A Hierarchically Developed Surface Reaction Kinetics for Oxidation of H₂, CO, and CH₄, WGS as well as Steam and Dry Reforming of Methane over Rh/Al₂O₃

Canan Karakaya¹, Lubow Maier², Olaf Deutschmann¹,²∗

¹ Institute of Chemical Technology and Polymer Chemistry, ² Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT)
76131 Karlsruhe (Germany)
*deutschmann@kit.edu

Introduction

Rhodium is known as very active catalyst for oxidation as well as steam and dry reforming of light and heavier hydrocarbons, and also for water-gas-shift (WGS), and reverse WGS, hydrogen and CO oxidation, and preferential CO oxidation. Several studies were published to reveal the reaction paths of these catalytic processes, e.g. [1-3]. In particular, experimentally determined spatial concentration and temperature profiles within monolithic and channel structures recently led to a better understanding of partial oxidation of methane over Rh [3, 4]. However, so far, no unique reaction mechanism has been presented to model all those reactions over Rh at once.

Using a stagnation-flow reactor (SFR) with a Rh/Al₂O₃ coated disk [5] and a flow reactor with monolithic catalysts [6] as well as many experimental observations from literature, the authors developed a novel multi-step surface reaction mechanism, which models all the catalytic reaction over Rh/Al₂O₃ mentioned above without any specific adaptation of kinetic parameters.

Methods

The experiments conducted in SFR facilitates computational modeling of heterogeneously catalyzed gas-phase reactions in a simple flow regime under technical relevant conditions. The catalytic surface can be treated zero-dimensional, i.e., no lateral variations on the catalyst on a macroscopic scale. Therefore it can easily be coupled with the one-dimensional convective and diffusive mass and heat transport in the reactive flow field, which allows to distinguish between intrinsic kinetics and mass and heat transfer limitations of the overall reaction rate. Many possible reaction paths of the system H₂O/O₂/CO/CO₂/H₂O/CH₄ over Rh/Al₂O₃ are considered. Experiments are conducted by following a hierarchy, i.e., the complexity of the reaction kinetics was step-wise increased starting from H₂ oxidation, via CO oxidation, preferential oxidation of CO in H₂, water-gas shift and reverse water-gas shift reactions and ending up with partial oxidation, steam reforming (SR), and dry reforming of CH₄. In the them manner, a thermodynamically consistent elementary-step-like reaction mechanism of altogether 48 steps among five gas-phase and thirteen surface species with the associated kinetic expressions was developed for the system H₂O/O₂/CO/CO₂/H₂O/CH₄ over Rh/Al₂O₃. The mean-field approximation is applied to describe the Langmuir-Hinshelwood like reactions. The mechanism was coupled with mass and heat transport models to numerically simulate the experiments. Conversions, selectivities, ignition temperatures, and spatial concentrations profiles were computed and compared with the experimental data for a wide range of mixture composition and temperature.

Results and Discussion

The model agrees well with all experimentally measured data. For example, it is shown that a considerable amount of CO₂ is produced at low temperatures (< 873 K) by WGS reactions, which could only be modeled by the implementation of reactions of a carboxyl group (COOH). Figures 1 and 2 exemplarily show the dependence of species concentrations on the distance from the catalyst in a SFR and as function of temperature in a monolithic catalyst.

Fig. 1: Comparison of the experimental (symbols) and the predicted (lines) mole fractions along the boundary-layer for (a) steam reforming of CH₄, S/C=1.06, and (b) partial oxidation of CH₄, C/O=0.99 at 973 K in the SFR.

Fig. 2: Comparison of the experimental (symbols) and the numerical simulations (lines) for steam reforming of CH₄, S/C=2.0 in a monolithic catalyst.

Significance

A novel reaction mechanism with the associated kinetic expressions is developed for oxidation of H₂, CO, and CH₄, WGS as well as steam and dry reforming of methane over Rh/Al₂O₃, which is tested over a wide range of fuel-to-oxygen ratios and temperatures. The mechanism has been shown to be of great benefit reactor simulations in industry and fundamental research.

References