

Development of a Hybrid Model to Account for Catalyst Deactivation in Reactor Models

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Introduction

The aging of heterogeneous catalysts is an unavoidable problem in the chemical industry [1, 2]. Chemical and physical phenomena such as coking, sintering, poisoning and solid state transformation lead to a reduction or blockage of the active sites of the catalyst [1]. Progressive deactivation of the catalyst is usually observed by a decrease in key performance indicators such as reactant conversion and product selectivity. In industrial practice, deactivation is usually counteracted by uniformly increasing the temperature of the cooling medium. However, this not only accelerates the reaction rates, but also promotes aging phenomena that lead to even faster deactivation. Xie and Freund [3] have shown that a significantly higher lifetime-averaged selectivity and catalyst lifetime can be achieved by optimal temperature control. However, the interaction of different deactivation phenomena makes it difficult and time-consuming to develop parametric deactivation models. A possible alternative is the use of a black-box model (e.g. an artificial neural network) to take into account for the dynamics of catalyst deactivation. The combination with the parametric reactor balance equations and the reaction kinetics without considering deactivation leads to a so-called hybrid model [4]. Such a hybrid model is expected to provide better generalization and extrapolation capabilities compared to a purely data-driven model.

Methodology: Extension of a kinetic model

Detailed kinetic measurements for the methanation of carbon dioxide over a nickel catalyst were performed using a laboratory gradient-free reactor (Berty reactor). Based on the experimental data collected in the Berty reactor, a new kinetic model for CO₂ methanation at constant catalyst activity was developed [5]. In addition, the influence of deactivation on the conversion of the reactants, i.e. X_{CO_2} and X_{H_2} as well as on the product selectivity S_{CH_4} was observed. A systematic experimental design was performed to study deactivation as a function of temperature, pressure and gas composition. A hybrid model is developed which is able to describe the decreasing

reaction rates. For this purpose, different model approaches are compared with each other. Based on the interpolation and extrapolation capabilities of the models, an appropriate modeling approach is selected to consider deactivation.

Results: Catalyst deactivation model

It was found that for the reaction system under investigation the kinetics are nonseparable. The activity of the catalyst is therefore not only a simple pre-factor but also influences the temperature dependency of the kinetics. To account for this, additional time dependent variables were added to the existing kinetics to account for the catalyst deactivation, and their progression over time was extracted from the measured data. The time courses of the additional variables were used for the training of a black box model. By linking the black box model with the known kinetics, a hybrid model is obtained which is able to describe the decreasing reaction rates over a wide range of temperatures (350 °C - 450 °C) and pressures (3 bar - 8 bar).

Conclusion and outlook

In this study, catalyst deactivation for a reaction system with nonseparable kinetics is taken into account with a hybrid model. For this purpose, data were collected from a laboratory plant over a wide range of reaction conditions. Different modeling approaches are compared using appropriate criteria. The methodology is developed and exemplified for the CO₂ methanation reaction. In further studies, the hybrid model can be used in dynamic optimizations, e.g. to optimize the methane selectivity over the catalyst lifetime or to extend the catalyst lifetime.

References

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