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Direct comparison of Urea-SCR and NH₃-SCR activities over acidic oxide and exchanged zeolite prototype powdered catalysts.

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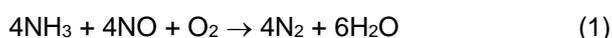
Abstract

In order to develop new NO_x selective catalytic reduction (SCR) catalysts for automotive application, the DeNO_x catalytic activity is commonly evaluate at the laboratory scale using NH₃ as reductant. However, NH₃ is not directly used on board: an ammonia precursor based on urea aqueous solution is injected in the exhaust pipe upstream the SCR catalyst. It is admitted that ammonia is then obtained by two successive reactions: the thermal decomposition of urea, leading to HNCO and NH₃, and the HNCO hydrolysis, providing the second molecule of NH₃. However, the complete availability of ammonia from urea could be not achieved before the SCR catalyst. Then, the influence of the SCR catalyst on these reactions may impact the NO_x reduction efficiency. With the aim to study the possible role of the SCR catalyst on the ammonia availability, an innovative synthetic gas bench adjusted to powdered material was developed, allowing the direct comparison of the use of gaseous NH₃ or urea (injected aqueous solution) for the NO_x conversion, depending on the temperature (200-500°C). This work presents results obtained with an oxide based prototype SCR catalyst in comparison with a patented Fe-exchanged zeolite, evaluated in both standard and fast SCR stoichiometry. This study points out that, in contrast with the exchanged zeolite, the evaluated oxide based catalyst may not allow an optimal NO_x conversion because of a lack in ammonia availability, attributed to insufficient activity in HNCO hydrolysis.

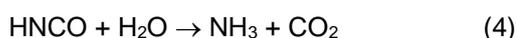
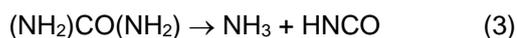
Keywords: Urea; NH₃; SCR; residence time; oxide; zeolite.

1. Introduction

Recent regulations for Diesel or lean-burn engines like Euro 6/VI tend to impose three different catalytic processes to treat the exhaust gas, including (i) an oxidation catalyst for CO and unburned hydrocarbons, (ii) a particulate filter for soot trapping and combustion, and (iii) a specific process for NO_x reduction. Concerning the NO_x treatment, two main technologies are usually proposed. The NO_x storage reduction (NSR) process works in transient condition, with alternating oxidizing and reducing phases [1]. It doesn't need additional reductant other than fuel, but the main drawbacks are fuel overconsumption, ageing (thermal ageing, poisoning) and NO_x reduction selectivity. The second technology is adapted from the NO_x selective catalytic reduction (SCR) by ammonia developed in the 1970' for stationary source application. The NH₃-SCR reactions are mainly known as "standard-SCR" (Eq. 1) and "fast-SCR" (Eq. 2) depending on the NO₂/NO_x ratio, both reactions respecting the NH₃-NO_x stoichiometry 1-1.



However, the implementation of the NH₃-SCR process into passenger cars and heavy duty vehicles requires the use of an ammonia precursor, usually an urea aqueous solution. Ammonia is then obtained by two consecutive reactions: urea thermolysis (Eq. 3) and HNCO hydrolysis (Eq. 4):



Unfortunately, NH₃ may be not fully available due to a limited urea decomposition/hydrolysis. It leads to an imbalance in the SCR stoichiometry and it may cause deposit formation due to formation of biuret, cyanuric acid, ammelide, ammeline...[2].

In addition, the implementation of a particulate filter in the exhaust pipe, which induces strong exothermic reactions, does not allow the use of conventional vanadium based SCR catalysts. To reach the required high thermal stability, new SCR materials are developed. They are usually firstly evaluated in DeNO_x efficiency at the laboratory scale in NH₃-SCR. However, this is not the on-board reductant, but only few works deal with urea-SCR at the laboratory scale [3,4], especially with powdered catalysts.

In order to evaluate these new catalysts in both urea-SCR and NH₃-SCR conditions, an innovative experimental synthetic gas bench was developed in our laboratory, specially designed for powdered samples, with the aim to obtain a direct comparison of both reductants. In the case of urea-SCR, the residence time between urea injection zone and the catalytic bed is a key parameter. This work presents the catalytic behaviour in terms of NO_x and NH₃ conversions over an oxide based prototype SCR catalyst, in comparison with a patented Fe-exchanged zeolite, for standard and fast conditions.

2. Materials and Methods

Two powdered samples were evaluated in this study, an oxide based catalyst and a zeolite based catalyst. The oxide was a modified acidic zirconia provided by Solvay, as proposed in [5]. It is denoted aZr. It was evaluated after hydrothermal ageing at 600°C and exhibited a specific surface area of 50 m²/g. Note that this solid appears very stable since its specific surface area was measured at 47 m²/g after hydrothermal ageing at 850°C. The second evaluated catalyst was a patented Fe-zeolite catalyst

[6], denoted as Fe-zeo. Before use, the catalysts were sieved in the 0.1-0.25 mm range and the apparent densities were approximately 0.77 g cm³ and 0.29 g cm³ for aZr and Fe-zeo, respectively.

The DeNO_x efficiency was evaluated in “standard SCR” and “fast-SCR” conditions using the following mixture: 400 ppm NO_x (*i.e.* 400 ppm NO in standard-SCR, or 200 ppm NO+200 ppm NO₂ in fast-SCR), 200 ppm urea or 400 ppm NH₃, 10% O₂, 8% H₂O, 10% CO₂ (total flow rate 20 L.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 ($\phi=50\mu\text{m}$) into a heated zone at 200°C upstream the catalytic bed. The liquid flow rate (19 $\mu\text{L}\cdot\text{min}^{-1}$) was controlled by a HPLC micro pump ($\Delta P=9-10$ bar). The catalyst (100 mg) was placed in a quartz reactor and positioned in an electric furnace. The residence time (noted Tr, corresponding to the elapsed time for the gaseous mixture between urea injection zone and the catalytic bed) was varied between 6.1 s and 4.0 s depending on the location of the catalytic bed in the oven. Note that the velocity of the urea ejection at the nozzle outlet is not taken into account for the Tr calculation. A scheme of the experimental bench is presented in Online Resource 1.

Supplementary tests were performed in order to evaluate the behaviour of materials in the oxidation of NH₃ or urea. Selective catalytic oxidation (SCO) tests were performed with the same mixture as for SCR tests, except that NO_x were removed. All catalytic activities were evaluated in the 200-500°C temperature range, by step of 50°C. Reported data were recorded after stabilization. The gas composition was monitored with a MKS 2030 Multigas infrared analyser for NO, NO₂, N₂O, HNCO, NH₃, CO, CO₂ and H₂O. The urea conversion was calculated taking into account that the introduced urea is fully converted into NH₃ at the analyser level without catalyst.

NH₃-TPD were performed under a flow containing CO₂, O₂ and H₂O (each at 10%) balanced in N₂ from 120°C up to 550°C (5°/min) after adsorption and purge at 100°C.

3. Results and Discussion

The aim of the study was to evaluate SCR catalysts at the laboratory scale with the on-board reductant: an urea aqueous solution. However, the conversion obtained with gaseous ammonia (NH₃-SCR) using the same apparatus is required as reference for the direct comparison of both reductant. Results are presented in the next section.

3.1 NH₃-SCR.

NO_x and NH₃ conversions obtained in standard SCR condition (only NO as NO_{x inlet}) using ammonia as reductant agent are reported in Fig. 1.

Over the zirconia based catalyst (aZr), the NO_x conversion starts at 48% at 200°C, it reaches a maximum of 93% near 350°C and it then decreases slowly to 87% at 500°C. Taking into account the ammonia conversion depicted in Fig.1B, it appears that the NH₃ conversion / NO_x conversion ratio is very close to 1 until 400°C, indicating that the DeNO_x process respects the fast and/or standard SCR stoichiometry (Eq. 1 and 2). For higher temperatures, this ratio increases and reaches 1.16 at 500°C (Fig. 1C). This NH₃ over-conversion at high temperatures is explained by the NH₃ oxidation by O₂ [7].

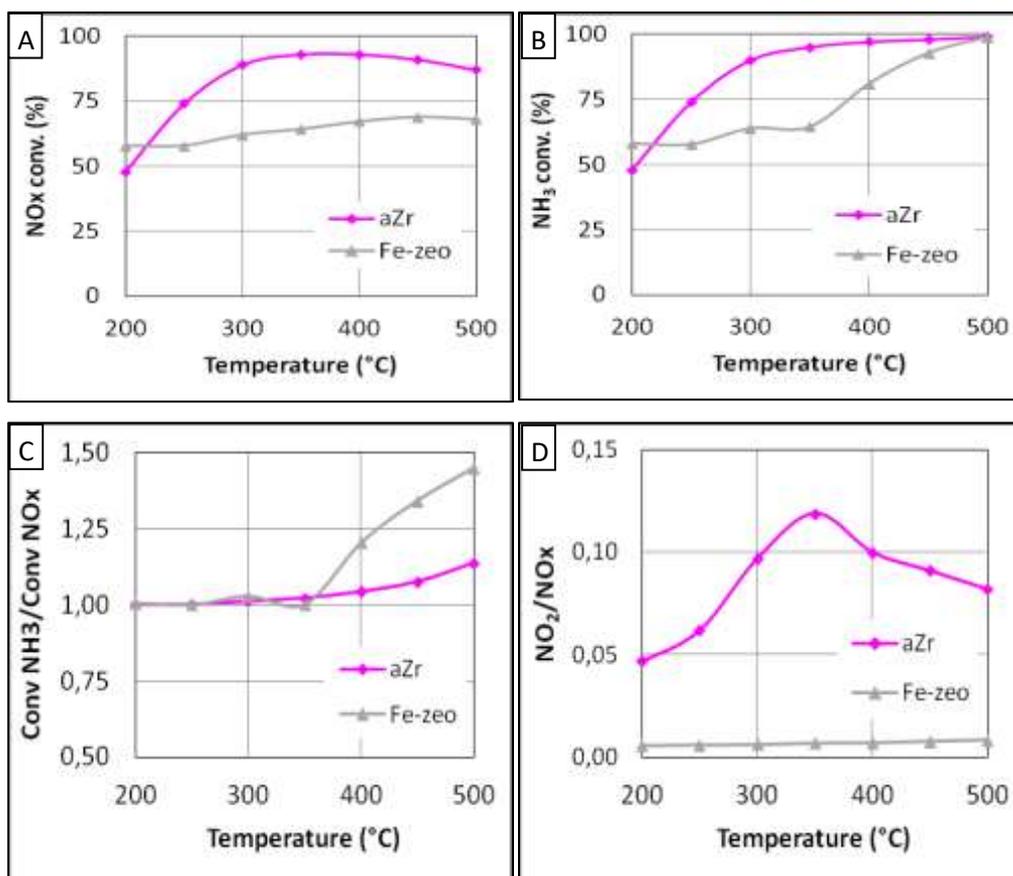


Fig. 1 standard-SCR activity obtained with gaseous NH_3 as introduced reductant over aZr (—) and Fe-zeo (—) catalysts. NO_x conversion (A), NH_3 conversion (B), NO_x conversion / NH_3 conversion ratio (C), and NO_2/NO_x outlet ratio (D)

In this standard SCR condition, a lower NO_x conversion is observed with the Fe-zeo sample compared with aZr. The NO_x conversion slowly increases with temperature, it varies between 58% and 69% in the 200-500°C temperature range, with a maximum at 450°C. The NH_3 conversion is equal to the NO_x conversion until 350°C, but the NH_3 conversion significantly differs for higher temperature, reaching 100% at 500°C. The “ NH_3 conversion / NO_x conversion” ratio was then 1.45 (Fig. 1C). It can be attributed to a pronounced oxidation of NH_3 , most meaningful than over the acidic zirconia.

Comparison of both catalysts also shows that nearly no NO_2 is emitted outlet with Fe-zeo (Fig. 1D) whereas 5-10 ppm NO_2 are detected using aZr. One assumption can be a lower activity in the oxidation of NO to NO_2 of Fe-zeo, but it can be also attributable to a full consumption of the generated NO_2 by a fast-SCR stoichiometry (eq. 2). In fact, Fe-zeo exhibited high De NO_x efficiency in fast-SCR condition (section 3.2.3), and NO oxidation tests performed at 200°C showed that the exchanged zeolite is more active than the aZr oxide based sample: the NO oxidation into NO_2 reached 25% and almost 0%, respectively (tests not shown). Then, it confirms the preferential fast SCR stoichiometry pathway for NO_x reduction on this zeolite material.

3.2 Urea-SCR.

3.2.1 Standard-SCR condition

Urea-SCR tests were firstly performed in “standard” conditions with various residence times (Tr) between the urea injector and the catalytic bed. For both studied catalysts, results obtained with residence time of 6.1 s (not shown) or 5.2 s are very close to those obtained with gaseous ammonia (Fig. 2). Taking into account that NH₃ is assumed to be the effective reductant, these results suggest that NH₃ is sufficiently available to ensure the expected NO_x reduction.

On the opposite, the NO_x reduction can be affected when the residence time is decreased to 4.0 s, especially with the aZr catalyst at low temperatures (Fig. 2A). For instance, the NO_x conversion is two times lower at 250°C. On the opposite, this limitation was not clearly evidenced over Fe-zeo (Fig. 2B). This direct comparison between reductant agents (NH₃ vs. urea) and catalyst composition illustrates that at least a part of the successive reaction of urea decomposition (Eqs. 3, 4) can be catalysed. Moreover, even if the considered residence times are significantly higher than in real SCR process, a residence time of 4.0 s appears sufficiently low in the used experimental setup to highlight significant differences depending on the introduced reductant and the catalysts formulation.

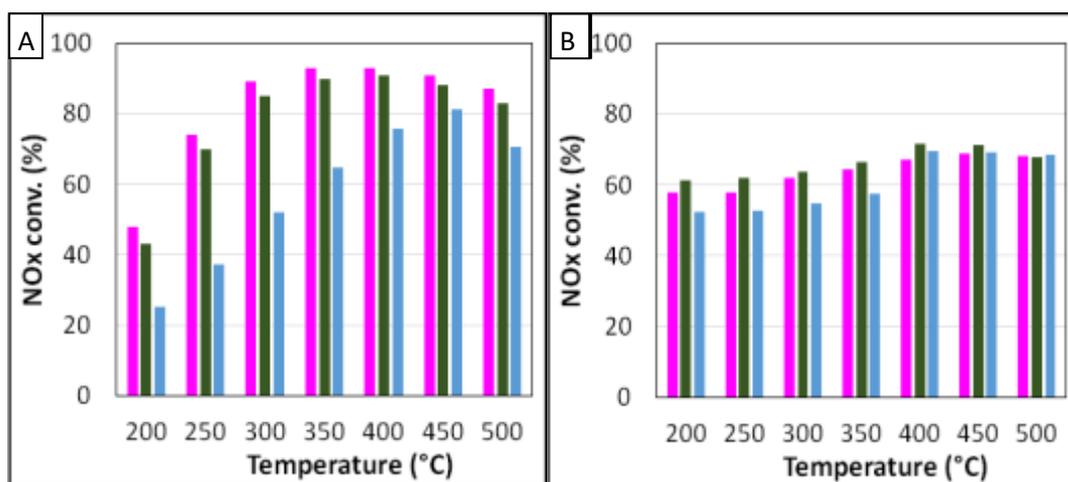


Fig. 2 Influence of urea residence time (■: Tr = 5.2s.; ■: Tr = 4.0 s.) in “standard-SCR” condition compared with the use of gaseous NH₃ (■). (A) aZr catalyst, (B) Fe-zeo catalyst.

Various hypothesis can be proposed to explain the drop in DeNO_x efficiency observed with the acidic zirconia catalyst for shorter urea residence time: (i) a catalyst poisoning due to deposit formation, as presented in the introduction section [2]; (ii) a lack of available NH₃ due to incomplete urea decomposition and/or H₂NCO hydrolysis (eq. 3 and 4); (iii) a lack of available NH₃ due to reactivity of the reductant(s) without NO_x reduction; (iv) a change in the SCR stoichiometry (attributable for instance to the following reactions $4\text{NH}_3 + 3\text{NO}_2 \rightarrow 3.5\text{N}_2 + 6\text{H}_2\text{O}$ and/or $4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}$).

3.2.2 Investigation of the DeNO_x efficiency decrease over aZr catalyst for urea Tr = 4.0 s.

Additional tests were performed in order to clarify the reason for the loss in NO_x conversion over aZr when the residence time dropped to 4.0 s. As the developed apparatus allows the simultaneous use of

urea and gaseous NH_3 , it is possible to add gaseous NH_3 in the feed stream, in addition to the injection of urea with $\text{Tr} = 4.0$ s. The amount of added NH_3 was calculated to theoretically compensate the loss in NO_x conversion for each tested temperature. Results presented in Fig. 3 show that this addition of gaseous NH_3 led to a full recovery of the NO_x conversion obtained with a residence time of 5.2 s (full line). Then, the NO_x conversion with $\text{Tr} = 4.0$ s appears limited by a lack of NH_3 availability.

Besides, SCO tests were also carried out to determine the behaviour of materials in the oxidation of the introduced reductant, NH_3 or urea ($\text{Tr} = 4.0\text{s}$). Table 1 reports the reductant conversion expressed in NH_3 conversion. It clearly appears that the reductant conversion is significantly improved when urea is used. It is deduced that (i) the effective reactant is not only ammonia when urea is injected, and (ii) the reactive species are more reactive toward oxidation than NH_3 .

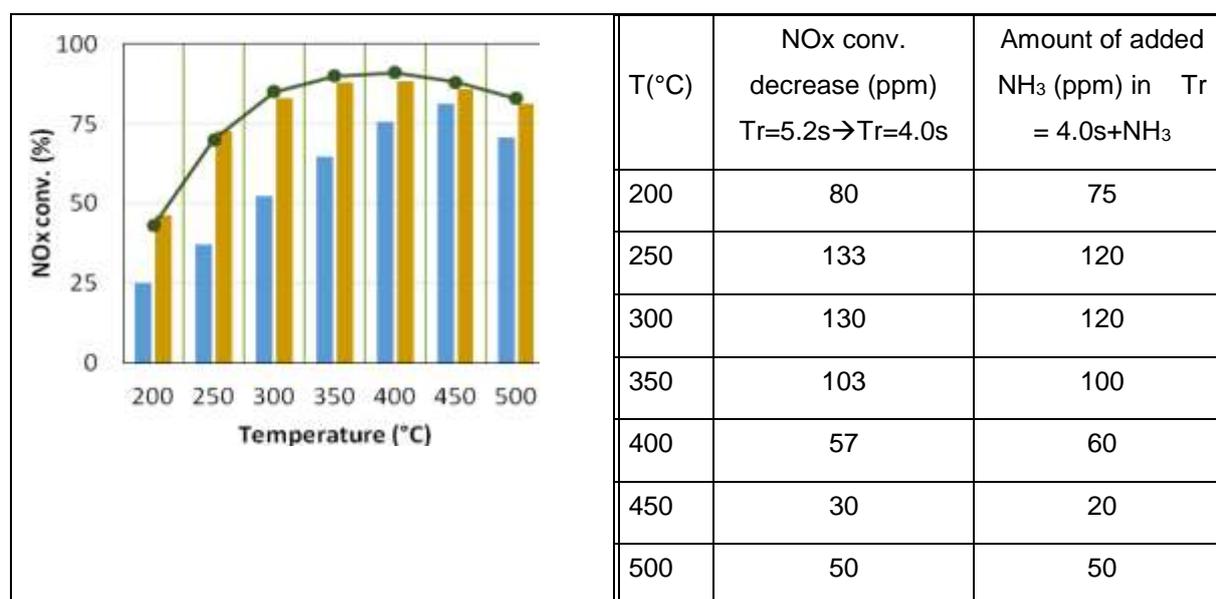


Fig. 3 aZr catalyst: influence of gaseous NH_3 addition (■) on the NO_x conversion obtained in “standard-SCR” condition with urea (■) at $\text{Tr} = 4.0\text{s}$. (—: $\text{Tr} = 5.2$ s.)

Table 1: reductant conversion over aZr in Selective Catalytic Oxidation (SCO) test (200 ppm urea or 400 ppm NH_3 , 10% O_2 , 8% H_2O , 10% CO_2)

Temperature (°C)	200	250	300	350	400	450
NH_3 conv. (%) with gaseous NH_3	0	5	8	15	28	47
“ NH_3 ” conv. (%) with urea ($\text{Tr} = 4.0\text{s}$)	0	19	30	31	38	49

A

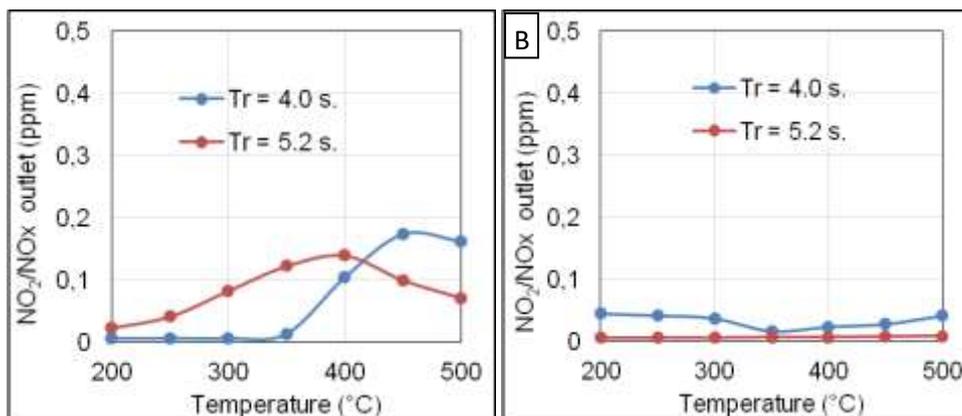


Fig. 4 NO₂/NO_x outlet ratio in “standard-SCR” for Tr = 4.0 s (—) and Tr = 5.2 s. (—). (A) aZr catalyst, (B) Fe-zeo catalyst

In addition, the urea residence time can also affect the NO₂/NO_x outlet ratio, depending on the catalyst formulation. For the exchanged zeolite, no clear effect of the urea residence time is observed in NO₂/NO_x outlet ratio (Fig. 4B). In fact, very low amount of NO₂ was emitted, whatever the urea residence time. These results are also in accordance with the test performed with gaseous ammonia (Fig. 1D). On the acidic zirconia sample, NO₂ can be emitted at low temperature for Tr = 5.2s (Fig. 4A) or using gaseous ammonia (Fig. 1D). On the contrary, no NO₂ was emitted until 350°C for the shorter urea residence time (4.0 s). It can be then supposed that the *in situ* produced NO₂ reacted with a product from the urea injection.

These results appear consistent with the previously detailed SCO tests which indicated an enhancement in the oxidation behaviour over the acidic zirconia catalyst when urea was injected with Tr = 4.0s instead of gaseous NH₃. The intermediate species, probably HNCO, is not only more reactive toward O₂, but also probably toward NO₂ (without NO_x reduction).

3.2.3 Fast-SCR condition

The detrimental effect of urea residence time on NO_x abatement was also examined in more favourable conditions for the NO_x reduction, namely the fast-SCR condition. Corresponding catalytic results for both samples are presented in Fig. 5. It appears that the NO_x conversion with Fe-zeo is then higher than over aZr. In fact, the NO_x conversion was highly improved over Fe-zeo in fast SCR condition compared with the standard SCR condition. It reached 87-97% in the whole studied temperature range, whatever the introduced reductant, gaseous ammonia or urea with Tr= 5.2-4.0 s.

The NO_x conversion is also improved with aZr in fast-SCR condition, which is particularly evidenced at low temperature: at 200°C, the NO_x conversion reached 68% in fast-SCR condition (Fig. 5B), compared to 48% in standard condition (Fig. 2A).

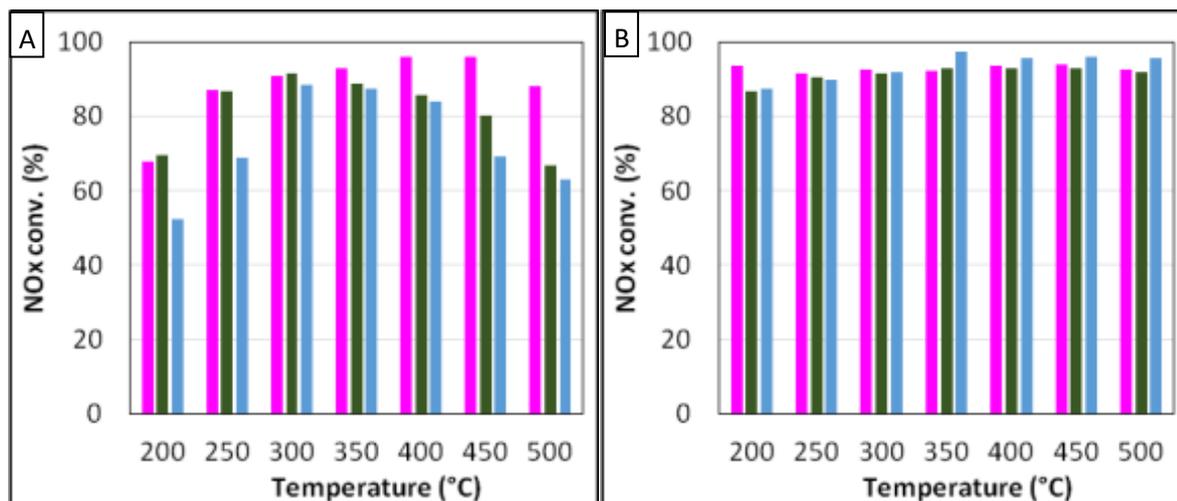


Fig. 5 Influence of urea residence time (■: $Tr = 5.2s$.; ■: $Tr = 4.0 s$.) in “fast-SCR” condition compared with the use of gaseous NH_3 (■). (A) aZr catalyst, (B) Fe-zeo catalyst

In addition, the detrimental impact of the shorter urea residence time is put in evidence again over the oxide-based sample, with a relative drop of about 25% at 200°C. Interestingly, the decrease of the urea residence time still has no influence over Fe-zeo catalyst. Note that the maximum N_2O outlet concentration is limited to 3 ppm at 500°C over aZr, and to 5 ppm at 350°C over Fe-zeo (recorded at stabilized temperatures), whatever the inlet condition (standard and/or fast).

3.2.4 Enhancement of DeNOx efficiency over the acidic zirconia oxide in standard-condition

Finally, the presented results suggest that the double ammonia formation from urea is not achieved at the catalyst level over the acidic zirconia oxide for shorter urea residence time ($Tr = 4.0 s$.), whatever the SCR conditions, namely standard or fast. The urea thermolysis (Eq. 3) is endothermic and thermally assisted compared to the HNCO hydrolysis which is exothermic. With pure urea, thermal decomposition can occur whereas the isocyanic acid is stable in the gas phase [8]. However, HNCO hydrolysis is catalysed on many solid oxides [9]. It is proposed that the rate of HNCO hydrolysis is much higher than the rate of the SCR reaction at low to medium temperatures on usual SCR catalysts.

However, both Eq.3 and Eq.4 reactions can be catalysed by transition metal oxides and the limiting step for ammonia formation also depends on the temperature [10]. Based on the results reported by Bernhard *et al* [10], 100 mg of single oxide (TiO_2 , 43 m^2/g ; ZrO_2 , 46 m^2/g ; Al_2O_3 , 185 m^2/g) were added just ahead the aZr catalytic bed. These oxides were selected in regards to their respective behaviours in urea thermolysis and HNCO hydrolysis, but they don't exhibit any DeNOx activity (results not shown). The DeNOx efficiencies of these dual bed catalytic systems were evaluated in standard condition.

A partial recovery of the NOx conversion was observed (Table 2) according the following order: $ZrO_2 > TiO_2 > Al_2O_3$, which also corresponds to the reactivity toward the HNCO hydrolysis reported in [10]. It is concluded that the decrease in the DeNOx efficiency over aZr when the urea Tr is decreased to 4.0 s is mainly attributable to a lack in the HNCO hydrolysis. In opposition, Fe-zeo is able to convert HNCO into NH_3 , or to use directly HNCO to reduce NOx, in both standard and fast SCR conditions.

Table 2: NO_x conversion in standard-SCR condition using urea (Tr =4.0s) as reductant: influence of the single oxide addition (100 mg) ahead the aZr catalytic bed.

Temperature (°C)	200	250	300	350	400	450
NO _x conv. (%) ; aZr catalyst alone	25	37	52	64	75	81
NO _x conv. (%) ; Al ₂ O ₃ +aZr catalyst	31	48	58	67	81	83
NO _x conv. (%) ; TiO ₂ +aZr catalyst	27	48	62	71	83	84
NO _x conv. (%) ; ZrO ₂ +aZr catalyst	37	56	72	80	82	82

Additionally, both catalysts present very different acidity behaviour. Ammonia temperature programmed desorption (TPD) were performed in order to evaluate this parameter (profiles not shown). The aZr catalyst presented a maximum desorption near 300°C, and NH₃ desorption was finished at approximately 450°C. As expected, the zeolite based sample exhibited higher acidic properties: the desorption profile showed a maximum near 400°C, and it occurred until 570°C. In addition the amount of desorbed ammonia was approximately two times higher over Fe-zeo than over aZr. This significant difference in acidity strength and site number may intervene in the zeolite behaviour toward HNCO, in accordance with the results obtained with the addition of singles oxides: ZrO₂ is the more acidic material compared with Al₂O₃ and TiO₂.

4. Conclusions

This study, carried out at the laboratory scale, clearly demonstrates the interest to evaluate catalysts in urea-SCR rather than in NH₃-SCR. A possible divergence in terms of DeNO_x efficiency is evidenced depending on the nature of the reductant agent, *i.e.* gaseous ammonia or aqueous urea, in respect to the catalyst formulation, *i.e.* oxide or zeolite-based materials. Particularly, the influence of the urea residence time is more detrimental to the acidic zirconia oxide compared to iron exchanged zeolite. In fact, using urea aqueous solution, the evaluated aZr catalyst may not allow an optimal NO_x conversion because of a lack in ammonia availability, attributed to insufficient activity in HNCO hydrolysis. The drop in DeNO_x efficiency noticed over acidic zirconia sample for shorter urea residence time is evidenced whatever the inlet condition, namely standard or fast SCR. In contrast, the evaluated Fe-zeo did not exhibit such limitations, demonstrating the role of the catalyst in urea-SCR compared to NH₃-SCR and the interest to develop specific materials active with urea rather than with gaseous ammonia.

In addition, results suggest that HNCO is more reactive toward oxidation than ammonia over acidic zirconia. In order to highlight this probable inconvenient, SCR tests with excess of NO₂ will be investigated in a near future.

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