

MECHANISTIC AND KINETIC ANALYSIS OF THE NO₂ SCR REACTION AND N₂O FORMATION OVER Fe- AND Cu-ZEOLITE CATALYSTS FOR THE AFTERTREATMENT OF DIESEL EXHAUSTS

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Summary

Urea/NH₃-SCR is presently considered a key technology for the control and abatement of NO emissions from Diesel engines; the presence of a DOC catalyst upstream from the SCR unit warrants significant amounts of NO₂ entering the SCR reactors together with NO.

In this work new zeolite-based catalysts promoted by Fe and by Cu were investigated: reactivity tests were performed to allow a quantitative comparison, whereas systematic mechanistic experiments were run to elucidate the major reaction pathways, with particular focus on the NO₂/NH₃ reacting system and on formation of N₂O. The bulk of information was then used to develop a dynamic kinetic model in close agreement with all the details of the SCR catalytic chemistry.

Keywords: Diesel exhaust aftertreatment, Diesel emission control, NH₃ SCR, NO₂, N₂O

Introduction

NH₃/urea SCR is considered one of the most promising technologies for the abatement of NO_x emissions from Diesel vehicles [1]. Extensive work has been devoted in the last two decades to study the “standard” SCR reaction ($2\text{NH}_3 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$) for DeNO_xing of stack gases from power plants, but mobile applications call for a greater low-T activity. Commercial SCR catalysts include Fe- and Cu-promoted zeolite based systems used in the form of washcoated cordierite monoliths [2,3]. An onboard Diesel Oxidation Catalyst upstream of the SCR converter can partially convert NO to NO₂, which greatly enhances the deNO_x efficiency due to the “Fast” SCR reaction ($2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$). Under specific operating conditions and in the presence of excess NO₂ in the reacting system also the “NO₂” SCR reaction ($8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$) can significantly contribute to the overall deNO_x process. However, the NH₃-SCR chemistry, catalytic mechanism and kinetics when both NO and NO₂ in different amounts are fed to the SCR reactor are only now being elucidated.

In this paper we investigate mechanistic aspects of the NO₂ SCR reaction over both Fe- and Cu-zeolite catalysts: reactivity tests were performed to allow a quantitative comparison, whereas systematic mechanistic experiments were run to elucidate the major reaction pathways in the NO₂-NH₃ reacting system. The bulk of information was then used to develop a dynamic kinetic model in close agreement with all the details of the SCR catalytic

chemistry, with particular focus on the undesired N₂O formation.

Experimental

Dynamic (step-response, temperature-programmed) kinetic experiments were performed in a flow-microreactor loaded with powdered catalyst (80 mg) obtained by grinding and sieving (140-200 mesh) the commercial washcoated monolith. Runs were performed in a wide temperature range (50-500°C) feeding NH₃ (0-1000 ppm), NO (0-1000 ppm), NO₂ (0-1000 ppm) in the presence of water (1% v/v) and oxygen (2% v/v) in He. The temporal evolution of NH₃, NO, NO₂, N₂O and N₂ was continuously monitored by a quadrupole mass spectrometer (Balzers QMS 200) coupled in a parallel arrangement with a UV analyzer (ABB LIMAS 11HV) able to detect NO, NH₃ and NO₂. More details are presented elsewhere [2].

Results and discussion

Catalysts activity in the NH₃-SCR of NO₂ – Steady state experiments were carried out over both Cu and Fe zeolite catalysts in order to study the reactivity of the NH₃-NO₂ reacting system. Over both catalytic systems, as already discussed in the literature [2,3], ammonium nitrate formation was observed below 225°C, while the main reaction occurring in the 250-550°C T-range was the so-

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called 'NO₂-SCR' reaction; significant N₂O evolution was also observed in the same temperature region.

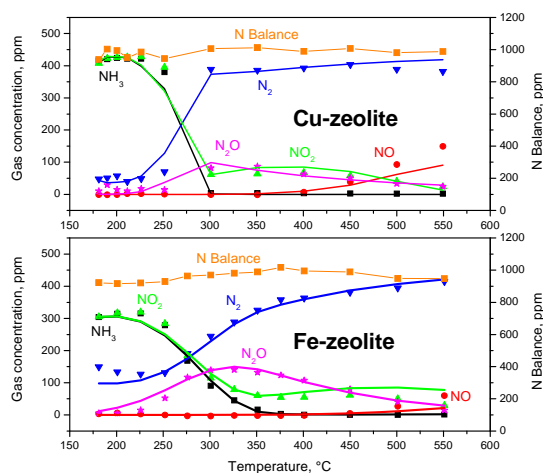


Figure 1 – Steady state NH₃-SCR reactivity of NO₂ over the tested Cu and Fe-zeolite catalysts. Symbols: experimental results; lines: model fits.

However, as clearly evident from figure 1, the reactivity of the two systems is dramatically different. Indeed the light-off of the NO₂-SCR reaction is more gradual over the iron zeolite than over the copper based system, and it is coupled with a greater evolution of N₂O.

Mechanistic analysis – In order to rationalize the mechanistic aspects of the different catalytic behaviours of the two systems, the 'NO₂-SCR' reaction was investigated by means of transient reactivity experiments over both catalysts. Previous work performed over the iron zeolite catalyst [4] evidenced a key role played by surface nitrates. Indeed, it was found that nitrates stored onto the catalyst were reduced by NH₃ with a T-threshold and T-dependence similar to those of the NO₂-SCR: this indicated that such a reaction actually results from nitrates formation from NO₂ and their reduction by NH₃. When dynamic methods were applied to the copper zeolite catalyst, it was found that the same prevailing reaction mechanisms are operating; furthermore, it was found that the different activity of the two systems in the NO₂-SCR reaction could be possibly related to the different stability, and thus reactivity, of surface nitrates, that clearly appears from inspection of Figure 2. The lower stability of nitrates formed over the Fe-zeolite catalyst can also nicely explain the higher formation of N₂O, if compared to the copper based catalyst, N₂O being likely the decomposition product of surface ammonia-nitrate complexes.

In order to further address the formation and the role of N₂O in the SCR chemistry, new experiments are now being carried out: the reactivity and the kinetics of the reactions between N₂O and both ammonia and NO₂ will be analysed over the two catalytic systems.

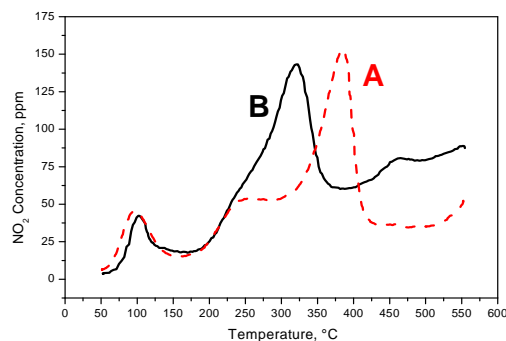


Figure 2 – Temperature programmed desorption/decomposition of surface nitrates formed by NO₂ adsorption at 200°C; NO₂ evolution vs. temperature over Cu- (A) and Fe-zeolite (B) catalysts.

Detailed kinetic modeling – A detailed kinetic model was derived from the above mentioned mechanistic scheme, that includes elementary steps reflecting the key role of surface nitrates in the SCR chemistry in the presence of NO₂. The rate parameters of the reaction steps were estimated by multiresponse nonlinear regression of the dynamic runs, namely TPD and TPSR experiments. Subsequently, the kinetics were validated against other independent NH₃-NO₂ reactivity runs. Such a detailed kinetic model was able to describe not only the overall activity of the reactions occurring when feeding NO₂ and ammonia (see solid lines in Figure 1), but also detailed reactions steps, including NO₂ adsorption in the form of nitrites and nitrates, decomposition of nitrites to nitrogen via reaction with ammonia, reversible reduction of nitrates to nitrites by NO, and direct reduction of nitrates to N₂ by ammonia. The analysis of the kinetic parameter estimates also confirmed that the different stability of surface nitrates is of key importance in order to describe the different reactivity in the NO₂-SCR reaction over the two investigated catalytic systems.

Acknowledgements

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References

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