

Coupling of spatially and temporally resolved reaction kinetic data in a channel type reactor with a novel kinetic model describing transient reactor behavior

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Highlights

- Kinetic investigation in a channel type reactor including DRIFTS measurements.
- Coupling of novel kinetic model with experimental data of surface kinetics.
- Comparison of various reactor models of different complexity.
- Identification of most suitable model for describing transient reactor behavior.

1. Introduction

Rising global temperatures due to the anthropogenic greenhouse gas emissions led to the necessity to increase the share of renewable electricity in power generation. Since renewable energy sources such as solar or wind often strongly fluctuate, it is crucial to use storage technologies such as CO₂ methanation as a so-called power-to-X technology. The development of new reactor concepts based on suitable kinetic models in order to achieve the highest possible reactor performance under fluctuating inlet conditions is becoming increasingly important. To allow for an accurate description of the methanation reactor's behavior during transient operation, current research aims at establishing non-steady-state kinetic models. Previous work has shown that the concentration of reaction intermediates on the catalyst surface play a key role in reaction dynamics [1]. Therefore, investigation of these surface species under reaction conditions is crucial for an improved understanding and a more suitable description of the reaction mechanism.

2. Methods

The CO₂ methanation reaction was investigated using an in-house developed reactor with multiple taps along the reaction coordinate, allowing for spatially and temporally resolved gas phase sampling in between dedicated reaction zones [2]. The reactor further allows for optical access, which was used to gather data on adsorbed species on the catalyst's surface via DRIFTS (**Figure 1**). This data was subsequently used for parametrization of a novel kinetic model.

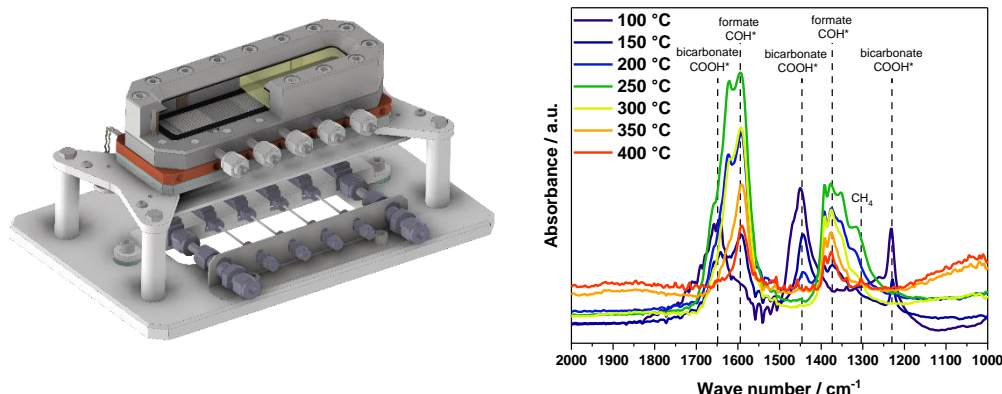


Figure 1. (a) CAD drawing of the reactor used to gather temporally and spatially resolved in operando data. (b) DRIFTS spectra of catalyst surface at different TR ($p_R = 5$ bar, $SV = 4.6$ mlN min⁻¹ mg_{cat}⁻¹, CO₂:H₂ = 1:4 with 50 vol.-% N₂).

Before fitting kinetic models to the experimental data, the reactor was investigated in detail using various methods. A CFD model of the reactor was implemented in ANSYS Fluent® to investigate the influence of sampling and flow phenomena on the experimental data. The results of the CFD simulations were compared with simpler models, using 1- and 2-dimensional pseudo-homogenous and heterogeneous

reactor models under isothermal conditions. In addition to these different reactor models, various kinetic models ranging from simple power law models to detailed microkinetic models for the methanation were implemented and their performance was compared with experimental data. Special focus was on the implementation of a novel dynamic kinetic model approach (Rate affecting step, RAS model) recently proposed by our group [1]. This model is capable of describing the surface coverage of reaction intermediates on the catalyst surface and thus can be coupled with the gathered data from the DRIFTS measurement with reasonable effort.

After implementation of the mathematical reactor models, simulations were performed for different operation conditions. The temperature was varied from 200 to 450 °C and the pressure from 1 to 10 bar. A volume flow range from 100 to 500 N ml min⁻¹ and varying feed compositions were simulated, covering the whole operational range of the reactor.

3. Results and discussion

The simulations show, depending on the model complexity and the used kinetic model, a good agreement with experimental data (see **Figure 2**). The kinetic models were reparametrized to describe the data more accurately. The different models were evaluated regarding computational effort and accuracy in describing the reaction progress. Especially for the use in parameter estimation of kinetic models, lower model complexity is beneficial for reducing calculation time.

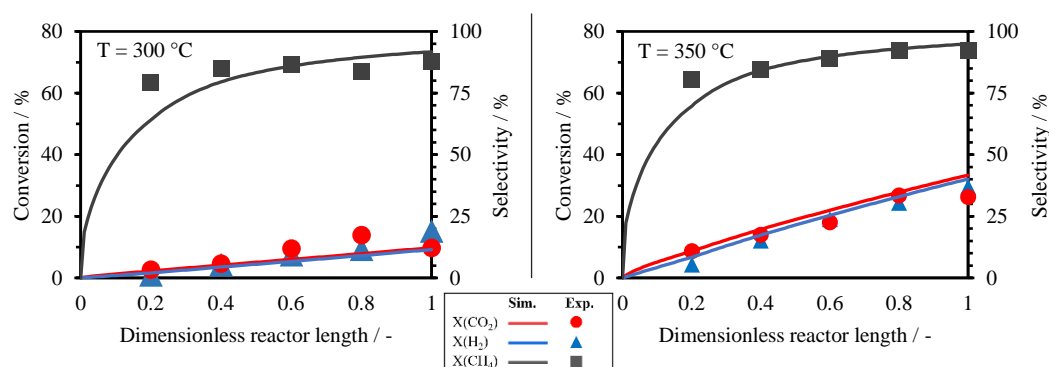


Figure 2. Comparison of experimentally determined spatially resolved conversion and selectivity data versus simulation results of a PFR model at different temperatures. At Temperature $T = 300$ and 350 °C as indicated, $p_R = 5$ bar and $SV = 4$ mL_N min⁻¹ mg_{cat}⁻¹, $m_{cat} = 121.7$ mg with stoichiometric feed ($CO_2/H_2 = 1:4$), 50 vol.-% diluted with N_2 .

Using the experimental data, the RAS kinetic model approach describing the surface reactions according to Langer et al. [1] was reparametrized. As a result, the model shows good agreement with the data from the experimental reactor and is suitable for describing transient behavior.

4. Conclusions

The simulation studies of the reactor show that, while models that are more complex can offer improved accuracy, the computational effort increases significantly. As a consequence, the choice of the model is always a trade-off. A sufficiently accurate model was chosen and successfully reparametrized to describe the experimental data in a satisfactory manner.

Special focus was on reparametrizing the RAS model recently proposed by our group [1] for transient simulation of the methanation reaction. This was achieved by including data from DRIFTS measurements [2] as well as the data gathered from the gas phase analysis. The reparametrized model can be used to describe transient effects during dynamic reactor operation more accurately and to develop operation strategies and optimized reactor concepts in the context of power-to-X applications.

References

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Keywords

Transient reactor operation; CO_2 methanation; Reaction kinetics.