A fundamental study of the enhanced SCR reaction over a Fe-zeolite catalyst for mobile applications

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Introduction
Due to the tightening emission limits and to the strategies for lower fuel consumption, which reduce the mean temperature of the aftertreatment converters, more effective aftertreatment technologies are under investigation. One way to improve the DeNOx efficiency at low T is by means of the Fast SCR reaction (F-SCR) (2), which involves an equimolar amount of NO and NO2 and is associated with a higher NOx reduction efficiency in the low temperature region [1] than the Standard SCR (S-SCR) (1):

\[
2 \text{NH}_3 + 2 \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \quad (1)
\]

\[
2 \text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \quad (2)
\]

Moreover, it was recently discovered that addition of aqueous solutions of NH4NO3 (AN) to a NO–NH3 containing feed results in the occurrence of the “Enhanced SCR” (E-SCR) reaction (3) over both V2O5–WO3/TiO2 and Fe–ZSM-5 commercial catalysts [2, 3], 2NH3 + 2NO + NH4NO3 → 3N2 + 5H2O (3)

Between 180-350°C reaction (3) shows a very high DeNOx efficiency, similar to the F-SCR. The aim of this work is to figure out the fundamental and practical aspects still not fully understood of the AN reactivity. Moreover, using the collected experimental data, a kinetic model will be developed in order to describe quantitatively the E-SCR chemistry.

Materials and Methods
Both NH3-SCR and Enhanced-SCR (E-SCR) reactions were investigated over core monolith samples (about 6 cm3) drilled from a commercial Fe-Zeolite (supplied by Umicore) washcoated on cordierite monoliths. In order to cover the most representative conditions, both isothermal steady-state and transient runs were carried out within the T=150–500°C and GHSV = 35000-100000 h⁻¹ ranges. The catalyst samples were loaded in a stainless steel reactor tube placed in an oven with N2 as balance gas. Typical feed concentrations of NOx (NOx/NO = 0.5) and NH3 during the activity runs were 500 ppm, with 0-8 % O2 and 5 % H2O v/v. Moreover, an aqueous solution of ammonium nitrate (AN) was also dosed to the reactor using an HPLC pump (Gilson 305). The solution concentrations and the pump flow rates were calibrated in order to result in NH4NO3 feed concentrations in the 100-350 ppm range. The reactor outlet concentrations of NO, NH3, NO2 and of N2O were continuously monitored using a UV-analyzer and an ND-IR-analyzer, respectively.

Results and Discussion
The potential of the AN to improve the low temperature activity was first investigated via steady state runs carried out feeding 500ppm of both NH3 and NO, 5% of H2O and 8% of O2 in the presence of 100, 200 and 250ppm of AN. The beneficial effect of AN was clearly apparent. Already at low temperature (180°C), on feeding just 100ppm of AN, the performance of the catalyst was boosted with a gain in NOx conversions of ~35% if compared to the case of the S-SCR where no AN was fed. When feeding a stoichiometric amount of AN (250ppm) according to reaction (3), the performance of the catalyst was further improved approaching the activity of the F-SCR for NH3 conversion. A set of transient (TRM) runs were also carried out without O2 at 200°C varying the GHSV. Figure 1 shows the TRM run performed at 75 kh⁻¹ (feed AN = 250 ppm) feeding 500 ppm of NO. At t = 11168 s the H2O pump was switched on to feed 5% of H2O + 250ppm of AN: the NO concentration dropped suddenly to roughly 270 ppm and at the same time, NO2 was formed, its outlet concentration increasing up to an average value of 230 ppm.

Figure 1 – Transient run. NO=500 ppm, AN=250 ppm, H2O=5%; T=200 °C, GHSV=75000 h⁻¹

The TRM data indicate that already at 200°C AN was able to oxidize NO to NO2 quantitatively, according to NO + NH4NO3 → NO2 + N2 + 2H2O (4)

Upon adding NH3 to the feed, then, the E-SCR (3) started to occur, resulting from a two-steps mechanism, (4)+(2). The evidence on the AN chemistry and all the results from the kinetic runs are currently being used to develop a kinetic model of the Enhanced SCR reaction.

Significance
The E-SCR reaction can help in the direction of further reduction of NOx in lean engine exhausts, due to its strong promoting effect at low T. This concept could also result in cost reduction, since the E-SCR chemistry enables optimal Fast SCR DeNOx activities by situ NO oxidation, without necessarily relying on costly PGM based DOC units upstream.

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References