

NOVEL MODELS FOR CATALYST LOADING AND AGING EFFECTS IN EXHAUST-GAS AFTER-TREATMENT CATALYSTS

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Summary

Abatement of pollutant emissions over Pt/Al₂O₃ containing catalytic converters of lean operated engines is studied. Several close-to-production model catalysts with varying catalyst loadings and aging steps are characterized. Conversion was investigated in a flow reactor using varying exhaust-gas mixtures and temperatures. The performance of the monolithic catalysts is modeled by a two-dimensional flow field description of a single channel coupled with models for washcoat diffusion and multi-step reaction mechanisms. It is shown that, in principle, the catalytic active surface area determined by CO-TPD can serve as parameter to model the varying catalyst loading and aging without any adaption of the kinetic data of the reaction mechanism.

Keywords

Rational design of catalysts, Computational catalysis, Complex reacting flow, Environmental Reaction Engineering

Introduction

In spite of the enormous achievements in the after-treatment of exhaust-gas emissions, the worldwide increasing number of vehicles represents a serious environmental problem due to vehicles' raw emissions, in particular, carbon dioxide, which has a strong impact on the greenhouse effect. A more efficient fuel consumption can be put into effect by diesel and lean operated engines, i.e., in excess of oxygen. Here, the problem is the formation of nitrogen oxides (NO_x). Since improvements of the combustion process itself are not sufficient to meet future legislative limits, the development of a technique for the after-treatment of NO_x is urgently needed.

One of the most promising approaches is the NO_x-Storage and reduction Catalyst (NSC)^[1] which utilizes the NO_x storage on barium sites to form nitrates during the lean phase and their reduction to nitrogen in a rich atmosphere. Detailed models, which are based on physical and chemical processes on the molecular level, are indispensable to exploit the full potential of this technique. A first step to model complex catalysts consisting of several components with different promoting and storage effects as well as interactions among them is the development of reliable models for single components. Due to the limited thermal stability of the NSC it is fundamental that the effect of aging on all components have to be considered to determine the most sensitive amongst them. In this work, the influence of platinum loading and aging effects on conversion is investigated.

Catalyst characterization

Three samples with different platinum loadings (20, 60, 120 g/ft³) have been manufactured by a commercial catalyst supplier. Several defined hydrothermal aging steps (700, 850, 950°C, 10% water, air, 16 hours) have been applied to the catalyst with the highest platinum loading. The model catalysts have been extensively characterized by several chemical and physical methods. BET isotherms were used to investigate the effect of aging on the washcoat structure. CO-TPDs show a linear dependency between noble metal loading or aging temperature and catalytic surface area within the considered limits. To measure geometric parameters of the coated channels light microscopy was used, whereas for the nanoscale platinum particles electron microscopy combined with EDX for component identification is consulted. As example HR-SEM pictures are shown in Figure 1. All results are implemented into the catalyst model for numerical simulation.

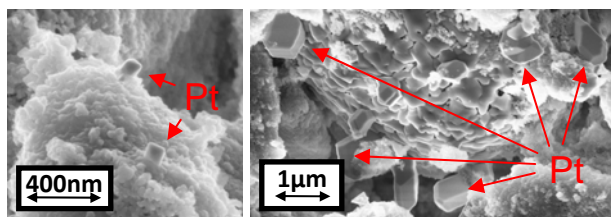


Figure 1: HR-SEM pictures of aged 120 g/ft³ loaded Pt catalyst (left 700°C; right 950°C)

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Kinetic data measurements

Small slices of monolith catalysts (400cpsi) have been studied under realistic flow conditions ($SV = 40.000 \text{ h}^{-1}$) with synthetic exhaust gas. The experiments were carried out in an isothermal flat-bed reactor^[2]. Within this, five thin slices of a monolithic catalyst (30 mm x 40 mm, one channel height) were placed behind one inert slice for gas preheating and uniform inlet flow distribution.

Lateral withdrawals after each slice allow the measurement of gas concentration profiles along the catalyst length that are obligatory for spreading the conversion of all catalyst samples with differing catalytic activity. Gas analysis was accomplished with SI-mass spectroscopy (MS4). Lean steady-state experiments with concentration variation of single gas components as well as complex gas mixtures have been investigated.

Modeling approach

The numerical simulation is based on the DETCHEM software^[3], which couples detailed chemistry models and computational fluid dynamics (CFD). The core is a library for the description of species properties based on atomistic models and for reactions among gas-phase and surface species based on elementary-step reaction mechanisms.

Due to the experimental set-up, a single channel model is sufficient. Therefore, the DETCHEM^{CHANNEL} code is applied here, which computes the two-dimensional flow field in a single channel using the boundary-layer assumption. Radial transport models include composition and temperature dependent transport coefficients in the gas phase and an effectiveness factor approach for diffusion and reaction in the washcoat. The reaction mechanism consists of 75 elementary-step like reactions with kinetic data based on a newly developed platinum mechanism^[4]. The catalytic active surface of the catalyst measured by chemisorptions serves as parameter to account for both varying loadings and hydrothermal aging. Variation of the platinum loading and aging temperature is shown to also change dispersion, particle size distribution and washcoat structure. Therefore, the question arises whether a single model parameter (the local active catalytic surface area) is sufficient to account for the varying loading and aging temperature. Albeit, varying particle sizes and washcoat morphology may also lead to varying turn-over-frequencies (TOF).

Results and discussion

A qualitative agreement between experimentally measured and numerically predicted conversion was achieved using the same reaction mechanism for all cases considered. That means the surface reaction rates (TOF) do not or only slightly vary for the different particle size distributions (loadings). The modeling approach proposed works well, the model can account for the loading variation and aging temperatures by choosing the catalytic surface area (model parameter) according to the chemisorptions measurement.

However, in order to improve agreement, the kinetic parameters of the previously published mechanism were fine tuned. Experimental results from the catalyst with the highest loading were partly used as reference for a random-walk parameter optimization algorithm. Activation energies were allowed to change by no more than 5 kJ/mol, pre-exponential factors by no more than factor 10. Thermodynamic consistency of the resulting mechanism was ensured.

It turned out that the adjusted mechanism gives very good agreement between experiment and simulation for all platinum loadings and hydrothermal aging steps at widely varying temperature and gas composition. The model is able to explain several kinetic inhibiting effects of the system.

Conclusions

By developing a reliable model for a platinum catalyst the first step for simulation of a NSC is achieved. Considering the decrease of noble metal dispersion of hydrothermal aged catalyst this model enables prediction of conversion of exhaust gas for catalysts with reduced activity. The simulations can now support optimization of catalyst loadings, also concerning a more economical spatially varying distribution, and catalyst stability by identifying the most sensitive components or even reaction steps most affected by hydrothermal aging.

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