DYNAMICALLY OPERATED FIXED BED REACTORS FOR CO_2 METHANATION: STRATEGIES TO MITIGATE CATALYST DEACTIVATION

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Abstract

Due to the fluctuating power generation from renewable sources, reactors within the power-to-X process concepts such as, e.g., the CO_2 methanation are confronted with partly strongly fluctuating feed flows. Dynamic reactor operation, however, can lead to temporally critical hot spots or unfavorable gas phase conditions, which increase the deactivation rate of the catalyst and shortens its lifetime. To investigate these effects we developed a kinetic model for the methanation reaction, which describes the reaction kinetics as well as the catalyst deactivation based on experiments conducted in an ideally mixed Berty-type reactor. Based on this results, we are able to model and design a load flexible industrial-scale fixed-bed reactor describing catalyst deactivation in dynamic operation. This in turn provides a basis for the derivation of adapted policies for dynamic operation to minimize catalyst.

Keywords

Dynamic Reactor Operation, CO_2 Methanation, Catalyst Deactivation.

Introduction

The transition of the energy sector from fossil fuels to sustainable alternatives is currently of great interest to researchers. In this context, hydrogen is considered to play a crucial role. However, the storage, distribution and reuse of hydrogen is associated with serious challenges. Power-to-X (PtX) technologies such as methanation are being discussed for the further processing of green hydrogen to overcome these drawbacks. In case of CO_2 methanation, hydrogen is converted to methane using CO_2 from abundant sources such as industrial exhaust gases or from direct air capture. The methane produced can be easily stored, distributed, and used as a natural gas substitute by utilizing existing natural gas infrastructure. In this scenario, decentralized small- to medium-sized plants are built directly at sites where renewable energy is produced and CO_2 sources are available. Hydrogen is provided on site by water electrolysis, which can follow the fluctuations of renewable energy generation comparatively easily. However, for the subsequent process units in PtX plants, dealing with these fluctuations is much more challenging. To operate such plants economically, expensive storage facilities for hydrogen and CO_2 should preferably be avoided. This implies that fluctuations in the reactant supply will 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 load-flexible 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

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targeting the catalyst packing and reactor scale (Fischer and Freund, 2020, Fischer and Freund 2021). While these methods can be used to design load flexible reactors that are safe in operation, the effect of load changes on catalyst deactivation has not been considered. This aspect, however, is of particular interest because dynamic effects can significantly 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 on 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 (see Figure 1). 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.

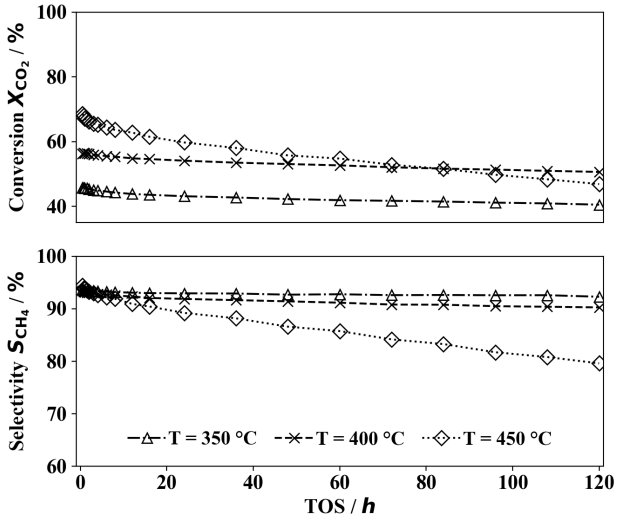

Figure 1: Change in CO_2 -Conversion (X_{CO2}) and Selectivity of the catalyst towards Methane (S_{CH4}) due to deactivation with increasing time on stream (TOS) for different temperatures

Dynamic Reactor Operation: Design and Operation to Avoid Catalyst Deactivation

By using the holistic kinetic model in a simulation study, we are able to investigate the reactor behavior over the whole catalyst lifetime with a special focus on dynamic operation. 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, to achieve 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.

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