

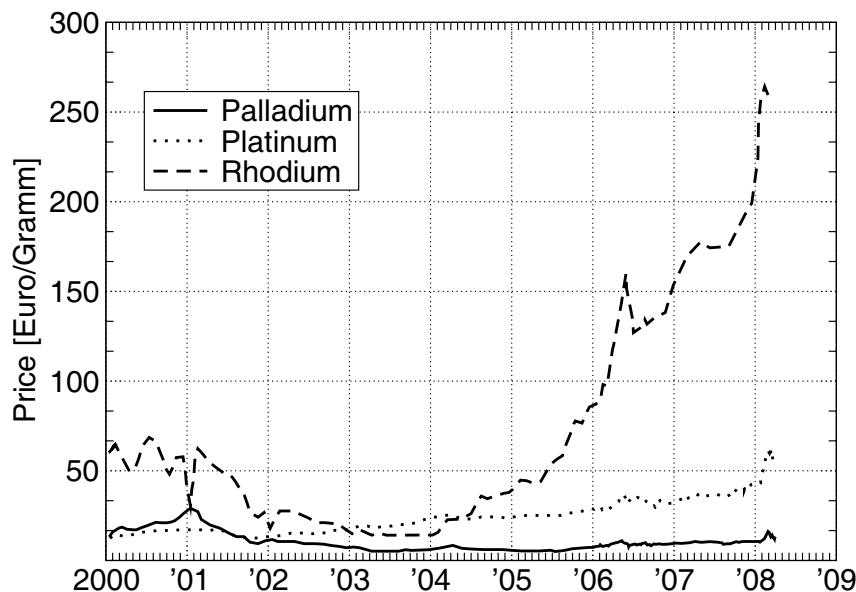
# 1 Introduction

The complex interactions between chemical kinetics and transport phenomena of mass, momentum and energy lead to incomplete fuel combustion, which is the origin of pollutant formation of internal combustion engines. Due to the steadily increasing number of passenger cars worldwide, the total amount of vehicle emissions has risen significantly during the last decades. In particular the air pollution problems of Los Angeles, California, led to the introduction of the first pollutant emission legislation in the 1970's. Similar problems in other urban areas with a high traffic density, and in particular the recognition of the adverse effects of toxic pollutants on human health have spread the demand for emission control devices in other countries. Pollutant emissions from vehicle exhaust gas are regulated by emission standards. Among those the main and most progressive legislations have been established by the United States of America and the United Nations Economic Commission for Europe (ECE). Moreover, intensions to regulate the non-toxic carbon dioxide ( $\text{CO}_2$ ) emissions are currently discussed, because of its contribution to global warming.

Vehicle exhaust gas emission control devices have continuously been improved to meet the constantly tightened standards. A cornerstone in automobile emission technology was the development of oxygen sensors, which enabled the control of the air to fuel ratio within a narrow window around the stoichiometric air to fuel ratio in a closed loop engine control management systems. For automobile manufacturers this was the key to a large scale introduction of so-called "three-way catalysts", which convert nitric oxides, carbon monoxide, and unburned hydrocarbons simultaneously at stoichiometric conditions. Three-way catalyst technology is still extensively used for the purification of automotive exhaust gases, usually in combination with monolithic (honeycomb) reactors.

The overall conversion efficiency of the reactor depends on the transport phenomena of heat and mass, as well as the heterogeneous kinetics at the gas-solid interface (Bird et al., 2002, Deutschmann, 2001, Hayes and Kolaczkowski, 1997). An ongoing reduction of tailpipe emissions requires a substantial understanding of all relevant processes involved in the formation and depletion of pollutants. During the vehicle lifetime thermal and chemical ageing processes inside the catalyst gradually reduce its pollutant conversion performance. The demand for effective and long lasting exhaust gas aftertreatment systems has led to the development of high cell density catalysts in closed coupled positions with improved chemical characteristics. At the same time the catalyst design must fulfil conflicting objectives concerning the engine power output and fuel efficiency. Additional aggravation is introduced by cost reasons, because of the rise in precious metal prices

over the last years<sup>1</sup>, which is illustrated in Fig. 1.1. In combination with the costly and time consuming experimental characterization of catalytic converters, numerical simulations offer a promising alternative. In particular during the early phase of the engine development process a simulation tool is required to predict the conversion efficiency of an aged catalyst, when corresponding hardware is not available.



**Fig. 1.1:** Development of the price for different precious metals.

In the past three decades, several one-dimensional plug flow models were developed (Ahn et al., 1986, Kirchner and Eigenberger, 1996, Montreuil et al., 1992, Oh and Cavendish, 1982, Onorati et al., 2002, Pattas et al., 1994, Siemund et al., 1996). They apply global parameter kinetics, due to the scarcity of available kinetic data of heterogeneous catalytic reactions on the surface of porous media. Most early models incorporated only simplified oxidation kinetics based on the work of Voltz et al. (1973), who studied the catalytic oxidation of carbon monoxide and propene on platinum packed bed reactors. Subramaniam and Varma (1985) proposed reaction rate expressions for NO reduction kinetics. Pattas et al. (1994) were the first to compare experimental data to the simulation results of their three-way catalyst model. Montreuil et al. (1992) presented a reaction mechanism, which uses a blending factor to interpolate between two sets of kinetic parameters for rich and lean conditions. Moreover, they were the first to suggest a systematic tuning methodology for global heterogeneous reaction kinetics. Pontikakis and Stamatelos (2001) tuned the kinetic parameters of a fundamental reaction mechanism for three-way catalysts presented by Koltsakis et al. (1997) to match experimental data of an FTP75 drive cycle. However, the results were not compared to stationary experiments.

<sup>1</sup>The data are taken from <http://www.kitco.com/> and <http://www.rohstoff-preise.de/>.

---

In this work a global reaction mechanism for three-way catalysts is developed including 16 reactions and 12 gas phase species. The reaction mechanism is combined with an empirical oxygen storage model and validated against a number of different real engine experiments carried out on both fresh (not aged) and aged catalysts. Once the mechanism is validated against the fresh system, the adaption to the aged system is achieved solely by the reduction of the available reactive surface area of the washcoat, without tuning the individual reaction parameters. Finally the parameter set of the aged system is used to simulate a FTP75 drive cycle and the results are compared to experimental data of the same catalyst without further tuning.

After this introduction the transient one-dimensional catalyst model is derived in chapter 2. First a short introduction to the structure of monolithic reactors is given. The governing equations for catalytically reacting flows are presented in three steps, namely the set of conservation equations for the gas phase, for the solid phase, and the coupling of the two phases. After a brief revision of the modeling concepts of homogeneous and heterogeneous reaction rates, the model equations are derived from the transient three-dimensional reacting Navier-Stokes equations. Finally the numerical setup is briefly addressed.

Chapter 3 focuses on the relevant transport processes inside the monolithic reactor channel and the adequacy of the transport models applied here. The relevant transport phenomena can be divided into intraphase transport (porous diffusion), which is shortly reviewed, and interphase transport at the gas-solid interface. The latter is discussed in more detail. Therefore the local distributions of Nusselt and Sherwood numbers inside a monolith channel are resolved using a two-dimensional model. The cases of non-reacting and reacting conditions at the channel wall are discussed and subsequently compared to according *a priori* correlations.

The subject of chapter 4 is the development and validation of the reaction mechanism. The concept of Langmuir-Hinshelwood-Hougen-Watson type rate expressions is shortly reviewed, before the set of global heterogeneous reaction equations is presented. The necessity to calibrate the lumped parameter kinetics of global reaction mechanisms motivates the application of advanced optimization algorithms. A brief introduction is then given to the theoretical background of multi-objective optimization problems and a selection of algorithms. In a benchmark considering relevant optimization problems the most suitable algorithm is evaluated. In the subsequent step this algorithm is used to calibrate the kinetic parameters of the reaction mechanism to match the conversion behavior of a fresh catalyst. The computed conversion characteristics are compared with experimental data derived from a test suite comprising four different operating conditions. In a second step the kinetic model is then used to simulate the conversion behavior of an aged catalyst. The adaption of the kinetic model is achieved only by the reduction of

the available surface area. Again the computed conversion characteristics are compared to measured data. Finally an empirical oxygen storage model is included.

In chapter 5 the catalyst model for the aged system is used to predict the tailpipe emissions during real drive cycle conditions. First the vehicle emission legislations of Europe and the U.S. are summarized, including the relevant emission test cycles. The boundary conditions of the drive cycle simulations are addressed, followed by the presentation of the results. In the subsequent discussion the quality of the computed results are evaluated by comparison with according experimental data. Finally a catalyst design parameter study is presented as a typical application of the model within the development process of exhaust gas aftertreatment systems.