

# DYNAMIC METHODS IN CATALYTIC REACTION ENGINEERING: APPLICATIONS TO THE INVESTIGATION OF THE NH<sub>3</sub>-SCR REACTIONS FOR DIESEL EMISSION CONTROL

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## Summary

For the case of the NH<sub>3</sub>-SCR reactions over V-based and metal-exchanged zeolite catalysts, we use step response and temperature-programmed experiments in a fixed-bed tubular micro reactor in order to: i) identify the adspecies and evaluate their storage capacities; ii) investigate the individual steps of proposed mechanistic schemes; iii) discriminate rival mechanistic hypotheses; iv) analyze the related surface kinetics. Results show that transient response techniques can yield a high level of mechanistic and kinetic information under process relevant conditions.

## Keywords

catalytic kinetics, transient response methods, Diesel exhaust aftertreatment, NH<sub>3</sub> SCR.

## Introduction

Diesel vehicles are responsible for significant polluting emissions of nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM): NH<sub>3</sub>- or urea-SCR (Selective Catalytic Reduction) is emerging in Europe as the most promising technology for the abatement of NO<sub>x</sub> from heavy-duty vehicles, and possibly from passenger cars as well. Since Diesel emission limits are expected to be further reduced in the near future, the automotive industry is focusing worldwide on the development of enhanced on-board SCR DeNO<sub>x</sub> systems, a task which necessarily calls for improved understanding of the SCR catalytic mechanisms and of the related kinetic aspects. The operating conditions of exhaust aftertreatment devices are intrinsically transient, involving continuous changes in temperature and flow rate over extended ranges: a quantitative description of the process rates is therefore much more demanding than in stationary applications, and naturally relies on transient reaction analysis. Taking the case of the NH<sub>3</sub>-SCR reactions over V-based and metal-exchanged zeolite catalysts as an example, it is the purpose of the present paper to demonstrate that such dynamic methods are powerful tools not only to study transient catalytic kinetics, but also to identify and demonstrate mechanistic features of catalytic reactions under process relevant conditions.

## Experimental and modeling methods

We used an experimental setup specifically designed in view of transient kinetic studies<sup>1</sup>. Dynamic NH<sub>3</sub>-SCR reaction runs were performed at T = 150 – 550 °C over

state-of-the-art V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and metal-exchanged zeolite commercial catalysts loaded in a quartz microflow tubular reactor (i.d. = 7 mm) in the form of powders (W<sub>c</sub> = 60-100 mg). The powdered catalyst was obtained by crushing and sieving the original extruded or washcoated honeycomb monoliths to a size (d<sub>p</sub> ~90 μm) suitable to rule out mass transfer limitations. Typical feed concentrations of NO<sub>x</sub> and NH<sub>3</sub> were 500 ppm, along with 2-10% O<sub>2</sub> and 1-10% water v/v, Ar as a tracer and balance He. The space velocity was set to high values to secure partial conversions at all temperatures. Fast switch valves were adopted to execute step changes in the feed composition. Continuous analysis of outlet gases was performed by a UV-analyzer (ABB LIMAS-11HV) for NO, NO<sub>2</sub>, NH<sub>3</sub>, in parallel with a MS (Balzer QMS 200) for N<sub>2</sub> and N<sub>2</sub>O, thus permitting the evaluation of N-balances. Care was taken to minimize all dead volumes in the rig. Altogether, the experimental configuration afforded to collect intrinsic kinetic information in a chemical regime during fast reaction transients under isothermal conditions, thus greatly facilitating the kinetic analysis, which in fact relied on a simple isothermal dynamic PFR model. The rate parameters were estimated by multiresponse nonlinear regression, using the temporal evolution of the outlet concentration traces of NH<sub>3</sub>, NO, NO<sub>2</sub>, N<sub>2</sub> and N<sub>2</sub>O as the fitted experimental responses.

## Results and discussion

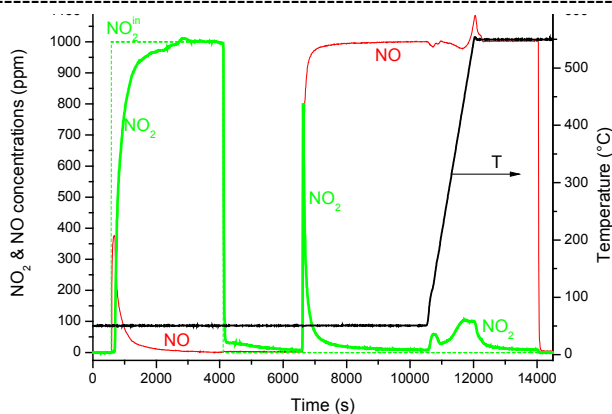
*Storage of adspecies* – NH<sub>3</sub> step feed runs followed by TPD have been traditionally used to estimate ammonia

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storage capacities and  $\text{NH}_3$  adsorption-desorption kinetics. We applied the same approach to show that also  $\text{NO}_2$  is chemisorbed onto SCR catalysts via i) disproportionation to surface nitrites and nitrates, ii) oxidation of nitrites to nitrates with  $\text{NO}$  evolution, and to estimate the related rates and capacities. Surface nitrates play a key (but overlooked) role in the important Fast SCR mechanism<sup>2,3</sup>, as shown below.

*Analysis of mechanistic steps* – A set of transient runs was designed to address systematically the individual steps in the overall  $\text{NO}$ - $\text{NO}_2$ - $\text{NH}_3$  SCR mechanism over an Fe-zeolite catalyst, including adsorption of ammonia, adsorption of  $\text{NO}_2$  in the form of nitrites and nitrates, decomposition of nitrites to nitrogen via reaction with ammonia, reversible reduction of nitrates to nitrites by  $\text{NO}$ , and direct reduction of nitrates to  $\text{N}_2$  by ammonia. Figure 1 shows e.g. a composite run whereby the catalyst is first saturated with nitrates at  $50^\circ\text{C}$  by exposing it to  $\text{NO}_2$ ; in the second stage the stored nitrates are almost completely reduced by  $\text{NO}$ , with  $\text{NO}_2$  evolution, already at the very low initial temperature; nitrates decomposition is then completed in the final T-ramp.

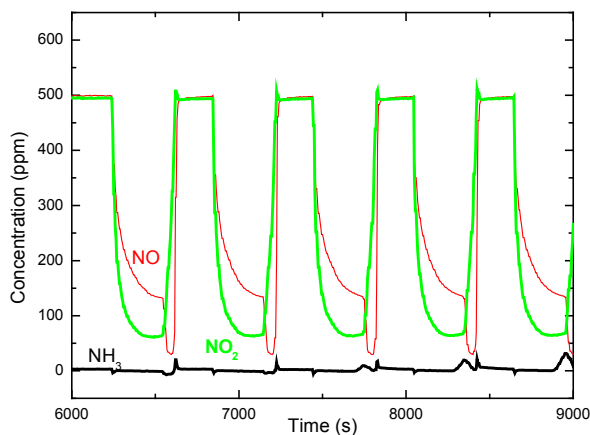


**Figure 1** - Reactivity of  $\text{NO}$  with preadsorbed  $\text{NO}_2$  over a Fe-zeolite catalyst.  $T=50^\circ\text{C}$ .

Notably, the crucial reduction of nitrates by  $\text{NO}$  did not occur at  $T < 150^\circ\text{C}$  in an identical experiment but in the presence of  $\text{NH}_3$ , which points out a low-T blocking action of ammonia on the key intermediates, i.e. the surface nitrates, likely due to formation of  $\text{NH}_4\text{NO}_3$  adsorbed precursors<sup>4</sup>. Further mechanistic insight was provided by similar experiments probing the reactivity of  $\text{NH}_3$  with adsorbed  $\text{NO}_2$ , of  $\text{NO}_2$  with adsorbed  $\text{NH}_3$ , and of  $\text{NO}+\text{NH}_3$  with surface nitrates.

*Discrimination of mechanistic models* – Transient reaction analysis can be applied also to challenge alternative mechanistic proposals. As an example, Figure 2 compares the  $\text{NO}$  and  $\text{NO}_2$  evolutions observed over a V-based SCR catalyst when pulsing ammonia to a feed stream containing 500 ppm each of  $\text{NO}$  and  $\text{NO}_2$ . The differences in the dynamics of  $\text{NO}$  and  $\text{NO}_2$  clearly rule out the

possibility that  $\text{NO}$  and  $\text{NO}_2$  react with  $\text{NH}_3$  directly from the gas phase via formation of  $\text{N}_2\text{O}_3$ , as suggested in the literature.



**Figure 2** –  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  dynamics during fast  $\text{NH}_3$  pulses to a  $\text{NO}+\text{NO}_2$  feed over a  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  SCR catalyst.  $T=200^\circ\text{C}$ .

*Surface kinetics* – A selection of the transient runs for mechanism identification performed over a commercial Fe-zeolite based catalyst, consisting of temperature programmed desorption (TPD) and temperature programmed surface reaction (TPSR) experiments, were used to estimate the intrinsic kinetic parameters of the mechanism steps in the full range of  $\text{NO}_2$  feed contents, i.e.  $0 \leq \text{NO}_2/\text{NO}_x \leq 1$ . Subsequently, the detailed kinetic model was validated against other independent  $\text{NH}_3$ - $\text{NO}/\text{NO}_2$  reactivity runs. The work was focused on the SCR reactivity in the presence of  $\text{NO}_2$ , since the kinetics of the more simple Standard-SCR reacting system ( $\text{NO}$ - $\text{NH}_3$ - $\text{O}_2$ ) have been already addressed extensively in the literature<sup>5</sup>. The resulting kinetic model can be used to simulate and analyse in details the SCR catalytic chemistry.

## Acknowledgements

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