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Study of the remarkable reactivity of HNCO/urea with NO₂ in the NO_x SCR by urea process over an oxide-based catalyst.

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An exceptional reactivity between NO₂ and probably HNCO was demonstrated over an oxide-based catalyst during NO₂-SCR experiments with urea as injected reductant. This was observed when only NO₂ was used as NO_x, but not with gaseous NH₃ as reductant. Roughly, one third the injected reductant reacted with NO₂ and two thirds appeared oxidized by O₂, the main product being N₂. 28 reactions may be involved in the observed results. A cooperative effect of NO₂ with O₂ was demonstrated and the observed global stoichiometry did not depend on the NO₂ concentration for (NO₂/eq. NH₃)_{inlet} ratio ≤ 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_x 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_x by NH₃ (NH₃-SCR), initially developed for stationary sources in the 1970s' is one of the most efficient way to reduce NO_x into N₂ in excess of oxygen. Several stoichiometries are involved depending on the NO₂/NO_x ratio. The "standard-SCR" (eq. 1) and "fast-SCR" (eq. 2) are generally considered, both respecting a NH₃/NO_x ratio of 1. However, other stoichiometries are possible like the "NO₂-SCR" reactions, which involve various NH₃/NO_x ratio depending on the participation of oxygen, as illustrated by eq. 3 and 4.

"standard-SCR", NH₃/NO_x stoichiometry: 1

"fast-SCR", NH₃/NO_x stoichiometry: 1

"NO₂-SCR", NH₃/NO_x stoichiometry: 1.33

"NO₂-SCR", NH₃/NO_x stoichiometry: 2

The implementation of the NH₃-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 NH₃ and HNCO (eq. 5), and HNCO is then hydrolysed into a second molecule of NH₃ (eq. 6), providing the reductant species for the NH₃-SCR process (eq. 7).

Unfortunately, urea decomposition may be uncomplete before or on the catalyst.¹ For instance, at low temperature (T<180°C), undesired by-compounds such as cyanuric acid, ammelide, biuret can be observed,² 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 NH₃ 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 NH₃ or urea (aqueous solution) as NO_x reductant species.³ The urea residence time between the injection zone and the catalytic bed is a key parameter of the deNO_x efficiency. For short urea residence time, a significant decrease of the NO_x reduction efficiency was observed over a prototype SCR catalyst provided by Solvay, when switching from gaseous NH₃ to urea aqueous solution, especially in "standard-SCR" condition.⁴ 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_x reduction with urea can be attributed to a lack in NH₃ availability due to limitations in HNCO hydrolysis.³ 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_x selective catalytic reduction was evidenced varying the NO₂/NO_x inlet ratio from 0 to 1.⁵ Particularly, it was showed that a mix of both NO and NO₂ (Fast-SCR condition) was able to react with HNCO and contribute to the NO_x reduction pathway of the Urea-SCR process. Additionally, it was observed that HNCO is highly reactive toward NO₂ alone (without introduced NO), but without supplementary NO_x 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 NO₂, 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 NO₂/NO_x 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 H₃PO₄,⁶ by reaction of sodium cyanate (NaOCN) with gaseous HCl,⁷ by thermal decomposition of cyanuric acid (a trimer of HNCO) or under primary vacuum,⁸ or using a permeation source which sublimates solid cyanuric acid at 250°C in a flow of dry nitrogen.⁹ 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/NH₃ 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 NH₃ 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 NH₃-SCR and Urea-SCR is described in Figure S1 (supplementary information file). The deNO_x efficiency of the powdered catalyst (100 mg) was evaluated in “NO₂-rich SCR” and “NO₂-only SCR” conditions using the realistic mixtures depicted in Table 1.

The total flow rate is fixed at 20 L h⁻¹, which corresponds to a GHSV of about 160,000 h⁻¹. For water and urea addition, an aqueous solution containing urea (1.33 10⁻¹ 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⁻¹) was controlled by a HPLC micro pump (Jasco PU-2085, ΔP_{pump}=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_R*, 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_R* = 4.0 s are presented in comparison with the use of gaseous ammonia, since the results obtained with *t_R* = 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, NO₂, N₂O, HNCO, NH₃, CO, CO₂ and H₂O. 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 NH₃ is detected and the reductant outlet concentration is expressed as equivalent detected ammonia, denoted “NH₃(eq)”. Note also that without catalyst, no evolution of the gas composition was recorded during the SCR experiments, whatever the studied temperature.³ 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 m² g⁻¹. Before experiments, catalyst was pre-treated at 550 °C under oxidant atmosphere (10 % O₂; 10 % CO₂ balanced in N₂). Supplementary tests were also performed with the addition of 150 mg ZrO₂ (Solvay) upstream the SCR catalyst. ZrO₂ addition was demonstrated to allow the recovery of the activity in standard SCR condition (NO₂/NO_x = 0),³ due to its catalytic activity in HNCO hydrolysis.¹⁰

Table 1. Gas feed compositions of for Urea-SCR catalytic tests (total flow rate 20 L h⁻¹).

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

Results and discussion

As presented at the end of the introduction section, an unexpected reactivity was observed in urea-SCR when only NO₂ was used as NOx (NO₂-only condition, NO₂/NO_{x,inlet} = 1) compared with NO₂-rich condition (NO₂/NO_{x,inlet} ratio of 0.7).⁵ 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 NO₂-NO mixtures.

SCR experiments with NO₂/NO_x = 0.7.

NO_x and reductant conversions obtained in NO₂-rich SCR condition are reported in Figures 1A and 1B, respectively.

NO_x conversion with gaseous ammonia as reductant reached 52 % at 200°C and increased until 75% at 400°C. In this temperature range, the corresponding NH₃ conversion values were very similar. For higher temperature, NH₃ conversion still increased whereas NO_x 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 deNO_x efficiency, especially at low temperature: the NO_x conversion at 200°C then reached 40%.

As previously showed in standard and fast-SCR condition,^{3,4} the addition of ZrO₂ upstream the aZr SCR catalyst allowed again a satisfactory recovery of the NO_x conversion in NO₂-rich SCR condition. As a consequence, the conclusion highlighted in the previous works is still appropriate: the decrease in NO_x 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 NO_x and reductant conversions appeared similar until 350°C, then respecting the fast and standard stoichiometry (Eq. 1 and Eq. 2), whereas the NO₂-NH₃ SCR stoichiometry induces a greater conversion of ammonia than NO_x, as reported in Eq. 3 and Eq. 4.

Considering the NO₂/NO_x inlet ratio (0.7), the NO_x conversion is theoretically limited to 60% respecting the fast SCR stoichiometry (the standard SCR reaction is assumed to be disfavoured in this condition including NO₂ in the inlet gas). Nevertheless, the recorded NO_x conversions in the 300-400°C temperature range were significantly higher than 60 % (75 % at 400°C, whatever the reductant agent urea or gaseous NH₃).

The NO_x over-conversion is then attributed to an *in situ* NO production by NO₂ 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 NO₂ decomposition).

To confirm this assumption, the activity of aZr catalyst in NO – NO₂ balance in absence of reductant was studied. Note that there was no evolution of the NO – NO₂ balance depending on the temperature when tests were performed without catalyst. Results obtained with (NO₂/NO_x)_{inlet} = 0.7 are reported in Table 2. As expected, the aZr catalyst influenced the NO₂/NO_x outlet ratio. A decrease of the NO₂ concentration was observed with temperature. For instance, at 400°C, 51 ppm of NO were supplementary provided by the NO₂ decomposition. This concentration is higher than the theoretical concentration needed to reach the observed NO_x conversion respecting the fast SCR stoichiometry. Obviously, it is assumed that NO_x conversion occurred respecting the fast-SCR stoichiometry for NO₂/NO_x inlet ratio of 0.7. Considering this inlet ratio, note that NO₂ conversion into NO for T<400°C appeared contradictory with the thermodynamic expectation which predicts an increase of the NO₂ concentration in this temperature range. In fact, the amounts of reduced NO₂ into NO for NO₂/NO_x = 0.7 were similar to those observed with NO₂/NO_x = 1 (Table2), which are then consistent with the thermodynamic expectation. One possible explanation is that the catalyst was mainly covered by NO₂ compared with NO for NO₂/NO_x inlet ratio of 0.7.

Figure 1. Full lines: NO_x (A, C) and NH₃(eq) (B, D) conversions recorded with NO₂/NO_x = 0.7 or 1 ; dotted lines in C : recorded outlet NO concentration. Reductant used: gaseous ammonia (—), urea with t_R = 4.0 s (—); urea with t_R = 4.0 s with addition of ZrO₂ upstream the SCR catalyst (—).

Table 2. NO – NO₂ balance over aZr catalyst versus temperature in absence of reductant for NO₂/NO_x inlet ratio of 0.7 and 1. Inlet gas mixture: 400ppm NO_x, 8 % H₂O, 10 % O₂ and 10 % CO₂.

T (°C)	NO-NO ₂ thermodynamic equilibrium				NO ₂ /NO _x inlet = 0.7 (120 ppm NO, 280 ppm NO ₂)			NO ₂ /NO _x inlet = 1 (400 ppm NO ₂)		
	with 10% O ₂		without 10% O ₂		NO ₂ (ppm)	NO (ppm)	NO ₂ →NO (ppm)	NO ₂ (ppm)	NO (ppm)	NO ₂ →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 NO₂ reduction tests (400 ppm NO₂, total flow rate 20 L h⁻¹) at (A): 200°C, (B): 300°C and (C): 400°C.

SCR experiments with NO₂/NO_x = 1.

NH₃-SCR with NO₂/NO_x = 1, NO involvement. SCR measurements without NO in the inlet gas mixture (“NO₂-only” SCR condition, NO₂/NO_x=1) are presented in Figures 1C and 1D. Using ammonia as reductant agent, the NH₃ conversion was decreased compared with (NO₂/NO_x)_{inlet} = 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 NO₂ into NO in absence of reductant. Nevertheless, the NO formation in this condition was not sufficient to assure the DeNO_x 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 NO₂ decomposition behaviour.

To check the possible role of the redox state of the catalyst, the activity of the aZr catalyst in NO₂ decomposition was studied at 200, 300 and 400°C after an oxidative pre-treatment (15 min under 10 % O₂ balanced in N₂) or a reducing one (15 min under 5 % H₂ balanced in N₂) carried out at the same temperatures (a purge of 15 min under N₂ was performed before NO₂ 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 NO₂ balanced in N₂. 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 % O₂. 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 NO₂ decomposition into NO was significantly enhanced by a reducing pre-treatment. Thus it is assumed that the presence of reductant agents such NH₃ during SCR experiments favourably interferes in the NO₂ decomposition over the aZr sample, justifying the observed equivalent ammonia and NO_x conversions reported in Figure 1 even for the “NO₂-only” SCR condition.

Urea-SCR with NO₂/NO_x = 1: O₂ involvement. Switching from gaseous ammonia to urea obviously strongly interfered in reductant

reactivity when only NO₂ was injected as NO_x (Figures 1C and 1D). The reductant species were then surprisingly almost fully converted, whereas a decrease of the NO_x 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 “NO₂-only” SCR test was performed with NH₃ (dotted line, Figure 1C). Again, addition of ZrO₂ upstream the SCR catalyst induced similar results than those obtained with gaseous ammonia (black and yellow curves). Detailed experimental data obtained in “NO₂ 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:

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 NO₂ and 658 ppm N[°] 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 NO₂ is recognized as a more powerful oxidant agent than O₂, oxygen contribution has to be considered as co-oxidant agent in the gas mixture.

To balance Eq. 8 with O₂, 184 ppm O₂ are needed (which correspond to 368 ppm O[°]), leading to Eq. 9.

Compared with gaseous ammonia, the higher reactivity of urea and its by-products (assumed to be mainly HNCO) toward oxidation by O₂ was previously demonstrated,³ especially in the 250-400°C temperature range. However, at 200°C, there was no oxidation of the reductant, whatever the injected species (NH₃ or urea). As a consequence, results reported Figure 1 in NO₂-only SCR condition demonstrate the high reactivity of the reductants other than NH₃ toward oxidation by NO₂ (a more powerful oxidative agent than O₂), but participation of O₂ is also evidenced. Reaction products are mainly nitrogen but NO is also produced.

To confirm the participation of O₂ 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 O₂ concentrations of 2 ppm, <50 ppm and <100 ppm in CO₂, NO₂, and N₂ gas cylinders, respectively.

Corresponding results reported in Figure 3 (blue lines) show that removing O₂ from the inlet mixture led to a slight increase of the NO_x conversion. Interestingly, while nearly no ammonia was detected in presence of O₂, NH₃ emission significantly increases in absence of oxygen (blue curve, Figure 3B), highlighting the reactivity of O₂ with urea by-products. However, the amount of residual ammonia remains lower than that observed in NH₃-SCR condition, illustrating certainly the residual traces of oxygen in the experimental setup. Note that in Eq. 9, only 184 ppm O₂ (368 ppm O[°]) are estimated involved in N^{-III} species oxidation. This result tends to confirm that the reactivity of urea by-products toward oxidation is enhanced in “NO₂ only” condition and much higher than with NO₂ alone, or O₂ alone as previously described in ref. 3. Similar results were also reported by Takeda *et al.*¹¹ which studied the reaction of adsorbates derived from cyanuric acid on an exchanged Cu zeolite with NO_x and O₂. Authors reported that the reaction rate of HNCO oxidation is much higher with a mixture of NO_x + O₂ than that with O₂, as also well known for soot combustion.¹²

Table 3. Experimental data obtained at 200°C in “NO₂ only” SCR (gas mixture reported in Table 1, urea =200 ppm, t_R = 4.0 s): N-species balance.

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

Figure 3. Effect of oxygen on the Urea-SCR behaviour in NO₂-only SCR (NO₂/NO_x=1) over aZr catalyst. (A): NO_x conversion; (B): (NH₃)_{eq} conversion

(▲): 400 ppm NO₂, 200 ppm urea, 8 % H₂O, 10 % O₂, 10 % CO₂.

(●): 400 ppm NO₂, 200 ppm urea, 8 % H₂O, 0 % O₂, 10 % CO₂.

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 NH₃, and (ii) O₂ 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 NH₃ is equivalent to the amount of converted NO_x, and no over production of NO_x 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_x were converted and 12 ppm of NH₃ were emitted at 200°C. Assuming a fast-SCR stoichiometry, the corresponding amount of formed NH₃ is 98 ppm (86+12) and an equal quantity of NO and NO₂ is assumed to be reduced into N₂ (43 ppm of NO and 43 ppm of NO₂). As a consequence, only 85 ppm of NO₂ (128_{disappeared} - 43_{reacted with NH₃}) 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 NH₃ induces an incomplete urea thermolysis and/or HNCO hydrolysis.

Figure 4. Reaction pathways corresponding to hypothesis #1. Note that the NH₃ 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^{-III} oxidation state (NH₂CONH₂, 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 NO₂ converted into NO (85 ppm), it results in a lack of oxidation agent to oxidize the remaining reductant species into N₂. Then, the contribution of O₂ is needed to respect the observed N-balance. Note that only 182.5 ppm O₂ 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 NH₃ generation. Corresponding calculations from experimental results are illustrated in Figure 5.

In this hypothesis, the urea thermolysis is achieved, producing 200 ppm of NH₃ and 200 ppm HNCO. It is assumed that NH₃ reacts following the fast-SCR reaction while HCNO reacts via a more complex way, as detailed below. Considering that 12 ppm NH₃ are recorded at the outlet, 188 ppm NH₃ are supposed to react with 94 ppm NO and 94 ppm NO₂. As 42 ppm of NO is emitted, then 94+42=136 ppm of NO are generated from NO₂ 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 NO₂ in the inlet mixture). Again, based on the fast-SCR stoichiometry, the corresponding amount of reacted NH₃ for NOx reduction is 86 ppm. As 188 ppm NH₃ are supposed to disappear, 102 ppm of ammonia (188-86) have to be additionally converted by reaction with 102 ppm NOx (no NH₃ – O₂ reactivity was recorded at 200°C³). 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 NO₂ (272_{out}+94_{converted}) and 136 ppm NO (42_{out}+94_{converted}). The reaction of 200 ppm of NH₃ (obtained by urea thermolysis) respecting the fast-SCR stoichiometry leads to 272 ppm NO₂, 42 ppm NO and 12 ppm NH₃ as reported in Table 3.

To obtain the theoretical calculated NOx composition (366 ppm NO₂ and 136 ppm NO) taking into account that 400 ppm NO₂ are initially introduced, 34 ppm NO₂ 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 N₂. Again, a lack in oxidizing species appears, indicating the participation of O₂. The proposed equation 12 respects this proposed pathway:

To conclude, both hypothesis #1 and #2 point out the participation of O₂ in addition to NO₂ to oxidize the reductant species (other than ammonia³) 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 ZrO₂, an active material in HNCO hydrolysis, allowed the recovery of the same DeNOx behaviour than that obtained with gaseous NH₃. Remarkably, no emission of NO was then observed using this dual bed catalytic configuration (ZrO₂+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 NO₂ is a much more powerful oxidizer than O₂, the participation of O₂ in the total reductant consumption in NO₂-only SCR condition is evidenced, even at low temperature (200°C) for

which no reactivity with O₂ was previously observed.³ A synergy effect between NO₂ and O₂ is not excluded.

Urea-SCR with NO₂/NOx = 1: possible involved reactions and observed stoichiometry. Results reported in the previous section demonstrates the oxidation of N^{-III} species by both NO₂ and O₂. 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^{-III}) reductant species may react with NO₂ to form N₂ (A type reactions);
- (N^{-III}) may react with NO₂ to form N₂ (from N^{-III}) and NO (from NO₂) (B type reactions);
- (N^{-III}) may react with NO₂ to form NO (from N^{-III}) and N₂ (from NO₂) (C type reactions);
- (N^{-III}) may react with NO₂ to form NO (D type reactions);
- E type and F type reactions correspond to the (N^{-III}) oxidation by O₂ into N₂ and NO, respectively.

All these generic reaction are reported in Table 4. For each reaction involving N^{+IV} species (i.e. NO₂), NO₂ can be partially substituted by ½ O₂ 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 NO₂-SCR probably results in a combination of these reactions. In addition, the probable role of NO as intermediate species of the DeNOx process by NO₂, as proposed in Figure 4 (hypothesis # 1), is not considered. Nevertheless, in order to have a better view of the global stoichiometry, new NO₂-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 NO₂ 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 NO₂ concentration range and the other for higher NO₂ inlet concentrations.

Until 400 ppm NO₂, the NOx conversion was rather stable, at approximately 27-28%. It indicates a kinetic order close to 1 for NO₂. Interestingly, in this 0-400 ppm NO₂ inlet concentration range, NH₃, NO and NO₂ outlet concentrations exhibited linear evolutions, as well as calculated N₂ 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 NO₂ inlet concentrations) on the observed balance between the involved reactions

Table 4. Generic reactions possibly involved in the observed results in NO₂-SCR.

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

*in which N^{-III} species are urea, HNCO or NH₃.N^{+IV} species is NO₂N^{+II} species is NON[°] species is N₂O[°] species is O₂

Figure 6. NO_x conversion (dotted line) and outlet mixture composition (full line) in NO₂-SCR experiments depending on the NO₂ inlet concentration. T = 200°C; urea t_R = 4.0s.

If "x" is the NO₂ inlet concentration, the slope for outlet reductant concentration, recorded as NH₃ species, was fixed to -0.95x. It means that the reductant consumption was equal to 95 % of the NO₂ inlet concentration, whatever the NO₂ inlet concentration in the 0-400 ppm range. The slope for outlet NO_x species was 0.72x, indicating that the ammonia consumption was around 3.4 times higher than the NO_x consumption (0.95/(1-0.72)). Moreover, 64 % of the injected NO₂ did not react while 8 % appeared reduced into NO (NO may also come from N^{III} oxidation by O₂, reaction F in Table 4). NO₂ reduction rate into N₂ cannot be rigorously calculated since N₂ may come from NO₂ reaction with N^{III} (A, B, C type reactions, corresponding to 16 different reactions, table 4) or from N^{III} oxidation by O₂ (reaction (E)).

Finally, the general observed stoichiometry for the 0-400 ppm NO₂ inlet range can be summarized as follow:

Simplified as:

To balance these products, O₂ 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 NO₂.

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 NH₂CONH₂ + 36 NO₂ + 36 O₂ = 66 N₂ + 96 CO₂ + 48 H₂O.

For NO₂ inlet concentrations higher than 400 ppm, the NO_x conversion was decreased because the reductant species was then almost fully converted (Figure 6). The NO₂ outlet slope was close to 1 which indicates that there was no supplementary NO₂ reduction when the NO₂/eq. NH₃ ratio was higher than 1. However, the NO outlet slope increased from 0.08 to 0.15 and the N₂ 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 N₂).

Finally, the observed balance between the numerous possible reactions was the same for all (NO₂/eq. NH₃)_{inlet} ratio ≤ 1. Roughly, concerning the reductant species, one third reacted with NO₂ and two third appeared oxidized by O₂. The global nitrogen selectivity reached 94 % in N^o (N₂) and 6 % in N^{II} (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_x reduction and reductant oxidation is temperature dependent. While the reductant was fully converted in the 200-500°C temperature range, the highest NO_x 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 NO₂ or O₂ was slightly modified. More than 40 % of the injected reductant apparently reacted with NO₂ (considering that NO came from NO₂ 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 NO₂-SCR experiments with urea as injected reductant demonstrated an exceptional reactivity between NO₂ and probably HNCO. This was observed only when NO₂ alone was used as NO_x, but not with gaseous NH₃ as reductant. Coarsely, at 200°C, one third the reductant from urea injection reacted with NO₂ and two thirds appeared oxidized, the main product being N₂. 28 reactions may be involved in the observed results. For sure, a cooperative effect of NO₂ with O₂ was demonstrated and the observed global stoichiometry did not depend on the NO₂ concentration for (NO₂/eq. NH₃)_{inlet} ratio ≤ 1.

Conflicts of interest

There are no conflicts of interest to declare.

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