**Modelling and Simulation of Porous Catalyst Pellets for Unsteady-State co-Methanation of CO/CO2 mixtures: Comparison of Diffusion Models**

Jannik Schumacher1, Dominik Meyer1, Jens Friedland1, Robert Güttel1

*1 Institute of Chemical Engineering, Ulm University, Ulm, Germany*

*\*Corresponding author: Jannik.schumacher@uni-ulm.de*

**Highlights**

* Unsteady-state methanation is modelled and simulated on the pellet scale.
* Different diffusion models are compared with respect to their dynamic effects.
* The exchange of CO2 with CO is used as a model experiment of a dynamic process.

**1. Introduction**

The methanation process is a promising part of a sustainable energy supply and infrastructure via the power-to-gas (PtG) process. However, since the availability of renewable energy and carbon sources is fluctuating, the methanation has to work under unsteady-state conditions as well, depending on the upstream storage capacities [1]. One of the main challenges arising from this situation is the dynamic behavior of the porous catalyst pellets used for methanation, where heat and mass transfer occur simultaneously with the chemical reaction. Dynamically changing spatial profiles of temperature and concentrations develop, which are coupled non-linearly. Since the measurement of those profiles, especially under operando-conditions is very challenging [2], modelling and simulation provides a powerful tool for analyzing the occurring dynamic processes. Among methanation of pure CO2 and CO a mixture of both carbon oxides is of interest especially when considering process gases, such as coke oven gas, as carbon source. However, when switching from CO2 to CO-methanation or between various mixtures of both, the dynamic profiles change in an unpredictable way, which originates from the different reaction mechanism for CO and CO2 hydrogenation. Thus, the present contribution analyses the dynamic behavior at particle scale based on modelling and simulation.

**2. Methods**

This work puts emphasis on the comparison of different diffusion models under isothermal and unsteady-state methanation conditions as a basis for reliable simulation results. The compared diffusion models comprise, but are not limited to, the models by Fick and Wilke-Bosanquet as well as the dusty-gas model [3]. The models are evaluated based on accuracy and numerical effort. Due to a lack of experimental data for validation the dusty-gas-model is assumed as the most accurate model, since it is the most complex one and thus probably considers all relevant effects on diffusion. Thus, the alternative (and simpler) models are compared to the results of the dusty-gas model as benchmark. The model equations for the unsteady-state reaction-diffusion problem are implemented to Aspen Custom Modeler for simulation. The diffusion models in accordance to Solsvik et al. [4] are used, while the reaction kinetics are taken from Xu and Froment [5]. For simulation typical methanation conditions are chosen with respect to temperature, pressure and reactant composition. The catalyst pellet is assumed to be isothermal, in order to avoid super-imposed temperature influences. The effects at reactor scale are neglected, as well as external heat and mass transfer resistances, in order to isolate the diffusion effects. The dynamic profiles when exchanging CO2 with CO are calculated with respect to the different diffusion models.

**3. Results and discussion**

As example Figure 1a shows the simulated steady-state profiles of the methane molar fraction in the CO2-methanation process for different diffusion models. It is obvious that the choice of the diffusion model is a critical part in the modelling and simulation process. Although the concentration profiles calculated with the dusty gas model and the Wilke-Bosanquet are highly different, the surface methane fluxes and consequently the effective reaction rates are quite similar (Figure 1b). Based on the systematic evaluation of diffusion models under steady-state conditions, the dynamic behavior of the concentration profiles is analyzed by changing the switching frequency between H2/CO and H2/CO2 as well as for different H2/COx gas mixtures (not shown in abstract). From the obtained results the impact of mass transport on the behavior of the catalyst pellet is evaluated.

a)

b)

**Figure 1.** a) Steady-state methane concentration profiles for CO2-methantion with different diffusion models, b) steady-state flux density of methane across the external surface of the catalyst pellet.

**4. Conclusions**

While the effective reaction rates in the CO2-methantation process are quite similar for the studied diffusion models, the dynamic behavior of the profiles is expected to differ, since the concentrations are highly different.

**References**

1. J. Lefebvre, M. Götz, S. Bajohr, R. Reimert, T. Kolb, Fuel Process. Technol. 132 (2015) 83–90.
2. T. Titze, C. Chmelik, J. Kullmann, L. Prager, E. Miersemann, R. Gläser, D. Enke, J. Weitkamp, J. Kärger, Angew. Chem. 127 (2015) 5148–5153.
3. R. Krishna, J.A. Wesselingh, Chem. Eng. Sci. 52 (1997) 861–911.
4. J. Solsvik, S. Tangen, H.A. Jakobsen, Ind. Eng. Chem. Res. 51 (2012) 8222–8236.
5. J. Xu, G.F. Froment, AIChE Journal 35 (1989) 88–96.