DETAILED KINETIC ANALYSIS OF NH_3-NO/NO_2 SCR CHEMISTRY OVER Fe- AND Cu-ZEOLITE CATALYSTS

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Introduction

SCR has become the technology of choice for the abatement of NOx emissions from heavy-duty vehicles, and it has been recently introduced also in passenger cars. The current challenge for Diesel vehicles both in Europe and in the US markets is the achievement of a substantial reduction of CO_2 emissions while bringing NOx emissions below the upcoming stringent Euro VI and US Tier 2 Bin 5 limits[1].

As the new test cycles require catalysts active at very low temperature, the "Fast" SCR reaction used in present SCR-based after treatment converters to enhance the low-T DeNOx activity, plays and will play even more in the near future a critical role in the development and optimization of SCR systems[2].

Different metal exchanged (Fe and Cu) commercial zeolite based catalysts are investigated in this study under experimental conditions representative of real applications, to analyse each individual reaction step of the complete NO/NO_2 + NH_3 + O_2 SCR reacting system. The identification of the SCR kinetic mechanisms, and of the role of the related surface species, as well as the development of a detailed kinetic model will be herein presented.

Materials and Methods

Transient kinetic experiments of various nature (step-response, temperature-programmed) were performed in representative T-ranges in a flow-microreactor loaded with powdered catalyst obtained by grinding and sieving the commercial washcoated Fe- and Cu-zeolite monoliths. Typical feed gas compositions were NH_3 (0-500 ppm), NO+NO_2 = NO_x (0-500 ppm), O_2 (0-6% v/v), H_2O (1-10% v/v), at 70-320 cm^3/min (STP) flow rates. The reactor outlet was connected to a quadrupole mass spectrometer (Balzers QMS 200) and to a UV-analyzer (ABB LIMAS 11HV) in parallel for continuous analysis of gases. More details are presented elsewhere [3].

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Results and Discussion

The bulk of transient experiments addressing the mechanistic features of the complete reacting system NO/NO_2 + NH_3 + O_2 over both the considered catalysts were found consistent with a scheme[3] based on: 1) NH_3 adsorption–desorption; 2) NO_2 disproportion and heterolytic chemisorption in the form of surface nitrites and nitrates; 3) reversible oxidation of nitrites by NO_2 to form nitrates and NO; 4) thermal decomposition of nitrates to NO_2 and oxygen; 5) reaction of nitrites with NH_3 to form N_2 via decomposition of unstable ammonium nitrite; 6) ammonia oxidation by surface nitrates with formation of nitrogen.

A dual-site micro-kinetic model of the Fast- and NO_2-SCR reactions was developed on the basis of such a scheme. It includes eight elementary steps, and reflects the key role of surface nitrates in the SCR chemistry in the presence of NO_2. It accounts for the competition between the rates of nitrates reduction by NO, associated with the Fast SCR reaction, and by NH_3, associated with the NO-SCR reaction. It also accounts for the blocking action of ammonia on the nitrates reduction by NO, which critically limits the low-T Fast-SCR activity [4].

The micro-kinetic model was coupled with lumped kinetics for the other SCR reactions, namely NH_3 adsorption/desorption and oxidation, NO oxidation, Standard– and Slow-SCR reactions. The rate parameters of all the 13 elementary and global reaction steps were estimated by multiresponse nonlinear regression according to a sequential strategy based on dedicated transient runs over the Fe-zeolite catalyst. Figure 1 shows e.g. that the model is

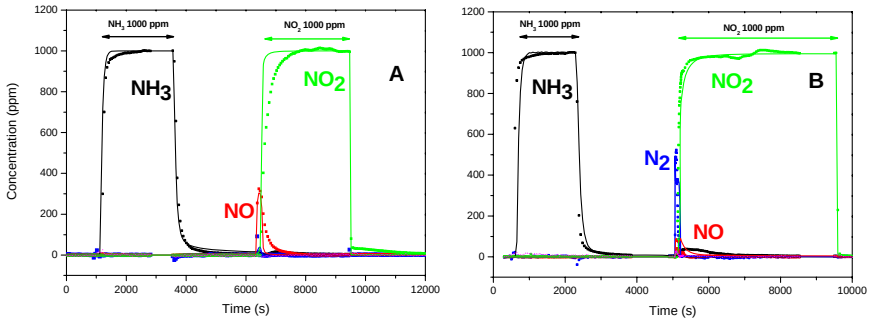

Figure 1 – Fit of step response runs with NO_2 feed to NH_3 saturated Fe-zeolite catalyst at 50 °C (A) and 200 °C (B). Notice the evolution of NO in A and of N_2 in B.

able to reproduce the switch from evolution of NO (at 50°C) to evolution of N_2 (at 200°C) observed on exposing to NO_2 the Fe-zeolite catalyst presaturated with NH_3. The extension of the same kinetic approach to the Cu-zeolite catalyst is in progress.

Significance

To our knowledge, no other mechanistic kinetic models of both Fast- and NO_2 - SCR reactions over Fe- and Cu-zeolites have been so far reported in the literature.

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