Influence of catalyst dynamics on fixed bed methanation reactor design and operation

Moritz R. Langer, Hannsjörg Freund

Institute of Reaction Engineering and Catalysis,

TU Dortmund University, Dortmund, Germany

Power-to-X (PtX) technologies as storage and distribution solutions for renewable energy are of major interest in current research and development. The main concept of PtX technologies is to convert renewably produced hydrogen with additional reactants to platform products, which can be easily stored and reused later on. As an example, methane can be produced in catalytic fixed bed reactors from hydrogen and CO_2. The produced methane can be stored, distributed and used as natural gas substitute by exploiting the existing natural gas infrastructure. The concept for such methanation plants will be to build small- to medium-sized plants directly at sites where the reactants are available, for instance at wind power plants or in the vicinity of industrial CO_2 sources. To operate such plants economically, expensive storage facilities for hydrogen and/or CO_2 should be avoided. This implies that fluctuations in the reactant supply will propagate to the plant and thus also to the catalytic reactors. However, commonly fixed bed reactors are operated at steady state conditions with only little fluctuations. Therefore, there is a lack of experience in the design and operation of reactors under highly dynamic conditions. To fill this knowledge gap, current studies address this issue on a numerical basis. Among others, Kreitz et al. investigated the system response of a fixed bed reactor after imposing a forced oscillation of the gas inlet composition [1]. Furthermore, Fischer and Freund presented a methodology to integrate the reactor dynamics into the optimization of fixed bed reactors [2]. In both studies, the focus was on the reactor scale, and a reaction kinetic expression was used based on a Langmuir-Hinshelwood type mechanism [3]. As already pointed out by the authors of these studies, the underlying steady state assumptions of the reaction kinetic model are questionable as they cannot depict dynamic effects regarding sorption processes and possible changes in the reaction mechanisms [4,5]. To the best knowledge of the authors, so far no numerical study exists which investigates the dynamic behavior of technical fixed bed methanation reactors using a kinetic model, which describes the dynamic behavior of the catalyst at relevant reaction conditions.

In this contribution, we analyze the influence of catalyst dynamics on the dynamic operation of fixed bed methanation reactors. Therefore, a semi-mechanistic kinetic model approach (RAS model) based on so-called rate affecting steps and considering the change in surface coverages is used. With this model, it is possible to describe the dynamic behavior of the catalyst surface. The technical reactor is described using a heterogeneous reactor model. The dimensions of the reactor are optimized according to the multi-steady-state method developed in our group [6]. Based on this model, relevant scenarios such as step changes of the inlet composition or start-up and shut-down cycles of the reactors are simulated. The results are analyzed in regards to the product specifications, temperature constraints and elapsed time until steady state is reached. Furthermore, to highlight the influence of the catalyst dynamics, the results are compared to simulations in which the catalyst dynamics are neglected (see Fig.1). Finally, this contribution demonstrates potentials for optimizing the dynamic operation of fixed bed reactors.

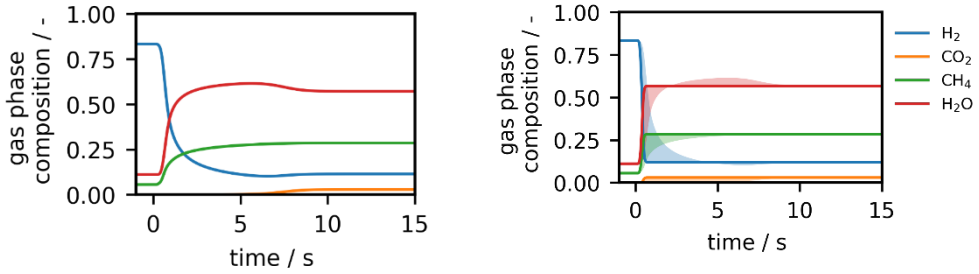

Figure 1: Simulation of the outlet composition of an isothermal PFR. Left: using the RAS model, which is able to depict catalyst dynamics. Right: using a kinetic model, which neglects catalyst dynamics. The shaded areas indicate the difference to the RAS model. At time t = 0 s, a change of inlet composition was simulated from hydrogen excess (H2/CO2 = 19/1 mol/mol) to stoichiometric feed composition. Reaction conditions: T = 300°C, p = 10 bar, flowrate = 0.5 ml_{STP} min^{-1} mg_{cat}^{-1}.

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