

REACTIVITY OF COMMERCIAL FE- AND CU-PROMOTED ZEOLITE CATALYSTS IN THE NH_3 - NO/NO_2 SCR FOR DIESEL EXHAUST AFTERTREATMENT

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Introduction

Urea/ NH_3 -SCR is presently considered a key technology for the control and abatement of NOx emissions from Diesel engines. The technology was introduced in the market for heavy duty applications already in 2005 [1], based on the use of extruded honeycomb monolith catalysts constituted of V_2O_5 - WO_3 - TiO_2 . However, the low stability of titania at high temperatures, the tightening of the NOx emission limits for both HD and LD vehicles that calls for higher activity at low T, and the issues related to vanadium toxicity have now motivated the introduction of new zeolite-based catalysts promoted by transition metals like Fe, Cu.

In this work two commercial zeolite SCR catalysts, promoted by Fe and by Cu, respectively, were investigated in details: reactivity tests were performed to allow a quantitative comparison, whereas systematic mechanistic experiments were run to elucidate the major reaction pathways in the complex NO/NO_2 - NH_3 reacting system.

Materials and Methods

Catalytic activity tests were performed both under steady state and transient conditions. 80 (Fe-Zeolite) and 60 (Cu-Zeolite) mg of the original monolith samples crushed to powder (140-200 mesh) were loaded in a flow microreactor in order to obtain intrinsic kinetic data. Runs were performed in a wide temperature range (50-550°C) feeding NH_3 (0-500-1000 ppm), NO (0-500-1000 ppm), NO_2 (0-500-1000 ppm) in the presence of water (3% v/v) and oxygen (2% v/v) in He. The temporal evolution of NH_3 , NO, NO_2 , N_2O and N_2 was continuously monitored by a mass spectrometer coupled in a parallel arrangement with a UV analyzer able to detect NO, NH_3 and NO_2 .

Results and Discussion

Both the Fe- and the Cu-zeolite catalysts were active in all the reactions typical of the complete (NO/NO_2 - NH_3) SCR reacting system, namely NH_3 and NO_2 adsorption (the latter disproportionating to form nitrate ad-species), NH_3 and NO oxidation, Standard-SCR ($4\text{NH}_3+4\text{NO}+\text{O}_2\rightarrow 4\text{N}_2+6\text{H}_2\text{O}$), ammonium nitrate formation ($2\text{NH}_3+2\text{NO}_2\rightarrow \text{N}_2+\text{NH}_4\text{NO}_3+\text{H}_2\text{O}$), N_2O formation ($2\text{NH}_3+2\text{NO}_2\rightarrow \text{N}_2+\text{N}_2\text{O}+3\text{H}_2\text{O}$), Fast-SCR ($4\text{NH}_3+2\text{NO}+2\text{NO}_2\rightarrow 4\text{N}_2+6\text{H}_2\text{O}$) and NO_2 -SCR ($8\text{NH}_3+6\text{NO}_2\rightarrow 7\text{N}_2+12\text{H}_2\text{O}$) [2,3]. However the Cu-Zeolite catalyst exhibited a higher NH_3 storage capacity, a higher NH_3 oxidation activity, a higher Std-SCR activity, and formed more stable surface nitrates. As opposite, the Fe-Zeolite was more active in the ammonium nitrate formation and in the Fast-SCR reaction. No relevant differences were found in the NO_2 -SCR reactivity. Fig.1 summarizes such results in terms of steady-state

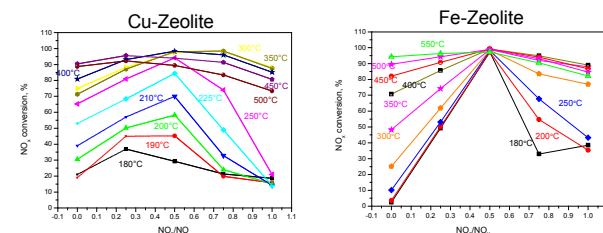


Fig.1 - NO_2/NO_x feed ratio effect on DeNOx activity over Cu- and Fe-zeolites catalysts

DeNOx performances at different temperatures collected varying the NO_2/NO_x feed ratio between 0 and 1

Transient dynamic tests performed over the Fe-zeolite catalyst by adsorbing NO_2 at low temperature (50°C) and contacting the so formed surface nitrates with different gases (e.g. NO, NH_3 , NH_3 +NO) lead us to propose the mechanism for both the Fast-SCR and the NO_2 -SCR where surface nitrates are key intermediates: in the Fast SCR they oxidize NO more efficiently and at lower temperature than oxygen does in the standard SCR, whereas they are reduced by ammonia when NO is not present in the feed mixture, as in the case of the NO_2 -SCR reaction. Besides, it was found that ammonia blocks the key reaction step $\text{NO}+\text{HNO}_3\leftrightarrow\text{HNO}_2+\text{NO}_2$ below 150°C, which represents an intrinsic limit for the low-T SCR activity.

The same kind of mechanistic experiments are being replicated over the Cu-based catalyst: preliminary results indicate that the prevailing mechanisms are similar to those proposed for the Fe-zeolite system, whereas some observed differences are possibly associated with the higher stability of nitrates formed on the Cu-based catalysts.

Significance

The detailed investigation performed over the Fe- and Cu-zeolite commercial SCR catalysts provides a conclusive and exhaustive summary of the reactivity of the complete (NO/NO_2 - NH_3) SCR reacting system, which is proven to be very similar over V-based and zeolite catalysts. Furthermore, the catalytic mechanisms involved in such a chemistry are identified, and this is preliminary to the development of mechanistic reaction kinetics to be included in transient mathematical models of SCR monolithic converters.

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