

## Investigations on Steady-State and Dynamic Hydrogenation of CO/CO<sub>2</sub>-Mixtures to Methane

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### 1. Introduction

The increasing utilization of regenerative resources in the chemical value chain induces new challenges in the operation strategy of chemical reactors. For example, the chemical storage of regenerative energy via the power-to-X process (PtX) provides an option to store fluctuating electrical energy by water electrolysis and subsequent hydrogenation of carbon oxides. The formed methane can be stored and transported in the existing gas grid. However, this scenario implies a dynamic behavior of the process chain, depending on the installed storage capacities. As the storage of large quantities of electrical energy and hydrogen is not yet feasible, the necessity of an unsteady-state operation of the methanation reactor becomes likely.

Interesting carbon sources for PtX amongst others are industrial exhaust gases, such as from blast furnace process or biomass gasification. Such sources contain mixtures of CO and CO<sub>2</sub> [1], which can be subject to strong fluctuations in composition and thus require simultaneous CO/CO<sub>2</sub> methanation. Some research has already been done for the simultaneous CO/CO<sub>2</sub> methanation under steady-state conditions for the last decades [2]. However, the range of CO/CO<sub>2</sub> mixtures studied so far is rather limited and suitable reaction kinetics are lacking for Nickel based catalysts. In addition to that, a profound understanding of the dynamic CO/CO<sub>2</sub> methanation is essential for the implementation of the CO/CO<sub>2</sub> methanation in a sustainable energy scenario based on fluctuating sources from renewables. Since this aspect is not yet covered in scientific literature, the present contribution will discuss the strong interrelation between the unsteady-state behavior of the reactor and the frequency of feed composition alteration for methanation on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Based on experimental results for the steady-state and unsteady-state case, conclusions on the effect of feed composition on the underlying transport mechanisms will be drawn.

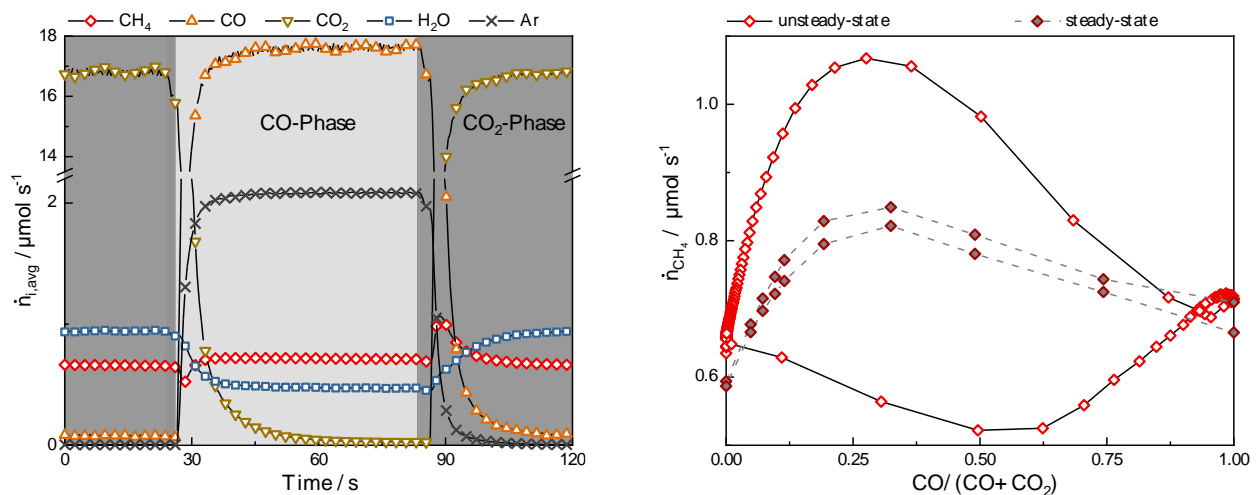
### 2. Methods

The experiments are performed in an isothermal packed-bed reactor (length 300 mm, diameter 4.5 mm) using a self-prepared Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (Ni loading 5 wt%, particle size 800 μm, 100 mg). Two gas lines with different compositions are switched by means of a 4-way valve with a period duration between 6 and 120 s and a split of 0.5. Both gas lines contain different inert gases as internal standards for the representation of the residence time behavior. The effluent was analyzed for unsteady-state experiments by a mass spectrometer with sampling time of 0.5 s providing sufficient temporal resolution and for steady-state experiments with a GC providing a maximal 2% error in the mass balance. Prior to dynamic experiments, the as-made catalyst was reduced and the catalytic behavior was studied under steady-state conditions for various feed compositions

and in a temperature range of 240 to 280 °C and a pressure of 2 bar. Subsequently, the dynamic experiments were performed under the same conditions.

### 3. Results and discussion

Figure 1 shows selected results in time and in phase plane for periodical switches between H<sub>2</sub>/CO/Ar and H<sub>2</sub>/CO<sub>2</sub>/He. The CH<sub>4</sub> trend at the reactor outlet shows a distinct maximum for the switch from CO rich to CO free phase and a minimum for the switch vice versa (Figure 1, left). This effect can be explained by the inhibiting effect of CO on the reaction system [2]. Since the mass balance is fulfilled and a limit cycle is reached for several consecutive periods, the data can be evaluated quantitatively. In this regard, Figure 1 (right) indicates an increase in methane productivity upon periodic operation, as indicated by the upward shift of the limit cycle compared to the expected steady-state system.



**Figure 1:** Temporal profiles of the molar flow rates of selected species (left) and phase plane of the molar flow rate of methane upon periodic exchange of CO with CO<sub>2</sub> compared to steady-state conditions (right); period duration 120 s, T = 553 K, p = 2 bar, H<sub>2</sub>/carbon source/inert = 4/1/1

### 4. Conclusions

We present experimental results on the steady-state and unsteady-state results of the simultaneous CO/CO<sub>2</sub> methanation on Ni-based catalysts. The different behavior of the reactive species indicates differences in interaction strength between those species and the active catalyst surface, which allows to deduce on the basic reaction mechanism. By quantitatively analyzing the dynamic change in the molar flow rate, we are able to determine a transient reaction rate for methane formation and can compare it to the steady-state case. Finally, we link the frequency response of each of the reactants to either the quasi steady-state, the full transient regime or the relaxed steady-state according to [4]. This provides to identify a tolerant operation window for the operation of a methanation reactor under fluctuating inlet compositions.

### References

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