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):

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

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

However, 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], (3)

 $2NH_3 + 2NO + NH_4NO_3 \rightarrow 3N_2 + 5H_2O$

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 N_2 as balance gas. Typical feed concentrations of NOx (NO₂/NOx = 0-0.5) 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 time = 11168 s the H₂O pump was switched on to feed 5% of $H_2O + 250$ ppm 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=75000h⁻¹

The TRM data indicate that already at 200°C AN was able to oxidize NO to NO₂ quantitatively, according to

 $NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O_3$ (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 in situ NO oxidation, without necessarily relying on costly PGM based DOC units upstream.

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References

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