

Mechanistic Kinetics based Simulation of Automotive NH₃ Oxidation Catalysts

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Introduction

Automotive catalysts for selective catalytic reduction of NO_x by NH₃ frequently are equipped with a short zone of an NH₃ oxidation catalyst. The purpose of this so called NH₃ slip catalyst is to allow a more aggressive dosing of NH₃ without increased NH₃ emissions. Due to its role in industrial nitric acid production, NH₃ oxidation on Pt is a very well investigated reaction. For this reason NH₃ oxidation on a simple Pt/Al₂O₃ model catalyst is used in this work, even though this catalyst (due to its high N₂O selectivity) is not the preferred catalyst for automotive applications.

NH₃ oxidation on Pt has been previously studied with a variety of theoretical and experimental methods like DFT calculations, UHV experiments, TAP reactor studies and micro reactor experiments under ambient pressure [1, 2, 3, 4]. Based on this extensive research detailed kinetic models have been developed [4, 5, 6]. It is one purpose of this contribution to investigate in how far the existing reaction mechanisms provide a valid description of NH₃ oxidation under automotive slip catalyst conditions (low NH₃ concentration, excess of O₂, low temperature, high space velocities).

We have recently demonstrated that elementary reaction mechanisms can be efficiently implemented in reactor simulations using a spline mapping of precomputed rate data. NH₃ oxidation is an interesting test case for this mapping approach since the mappings needs not only to reproduce the NH₃ conversion but also the selectivity towards the different products.

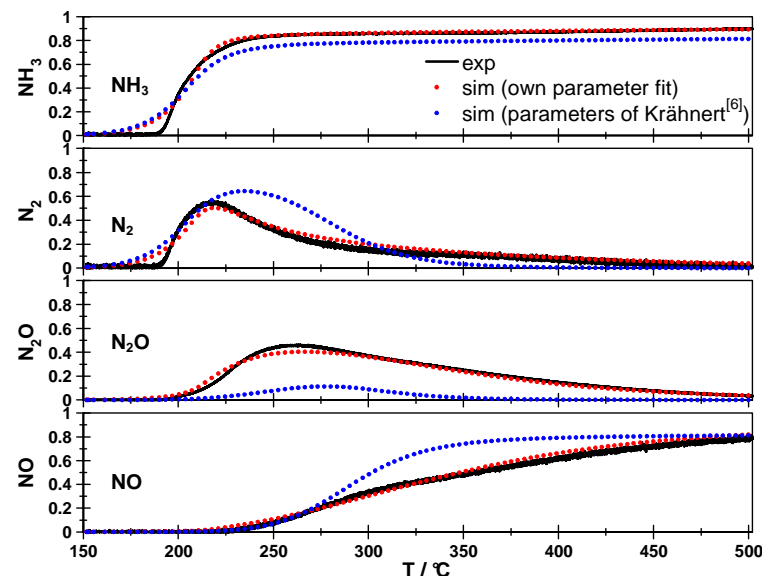
Finally, the NH₃ slip catalyst is interesting from a reactor engineering point of view since the catalyst is generally operated at very high space velocities so that diffusion limitation are expected to have some influence on conversion and product selectivity.

Results and Discussion

- NH₃ conversion and product selectivity in a monolithic Pt catalyst are studied in a model gas reactor with FTIR product analysis.
- Using the site concentration as a single adjustable parameter the literature mechanism from [1] reproduces the experimental results for NH₃ conversion and product selectivities surprisingly well (Fig 1). Only the N₂O selectivity is slightly underestimated.
- Adjustment of several parameters leads to an excellent fit to the experimental data (Fig. 1).
- A spline mapping of the effective rate data for NH₃ consumption and product formation is set up. The mapping reproduces the exact numerical solution with an error of less than 1.0 % and offers speed up of several orders of magnitude.
- A detailed model of one monolith channel including the diffusion in the washcoat is set up using the commercial simulation software Comsol with the surface chemistry implemented through the mapping approach.

- The detailed model is used to study the effect of external and internal diffusion limitation on NH₃ conversion and product selectivity. It is found that diffusion resistance significantly reduces the conversion of the catalyst at higher temperatures surprisingly with little effect on product selectivity.

Figure 1. Conversion of NH₃ and yields of N₂, N₂O, NO vs. temperature for a TPR (heating rate: 2 K/min, 300 ppm NH₃, 6 % O₂, 5 % H₂O, GHSV 300,000 h⁻¹) with Pt/Al₂O₃ on a monolith substrate. Yield of N₂ is calculated from the mass balance. Experimental results are compared with simulation results for the Krähnert parameter set and the fitted parameter set.



References

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