

NO_x SCR by urea: evidence of the reactivity of HNCO, including a specific reaction pathway for NO_x reduction involving NO+NO₂.

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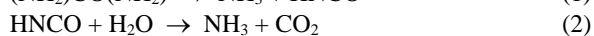
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ABSTRACT: To treat the NO_x emissions from diesel vehicles, NO_x selective catalytic reduction (SCR) process by NH₃ requires the use of a precursor: an urea aqueous solution. Using an innovative experimental synthetic gas bench adjusted to powdered catalysts and allowing the use of urea or ammonia, the competitive reactivity of the HNCO intermediate species was evidenced. This intermediate species was found to be highly reactive toward NO₂, without NO_x reduction. During the SCR process, a mix of both NO and NO₂ was evidenced to react with HNCO and contribute to the NO_x reduction efficiency, resulting in an original pathway.

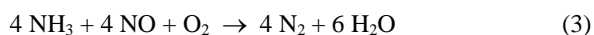
KEYWORDS. NO_x reduction, SCR, urea, HNCO, reaction pathways.

1. INTRODUCTION

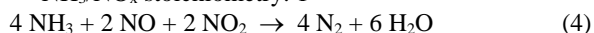
Automotive traffic is well-known to be responsible for air pollution, which causes environmental and human health disturbances. Catalytic converters are suitable to purify exhaust gases, but for Diesel engines operating in oxygen excess, NO_x reduction into N₂ is particularly challenging. To meet the severe current standards like Euro 6/VI, the implementation of a specific process, such as the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR), is required. The use of an aqueous urea solution as ammonia precursor was adopted by the automotive industry as a safe and operational adaptation of the NH₃-SCR technology. Ammonia is then obtained by two consecutive reactions: the “urea thermolysis” (Eq. 1) leading to NH₃ and HNCO, and the “HNCO hydrolysis” (Eq. 2), leading to the second NH₃ molecule to provide the expected amount of reductant.



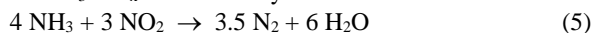
Ammonia then reduces NO_x with different reaction stoichiometry described by Eqs 1 to 4. These reactions are usually denoted as “standard-SCR” (Eq. 3), “fast-SCR” (Eq. 6) and “NO₂-SCR” (Eq. 5 and 6) reactions and involve different NO₂/NO_x and NH₃/NO_x ratios.¹⁻⁵



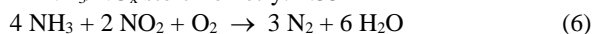
NH₃/NO_x stoichiometry: 1



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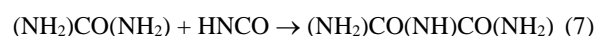
NH₃/NO_x stoichiometry: 1.33



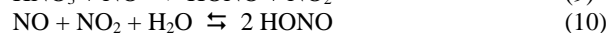
NH₃/NO_x stoichiometry: 2

Unfortunately, incomplete urea decomposition may occur⁶ thus entailing a mixture of NH₃, HNCO and urea on the SCR

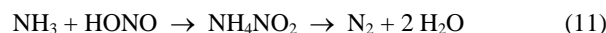
catalyst. The HNCO intermediate exhibits high reactivity and reacts not only with H₂O to produce NH₃, but also with condensed urea, leading to formation of solid deposits for T ≤ 180°C, as biuret (Eq. 7).⁷



In addition, it was recently demonstrated that HNCO appears more reactive toward O₂ than NH₃. Selective catalytic oxidation (SCO) experiments show a reductant oxidation at 300°C of about 30% for Urea-SCO compared to 8% for NH₃-SCO.⁸ These undesired side-reactions can lead to the deactivation of the catalyst by poisoning, and also induce an undesired overconsumption of the injected reductant. To avoid these drawbacks, deeper understanding of Urea-SCR pathways in urea availability and ammonia release is of the most interest. In fact, significant efforts have been undertaken to describe total urea decomposition reaction^{3,7,9} assuming that NO_x reduction is thereafter correlated to NH₃ yield and follows similar pathways than those demonstrated when ammonia is directly used as reductant. The first step assumed for NH₃-NO/NO₂-O₂ gas mixture over exchanged zeolites and oxides-based catalysts is the NO₂ disproportionation to nitrous and nitric acid (Eq. 8) followed by the nitric acid reduction by NO (Eq.9)³, leading to the overall reaction (10).



HONO is therefore a key intermediate which can react with NH₃ to form ammonium nitrite which easily decompose into N₂ (Eq. 11).¹⁰⁻¹²



The combination of reactions (10) and (11) corresponds to Eq. (4), *i.e.* the “fast-SCR” stoichiometry.

Finally, the urea decomposition to ammonia and side-reactions are well known, as well as the mechanism of the NO_x reduction by NH₃. However, detailed pathways in the NO_x SCR process by urea or its by-products remains poorly documented. We present herein the behavior of an acidic zirconia based catalyst (denoted aZr, provided by Solvay¹³) in Urea-SCR. The direct comparison of NH₃ or urea as reductant allow us to point out different behaviors, and the variation of the (NO/NO₂) inlet ratio is use to address the role of NO₂ in the involved reactions during the NO_x SCR process using urea.

2. EXPERIMENTAL

A synthetic gas bench adjusted to powdered catalysts allowing direct comparison of NH₃-SCR and Urea-SCR reactions at the laboratory scale was recently developed to easily act on the experimental parameters and directly compare the use of both reductants, urea or ammonia.⁸ The experimental set-up for catalytic test is detailed in the Supporting Information (SI) file (Figure S1). Two urea residence times (elapsed time for the gaseous mixture between urea injection zone and the catalytic bed) were examined: 5.2 s and 4.0 s. They are well away from the requirements encountered in real conditions (order of magnitude: one second) but sufficiently low to observe differences in the pathways related to the use of urea over the studied catalyst. Note that without catalyst, the complete urea decomposition into ammonia is achieved at the analyzer level (all pipes of the apparatus are heated at 200°C, the residence time between urea injection and analyzer is around 34 s). Consequently, only NH₃ is detected (HNCO is never observed) and the outlet urea concentration is expressed as equivalent ammonia, and denoted “NH_{3(eq)}”. The NO₂ to NO_x inlet ratios were fixed at 0, 0.5, 0.7 and 1 (Table S1). The compositions of the feed gas and effluent stream were monitored continuously using online MKS Multi-gas infrared analyzer for NO, NO₂, N₂O, HNCO, NH₃, CO, CO₂ and H₂O.

3. RESULTS AND DISCUSSION

Figure 1 reports the effect of the urea residence time on the NO_x conversion for various NO₂/NO_x inlet ratios. For the longer urea residence time ($t_R=5.2$ s), results are similar than those obtained with gaseous NH₃ as reductant, proving that the availability of NH₃ is then satisfactory (Figure S2, SI file).

When the urea residence time is decreased to 4.0 s, a drop in NO_x conversion is clearly denoted (Figure 1). The most significant loss of activity is observed for the standard SCR condition, when only NO is introduced as NO_x (Figure 1A, NO₂/NO_x=0). It was previously evidenced that the observed activity loss is not attributed to a catalyst surface deactivation caused by deposit formation (Figure S3, SI file) but to a lack of available NH_{3(eq)} due to an incomplete HNCO hydrolysis, that induces the presence of HNCO at the aZr catalyst level.⁸

Increasing the proportion of NO₂ in the reaction mixture (Figure 1B and 1C, NO₂/NO_x = 0.5 and 0.7, respectively) leads to reduce the drop of deNO_x activity for urea residence time of 4.0 s compared to NO_x reduction in standard condition (NO₂/NO_x = 0, Figure 1A). These results seems to indicate that the presence of NO₂ interferes in the reductant availability and/or in NO_x reduction reactions involved in Urea-SCR. To highlight the specific reactivity of NO₂ in NO_x reduction mechanism, Urea-SCR and NH₃-SCR experiments were especially carried out in NO₂-only condition (NO₂/NO_x inlet = 1).

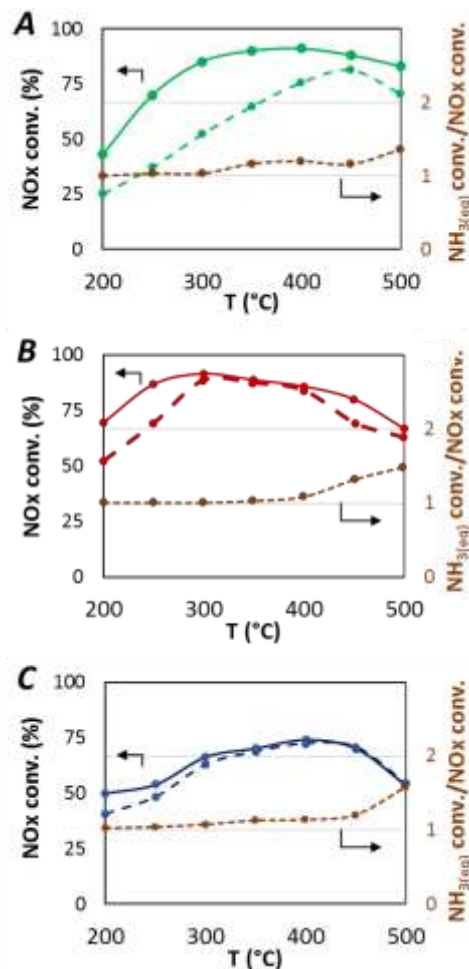


Figure 1. Effect of urea residence time on NO_x conversion (full line: $t_R=5.2$ s; dotted line: $t_R=4.0$ s) and NH_{3(eq)}/NO_x conversion ratio at $t_R=4.0$ s for various NO₂/NO_x inlet ratio over aZr catalyst. GHSV = 160000 h⁻¹; NO_x = 400 ppm, urea = 200 ppm, H₂O = 8 %, O₂ = 10 %, CO₂ = 10 %.

A: NO₂/NO_x = 0; B: NO₂/NO_x = 0.5; C: NO₂/NO_x = 0.7

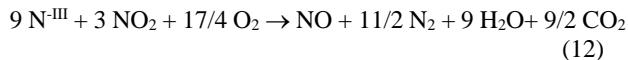
3.1. Specific Reactivity of HNCO with NO₂

In order to study the reactivity of HNCO with NO₂, specific SCR tests were performed with NO₂ only in the inlet gases (NO₂/NO_x)_{inlet} ratio = 1. For NH₃-SCR, results reported in Figure 2A show that ammonia and NO_x conversions are the same until 350°C, with conversion rates between 30 and 50 %. For higher temperatures, NH₃ oxidation was clearly evidenced.⁵ Additionally, there is nearly no NO emission when gaseous NH₃ is used as reductant agent.

To the opposite, concerning urea-SCR experiments, it clearly appears from Figure 2B that reductant is surprisingly fully converted in the whole studied temperature range. At the same time, NO is produced in substantial amounts (around 40 ppm).

These divergent results between urea and ammonia confirm an incomplete urea hydrolysis, in agreement with SCO experiments previously reported in Ref. 8. The urea by-product, assumed to be HNCO, also exhibits a particularly high reactivity with NO₂ (Figure 2B) in the 200-500°C temperature range. Taking into account the outlet NO, NO₂ and NH₃ concentrations, the contribution of O₂ as co-oxidant agent has to be considered in addition to nitrogen dioxide to fully convert the reductant

agent. Note that the beneficial effect of NO₂ on the HNCO oxidation rate by O₂ was previously reported by Takeda and Iwamoto over exchanged Cu zeolite.¹⁴ The stoichiometry and possible reaction pathways involving urea by-products, NO₂, NO and O₂ over aZr catalyst are detailed in the SI file. At 200°C, the global stoichiometry respecting the observed results is close to Eq (12) (N^{III} species correspond to the reductant species from urea, coefficient for H₂O and CO₂ are calculated from urea injection).



This particular reactivity between HNCO and NO₂ was also expected to occur for NO₂/NO_x inlet ratio of 0.5 and 0.7. The behaviour of the reductant during SCR reactions can be monitored by the NH_{3(eq)}/NO_x conversion ratio. It appears from Figure 1 that this ratio remains close to 1 in the 200-400°C temperature range, which induces a standard or fast SCR stoichiometry (Eq. 3 and 4). An over-consumption of reductant is denoted only for temperature higher than 400°C, whatever the NO₂/NO_x inlet ratio. It is commonly assigned to a reductant reactivity with O₂.^{5,8}

Finally, HNCO intermediate species could react easily with NO₂ or NO₂+O₂. However, these results do not explain how NO₂ acts in the urea-SCR mechanism for NO_x reduction, since the effect of shortened urea residence time in NO_x conversion dissipates together with the increase of NO₂ in the inlet gas mixture, without over consumption of reductant (Figure 1).

3.2. Reactivity of HNCO with NO versus (NO+NO₂)

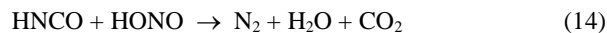
For urea-SCR, a NO_x conversion of 70 % is denoted at 250°C in fast-SCR condition (Figure 1B), showing that 70 % of the NH_{3(eq)} reductant is converted at t_R=4.0 s (NH_{3(eq)}/NO_x = 1 in inlet and outlet gas mixtures).

To the opposite, only 37 % of NO_x conversion is achieved in standard condition (t_R=4.0 s) whereas a maximum of around 70 % could be reached in the case of an optimal ammonia availability, as illustrated in Figure 1A for t_R=5.2 s. Consequently, the drop in deNO_x efficiency observed in standard-SCR condition for shortened urea residence time is not only related to a lack of NH_{3(eq)} due to an incomplete HNCO hydrolysis, but also to a defective activation of HNCO reductant by NO. Additionally, it is evidenced that the presence of both NO and NO₂ beneficially interfere at the catalytic level with urea by-products, assumed to be HNCO, allowing a better use of the reductant species supported by a higher deNO_x efficiency. This NO_x reduction enhancement can be described by reaction (13).



In fact, in the established mechanism for NO_x SCR by NH₃, as well as in reactional pathways mentioned when alcohols or hydrocarbon are used as reductant^{15,16}, the final step of deNO_x chemistry in lean media is the formation of N₂ by decomposition of ammonium nitrite (Eq. 11). It systematically involves the HONO intermediate species, which is formed by the overall reaction (10) respecting an optimal NO: NO₂ balance of 1:1, as for the “fast” SCR stoichiometry (Eq. 4). Consequently, a similar route in which HONO intervenes is postulated in the NO_x reduction with urea to support the observed experimental results (Figure 1). It is proposed that isocyanic acid reacts with nitrous

acid to yield nitrogen, as described in Eq (14), in which HONO is produced by reaction (10).



The sum of reactions (10) and (14, twice) corresponds to the global equation (13) of the “HNCO-SCR” route.

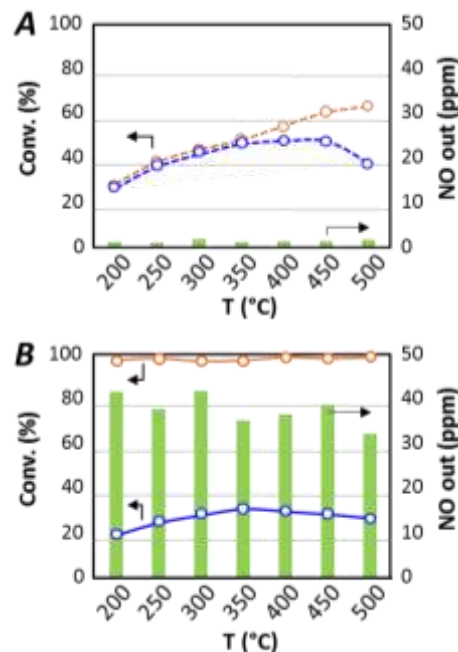
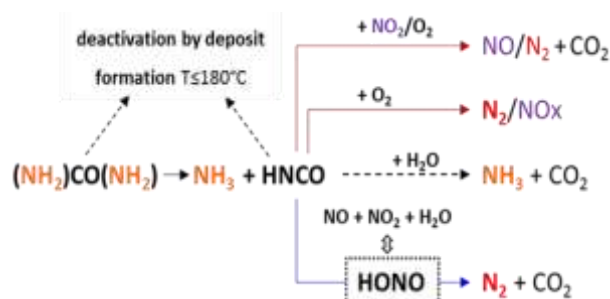


Figure 2. NO₂-only SCR (NO₂/NO_x=1) over aZr catalyst with (A): NH₃; (B): urea. (—): NO_x conversion; (—): NH_{3(eq)} conversion; (■): NO out emission. GHSV = 160000 h⁻¹; NO₂ = 400 ppm, NH₃ = 400 ppm or urea = 200 ppm, H₂O = 8 %, O₂ = 10 %, CO₂ = 10 %.

4. CONCLUSION

This work evidenced the high reactivity of HNCO toward the gas feed constituents in the NO_x SCR by urea process. The expected HNCO hydrolysis to yield ammonia can compete with other reactions, like oxidation by O₂ and especially NO₂, even if these oxidation reactions appear negligible during the SCR process over the studied catalyst. This study also evidences a new “HNCO-SCR” route involving both NO and NO₂, probably via the formation of HONO, which is commonly proposed as intermediate species in NO_x reduction mechanisms. Finally, the various competitive reactions regarding HNCO in the urea SCR process are highlighted in Scheme 1.



Scheme 1. Proposal of HNCO competitive reactivity for Urea-SCR with shortened urea residence time.

ASSOCIATED CONTENT

Supporting Information.

- Experimental Urea-SCR catalytic apparatus and test protocol.
 - Effect of reductant agent, NH₃ or Urea (t_R=5.2 s), depending on the (NO₂/NO_x) inlet ratio.
 - Characterization by TPD/TPO of the adsorbed species depending on the injected reductant.
 - Reductant consumption in NO₂-only Urea-SCR condition.
- This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

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