Dynamically Operated Fixed Bed Reactors for CO_2 Methanation: Strategies to Mitigate Catalyst Deactivation

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Introduction

Due to the unsteady power generation from renewable sources, reactors within Power-to-X process concepts such as, e.g., the CO_2 methanation are confronted with partly fluctuating feed flows. These fluctuations can propagate to the plant and thus also to the catalytic reactors. However, particularly the exothermic nature of the methanation reaction poses challenges for the operation of such reactors. These challenges are addressed in recent numerical studies by developing concepts for temperature control by catalyst particle design (Zimmermann et al., 2020) and by optimization methods targeting the catalyst packing and reactor scale (Fischer and Freund, 2020, Fischer and Freund 2021). The effect of load changes on catalyst deactivation has not yet been considered. This aspect, however, is of particular interest because dynamic effects can shorten the lifetime of the catalyst and thus need to be taken into account for design and operation of methanation reactors in power-to-gas applications.

Integrated Kinetic Modeling of Catalyst Activity and Deactivation Behavior

In this contribution, we present a kinetic model based on a Langmuir-Hinshelwood-Hougen-Watson approach for an industrial Ni/AlO_X catalyst, which is capable of describing both, catalytic activity over a broad operation range as well as catalyst deactivation according to the given conditions. For this, we used a lab-scale kinetic plant with a Berty-type reactor, which allows kinetic measurements in the absence of mass and heat transfer limitations and provides gradientless reaction conditions. To access the catalytic activity, measurements were performed within a broad operation range from 250 to 450 °C, 3 to 10 bar for CO_2 and CO (co-)methanation at various stoichiometric ratios. The deactivation behavior was investigated at long-term experiments up to 120 h time on stream, varying in temperature, pressure and the volume flow to catalyst mass ratio. On this basis, an integrated kinetic model could be parameterized, giving a holistic picture of kinetic activity over the catalyst lifetime in respect of its history.

Reactor Operation: Design and Operation to Avoid Catalyst Deactivation

Our investigation is based on the optimal reactor design and operation approach by Xie and Freund (2017) combined with the reactor design optimized according to the multi-steady-state operation method developed recently in our group (Fischer and Freund, 2021). Herein, an optimization problem is formulated to optimize the reactor design simultaneously for multiple steady state operating points within a desired load range, leading to a high load flexibility while ensuring the required product gas quality meeting the specifications for all scenarios. Using this obtained reactor design, we simulated fluctuating conditions of power-to-gas processes by defined ramp and step changes in the inlet gas composition (ratio of H_2 to CO_2) and in the volume flow at the reactor inlet. With these simulations, it is possible to identify reaction conditions, which particularly accelerate catalyst deactivation, and therefore should be avoided. From these observations, recommendations for adjusted operation policies can be derived for achieving a high catalytic activity over a long catalyst lifetime.

Conclusion

We developed a methodology to derive reactor operation policies under dynamic conditions to extend catalyst lifetime. The methodology was developed and exemplified for a methanation reactor as a representative for a PtX application, for which we were able to identify unfavorable operation conditions. For this purpose, we developed a holistic kinetic model capable of describing catalyst activity and its deactivation in respect of its history, using extensive data from laboratory experiments covering a broad range of reaction conditions. With this model, a reactor concept was developed that is specifically designed for a wide range of feed gas loads while ensuring the required specifications of the product gas stream.

References

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