



Effect of the NH_4NO_3 Addition on the Low-T NH_3 -SCR Performances of Individual and Combined Fe- and Cu-Zeolite Catalysts

R. Villamaina¹ · I. Nova¹ · E. Tronconi¹ · T. Maunula² · M. Keenan³

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Abstract

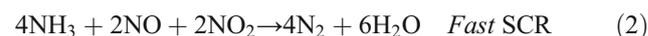
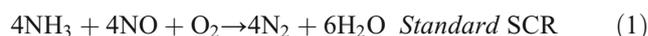
We have measured NO_x conversions and N₂O productions over Fe-BEA and Cu-SAPO catalysts and over their sequential arrangements under Enhanced SCR conditions, resulting from the addition of an aqueous solution of ammonium nitrate (AN) to the typical Standard SCR feed stream, and we have compared them to those observed under Standard and Fast SCR conditions. The expected strong enhancement of the poor low temperature activity of the Fe-BEA catalyst was confirmed: both NH₃ and NO_x conversions and N₂O formations similar to those of the Fast SCR reaction were achieved when cofeeding ammonium nitrate. On the other hand, the Cu-SAPO efficiency was drastically decreased by the addition of AN at low temperatures, possibly due to trapping of the ammonium nitrate salt within the SAPO zeolite, characterized by smaller pores than those of the BEA zeolite. The Cu-SAPO performances were recovered only at T > 250 °C with a huge release of N₂O due to the thermal decomposition of AN. The combined system with the Fe-zeolite sample placed upstream of the Cu-zeolite also exhibited outstanding low temperature deNO_x performances, with even lower N₂O production than over the Fe-zeolite only at the same Enhanced SCR (E-SCR) conditions.

Keywords NH_4NO_3 · Enhanced SCR · Low-T deNO_x activity · NH_3 -SCR · Cu-zeolite · Fe-zeolite

1 Introduction

The current well-established solution for the NO_x emission control on Diesel and/or natural gas lean-burn engines is represented by the NH₃ selective catalytic reduction (NH₃ SCR) [1, 2]. The NO_x abatement occurs over state-of-the-art catalysts, such as Fe-, Cu-zeolite and V-based catalysts [2–13], by means of the injection of urea, which, once decomposed to NH₃, can react with NO_x

producing harmless N₂ and H₂O, according to the main SCR reactions



The deNO_x performance of the SCR systems is strictly connected to the temperature of the exhaust gases. One big challenge is the improvement of the efficiency when the temperatures are too low for the SCR catalysts to be active and for the urea to effectively decompose. Moreover, the development of more efficient Diesel engines is leading to operating conditions with high contents of oxygen. Thus, such increasingly efficient engines produce higher amounts of NO_x as well as exhaust gases with increasingly lower temperatures, aggravating the task of the SCR converter. A way to maximize the NO_x conversion to N₂ in the mobile applications is by increasing the NO₂/NO molar feed ratio in order to promote the Fast SCR reaction (2). Since the NO_x gases, produced during the combustion, are composed mainly by NO (95%), the Standard SCR reaction (1) is the main reaction involved in the NO_x

✉ E. Tronconi
enrico.tronconi@polimi.it

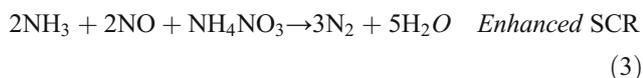
¹ Department of Energy, Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, 20156 Milan, Italy

² Dinex Finland Oy, Global Catalyst Competence Centre, P.O. Box 20, FI-41331 Vihtavuori, Finland

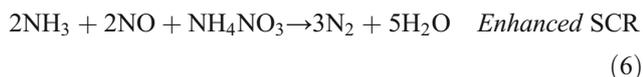
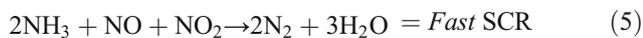
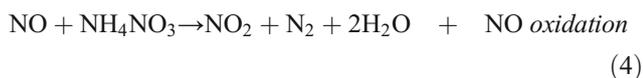
³ Ricardo UK Ltd, Shoreham Technical Centre, Shoreham-by-Sea BN43 5FG, UK

control, which is unfortunately characterized by a significantly lower efficiency than the Fast SCR (2) in the low temperature range [2]. The NO₂/NO molar feed ratio can be modified in the catalytic oxidation step mainly dedicated to the abatement of unburned hydrocarbon and CO, the Diesel Oxidation Catalyst (DOC) or/and Methane Oxidation Catalyst (MOC). The presence of NO₂ in the exhausts allows the improvement of the deNO_x efficiency of the SCR systems in the low T range, especially when the NO₂/NO molar ratio is 1/1 and the Fast SCR can take place (2). However, the oxidation activity of the DOC/MOC is strongly dependent on temperature and flow rate of the exhaust gases and, consequently, the optimal NO₂/NO feed ratio cannot be guaranteed for all the possible engine operating conditions [14].

In the last years, another catalytic route was proposed to overcome the issues connected to the presence of a proper amount of NO₂ in the gas mixture necessary to boost the typical poor deNO_x activity of Fe-zeolite or V-based catalysts in the low T range. This involves the addition of an aqueous solution of ammonium nitrate (NH₄NO₃) to a NO–NH₃ containing gas mixture, which determines the occurrence of the so-called Enhanced SCR reaction (3)



The E-SCR reaction was previously studied on Fe-zeolite and V-based catalysts [14–18] and it was demonstrated to be associated with superior NO reduction efficiencies in the 200–350 °C T range with respect to the Standard SCR reaction, allowing to approach the desired higher Fast SCR activity. It is worth emphasizing that this solution does not require the oxidation of NO to NO₂ upstream of the SCR converter since this oxidation is directly entrusted to the ammonium nitrate itself according to the reaction (4)



The produced NO₂ is, then, able to react further with the remaining NO and with NH₃ in accordance with the Fast SCR Reaction (5): the Enhanced SCR reaction (6), therefore, is the sequential combination of these two catalytic steps: (4) + (2) [17]. The Enhanced SCR and the Fast SCR are characterized by the same reaction mechanism, which differs only in their first step, existing a direct equivalence between AN and NO₂ [17].

The ammonium nitrate feed can be obtained by injecting or vaporizing an aqueous solution of ammonium nitrate upstream

of the SCR converter, together with the urea solution: indeed, single aqueous solutions containing both the reducing agent (urea) and the oxidizing additive (ammonium nitrate) are commercialized and available for this purpose [14].

This work aims at brushing up this concept since it gives interesting perspectives for the enhancement of the critical low temperature deNO_x activity without necessarily relying on the generation of NO₂ in the DOC/MOC. Since it was demonstrated to be a concept applicable to two classes of commercial SCR catalysts (V-based systems and Fe-exchanged zeolites), here we complete the study by investigating also the deNO_x performances of a Cu-promoted zeolite catalyst and of combined Fe- and Cu-zeolite systems under Enhanced SCR conditions, eventually comparing them with the Standard and Fast SCR data.

2 Experimental

Steady-state Standard SCR, Fast SCR and Enhanced SCR catalytic activity tests were performed over two NH₃-SCR catalysts, namely a thermally stable Cu-SAPO and a Fe-BEA, supplied in the shape of coated monoliths by Dinex Finland [19]. The Fe-BEA catalyst was coated onto a cylindrical rolled metallic substrate made of flat and corrugated thin (50 μm) AlCr foils (cell density of 600 cpsi). The coating load was about 150 g/L (40 g/m²). The dimensions of the tested sample were $L = 20$ mm, $D = 12.5$ mm, $V = 2453$ mm³. The Cu-SAPO catalyst was tested in the form of a coated ceramic honeycomb (400 cpsi). The coating load was about 140 g/L. The dimensions of the tested sample were $L = 41.8$ mm, $h = 7.7$ mm, $w = 7.7$ mm, $V = 2478$ mm³. The combined systems were realized putting both catalysts in series, so that 50% of the total catalyst volume was composed by the Cu-sample and 50% by the Fe-sample. The molar Si/Al₂ ratio in the zeolites was in the range of 25–40 to maintain a good hydrothermal stability. A small amount (< 15wt% of final coating) of binder was added in the coating process. The catalysts were hydrothermally (HT) aged at 700 °C for 20 h in air flow with 10% of water [2, 19]. Data on the sulphur resistance of both catalysts are also given in [19].

The experimental equipment used to carry out this work was described in our previous work [2]. Steady-state runs were performed in order to investigate the catalytic activities in a wide T range (150–550 °C), using defined reactant feed concentrations and temperature steps. The feed composition was representative of real after treatment systems: NH₃ = 500 ppm, NO_x = 500 ppm (NO₂/NO_x = 0–0.5), O₂ = 5% (v/v), H₂O = 5% (v/v) and balance N₂. Under Enhanced SCR conditions an aqueous solution of NH₄NO₃ was fed to the reactor: the ammonium nitrate feed concentration level of 200 ppm was achieved by properly diluting a master 2.5 M solution. Either liquid water or the AN + H₂O solution was metered by a volumetric piston pump (Gilson model 305): the

feed rate was around 0.025 ml/min \pm 0.0001 for GHSV = 75,000 h⁻¹. Afterwards, the liquid feed was vaporized in a hot pipeline kept at 190 °C, and then mixed with the other gaseous species and fed to the reactor. All the gaseous species (except N₂ and AN) were continuously monitored at the reactor outlet by a FT-IR gas analyser (Bruker MATRIX MG5).

3 Results

3.1 Enhanced SCR on Fe-BEA

In our previous work [2], we reported the investigation of two commercial SCR catalysts, a Fe-BEA and Cu-SAPO, under typical exhaust aftertreatment conditions for natural gas or duel fuel vehicles. Moreover, we demonstrated that the sequential arrangement of the two Fe- and Cu- monolith catalysts allowed to overcome the issues connected to the use of only one of these metal-promoted zeolite catalysts under Standard SCR conditions, namely the poor low-T deNO_x activity typical of Fe-zeolite catalysts and the lower selectivity in the high-T range of Cu-zeolites. Their combination (Fe followed by Cu), indeed, permitted to mitigate these drawbacks keeping only the advantages of the two catalytic systems, i.e. the outstanding low-T deNO_x efficiency of the Cu-zeolite and the high-T selectivity and activity of the Fe-zeolite. The Cu-zeolite, in fact, placed after the Fe-zeolite, compensated the poor Fe- catalyst activity at low temperature, thus achieving greater overall deNO_x performances under Standard SCR conditions.

An alternative way to improve the low-T deNO_x efficiency of Fe-zeolite systems, however, was already proposed and discussed in the literature [14–18]: the addition of AN to the feed stream, indeed, was demonstrated to increase significantly the low-T Standard SCR NO_x conversions over Fe-zeolite catalysts. Figure 1 compares the NO_x steady-state conversions collected under Standard SCR conditions (GHSV = 75,000 h⁻¹, NH₃ = 500 ppm, NO = 500 ppm, H₂O = 5% v/v, O₂ = 5% v/v) over the Fe-BEA and Cu-SAPO samples and their sequential combination (Fe + Cu) (already shown in [2]) with the NO_x conversions achieved on the Fe-BEA sample under the same Standard SCR conditions when 200 ppm of NH₄NO₃ were added to the gas feed mixture (Enhanced SCR). Figure 1 confirms that the AN dramatically boosts the NO_x conversion over the Fe-zeolite at temperatures below 300 °C, matching the well-known outstanding Standard SCR activity of the Cu-zeolite catalyst, or even overcoming it in the intermediate temperature range. Moreover, the Enhanced SCR activity of the Fe-zeolite sample outperformed the Standard SCR activity of the combined Fe- + Cu-zeolite system (Fig. 1).

Figure 2 directly demonstrates the ammonium nitrate addition effect on the Fe-zeolite sample by comparing the steady-

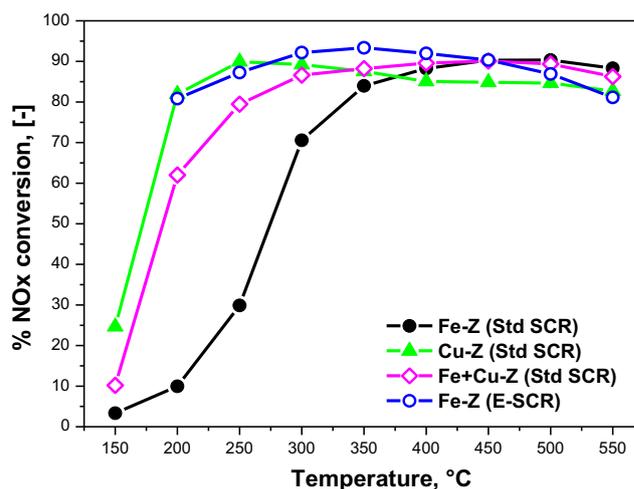
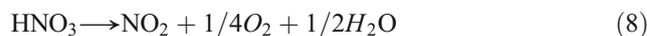


Fig. 1 Comparison of NO_x conversion under Std SCR conditions on Fe-BEA, Cu-SAPO, and Fe+Cu-zeolite catalysts and of NO_x conversion under E-SCR conditions on Fe-zeolite catalyst. GHSV = 75,000 h⁻¹, NH₃ = 500 ppm, NO = 500 ppm, O₂ = 5% v/v, H₂O = 5% v/v, T_{range} = 150–550 °C. Std SCR = NH₄NO₃/NO = 0; E-SCR = NH₄NO₃/NO = 2/5

state NO_x conversions and N₂O productions measured under Fast SCR, Standard SCR and Enhanced SCR conditions. As previously noted, the Enhanced SCR reaction resulted in a significantly higher deNO_x activity at low temperatures with respect to the Standard SCR reaction, approaching the activity of Fast SCR (Fig. 2a). In these tests, the adopted AN feed concentration was 200 ppm. As demonstrated by Marchitti et al. [17], the ammonium nitrate is able to oxidize NO to NO₂, according to reaction (4). Then the co-presence of NO, NO₂ and NH₃ allows the occurrence of the Fast SCR reaction. Considering that all the ammonium nitrate injected in our system oxidized NO to NO₂, the resulting NO₂/NO_x ratio was 2/5, a little lower than the ratio used under Fast SCR conditions (1/2), consistent with our E-SCR experiments remaining below the Fast SCR activity.

Even if the AN dosing is able to improve the NO_x conversions, the N₂O formation is a delicate aspect that needs to be controlled, being a strongly undesired by-product due to its high greenhouse potential. In fact, ammonium nitrate could be involved in other side reactions which are not advantageous for the deNO_x performances but, on the contrary, can contribute to the emission of more pollutants, losing that benefit obtained by injecting nitrate species for the reduction of NO_x. The ammonium nitrate, in fact, can decompose according to the following reactions [18]:



Reactions (7) and (8) determine the production of NH₃ and NO₂. In our systems, we observed a negligible formation of NO₂, which suggests that the nitrate ad-species possibly

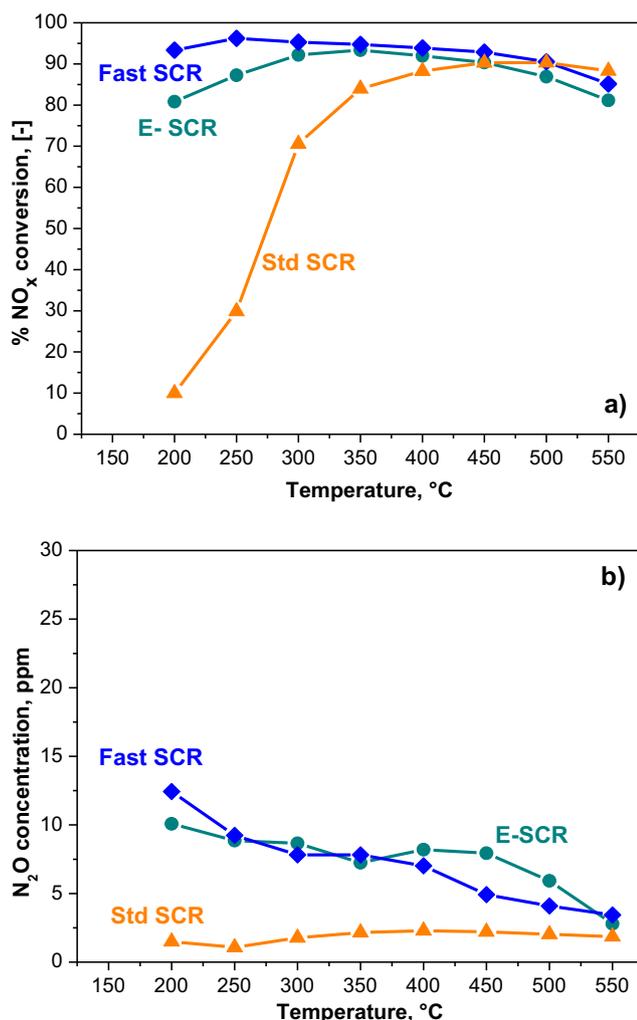


Fig. 2 Standard SCR, Fast SCR and Enhanced SCR reactions on Fe-BEA: **a** NO_x steady-state conversions, **b** N₂O steady-state productions, **c** N₂ Selectivity. GHSV = 75,000 h⁻¹, NH₃ = 500 ppm NO_x = 500 ppm, O₂ = 5% v/v, H₂O = 5% v/v, T_{range} = 200–550 °C. Std SCR: NO₂/NO_x = 0, NH₄NO₃/NO_x = 0; Fast SCR: NO₂/NO_x = 0.5, NH₄NO₃/NO_x = 0; E-SCR: NO₂/NO_x = 0, NH₄NO₃/NO = 2/5

formed by reaction (7) directly participate in SCR reactions [18]. On the other hand, traces of N₂O were detected, which are shown in Fig. 2b and compared with the amount of N₂O emitted under Standard SCR, Fast SCR conditions in the case of Fe-BEA. Figure 2c shows the N₂ selectivities computed as $[1 - 2 * N_2O_{production} / (NH_3 + NO + NH_4NO_3)_{consumption}]$, i.e. assuming that N₂O is the only side product of the SCR process. Even though the Standard SCR reaction is characterized by the worst activity performance, the NO-NH₃ reacting system shows the highest N₂ selectivity at any investigated temperature. The Fast and the E-SCR reactions, instead, contribute to a significant N₂O production (Fig. 2b). Moreover, they show also the same selectivity up to 450 °C, while at higher temperature the E-SCR reaction recovers the Standard SCR selectivity (Fig. 2c).

3.2 Enhanced SCR on Cu-SAPO

The Enhanced SCR reaction was carried out for the first time on a Cu-zeolite catalyst, specifically a Cu-SAPO sample, and compared with the data collected under Standard and Fast SCR conditions. The steady-state NO_x conversions and N₂O productions observed for the three reactions are compared in Fig. 3. For the Cu-SAPO catalyst, the situation was reversed with respect to Fe-BEA: at the lowest investigated temperature, the AN dosing worsened the good deNO_x efficiency achieved both under Standard and Fast SCR conditions. The negative impact of the addition of the AN aqueous solution could be ascribed to the porous structure of the zeolite itself. It is well known that the SAPO chabazite framework is associated with pores with a smaller size compared, for example, to those of the BEA zeolite [20]. At low temperatures (≤ about

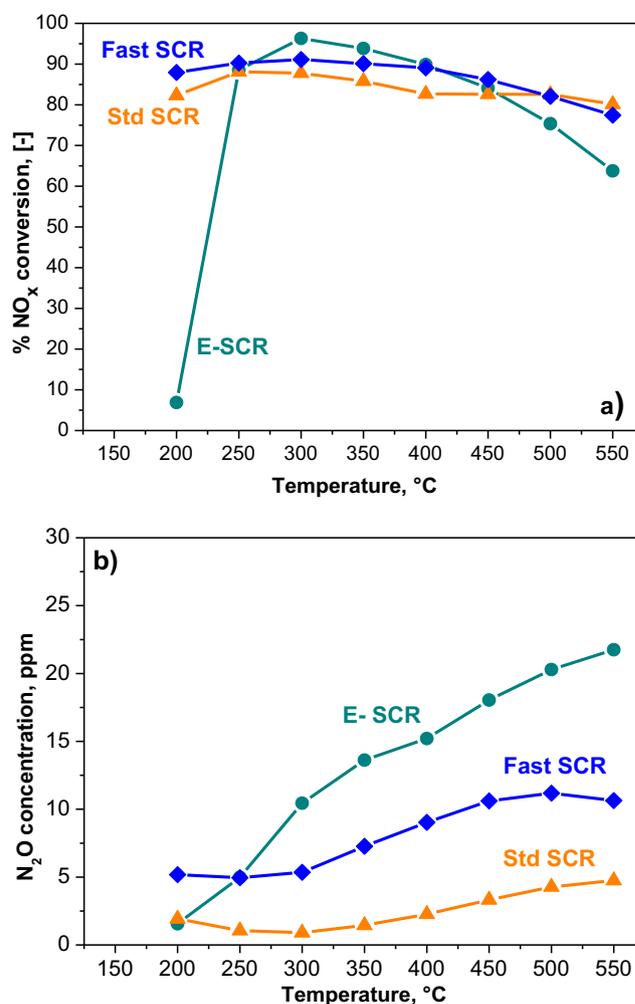


Fig. 3 Standard SCR, Fast SCR and Enhanced SCR reactions on Cu-SAPO catalysts: **a** NO_x steady-state conversions, **b** N₂O productions, **c** N₂ selectivity. GHSV = 75,000 h⁻¹, NH₃ = 500 ppm NO_x = 500 ppm, O₂ = 5% v/v, H₂O = 5% v/v, T_{range} = 200–550 °C. Std SCR: NO₂/NO_x = 0, NH₄NO₃/NO_x = 0; Fast SCR: NO₂/NO_x = 0.5, NH₄NO₃/NO_x = 0; E-SCR: NO₂/NO_x = 0, NH₄NO₃/NO = 2/5

200 °C), the ammonium nitrate salt can be trapped within the small pores of the zeolite, covering the active sites and thus inhibiting the SCR activity. Indeed, on increasing the temperature the activity was recovered, consistent with the fact that the ammonium nitrate was thermally decomposed according to reaction (9) releasing large amounts of N_2O , as shown in Fig. 3b.

Accordingly, the N_2 selectivity under E-SCR conditions remained lower than under Standard and Fast SCR conditions (Fig. 3c), confirming a negative impact of the NH_4NO_3 addition on the deNO_x performance of the Cu-SAPO catalyst.

3.3 Enhanced SCR Fe-BEA + Cu-SAPO: Effect of the Sequential Arrangement

We verified and shown in Fig. 1 that the addition of a Cu-SAPO catalyst after the Fe-BEA monolith can improve the NO_x removal efficiency over that of the Fe-zeolite alone. However, since in the low-T range, the combined system exhibited lower NO_x conversions under Std SCR conditions with respect to those achieved on the only Fe-zeolite catalyst under Enhanced SCR conditions; the very good activity of the combined system could be, theoretically, further improved by dosing ammonium nitrate and thus running the Enhanced SCR reaction over it. For the Fe+Cu-zeolite sequential system, Fig. 4a compares the Standard SCR NO_x conversions, already seen in Fig. 1, with those collected upon addition of 200 ppm of NH_4NO_3 to the Std SCR conditions (E-SCR) and those obtained under the Fast SCR conditions. This plot proves that the combination of these two strategies, namely the AN boosting effect and the combination of Fe and Cu catalysts, can enable outstanding deNO_x performance, already at 200 °C, even better than those obtained on the only Fe catalyst (at 200 °C the NO_x conversions is about 80% against the 86% of Fe+Cu). In addition, this combined catalytic system is beneficial also in terms of N_2O production: Fig. 4b illustrates, as seen for the Fe-zeolite catalyst, that E-SCR and Fast SCR reactions are characterized by similar N_2O formations and, consequently, similar N_2 selectivities (Fig. 4c). However, the measured N_2O concentration was always lower with respect to those detected on the only Fe-zeolite samples, confirming, also for this aspect, that the sequential arrangement is the best choice towards this application.

In our previous work [2], we checked also that the correct positioning of the Fe and Cu samples in the sequential arrangement is crucial in order to generate a synergy between the two catalysts. Under Standard SCR conditions, we observed a loss of selectivity when the Cu catalyst was placed prior to the Fe-sample, while in the low-T region, we observed similar behaviours. Consequently, our investigation was focused on the Fe+Cu-zeolite combined arrangement. In this work, we have studied the effect of the catalyst order on the

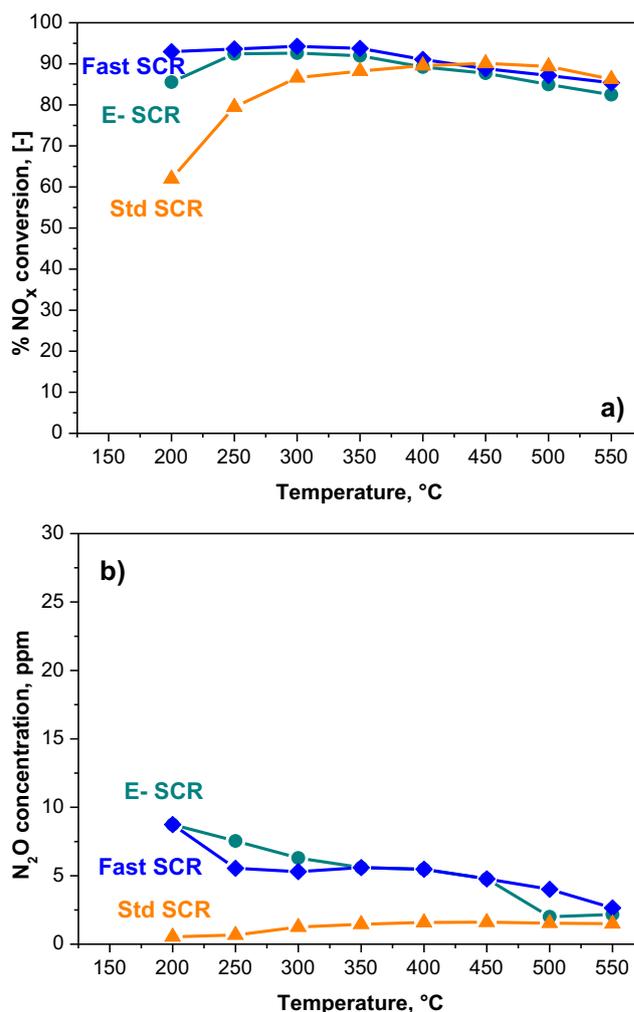


Fig. 4 Standard SCR, Fast SCR and Enhanced SCR reactions on the combined system Fe- + Cu-zeolite catalysts: **a** NO_x steady-state conversions, **b** N_2O steady-state productions, **c** N_2 Selectivity. GHSV = 75,000 h⁻¹, NH_3 = 500 ppm NO_x = 500 ppm, O_2 = 5% v/v, H_2O = 5% v/v, T_{range} = 200–550 °C. Std SCR: NO_2/NO_x = 0, NH_4NO_3/NO_x = 0; Fast SCR: NO_2/NO_x = 0.5, NH_4NO_3/NO_x = 0; E-SCR: NO_2/NO_x = 0, NH_4NO_3/NO = 2/5

Enhanced SCR performances, too. Figure 5 illustrates the sequential arrangement effect on the deNO_x performances under the Enhanced SCR conditions. Clearly, when the Cu-zeolite was placed upstream the beneficial effect of the ammonium nitrate addition was lost, the NO_x conversions (Fig. 5a) being even worse than those observed under Standard SCR conditions (no AN) on the Cu catalyst alone (Fig. 1), on the Fe+Cu samples (Fig. 1) and on Cu+Fe-samples (Fig. 1 in [2]). Moreover, even if in the low-T range the N_2O production on the Cu + Fe-sample is lower than that on the dual sample with reverse order (Fig. 5b), the two sequential combinations are similar in terms of N_2 selectivity (99% vs. 98%) (Fig. 5c). In the high-T region, instead, the Fe+Cu-sample overcomes the other in terms of N_2 selectivity and minimum N_2O formation.

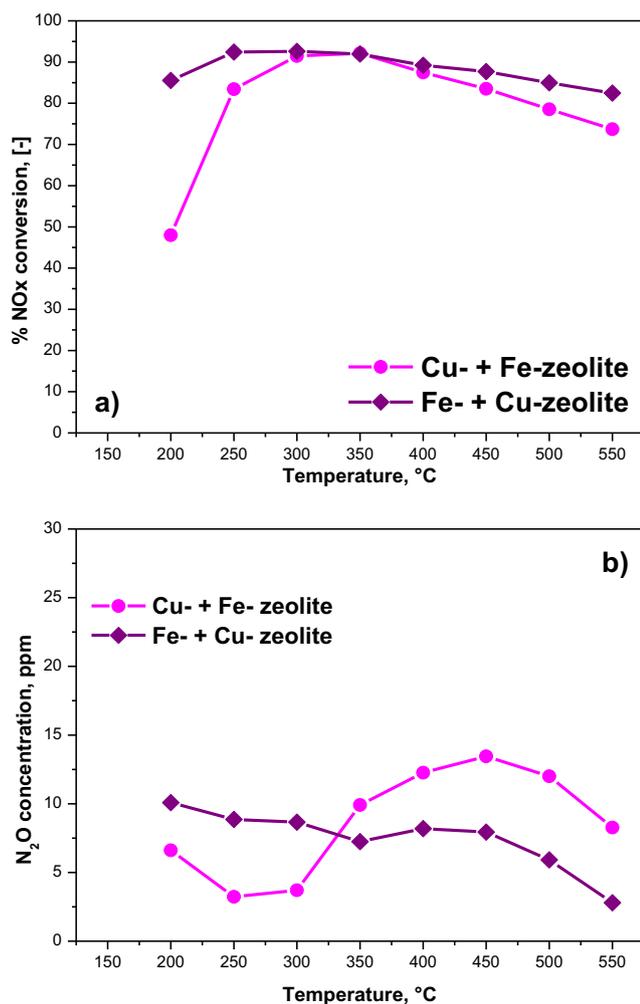


Fig. 5 Sequential arrangement effect (Fe+Cu-zeolite vs. Cu+Fe-zeolite) on the deNO_x performance under Enhanced SCR conditions: **a** NO_x steady-state conversions, **b** N₂O steady-state productions, **c** N₂ selectivity. GHSV = 75,000 h⁻¹, NH₃ = 500 ppm, NO = 500 ppm, O₂ = 5% v/v, H₂O = 5% v/v, NH₄NO₃ = 200 ppm, T_{range} = 200–550 °C

Such a negative impact of the AN dosing observed on Cu-SAPO in the previous section is in turn reflected on the sequential configuration in which the Cu-zeolite was placed before the Fe-zeolite (Fig. 5). Under Standard SCR conditions, the two configurations worked in a similar way in the low-T range [2]: in both cases, in fact, most of the reactants were converted over the Cu-zeolite catalyst. Indeed, when the Fe-BEA sample was placed upstream, being its activity lower than the following Cu-SAPO, the gases reacted in the second monolith sample. In the case of the reverse configuration, instead, NO and NH₃ were consumed in the upstream Cu-zeolite section while the following Fe-zeolite was hardly utilized. In the E-SCR reaction, however, the order of the two samples plays instead an important role. Indeed, being the Fe-BEA activity significantly promoted by the AN addition, when placed upstream the Fe-zeolite was able to convert most of the reactants, obtaining the good performances shown in

Fig. 1. When instead Cu-SAPO, which is adversely affected by AN, as observed in Fig. 3, was placed upstream, ammonium nitrate blocked the active sites at low temperature and in turn the consumption of the reactants moved to the second section, i.e. the Fe-BEA catalyst, which at those temperatures and without all the available ammonium nitrate feed showed its poor deNO_x efficiency.

Accordingly, the E-SCR reaction represents a promising and easy method to improve the activity of metal-promoted zeolite catalysts which are characterized by a poor activity in the low-T range, as seen for the Fe-BEA sample. However, it is important to pay attention to the zeolite structure: the smaller the pore size of the zeolite framework, the worse the performances.

4 Conclusions

In this work, the cofeed of ammonium nitrate according to the Enhanced SCR reaction was demonstrated to be an effective method to improve the typically poor low-T activity of NH₃-SCR Fe-zeolite catalysts. The dosage of an aqueous solution containing ammonium nitrate to Standard SCR conditions allowed to boost the overall NO_x conversion via the NO oxidation to NO₂ enabled by the ammonium nitrate, reaction (4). Once NO₂ is formed, the Fast SCR reaction can take place thanks to the co-presence of NO, NO₂ and NH₃. On the other hand, the Enhanced SCR conditions had a negative impact on the Cu-SAPO catalyst: the addition of ammonium nitrate to a catalyst based on a small-pore zeolite determined a dramatic loss of activity in the low temperature region and a huge release of N₂O due to the unselective thermal decomposition of NH₄NO₃ salt deposited within the zeolite structure. On the other hand, the sequential arrangement of a Fe-BEA catalyst followed by the Cu-SAPO sample under the E-SCR conditions showed outstanding performances, close to those corresponding to Fast SCR conditions even in the absence of NO₂ in the feed stream.

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