

# NO<sub>x</sub> SCR by urea: evidence of the reactivity of HNCO, including a specific reaction pathway for NO<sub>x</sub> reduction involving NO+NO<sub>2</sub>.

M. Seneque, F. Can,\* D. Duprez and X. Courtois\*.

Institut de Chimie des Milieux et des Matériaux de Poitiers (IC2MP), UMR 7285 CNRS-Université de Poitiers, Bâtiment B27, 4 rue Michel Brunet, TSA 51106, 86073 Poitiers Cedex 9.

\* xavier.courtois@univ-poitiers.fr

\* fabien.can@univ-poitiers.fr

### Experimental Urea-SCR catalytic apparatus and test protocol

DeNO<sub>x</sub> efficiency of the powdered aZr sample was evaluated in “standard SCR”, “fast SCR”, “NO<sub>2</sub>-rich SCR” and “NO<sub>2</sub>-only SCR” conditions using the following mixture: 400 ppm NO<sub>x</sub>, 200 ppm urea or 400 ppm NH<sub>3</sub>, 10 % O<sub>2</sub>, 8 % H<sub>2</sub>O, 10 % CO<sub>2</sub> (Table S1). The total flow rate is fixed at 20 L.h<sup>-1</sup>. For water and urea addition, an aqueous solution containing urea ( $1.33 \cdot 10^{-1}$  M, *i.e.* 0.794<sub>wt%</sub>) was vaporized via a micro-nozzle ( $\varnothing=50\mu\text{m}$ ), provided by The Lee Company, into a heated zone at 200°C upstream the catalytic bed.

The liquid flow rate ( $19 \mu\text{L min}^{-1}$ ) was controlled by a HPLC micro pump ( $\Delta P=10$  bar), provided by Jasco, PU-2085.

The powdered catalyst (100 mg) is placed in a quartz tubular micro-reactor (internal diameter of 8 mm) and its location can be changed in order to examine different residence time 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  $t_R$ ), which corresponds to the 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 is not considered for the  $t_R$  calculation. A scheme of the experimental bench is presented in Figure S1.

It is important to note that without catalyst, in Urea-SCR condition, complete urea decomposition into ammonia is fully achieved at the analyzer level, due to a long residence time between the catalyst and the analyzer of about 34 s (no HNCO is recorded). Consequently, only NH<sub>3</sub> is detected and the urea analysis is expressed as equivalent detected ammonia, denoted “NH<sub>3(eq)</sub>”.

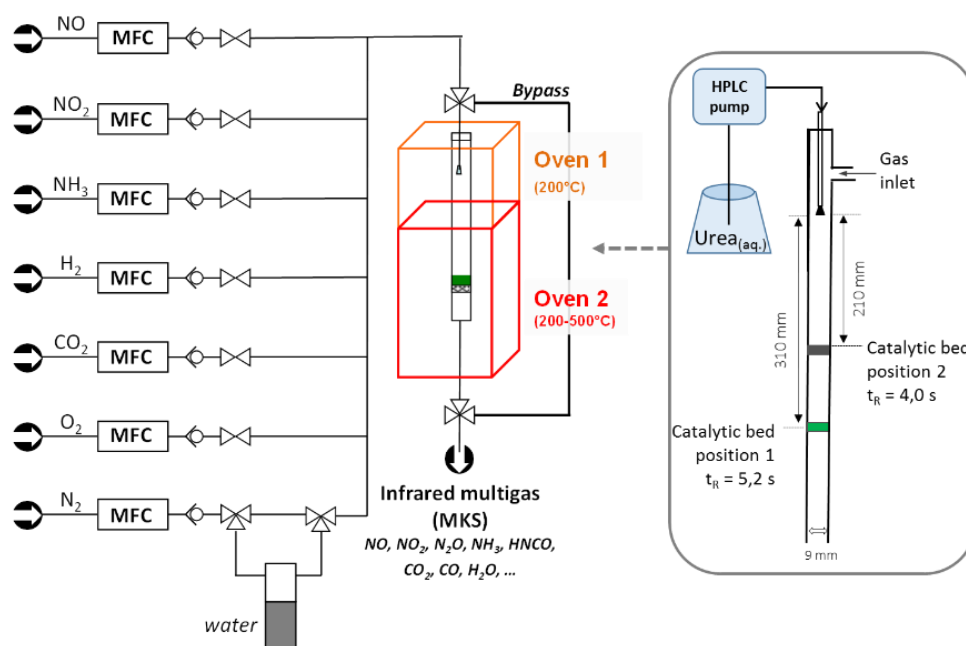
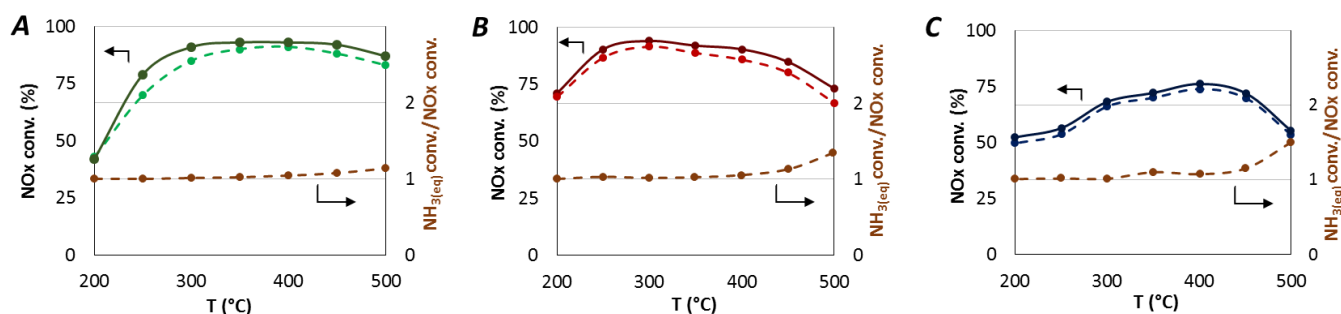


Figure S1. Experimental set-up for Urea-SCR.

**Table S1.** 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>	NO (ppm)	NO <sub>2</sub> (ppm)	Reductant (ppm)	O <sub>2</sub> (%)	H <sub>2</sub> O (%)	CO <sub>2</sub> (%)
Standard SCR	0	400	0	200 (urea) or 400 (NH <sub>3</sub> )	10	8	10
Fast SCR	0.5	200	200				
NO <sub>2</sub> -rich SCR	0.7	120	280				
NO <sub>2</sub> -only SCR	1	0	400				

Effect of reductant agent, NH<sub>3</sub> or Urea ( $t_R=5.2$  s), depending on the (NO<sub>2</sub>/NO<sub>x</sub>) inlet ratio.

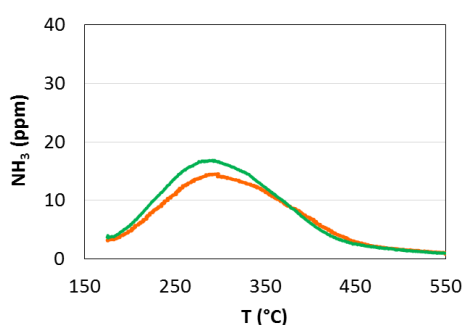


**Figure S2.** Effect of reductant agent: NH<sub>3</sub>-SCR (full line) and Urea-SCR at  $t_R=5.2$  s (dotted line) on NO<sub>x</sub> conversion and NH<sub>3</sub>/NO<sub>x</sub> conversion ratio for various NO<sub>2</sub>/NO<sub>x</sub> inlet ratio. GHSV = 160000 h<sup>-1</sup>; NO<sub>x</sub> = 400ppm, NH<sub>3</sub> = 400 ppm or urea = 200 ppm, H<sub>2</sub>O = 8%, O<sub>2</sub> = 10%, CO<sub>2</sub> = 10%. A: NO<sub>2</sub>/NO<sub>x</sub> = 0; B: NO<sub>2</sub>/NO<sub>x</sub> = 0.5; C: NO<sub>2</sub>/NO<sub>x</sub> = 0.7

The comparison of reductant agent in NO<sub>x</sub> conversion is reported in Figure S2 for NH<sub>3</sub>-SCR and Urea-SCR (urea residence time of 5.2 s). No significant modification of NO<sub>x</sub> conversion is observed depending of the NO<sub>2</sub>/NO<sub>x</sub> inlet ratio when urea is injected at  $t_R=5.2$  s. In addition, note that whatever the introduced reductant, the maximum N<sub>2</sub>O emission is limited to 3-4 ppm.

The “NH<sub>3</sub> conv./NO<sub>x</sub> conv.” ratio for NH<sub>3</sub>-SCR remains closed to 1 for all NO<sub>2</sub>/NO<sub>x</sub> inlet ratios, excepted at high temperature. The oxidation of ammonia is then denoted, it is more marked with the increase of the NO<sub>2</sub>/NO<sub>x</sub> inlet ratio. These results demonstrated the efficiency of urea in NO<sub>x</sub> SCR for this urea residence time (5.2 s).

Characterizations by TPD/TPO of the adsorbed species depending on the injected reductant.



**Figure S3.** Temperature programmed desorption curves depending on the adsorbed reductant agent. (—): NH<sub>3</sub>; (—): Urea.

Temperature programmed desorption (TPD) and oxidation (TPO) experiments were carried out to evaluate the nature of the adsorbed species on the surface of the catalyst depending on the reductant agent used (i.e. gaseous ammonia or urea).

100 mg of catalyst were placed in a quartz tubular micro-reactor. After a pretreatment at 550°C (5°C min<sup>-1</sup>) for 30 min under a flow containing CO<sub>2</sub>, O<sub>2</sub> (each at 10 %) and H<sub>2</sub>O (8 %) balanced in N<sub>2</sub> (total flow of 20 L h<sup>-1</sup>), the catalyst sample is cooled down at 175°C. After one hour of adsorption at 175°C under 400 ppm NH<sub>3</sub> (or 200 ppm urea at  $t_R=4.0$  s), 8 % H<sub>2</sub>O, 10 % CO<sub>2</sub>, 10 % O<sub>2</sub>, TPD experiments were performed up to 550°C (5°C min<sup>-1</sup>), and the outlet gas was continuously analyzed by an MKS Multigas infrared analyzer.

Results reported in Figure S3 show that most of the adsorbed species are desorbed before 450°C. In addition, TPD curves are very similar whatever the nature of adsorbed reducer (NH<sub>3</sub> or urea) and no other N-compounds than NH<sub>3</sub> was detected. In addition, temperature programmed oxidation (TPO) experiments performed after urea adsorption at 175°C gives rise to similar results to the inert gas desorption (TPD), in terms of desorption temperature range or products analyzed. These results tends to demonstrate that the polymerization of urea does not occur, since no oxidation product (NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, ...) is detected during TPO experiments until 550°C.

## Reductant consumption in NO<sub>2</sub>-only Urea-SCR condition (NO<sub>2</sub>/NO<sub>x</sub>)<sub>inlet</sub> = 1)

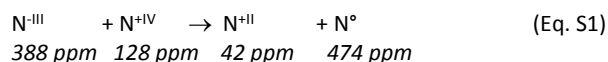
**Table S2.** Experimental data obtained in “NO<sub>2</sub> only” SCR (NO<sub>2</sub> in = 400 ppm; NO in = 0 ppm, urea =200 ppm, t<sub>R</sub> = 4.0 s) and detailed N-species balance at 200°C

“NO <sub>2</sub> only” SCR with urea					Detailed data recorded at 200°C			
T (°C)	NO out (ppm)	NO <sub>2</sub> out (ppm)	NO <sub>x</sub> conv. (%)	Reduct. conv. (%)		Inlet concentration (ppm)	Outlet concentration (ppm)	N <sup>III</sup> (ppm)
200	42	272	21	97	NO <sub>x</sub>	400	314	-86
250	38	253	27	98	NO <sub>2</sub>	400	272	- 128
300	42	235	31	97	NO	0	42	+42
350	35	233	33	97	NH <sub>3</sub> (eq)	400 (eq)	12	-388
400	36	236	32	99				
450	39	238	30	98				
500	32	254	28	99				

NO<sub>2</sub>-only SCR experiments (NO<sub>2</sub>/NO<sub>x</sub> inlet = 1) were especially performed to highlight the particular reactivity of NO<sub>2</sub> in NO<sub>x</sub> reduction mechanism when urea is injected as reductant agent.

Switching from gaseous ammonia to urea obviously strongly interferes in DeNO<sub>x</sub> pathways: the reductant species are then almost fully converted, whereas a decrease of the NO<sub>x</sub> conversion is observed. In addition, significant NO concentration is then detected while NO was nearly not recorded when “NO<sub>2</sub>-only” SCR test was performed with NH<sub>3</sub>. Detailed experimental data obtained in “NO<sub>2</sub> only” Urea-SCR (NO<sub>2</sub> in = 400 ppm; NO in = 0 ppm, urea =200 ppm, t<sub>R</sub> = 4.0 s) in the 200-500°C temperature range are reported in Table S2. To illustrate the global reaction stoichiometry, the temperature of 200°C was selected and the corresponding N-species balance is also reported in Table S2.

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



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

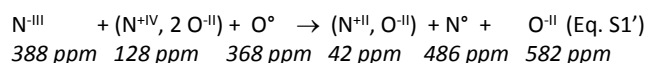
N<sup>IV</sup> species is NO<sub>2</sub>

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. S1)

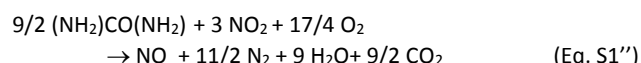
Taking into account the redox state of the involved N-species, Eq. S1 is not balanced. Oxidants should be added to Eq. S1 to keep electroneutrality. Although NO<sub>2</sub> is a more powerful oxidant agent than O<sub>2</sub>, NO<sub>2</sub> cannot be converted in a larger extent than 128 ppm to respect the recorded data. As a consequence, O<sub>2</sub> contribution has to be considered as co-oxidant agent in the gas mixture.

To balance Eq. S1, 368 ppm O<sup>°</sup> (which correspond to 184 ppm O<sub>2</sub>) are needed, leading to Eq. S1’.



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 oxides like H<sub>2</sub>O, CO<sub>2</sub>...

Considering that the injected reductant is initially urea, the corresponding stoichiometry of the overall reaction is close to reaction (Eq. S1’):



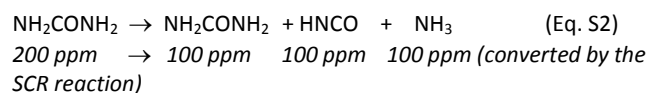
Finally, these calculations put in evidence the oxidation of N<sup>III</sup> species by both NO<sub>2</sub> and O<sub>2</sub>, even at low temperature (200°C). Similar results were also reported by Taketa and Iwamoto<sup>1</sup> which studied the reaction of adsorbates derived from cyanuric acid on an 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>.

In order to propose a better overview the possible reaction pathways based on data reported in Table S2 for T = 200°C, two relevant hypotheses are exposed. They both assume that ammonia is converted only following the Fast-SCR stoichiometry (2NH<sub>3</sub> + NO + NO<sub>2</sub> → 2N<sub>2</sub> + 3H<sub>2</sub>O), in accordance with results observed with gaseous NH<sub>3</sub>. In each hypothesis, O<sub>2</sub> plays a role in the overall reaction.

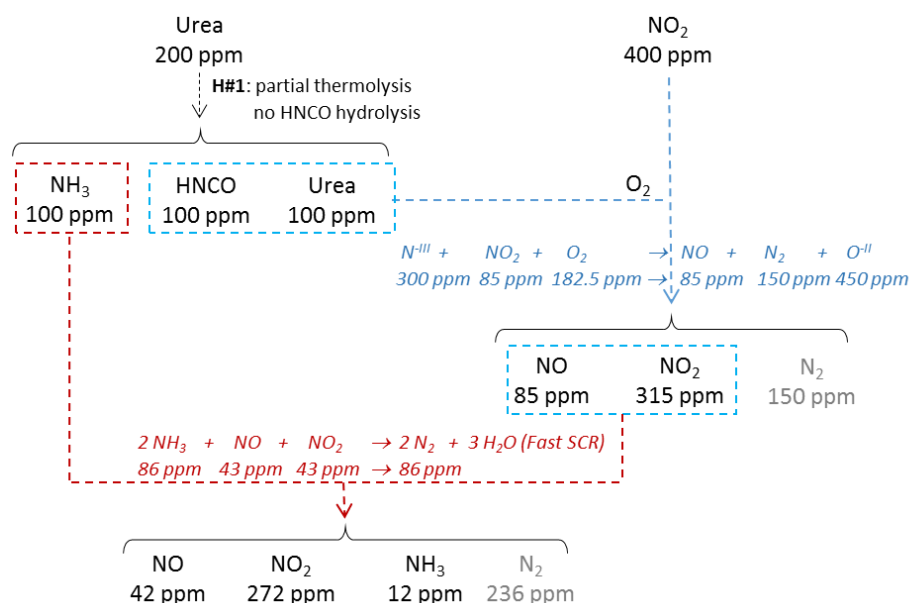
**Hypothesis #1:** The amount of generated NH<sub>3</sub> is equivalent to the amount of converted NO<sub>x</sub>, and no over production of NO<sub>x</sub> is considered.

Based on results reported in Table S2, 86 ppm of NO<sub>x</sub> are converted and 12 ppm of NH<sub>3</sub> are 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 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 remaining reductant, and simultaneously produced 85 ppm of NO.

Besides, the formation of only 98 ppm of NH<sub>3</sub> induces an incomplete urea thermolysis and/or HNCO hydrolysis. Consequently, the corresponding amount of reductant in the N<sup>III</sup> oxidation state (NH<sub>2</sub>CONH<sub>2</sub>, HNCO or NH<sub>3</sub>) is around 300 ppm, as for instance 100 ppm urea and 100 ppm HNCO as illustrated below (Eq. S2):

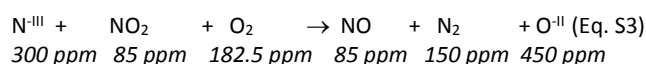


In regards of the amount of NO<sub>2</sub> converted into NO (85 ppm), it results in a lack of oxidation agent to oxidize the remaining reductant species into N<sub>2</sub>. Then, the contribution of O<sub>2</sub> is needed to respect the observed N-balance even if this represents a very small proportion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



**Figure S4.** 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.

Finally, the following reaction (Eq. S3) can be put forward for validating the hypothesis #1:



An overview of the pathways corresponding to this hypothesis is reported in Figure S4

**Hypothesis #2: The urea thermolysis is not the determining-step of NH<sub>3</sub> generation.**

In this hypothesis, the urea thermolysis is achieved and 200 ppm of NH<sub>3</sub> and HNCO each are obtained. It is assumed that NH<sub>3</sub> reacts by a fast-SCR reaction while HNCO reacts via a more complex way, as detailed below. Considering that 12 ppm NH<sub>3</sub> are recorded by the IR analyzer at 200°C, 188 ppm NH<sub>3</sub> are supposed to react. Based on the Fast-SCR stoichiometry, the corresponding theoretical amount of NO converted is 94 ppm (188/2), equal to the amount of converted NO<sub>2</sub>. As 42 ppm of NO is emitted, it induces that 94+42= 136 ppm of NO are generated from NO<sub>2</sub> reduction (it induces a total NOx over generation: 136 - 94 = 102 ppm).

As previously mentioned, 86 ppm of NOx are apparently converted (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> is 86 ppm. As a consequence, 102 ppm of ammonia (188-86) have to be additionally converted by reaction with NOx (there is no NH<sub>3</sub> – O<sub>2</sub> reactivity at 200°C, as showed by SCO experiments in a previous work<sup>2</sup>).

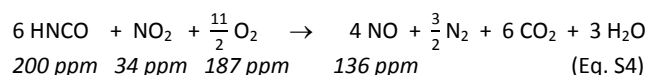
To respect the outlet measured NOx concentrations, it induced that the effective NOx concentration at the catalyst level reach 502 ppm (400+102) in order to assume the conversion of the expected 102 ppm of NH<sub>3</sub>.

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 S2.

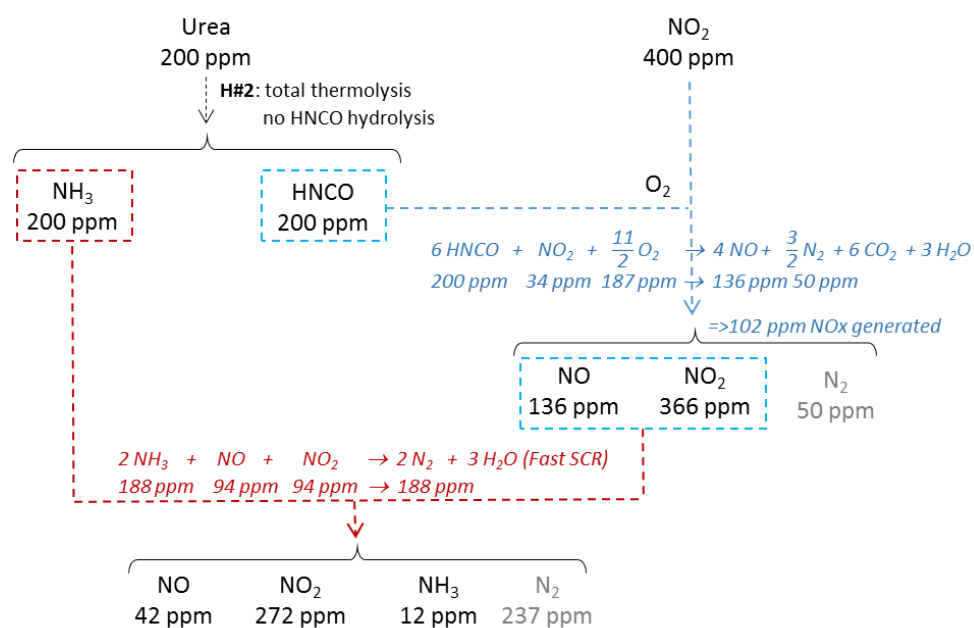
To obtained the theoretical calculated NOx composition (366 ppm NO<sub>2</sub> and 136 ppm NO) taking into account that 400 ppm NO<sub>2</sub> are initially introduced, 34 ppm NO<sub>2</sub> have to be converted together with the over formation of 136 ppm NO. In the same time, 200 ppm HNCO have to be 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 Eq. S4 respects this proposed pathway:



An overview of the pathways corresponding to this hypothesis is reported in Figure S5.

Finally, both hypothesis #1 and #2 point out the participation of O<sub>2</sub> in addition to NO<sub>2</sub> to “fully” oxidize the reductant species other than ammonia.

In order to evaluate the most probable hypothesis #1 or #2, supplementary experiments were performed adding 150 mg ZrO<sub>2</sub> upstream the aZr sample. ZrO<sub>2</sub> is an active material in HNCO hydrolysis as previously discussed in ref 8. In NO<sub>2</sub>-only SCR condition, ZrO<sub>2</sub> addition leads to the same results than those obtained with gaseous ammonia (results not shown), with also similar outlet NH<sub>3</sub> concentration. Then, these experimental results strongly suggest that HNCO is largely present at the catalyst surface (without excluding the possible presence of traces of urea) and support the hypothesis #2. On the contrary, the main drawback of the hypothesis #1 is the poor advancement in urea thermolysis (together with no HNCO hydrolysis), which doesn't fit with other reported results in this study.



**Figure S5.** Reaction pathways corresponding to hypothesis #2.

#### Reference

- (1) Takeda, T., Iwamoto, M., *Catal. letters*, **1996**, 38, 21-25.
- (2) Seneque, M., Can, F., Duprez, D., Courtois X., *Catalysts*, **2015**, 5, 1535-1553