NO<sub>2</sub>/eq. NH<sub>3</sub>)<sub>inlet ratio</sub> ≤ 1.

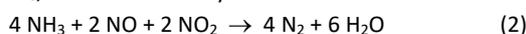
### Introduction

Air pollution from automotive traffic still induces severe environmental and human health damages despite the generalized implementation of catalytic converters to purify exhaust gases. Nevertheless, NO<sub>x</sub> treatment from engines operating in oxygen excess is still particularly challenging. To meet the current standards like Euro 6/VI, dedicated catalytic processes are required. The selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR), initially developed for stationary sources in the 1970s' is one of the most efficient way to reduce NO<sub>x</sub> into N<sub>2</sub> in excess of oxygen. Several stoichiometries are involved depending on the NO<sub>2</sub>/NO<sub>x</sub> ratio. The "standard-SCR" (eq. 1) and "fast-SCR" (eq. 2) are generally considered, both respecting a NH<sub>3</sub>/NO<sub>x</sub> ratio of 1. However, other stoichiometries are possible like the "NO<sub>2</sub>-SCR" reactions, which involve various NH<sub>3</sub>/NO<sub>x</sub> ratio depending on the participation of oxygen, as illustrated by eq. 3 and 4.

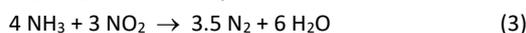
"standard-SCR", NH<sub>3</sub>/NO<sub>x</sub> stoichiometry: 1



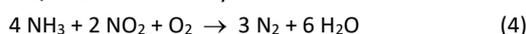
"fast-SCR", NH<sub>3</sub>/NO<sub>x</sub> stoichiometry: 1



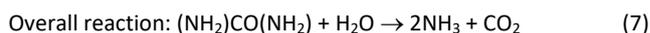
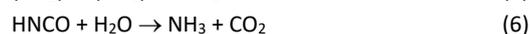
"NO<sub>2</sub>-SCR", NH<sub>3</sub>/NO<sub>x</sub> stoichiometry: 1.33



"NO<sub>2</sub>-SCR", NH<sub>3</sub>/NO<sub>x</sub> stoichiometry: 2



The implementation of the NH<sub>3</sub>-SCR process into vehicles requires the use of an ammonia precursor, provided by an urea aqueous solution (Adblue®) in the conventional process. After injection in the exhaust pipe, urea is firstly thermally decomposed into NH<sub>3</sub> and HNCO (eq. 5), and HNCO is then hydrolysed into a second molecule of NH<sub>3</sub> (eq. 6), providing the reductant species for the NH<sub>3</sub>-SCR process (eq. 7).



Unfortunately, urea decomposition may be uncomplete before or on the catalyst.<sup>1</sup> For instance, at low temperature (T<180°C), undesired by-products such as cyanuric acid, ammelide, biuret can be observed,<sup>2</sup> due to the high reactivity of HNCO intermediate species. Then, the conversion of urea to ammonia and/or the reactivity of by-products at the catalyst level have to be optimal. However, most studies performed at laboratory scale involve catalytic benches with NH<sub>3</sub> as reductant, especially because urea injection/vaporization is difficult to control. In order to evaluate powdered catalysts using the "real" reaction mixture, an innovative laboratory bench adapted to powdered catalysts (100 mg) was developed, allowing the use of NH<sub>3</sub> or urea (aqueous solution) as NO<sub>x</sub> reductant species.<sup>3</sup> The urea residence time between the injection zone and the catalytic bed is a key parameter of the deNO<sub>x</sub> efficiency. For short urea residence time, a significant decrease of the NO<sub>x</sub> reduction efficiency was observed over a prototype SCR catalyst provided by Solvay, when switching from gaseous NH<sub>3</sub> to urea aqueous solution, especially in "standard-SCR" condition.<sup>4</sup> However, the gas composition at the catalytic bed level is very difficult to assess because urea thermolysis and HNCO hydrolysis reactions are both strongly time and temperature dependent (in all gas analysis methods including heated sampling, a change of the mixture composition between the gas picking zone and the analysis cell is generally observed). Indirect methods were developed with addition of single oxides having specific activity either in urea thermolysis or HNCO hydrolysis. They showed that the decrease in NO<sub>x</sub> reduction with urea can be attributed to a lack in NH<sub>3</sub> availability due to limitations in HNCO hydrolysis.<sup>3</sup> Then, it was assumed that HNCO is largely present at the catalyst surface for the shorter urea residence time, even if traces of urea cannot be excluded.

More recently, the reactivity of HNCO in the NO<sub>x</sub> selective catalytic reduction was evidenced varying the NO<sub>2</sub>/NO<sub>x</sub> inlet ratio from 0 to 1.<sup>5</sup> Particularly, it was showed that a mix of both NO and NO<sub>2</sub> (Fast-SCR condition) was able to react with HNCO and contribute to the NO<sub>x</sub> reduction pathway of the Urea-SCR process. Additionally, it was observed that HNCO is highly reactive toward NO<sub>2</sub> alone (without introduced NO), but without supplementary NO<sub>x</sub> reduction. This point was just pointed out in ref. 5 and the purpose of the present work was to investigate this unexpected reactivity between HNCO and NO<sub>2</sub>, in order to clarify the involved stoichiometry/reaction(s). With this aim, the previously used SCR catalyst in ref. 5 was submitted to various reaction mixtures focussing on NO<sub>2</sub>/NO<sub>x</sub> inlet ratio of 0.7 and 1.

Note that the direct use of HNCO as reductant has been envisaged to support this work but isocyanic acid injection is subject to severe technical limitations. Indeed, HNCO is an unstable acid which is not commercially available. It can be obtained for instance by reaction of saturated KNCO with H<sub>3</sub>PO<sub>4</sub>,<sup>6</sup> by reaction of sodium cyanate (NaOCN) with gaseous HCl,<sup>7</sup> by thermal decomposition of cyanuric acid (a trimer of HNCO) or under primary vacuum,<sup>8</sup> or using a permeation source which sublimates solid cyanuric acid at 250°C in a flow of dry nitrogen.<sup>9</sup> This non-exhaustive list shows the technical complexity of the HNCO synthesis. Moreover, HNCO should not be in contact with water before the catalyst to avoid any hydrolysis, otherwise it would lead to a mix of reductant agents (HNCO/NH<sub>3</sub> with uncontrolled ratio). Finally, the direct use (and dosing) of HNCO in our catalytic conditions was considered as an unrealistic option. Only the direct comparison between the use of gaseous NH<sub>3</sub> or urea aqueous solution (with adequate residence time between the nozzle and the catalytic bed) allows us to point out the reactivity of HNCO.

## Experimental

The synthetic gas bench adjusted to powdered catalysts and allowing direct comparison of NH<sub>3</sub>-SCR and Urea-SCR is described in Figure S1 (supplementary information file). The deNO<sub>x</sub> efficiency of the powdered catalyst (100 mg) was evaluated in “NO<sub>2</sub>-rich SCR” and “NO<sub>2</sub>-only SCR” conditions using the realistic mixtures depicted in Table 1.

The total flow rate is fixed at 20 L h<sup>-1</sup>, which corresponds to a GHSV of about 160,000 h<sup>-1</sup>. For water and urea addition, an aqueous solution containing urea (1.33 10<sup>-1</sup> M, *i.e.* 0.794 wt%) was vaporized via a micro-nozzle (Ø=50 µm), provided by The Lee Company, into a

heated zone at 200°C upstream the catalytic bed. The liquid flow rate (19 µL min<sup>-1</sup>) was controlled by a HPLC micro pump (Jasco PU-2085, ΔP<sub>pump</sub>=10 bar).

The catalyst was placed in a quartz tubular micro-reactor (internal diameter of 8 mm) and its location can be changed in order to examine different residence times between the urea injection (placed upstream the catalytic bed into a heated zone at 200°C), and the catalytic bed, which is placed in a subsequent oven at temperature controlled between 200 and 500°C. The residence time (noted t<sub>R</sub>, elapsed time for the gaseous mixture between urea injection zone and the catalytic bed) was fixed at 5.2 s or 4.0 s. Note that the velocity of the urea ejection—at the nozzle outlet was not considered for this calculation. In this study, only tests performed with t<sub>R</sub> = 4.0 s are presented in comparison with the use of gaseous ammonia, since the results obtained with t<sub>R</sub> = 5.2 s were similar to those obtained with gaseous ammonia.

The compositions of the feed gas and effluent stream were monitored continuously using online MKS 2030 multigas infrared analyser for NO, NO<sub>2</sub>, N<sub>2</sub>O, HNCO, NH<sub>3</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O. It is important to note that without catalyst, in Urea-SCR condition, complete urea decomposition into ammonia is fully achieved at the analyser level, due to a long residence time between the catalyst and the analyser of about 34 s (all pipes are heated at 200°C, no HNCO is recorded). Consequently, only NH<sub>3</sub> is detected and the reductant outlet concentration is expressed as equivalent detected ammonia, denoted “NH<sub>3</sub>(eq)”. Note also that without catalyst, no evolution of the gas composition was recorded during the SCR experiments, whatever the studied temperature.<sup>3</sup> The studied catalyst, denoted aZr, was provided by Solvay. This material was developed for the urea-SCR process for vehicles equipped with a Diesel particulate filter (DPF). To ensure a high thermal stability, it is based on a modified zirconia with acidic and redox behaviours. Typical compositions are reported in patent WO2013037507 A1. The catalyst was previously hydrothermally aged 5 h at 600 °C and exhibited a specific surface area of 50 m<sup>2</sup> g<sup>-1</sup>. Before experiments, catalyst was pre-treated at 550 °C under oxidant atmosphere (10 % O<sub>2</sub>; 10 % CO<sub>2</sub> balanced in N<sub>2</sub>). Supplementary tests were also performed with the addition of 150 mg ZrO<sub>2</sub> (Solvay) upstream the SCR catalyst. ZrO<sub>2</sub> addition was demonstrated to allow the recovery of the activity in standard SCR condition (NO<sub>2</sub>/NO<sub>x</sub> = 0),<sup>3</sup> due to its catalytic activity in HNCO hydrolysis.<sup>10</sup>

**Table 1.** Gas feed compositions of for Urea-SCR catalytic tests (total flow rate 20 L h<sup>-1</sup>).

	NO <sub>2</sub> /NO <sub>x</sub> Inlet ratio	NO (ppm)	NO <sub>2</sub> (ppm)	Reductant (ppm)	O <sub>2</sub> (%)	H <sub>2</sub> O (%)	CO <sub>2</sub> (%)	N <sub>2</sub>
NO <sub>2</sub> -rich SCR	0.7	120	280	200 (urea)	10	8	10	balance
NO <sub>2</sub> -only SCR	1	0	400	or 400 (NH <sub>3</sub> )				

## Results and discussion

As presented at the end of the introduction section, an unexpected reactivity was observed in urea-SCR when only NO<sub>2</sub> was used as NOx (NO<sub>2</sub>-only condition, NO<sub>2</sub>/NO<sub>x,inlet</sub> = 1) compared with NO<sub>2</sub>-rich condition (NO<sub>2</sub>/NO<sub>x,inlet</sub> ratio of 0.7).<sup>5</sup> Obviously, these results were worthy of investigations to clarify the involved reaction(s) and to highlight competitive reactions of urea and its by-products with NO<sub>2</sub>-NO mixtures.

### SCR experiments with NO<sub>2</sub>/NO<sub>x</sub> = 0.7.

NOx and reductant conversions obtained in NO<sub>2</sub>-rich SCR condition are reported in Figures 1A and 1B, respectively.

NOx conversion with gaseous ammonia as reductant reached 52 % at 200°C and increased until 75% at 400°C. In this temperature range, the corresponding NH<sub>3</sub> conversion values were very similar. For higher temperature, NH<sub>3</sub> conversion still increased whereas NOx conversion decreased, indicating that a part of the reductant reacted with oxygen.

The use of an urea aqueous solution instead of gaseous ammonia led to the decrease of the deNOx efficiency, especially at low temperature: the NOx conversion at 200°C then reached 40%.

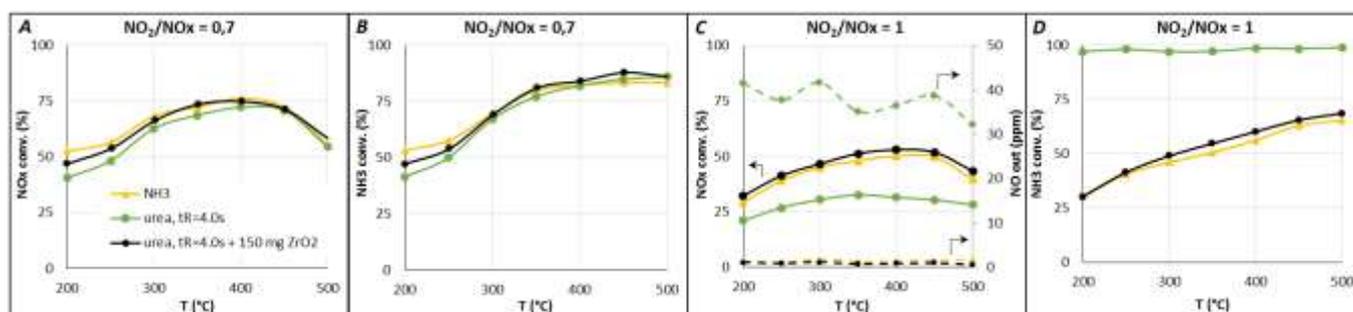
As previously showed in standard and fast-SCR condition,<sup>3,4</sup> the addition of ZrO<sub>2</sub> upstream the aZr SCR catalyst allowed again a satisfactory recovery of the NOx conversion in NO<sub>2</sub>-rich SCR condition. As a consequence, the conclusion highlighted in the previous works is still appropriate: the decrease in NOx efficiency using urea is attributed to a lack of suitable reductant, due to a poor activity in HNCO hydrolysis.

However, it is worth noting that NOx and reductant conversions appeared similar until 350°C, then respecting the fast and standard stoichiometry (Eq. 1 and Eq. 2), whereas the NO<sub>2</sub>-NH<sub>3</sub> SCR stoichiometry induces a greater conversion of ammonia than NOx, as reported in Eq. 3 and Eq. 4.

Considering the NO<sub>2</sub>/NO<sub>x</sub> inlet ratio (0.7), the NOx conversion is theoretically limited to 60% respecting the fast SCR stoichiometry (the standard SCR reaction is assumed to be disfavoured in this condition including NO<sub>2</sub> in the inlet gas). Nevertheless, the recorded NOx conversions in the 300-400°C temperature range were significantly higher than 60 % (75 % at 400°C, whatever the reductant agent urea or gaseous NH<sub>3</sub>).

The NOx over-conversion is then attributed to an *in situ* NO production by NO<sub>2</sub> decomposition. To respect the fast-SCR stoichiometry, this gain of conversion at 400°C requires a supplementary production of only 30 ppm of NO (from NO<sub>2</sub> decomposition).

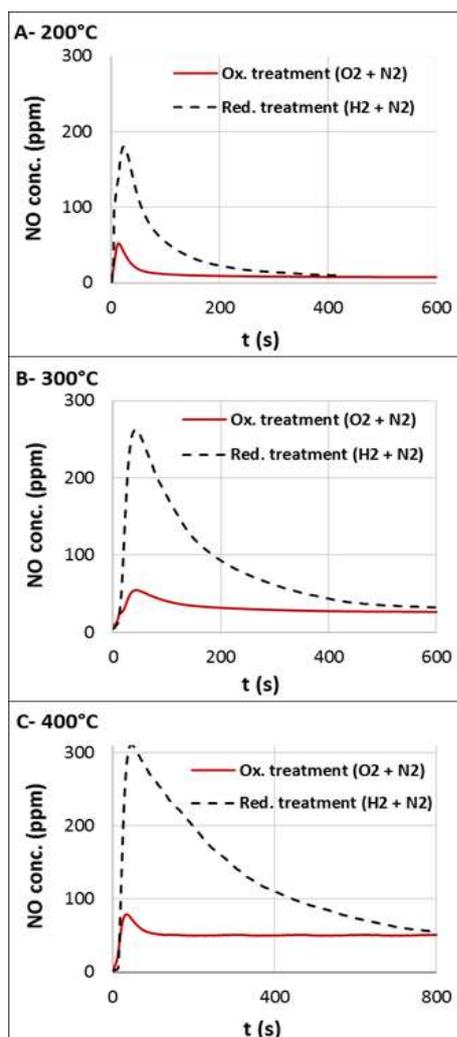
To confirm this assumption, the activity of aZr catalyst in NO – NO<sub>2</sub> balance in absence of reductant was studied. Note that there was no evolution of the NO – NO<sub>2</sub> balance depending on the temperature when tests were performed without catalyst. Results obtained with (NO<sub>2</sub>/NO<sub>x</sub>)<sub>inlet</sub> = 0.7 are reported in Table 2. As expected, the aZr catalyst influenced the NO<sub>2</sub>/NO<sub>x</sub> outlet ratio. A decrease of the NO<sub>2</sub> concentration was observed with temperature. For instance, at 400°C, 51 ppm of NO were supplementary provided by the NO<sub>2</sub> decomposition. This concentration is higher than the theoretical concentration needed to reach the observed NOx conversion respecting the fast SCR stoichiometry. Obviously, it is assumed that NOx conversion occurred respecting the fast-SCR stoichiometry for NO<sub>2</sub>/NO<sub>x</sub> inlet ratio of 0.7. Considering this inlet ratio, note that NO<sub>2</sub> conversion into NO for T<400°C appeared contradictory with the thermodynamic expectation which predicts an increase of the NO<sub>2</sub> concentration in this temperature range. In fact, the amounts of reduced NO<sub>2</sub> into NO for NO<sub>2</sub>/NO<sub>x</sub> = 0.7 were similar to those observed with NO<sub>2</sub>/NO<sub>x</sub> = 1 (Table2), which are then consistent with the thermodynamic expectation. One possible explanation is that the catalyst was mainly covered by NO<sub>2</sub> compared with NO for NO<sub>2</sub>/NO<sub>x</sub> inlet ratio of 0.7.



**Figure 1.** Full lines: NOx (A, C) and NH<sub>3</sub>(eq) (B, D) conversions recorded with NO<sub>2</sub>/NO<sub>x</sub> = 0.7 or 1 ; dotted lines in C : recorded outlet NO concentration. Reductant used: gaseous ammonia (—○—), urea with t<sub>R</sub> = 4.0 s (—□—); urea with t<sub>R</sub> = 4.0 s with addition of ZrO<sub>2</sub> upstream the SCR catalyst (—△—).

**Table 2.** NO – NO<sub>2</sub> balance over aZr catalyst versus temperature in absence of reductant for NO<sub>2</sub>/NO<sub>x</sub> inlet ratio of 0.7 and 1. Inlet gas mixture: 400ppm NO<sub>x</sub>, 8 % H<sub>2</sub>O, 10 % O<sub>2</sub> and 10 % CO<sub>2</sub>.

T (°C)	NO-NO <sub>2</sub> thermodynamic equilibrium				NO <sub>2</sub> /NO <sub>x</sub> inlet = 0.7 (120 ppm NO, 280 ppm NO <sub>2</sub> )			NO <sub>2</sub> /NO <sub>x</sub> inlet = 1 (400 ppm NO <sub>2</sub> )		
	with 10% O <sub>2</sub>		without 10% O <sub>2</sub>		NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> →NO (ppm)	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> →NO (ppm)
	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO (ppm)						
200	396	4	388	12	271	129	9	389	10	10
250	388	12	371	29	264	135	15	384	15	15
300	360	40	340	60	248	152	32	374	25	25
350	316	84	294	105	240	160	40	366	35	35
400	256	144	237	163	228	171	51	353	47	47



**Figure 2.** NO emission during NO<sub>2</sub> reduction tests (400 ppm NO<sub>2</sub>, total flow rate 20 L h<sup>-1</sup>) at (A): 200°C, (B): 300°C and (C):400°C.

#### SCR experiments with NO<sub>2</sub>/NO<sub>x</sub> = 1.

**NH<sub>3</sub>-SCR with NO<sub>2</sub>/NO<sub>x</sub> = 1, NO involvement.** SCR measurements without NO in the inlet gas mixture (“NO<sub>2</sub>-only” SCR condition, NO<sub>2</sub>/NO<sub>x</sub>=1) are presented in Figures 1C and 1D. Using ammonia as reductant agent, the NH<sub>3</sub> conversion was decreased compared with (NO<sub>2</sub>/NO<sub>x</sub>)<sub>inlet</sub> = 0.7. It started from 30 % at 200°C and continuously increased to 65 % at 500°C. Interestingly, ammonia conversion rate

is similar to NO conversion until 350°C, which indicates again a fast-SCR stoichiometry. No outlet NO was recorded (dotted line, Figure 1C).

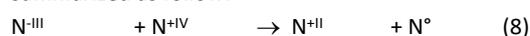
In fact, the fast-SCR stoichiometry is theoretically not possible in absence of NO in the inlet mixture. However, results reported in Table 2 illustrate that aZr catalyst is able to partially decompose NO<sub>2</sub> into NO in absence of reductant. Nevertheless, the NO formation in this condition was not sufficient to assure the DeNO<sub>x</sub> efficiency respecting the fast-SCR stoichiometry observed in Figures 1C 1D. However, experiments reported in Table 2 were performed without any reductant, which is not the case during the SCR tests. This could impact the redox state of the catalyst and its NO<sub>2</sub> decomposition behaviour.

To check the possible role of the redox state of the catalyst, the activity of the aZr catalyst in NO<sub>2</sub> decomposition was studied at 200, 300 and 400°C after an oxidative pre-treatment (15 min under 10 % O<sub>2</sub> balanced in N<sub>2</sub>) or a reducing one (15 min under 5 % H<sub>2</sub> balanced in N<sub>2</sub>) carried out at the same temperatures (a purge of 15 min under N<sub>2</sub> was performed before NO<sub>2</sub> introduction). The change of the NO emissions with time on stream are reported in Figure 2. Pulses of NO emission are always observed when switching from pre-treatment atmosphere to the mixture composed of 400 ppm NO<sub>2</sub> balanced in N<sub>2</sub>. Note that for each studied temperature, same NO concentrations were recorded at steady state (600-800 s.) whatever the pre-treatment mixture: 6 ppm at 200°C, 26 ppm at 300°C and 60 ppm at 400°C. All these values are lower than those calculated from thermodynamic data reported in Table 2 which also take into account the presence of 10 % O<sub>2</sub>. Then, the catalyst did not allow to reach the thermodynamic equilibrium with the used space velocity. Nevertheless, Figure 2 also put in evidence that the observed NO formation pulse was strongly dependent to the pre-treatment atmosphere and the temperature test. The maximum NO concentrations vary from 50 ppm to 310 ppm. Figure 2 clearly indicates that the NO<sub>2</sub> decomposition into NO was significantly enhanced by a reducing pre-treatment. Thus it is assumed that the presence of reductant agents such NH<sub>3</sub> during SCR experiments favourably interferes in the NO<sub>2</sub> decomposition over the aZr sample, justifying the observed equivalent ammonia and NO<sub>x</sub> conversions reported in Figure 1 even for the “NO<sub>2</sub>-only” SCR condition.

**Urea-SCR with NO<sub>2</sub>/NO<sub>x</sub> = 1: O<sub>2</sub> involvement.** Switching from gaseous ammonia to urea obviously strongly interfered in reductant

reactivity when only NO<sub>2</sub> was injected as NO<sub>x</sub> (Figures 1C and 1D). The reductant species were then surprisingly almost fully converted, whereas a decrease of the NO<sub>x</sub> conversion was observed, with a maximum lower than 40 %. In addition, significant NO concentration was then detected (30-40 ppm), while NO was not recorded when “NO<sub>2</sub>-only” SCR test was performed with NH<sub>3</sub> (dotted line, Figure 1C). Again, addition of ZrO<sub>2</sub> upstream the SCR catalyst induced similar results than those obtained with gaseous ammonia (black and yellow curves). Detailed experimental data obtained in “NO<sub>2</sub> only” SCR over the SCR catalyst in the 200-500°C temperature range are reported in Table S2 (supplementary information file). To illustrate the global reaction stoichiometry, the temperature of 200°C was selected and the corresponding N-species balance obtained with urea is reported in Table 3.

The overall reaction corresponding to data recorded at 200°C can be summarized as follow:



$$388 \text{ ppm} \quad 128 \text{ ppm} \rightarrow 42 \text{ ppm} \quad 474 \text{ ppm}$$

in which: N<sup>III</sup> species are urea, HNCO or NH<sub>3</sub>.

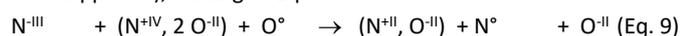
N<sup>IV</sup> species is NO<sub>2</sub>

N<sup>II</sup> species is NO

N<sup>°</sup> species is N<sub>2</sub> (474 ppm N<sup>°</sup> correspond to 237 ppm N<sub>2</sub>, calculated from N balance of Eq. 8)

Taking into account the redox state of the involved N-species, Eq. 8 is not balanced. It could be balanced with the involvement of 312 ppm NO<sub>2</sub> and 658 ppm N<sup>°</sup> but nitrogen dioxide cannot be converted in a larger extent than 128 ppm to respect the recorded data (Table 3). Consequently, another oxidant agent must be taken into account to obtain a balanced redox state. Although NO<sub>2</sub> is recognized as a more powerful oxidant agent than O<sub>2</sub>, oxygen contribution has to be considered as co-oxidant agent in the gas mixture.

To balance Eq. 8 with O<sub>2</sub>, 184 ppm O<sub>2</sub> are needed (which correspond to 368 ppm O<sup>°</sup>), leading to Eq. 9.



$$388 \text{ ppm} \quad 128 \text{ ppm} \quad 368 \text{ ppm} \rightarrow 42 \text{ ppm} \quad 474 \text{ ppm} \quad 582 \text{ ppm}$$

in which: O<sup>°</sup> species is O<sub>2</sub> (368 ppm O<sup>°</sup> correspond to 184 ppm O<sub>2</sub>)

O<sup>-II</sup> species are oxygenated compounds like H<sub>2</sub>O, CO<sub>2</sub>...

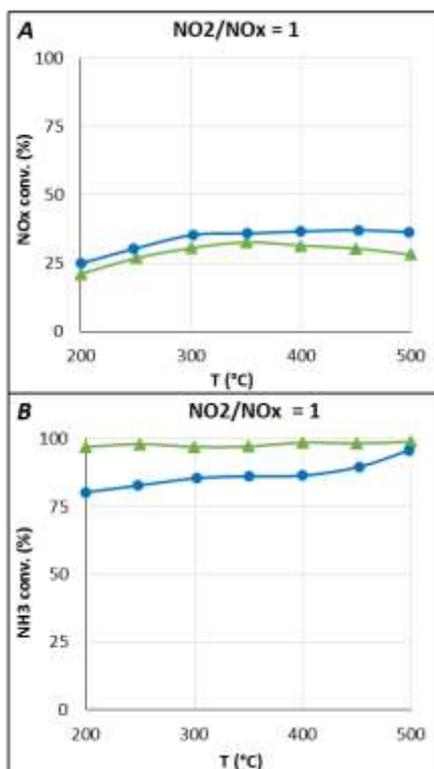
Compared with gaseous ammonia, the higher reactivity of urea and its by-products (assumed to be mainly HNCO) toward oxidation by O<sub>2</sub> was previously demonstrated,<sup>3</sup> especially in the 250-400°C temperature range. However, at 200°C, there was no oxidation of the reductant, whatever the injected species (NH<sub>3</sub> or urea). As a consequence, results reported Figure 1 in NO<sub>2</sub>-only SCR condition demonstrate the high reactivity of the reductants other than NH<sub>3</sub> toward oxidation by NO<sub>2</sub> (a more powerful oxidative agent than O<sub>2</sub>), but participation of O<sub>2</sub> is also evidenced. Reaction products are mainly nitrogen but NO is also produced.

To confirm the participation of O<sub>2</sub> in the reductant conversion, new catalytic tests in which oxygen was not introduced were performed. Unfortunately, even with high purity gases, traces of oxygen in the pipes are expected. Air Liquide gas supplier indicates O<sub>2</sub> concentrations of 2 ppm, <50 ppm and <100 ppm in CO<sub>2</sub>, NO<sub>2</sub>, and N<sub>2</sub> gas cylinders, respectively.

Corresponding results reported in Figure 3 (blue lines) show that removing O<sub>2</sub> from the inlet mixture led to a slight increase of the NO<sub>x</sub> conversion. Interestingly, while nearly no ammonia was detected in presence of O<sub>2</sub>, NH<sub>3</sub> emission significantly increases in absence of oxygen (blue curve, Figure 3B), highlighting the reactivity of O<sub>2</sub> with urea by-products. However, the amount of residual ammonia remains lower than that observed in NH<sub>3</sub>-SCR condition, illustrating certainly the residual traces of oxygen in the experimental setup. Note that in Eq. 9, only 184 ppm O<sub>2</sub> (368 ppm O<sup>°</sup>) are estimated involved in N<sup>III</sup> species oxidation. This result tends to confirm that the reactivity of urea by-products toward oxidation is enhanced in “NO<sub>2</sub> only” condition and much higher than with NO<sub>2</sub> alone, or O<sub>2</sub> alone as previously described in ref. 3. Similar results were also reported by Takeda *et al.*<sup>11</sup> which studied the reaction of adsorbates derived from cyanuric acid on an exchanged Cu zeolite with NO<sub>x</sub> and O<sub>2</sub>. Authors reported that the reaction rate of HNCO oxidation is much higher with a mixture of NO<sub>x</sub> + O<sub>2</sub> than that with O<sub>2</sub>, as also well known for soot combustion.<sup>12</sup>

**Table 3.** Experimental data obtained at 200°C in “NO<sub>2</sub> only” SCR (gas mixture reported in Table 1, urea =200 ppm, t<sub>R</sub> = 4.0 s): N-species balance.

gas	Inlet Conc. (ppm)	Outlet conc. (ppm)	Δ (ppm)
NO <sub>x</sub>	400	314	-86
NO <sub>2</sub>	400	272	-128
NO	0	42	+42
NH <sub>3</sub> (eq)	400 (eq)	12	-388



**Figure 3.** Effect of oxygen on the Urea-SCR behaviour in NO<sub>2</sub>-only SCR (NO<sub>2</sub>/NO<sub>x</sub>=1) over aZr catalyst. (A): NO<sub>x</sub> conversion; (B): (NH<sub>3</sub>)<sub>eq</sub> conversion

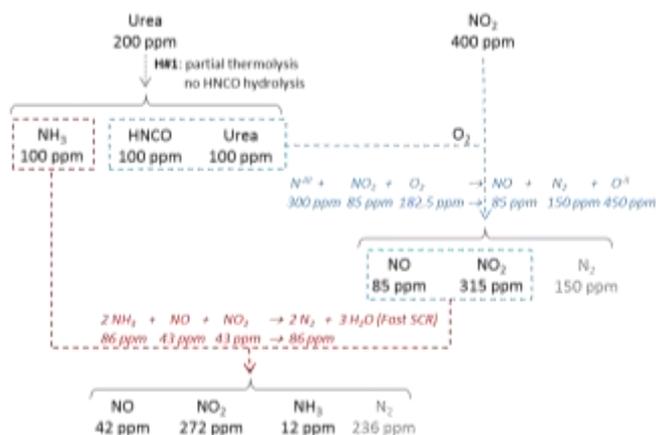
(▲): 400 ppm NO<sub>2</sub>, 200 ppm urea, 8 % H<sub>2</sub>O, 10 % O<sub>2</sub>, 10 % CO<sub>2</sub>.

(●): 400 ppm NO<sub>2</sub>, 200 ppm urea, 8 % H<sub>2</sub>O, 0 % O<sub>2</sub>, 10 % CO<sub>2</sub>.

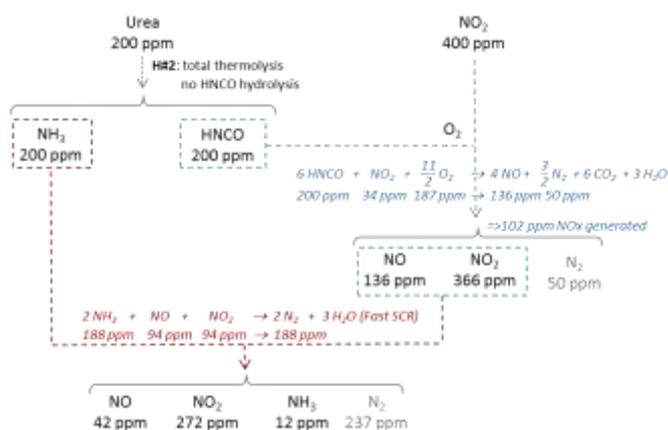
**Reaction schemes and nitrogen species balance at 200°C.** In order to explain the observed N-product evolution at 200°C (Table 3), different routes were envisaged. Assuming that (i) ammonia is converted only following the fast-SCR stoichiometry (eq. 2), in accordance with results observed with gaseous NH<sub>3</sub>, and (ii) O<sub>2</sub> contribution have to be considered in the overall reaction; as demonstrated in the previous section, two relevant reaction pathways were identified and described below.

**Hypothesis #1:** The amount of generated NH<sub>3</sub> is equivalent to the amount of converted NO<sub>x</sub>, and no over production of NO<sub>x</sub> from reductant oxidation is considered. Based on data reported in Table 3, calculations were performed and the corresponding reaction pathway is illustrated in Figure 4.

Experimental data showed that 86 ppm of NO<sub>x</sub> were converted and 12 ppm of NH<sub>3</sub> were emitted at 200°C. Assuming a fast-SCR stoichiometry, the corresponding amount of formed NH<sub>3</sub> is 98 ppm (86+12) and an equal quantity of NO and NO<sub>2</sub> is assumed to be reduced into N<sub>2</sub> (43 ppm of NO and 43 ppm of NO<sub>2</sub>). As a consequence, only 85 ppm of NO<sub>2</sub> (128<sub>disappeared</sub>-43<sub>reacted with NH<sub>3</sub></sub>) are involved in the full oxidation of the reductant, with simultaneously the production of 85 ppm NO. Besides, the formation of only 98 ppm of NH<sub>3</sub> induces an incomplete urea thermolysis and/or HNCO hydrolysis.

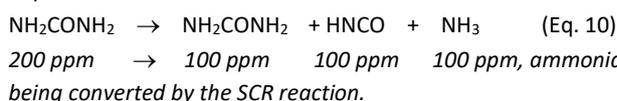


**Figure 4.** Reaction pathways corresponding to hypothesis #1. Note that the NH<sub>3</sub> formation should be limited at 98 ppm to perfectly fit with the calculations.



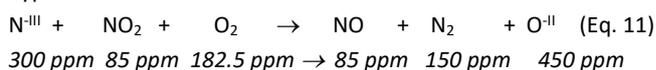
**Figure 5.** Reaction pathways corresponding to hypothesis #2.

Consequently, the corresponding amount of remaining reductant in the N<sup>-III</sup> oxidation state (NH<sub>2</sub>CONH<sub>2</sub>, HNCO) is around 300 ppm, as for instance 100 ppm urea and 100 ppm HNCO as illustrated below (Eq. 10):



In regards of the amount of NO<sub>2</sub> converted into NO (85 ppm), it results in a lack of oxidation agent to oxidize the remaining reductant species into N<sub>2</sub>. Then, the contribution of O<sub>2</sub> is needed to respect the observed N-balance. Note that only 182.5 ppm O<sub>2</sub> are needed, which represents a very small proportion of the oxygen included in the feed gas.

Finally, the following reaction (Eq. 11) can be put forward to illustrate hypothesis #1:



**Hypothesis #2:** The urea thermolysis is not the determining-step of NH<sub>3</sub> generation. Corresponding calculations from experimental results are illustrated in Figure 5.

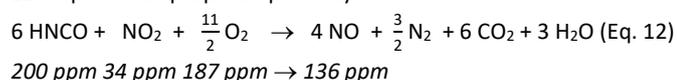
In this hypothesis, the urea thermolysis is achieved, producing 200 ppm of NH<sub>3</sub> and 200 ppm HNCO. It is assumed that NH<sub>3</sub> reacts following the fast-SCR reaction while HCNO reacts via a more complex way, as detailed below. Considering that 12 ppm NH<sub>3</sub> are recorded at the outlet, 188 ppm NH<sub>3</sub> are supposed to react with 94 ppm NO and 94 ppm NO<sub>2</sub>. As 42 ppm of NO is emitted, then 94+42=136 ppm of NO are generated from NO<sub>2</sub> reduction (total NOx over generation: 136-94=102 ppm).

As previously mentioned, 86 ppm of NOx are apparently converted (21 % NOx conversion for 400 ppm NO<sub>2</sub> in the inlet mixture). Again, based on the fast-SCR stoichiometry, the corresponding amount of reacted NH<sub>3</sub> for NOx reduction is 86 ppm. As 188 ppm NH<sub>3</sub> are supposed to disappear, 102 ppm of ammonia (188-86) have to be additionally converted by reaction with 102 ppm NOx (no NH<sub>3</sub> – O<sub>2</sub> reactivity was recorded at 200°C<sup>3</sup>). To respect the outlet measured NOx concentrations, the effective NOx concentration at the catalyst level reaches 502 ppm (400+102).

Based on this hypothesis, calculations give the following results:

502 ppm NOx are needed, respecting the balance of 366 ppm NO<sub>2</sub> (272<sub>out</sub>+94<sub>converted</sub>) and 136 ppm NO (42<sub>out</sub>+94<sub>converted</sub>). The reaction of 200 ppm of NH<sub>3</sub> (obtained by urea thermolysis) respecting the fast-SCR stoichiometry leads to 272 ppm NO<sub>2</sub>, 42 ppm NO and 12 ppm NH<sub>3</sub> as reported in Table 3.

To obtain the theoretical calculated NOx composition (366 ppm NO<sub>2</sub> and 136 ppm NO) taking into account that 400 ppm NO<sub>2</sub> are initially introduced, 34 ppm NO<sub>2</sub> have to be converted together with the over formation of 136 ppm NO. In the same time, 200 ppm HNCO have to be fully oxidized into N<sub>2</sub>. Again, a lack in oxidizing species appears, indicating the participation of O<sub>2</sub>. The proposed equation 12 respects this proposed pathway:



To conclude, both hypothesis #1 and #2 point out the participation of O<sub>2</sub> in addition to NO<sub>2</sub> to oxidize the reductant species (other than ammonia<sup>3</sup>) and respect the experimental results recorded in Figures 1C and 1D.

In order to evaluate the most probable hypothesis #1 or #2, supplementary experiments were performed. As previously presented in Figure 1, the addition upstream of ZrO<sub>2</sub>, an active material in HNCO hydrolysis, allowed the recovery of the same DeNOx behaviour than that obtained with gaseous NH<sub>3</sub>. Remarkably, no emission of NO was then observed using this dual bed catalytic configuration (ZrO<sub>2</sub>+aZr materials). These experimental results strongly suggest that HNCO is largely present at the catalyst surface (without excluding the possible presence of traces of urea) and hypothesis #2 appears the more realistic. The main drawback of the hypothesis #1 remains the poor advancement in urea thermolysis (together with no HNCO hydrolysis), which fits rather badly with other reported results in this study.

Finally, even if NO<sub>2</sub> is a much more powerful oxidizer than O<sub>2</sub>, the participation of O<sub>2</sub> in the total reductant consumption in NO<sub>2</sub>-only SCR condition is evidenced, even at low temperature (200°C) for

which no reactivity with O<sub>2</sub> was previously observed.<sup>3</sup> A synergy effect between NO<sub>2</sub> and O<sub>2</sub> is not excluded.

#### **Urea-SCR with NO<sub>2</sub>/NOx = 1: possible involved reactions and observed stoichiometry.**

Results reported in the previous section demonstrates the oxidation of N<sup>III</sup> species by both NO<sub>2</sub> and O<sub>2</sub>. However, considering all the reagents and products implied in the SCR process, numerous reactions may be involved leading to the observed results.

With a general overview, the possible generic reaction can be described as follow:

- (N<sup>III</sup>) reductant species may react with NO<sub>2</sub> to form N<sub>2</sub> (A type reactions);
- (N<sup>III</sup>) may react with NO<sub>2</sub> to form N<sub>2</sub> (from N<sup>III</sup>) and NO (from NO<sub>2</sub>) (B type reactions);
- (N<sup>III</sup>) may react with NO<sub>2</sub> to form NO (from N<sup>III</sup>) and N<sub>2</sub> (from NO<sub>2</sub>) (C type reactions);
- (N<sup>III</sup>) may react with NO<sub>2</sub> to form NO (D type reactions);
- E type and F type reactions correspond to the (N<sup>III</sup>) oxidation by O<sub>2</sub> into N<sub>2</sub> and NO, respectively.

All these generic reaction are reported in Table 4. For each reaction involving N<sup>IV</sup> species (i.e. NO<sub>2</sub>), NO<sub>2</sub> can be partially substituted by ½ O<sub>2</sub> until obtain reactions E and F. The corresponding stoichiometries considering HNCO as reductant are also reported in Table 4. Finally, it leads to 28 different reactions.

The observed behaviour in NO<sub>2</sub>-SCR probably results in a combination of these reactions. In addition, the probable role of NO as intermediate species of the DeNOx process by NO<sub>2</sub>, as proposed in Figure 4 (hypothesis # 1), is not considered. Nevertheless, in order to have a better view of the global stoichiometry, new NO<sub>2</sub>-SCR experiments were carried out at the selected temperature of 200°C. Unfortunately, due to technical limitations, it was not possible to vary the oxygen concentration in a controlled low level (see section 3.2.2). Varying the urea concentration was also aborted because new aqueous solution had to be prepared for each desired concentration, leading to un-continuous measurements which was not suitable.

As a consequence, only tests varying the NO<sub>2</sub> inlet concentration between 0 and 500 ppm were performed.

Corresponding results are reported Figure 6. Two different behaviours are distinguished: one in the 0-400 ppm NO<sub>2</sub> concentration range and the other for higher NO<sub>2</sub> inlet concentrations.

Until 400 ppm NO<sub>2</sub>, the NOx conversion was rather stable, at approximately 27-28%. It indicates a kinetic order close to 1 for NO<sub>2</sub>. Interestingly, in this 0-400 ppm NO<sub>2</sub> inlet concentration range, NH<sub>3</sub>, NO and NO<sub>2</sub> outlet concentrations exhibited linear evolutions, as well as calculated N<sub>2</sub> formation.

It indicates that the same global stoichiometry was respected at 200°C. As a consequence, there is no influence of a large reductant excess (i.e. for low NO<sub>2</sub> inlet concentrations) on the observed balance between the involved reactions

**Table 4.** Generic reactions possibly involved in the observed results in NO<sub>2</sub>-SCR.

Generic reactions*	Corresponding stoichiometries considering HNCO as reductant		
(A) type reactions	4 HNCO + 3 NO <sub>2</sub>	= 7/2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(A1)
	4 HNCO + 5/2 NO <sub>2</sub> + 1/2 O <sub>2</sub>	= 13/4 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(A2)
N <sup>+III</sup> + N <sup>+IV</sup> = N <sup>°</sup> + N <sup>°</sup>	4 HNCO + 2 NO <sub>2</sub> + O <sub>2</sub>	= 3 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(A3)
	4 HNCO + 3/2 NO <sub>2</sub> + 3/2 O <sub>2</sub>	= 11/4 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(A4)
	4 HNCO + 1 NO <sub>2</sub> + 2 O <sub>2</sub>	= 5/2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(A5)
	4 HNCO + 1/2 NO <sub>2</sub> + 5/2 O <sub>2</sub>	= 9/4 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(A6)
	4 HNCO + 3 O <sub>2</sub>	= 2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(E)
(B) type reactions	4 HNCO + 6 NO <sub>2</sub>	= 2 N <sub>2</sub> + 6 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B1)
	4 HNCO + 5 NO <sub>2</sub> + 1/2 O <sub>2</sub>	= 2 N <sub>2</sub> + 5 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B2)
N <sup>+III</sup> + N <sup>+IV</sup> = N <sup>°</sup> + N <sup>+II</sup>	4 HNCO + 4 NO <sub>2</sub> + O <sub>2</sub>	= 2 N <sub>2</sub> + 4 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B3)
	4 HNCO + 3 NO <sub>2</sub> + 3/2 O <sub>2</sub>	= 2 N <sub>2</sub> + 3 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B4)
	4 HNCO + 2 NO <sub>2</sub> + 2 O <sub>2</sub>	= 2 N <sub>2</sub> + 2 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B5)
	4 HNCO + 1 NO <sub>2</sub> + 5/2 O <sub>2</sub>	= 2 N <sub>2</sub> + 1 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B6)
	4 HNCO + 3 O <sub>2</sub>	= 2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(E)
(C) type reactions	4 HNCO + 5 NO <sub>2</sub>	= 4 NO + 5/2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(C1)
	4 HNCO + 4 NO <sub>2</sub> + O <sub>2</sub>	= 4 NO + 2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(B3)
N <sup>+III</sup> + N <sup>+IV</sup> = N <sup>+II</sup> + N <sup>°</sup>	4 HNCO + 3 NO <sub>2</sub> + 2 O <sub>2</sub>	= 4 NO + 3/2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(C2)
	4 HNCO + 2 NO <sub>2</sub> + 3 O <sub>2</sub>	= 4 NO + N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(C3)
	4 HNCO + 1 NO <sub>2</sub> + 4 O <sub>2</sub>	= 4 NO + 1/2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(C4)
	4 HNCO + 5 O <sub>2</sub>	= 4 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(F)
(D) type reactions	4 HNCO + 10 NO <sub>2</sub>	= 14 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D1)
	4 HNCO + 9 NO <sub>2</sub> + 1/2 O <sub>2</sub>	= 13 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D2)
N <sup>+III</sup> + N <sup>+IV</sup> = N <sup>+II</sup> + N <sup>+II</sup>	4 HNCO + 8 NO <sub>2</sub> + O <sub>2</sub>	= 12 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D3)
	4 HNCO + 7 NO <sub>2</sub> + 3/2 O <sub>2</sub>	= 11 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D4)
	4 HNCO + 6 NO <sub>2</sub> + 2 O <sub>2</sub>	= 10 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D5)
	4 HNCO + 5 NO <sub>2</sub> + 5/2 O <sub>2</sub>	= 9 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D6)
	4 HNCO + 4 NO <sub>2</sub> + 3 O <sub>2</sub>	= 8 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D7)
	4 HNCO + 3 NO <sub>2</sub> + 7/2 O <sub>2</sub>	= 7 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D8)
	4 HNCO + 2 NO <sub>2</sub> + 4 O <sub>2</sub>	= 6 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D9)
	4 HNCO + 1 NO <sub>2</sub> + 9/2 O <sub>2</sub>	= 5 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(D10)
	4 HNCO + 5 O <sub>2</sub>	= 4 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(F)
(E) type reaction	4 HNCO + 3 O <sub>2</sub>	= 2 N <sub>2</sub> + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(E)
N <sup>+III</sup> + O <sup>°</sup> = N <sup>°</sup>			
(F) type reaction	4 HNCO + 5 O <sub>2</sub>	= 4 NO + 4 CO <sub>2</sub> + 2 H <sub>2</sub> O	(F)
N <sup>+III</sup> + O <sup>°</sup> = N <sup>+II</sup>			

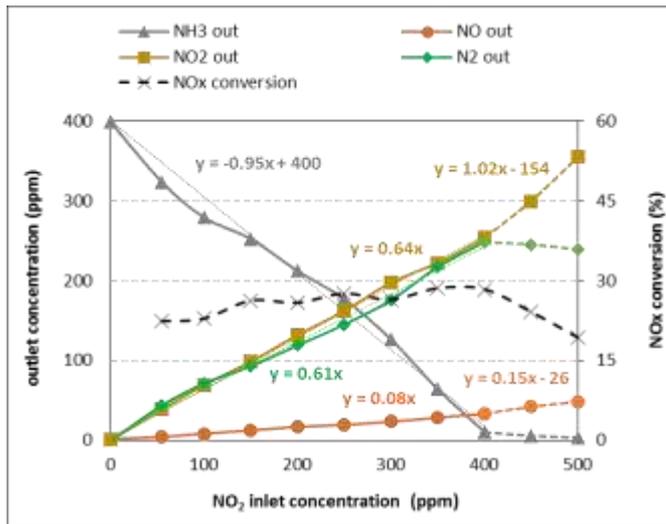
\*in which N<sup>+III</sup> species are urea, HNCO or NH<sub>3</sub>.

N<sup>+IV</sup> species is NO<sub>2</sub>

N<sup>+II</sup> species is NO

N<sup>°</sup> species is N<sub>2</sub>

O<sup>°</sup> species is O<sub>2</sub>



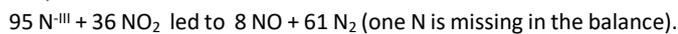
**Figure 6.** NO<sub>x</sub> conversion (dotted line) and outlet mixture composition (full line) in NO<sub>2</sub>-SCR experiments depending on the NO<sub>2</sub> inlet concentration. T = 200°C; urea t<sub>R</sub> = 4.0s.

If "x" is the NO<sub>2</sub> inlet concentration, the slope for outlet reductant concentration, recorded as NH<sub>3</sub> species, was fixed to -0.95x. It means that the reductant consumption was equal to 95 % of the NO<sub>2</sub> inlet concentration, whatever the NO<sub>2</sub> inlet concentration in the 0-400 ppm range. The slope for outlet NO<sub>x</sub> species was 0.72x, indicating that the ammonia consumption was around 3.4 times higher than the NO<sub>x</sub> consumption (0.95/(1-0.72)). Moreover, 64 % of the injected NO<sub>2</sub> did not react while 8 % appeared reduced into NO (NO may also come from N<sup>-III</sup> oxidation by O<sub>2</sub>, reaction F in Table 4). NO<sub>2</sub> reduction rate into N<sub>2</sub> cannot be rigorously calculated since N<sub>2</sub> may come from NO<sub>2</sub> reaction with N<sup>-III</sup> (A, B, C type reactions, corresponding to 16 different reactions, table 4) or from N<sup>-III</sup> oxidation by O<sub>2</sub> (reaction (E)).

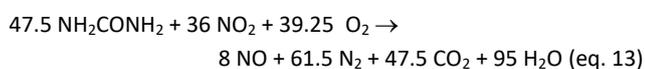
Finally, the general observed stoichiometry for the 0-400 ppm NO<sub>2</sub> inlet range can be summarized as follow:



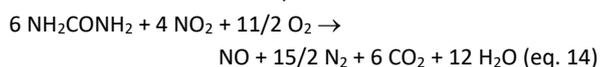
Simplified as:



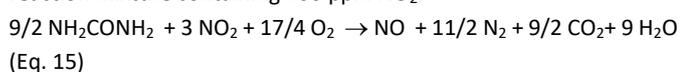
To balance these products, O<sub>2</sub> have to be included. Considering urea as initial reductant species, the reaction respects the following balance:



This reaction can be coarsely rounded to:



Note that this balance is rather close to that previously proposed in ref 5 (Eq. 15) which was deduced only from results obtained with the reaction mixture containing 400 ppm NO<sub>2</sub>.



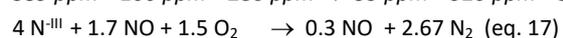
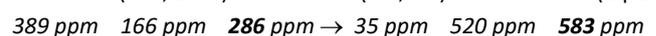
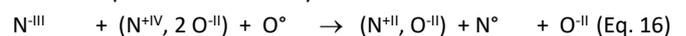
Taking into accounts reactions reported in Table 4, the observed stoichiometry could correspond to various combinations. For

instance, the combination (B6\*8) + (A3\*14) + (E \*1.4) gives the stoichiometry reported in eq. 13. Nevertheless, stoichiometry calculated from reaction A4 gives a result close to that reported in eq. 13 even if this reaction does not consider the NO formation. It would correspond to: 48 NH<sub>2</sub>CONH<sub>2</sub> + 36 NO<sub>2</sub> + 36 O<sub>2</sub> = 66 N<sub>2</sub> + 96 CO<sub>2</sub> + 48 H<sub>2</sub>O.

For NO<sub>2</sub> inlet concentrations higher than 400 ppm, the NO<sub>x</sub> conversion was decreased because the reductant species was then almost fully converted (Figure 6). The NO<sub>2</sub> outlet slope was close to 1 which indicates that there was no supplementary NO<sub>2</sub> reduction when the NO<sub>2</sub>/eq. NH<sub>3</sub> ratio was higher than 1. However, the NO outlet slope increased from 0.08 to 0.15 and the N<sub>2</sub> production appeared to rather decrease. As a consequence, a slightly higher part of the reductant appeared to be oxidized into NO (instead of apparently converted into N<sub>2</sub>).

Finally, the observed balance between the numerous possible reactions was the same for all (NO<sub>2</sub>/eq. NH<sub>3</sub>)<sub>inlet ratio</sub> ≤ 1. Roughly, concerning the reductant species, one third reacted with NO<sub>2</sub> and two third appeared oxidized by O<sub>2</sub>. The global nitrogen selectivity reached 94 % in N<sup>o</sup> (N<sub>2</sub>) and 6 % in N<sup>+II</sup> (NO). Unfortunately, current available results do not allow to rigorously attribute which combination of the possible reactions reported in Table 4 was really involved.

Nevertheless, data reported in Figure 1 also indicates that the balance between NO<sub>x</sub> reduction and reductant oxidation is temperature dependent. While the reductant was fully converted in the 200-500°C temperature range, the highest NO<sub>x</sub> conversion was recorded at 350°C, at 33 %, compared with 21 % at 200°C and 28 % at 500°C. At 350°C, the balance between the reductant reactivity with either NO<sub>2</sub> or O<sub>2</sub> was slightly modified. More than 40 % of the injected reductant apparently reacted with NO<sub>2</sub> (considering that NO came from NO<sub>2</sub> reduction). More precisely, the recorded data at 350°C corresponds to equation 16, also presented in equation 17 with a simplified stoichiometry.



Again, the closer corresponding reaction is still reaction A4 (Table4).

## Conclusions

The NO<sub>2</sub>-SCR experiments with urea as injected reductant demonstrated an exceptional reactivity between NO<sub>2</sub> and probably HNCO. This was observed only when NO<sub>2</sub> alone was used as NO<sub>x</sub>, but not with gaseous NH<sub>3</sub> as reductant. Coarsely, at 200°C, one third the reductant from urea injection reacted with NO<sub>2</sub> and two thirds appeared oxidized, the main product being N<sub>2</sub>. 28 reactions may be involved in the observed results. For sure, a cooperative effect of NO<sub>2</sub> with O<sub>2</sub> was demonstrated and the observed global stoichiometry did not depend on the NO<sub>2</sub> concentration for (NO<sub>2</sub>/eq. NH<sub>3</sub>)<sub>inlet ratio</sub> ≤ 1.

## Conflicts of interest

There are no conflicts of interest to declare.

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