NO/NO_2-NH_3 SCR reaction over a V-based catalyst for Diesel exhaust after treatmen

Isabella Nova*, Cristian Ciardelli, Enrico Tronconi
Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano (Italy)
**isabella.nova@polimi.it*

Introduction

NH_3/urea SCR is emerging as the most promising technology for the abatement of NO_x emissions from Diesel vehicles [1]. Extensive work has been devoted in the past to study the "Standard" SCR ($2NH_3 + 2NO + \frac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O$) for DeNOxing of stack gases from power plants, but mobile applications call for a greater low-T reactivity. An onboard Diesel Oxidation Catalyst upstream of the SCR converter can partially convert NO to NO_2, which greatly enhances the deNOx efficiency due to the "Fast" SCR reaction ($2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$). However, SCR chemistry, catalytic mechanism and kinetics in the presence of both NO and NO_2 are still largely unknown.

Materials and Methods

The NH_3 storage and oxidation, the NO+NH_3 ("Standard") and the NO/NO_2+NH_3 ("Fast") SCR reactions were studied according to a sequential approach in the 50-450°C T-range in the presence of water (1 - 10 % v/v) and oxygen (2 – 6 % v/v) over a commercial powdered V_2O_5-WO_3/TiO_2 catalyst (W_{cat}=160 mg) loaded in a micro-reactor: the temporal evolution of the outlet species concentrations (including N_2) upon variations of inlet reactant concentrations or after T-ramps was followed by a mass spectrometer in parallel with a UV-analyzer (ABB LIMAS 11HV) . The intrinsic transient kinetics of NH_3 adsorption-desorption-oxidation were first investigated by imposing rectangular step changes of the NH_3 inlet concentration (1000 ppm) at different temperatures in a continuous flow of O_2+H_2O+He. The dynamics of the NO + NH_3 and of the $NO/NO_2 + NH_3$ SCR reactions were then addressed by imposing stepwise perturbations to the NH_3 inlet concentration (1000 ppm) while continuously feeding NO (1000 ppm) or NO + NO_2 (= 1000 ppm) with NO_2/NOx ratios in the range 0 to 1 at different temperatures, while keeping constant the concentrations of the other reactants. The experimental results were analysed by means of a dynamic 1D heterogeneous PFR model, and fitted by multiresponse non-linear regression to provide estimates of the rate parameters.

Results and Discussion

In this paper we present the results of a systematic fundamental investigation of the chemistry and of the catalytic kinetic features of NH_3-NO/NO_2 reactions over a V-based commercial catalyst, and the related development of a dynamic simulation model of SCR converters for vehicle applications.

The reactions involved in the NH_3-NO/NO_2 SCR reacting system were investigated by an extensive set of various unsteady experiments over a powdered catalyst (160 mg), collected varying temperature (170-450°C) and the NO/NOx feed ration (0-1): by analysing the steady state concentrations of the reactants (NH_3, NO and NO_2) and of the products (N_2 and N_2O) it was possible first to identify the stoichiometries of all the reactions involved [2]. Then, a full proposal for the chemistry prevailing over V-based SCR catalysts when feeding NH_3-NO/NO_2 mixtures was developed, and validated on the basis of transient response experiments addressing both the overall reactivity in the Fast SCR reaction and also specific individual reaction steps. Such a mechanistic proposal can be summarized in the following steps: i) dimerization/disproportion of NO_2 and reaction with NH_3 and water to give ammonium nitrite and ammonium nitrate; ii) reduction of ammonium nitrate by NO to ammonium nitrite, which was proved to be the rate determining step of the "Fast SCR" reaction; iii) decomposition of ammonium nitrite to nitrogen [3].

Finally the role of vanadium and of its redox properties in such chemistry was addressed: it was found that nitrate species, which are produced in situ by NO_2 and H_2O, are the oxidizing agent in the "Fast SCR". Indeed, nitrates are known to be stronger oxidizing agents than oxygen, hence this explains the higher activity of the SCR reaction in the presence of NO_2 if compared with the Standard SCR reaction [4].

Based on such experimental evidence, a dual site Mars-Van Krevelen dynamic kinetic model was derived, which unifies Standard and Fast SCR into a single Redox-type approach. Intrinsic rate parameters were accordingly estimated and incorporated into a transient heterogeneous 1D+1D mathematical model of SCR monolith reactors together with the relevant geometrical and morphological characteristics of the monolith commercial catalyst. The obtained predictive model was validated first against transient SCR runs performed over honeycomb catalyst samples (up to 10 cm^3) in a laboratory rig, and then against extensive test bench data collected in full scale SCR monolith converters loaded with catalysts up to 43 litres in size, using real Diesel engine exhaust gases [5].

Significance

Simulation is becoming an essential tool for the development of after-treatment systems due to their growing complexity and integration. Because of the broad range of possible input conditions and design parameters a predictive simulation model has to be fully grounded on chemical and physical fundamentals. The transient model presented in this paper satisfies such requirements and is currently applied by DaimlerChrysler to design and optimization of SCR converter parameters (e.g. urea dosing strategy, size, cell density and position of the monolith catalyst) for a variety of applications: it has been successfully used for model-based development of the BlueTec© technology commercialized in 2005.

References

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