In situ axially-resolved measurement of CO intermediate product formation in CO_2 methanation

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Highlights

- Measurement of axially-resolved concentration profiles in CO_2 methanation.
- Continuous temperature profiles during the CO_2 methanation are obtained.
- The concentration of the intermediate product CO is quantified with a selectivity up to 12%.

1. Introduction

The increasing presence of renewable energies in the electricity market necessitates the development of long-term energy storage solutions, which can be achieved in the form of chemical components. One such solution is the CO_2 methanation, a power-to-gas process, which is seen as a crucial part to compensate the fluctuating availability of renewable energies [1]. Therefore, the comprehension of the reaction mechanism and the corresponding kinetic description is of supreme importance in designing efficient reactors and processes. The strongly exothermic CO_2 methanation reaction (R1, see Figure 1b insert) is part of a reaction network, which also comprises the endothermic reverse water gas shift reaction (R2, rWGS) and the consecutive exothermic CO methanation (R3), making it a demanding task to derive the reaction kinetics. Predominantly, published kinetics strongly rely on measured exit gas compositions of differential or integral laboratory reactors [2,3]. However, these face specific limitations like the operation with diluted feeds and neglected internal concentration and temperature gradients [4]. The aim of this study is to overcome these systematic limitations by the in situ axially-resolved measurement of the relevant species concentrations (CO_2, H_2, CO and CH_4) and temperature profiles with a special focus on the intermediate product formation of CO, to gain further understanding of the described reaction network (R1-R3). Varying temperatures, pressures and WHSVs are investigated.

2. Methods

For CO_2 methanation, alumina and silica supported Ni catalyst are produced via spray-drying. This technique for catalyst synthesis has proven to be advantageous, as several physical properties like loading, metal particle size and porosity can be controlled independently enabling the production of tailored catalysts [5,6]. Steady-state methanation experiments are carried out in plug flow tube reactor, which allows the measurement of axially-resolved concentration profiles of all involved species next to continuous temperature profiles. Sampling takes place through an inert capillary, which can be axially moved relative to the fixed bed. The gas composition is determined through gas chromatography. For the temperature measurement, a thermocouple is placed at the sampling hole of the capillary. Also, a series of temperature-programmed measurements is conducted next to physical characterization methods.

3. Results and discussion

Figure 1 depicts the obtained conversion profiles, temperature profiles and CO concentration profiles for two different inlet temperatures (573 K and 613 K).

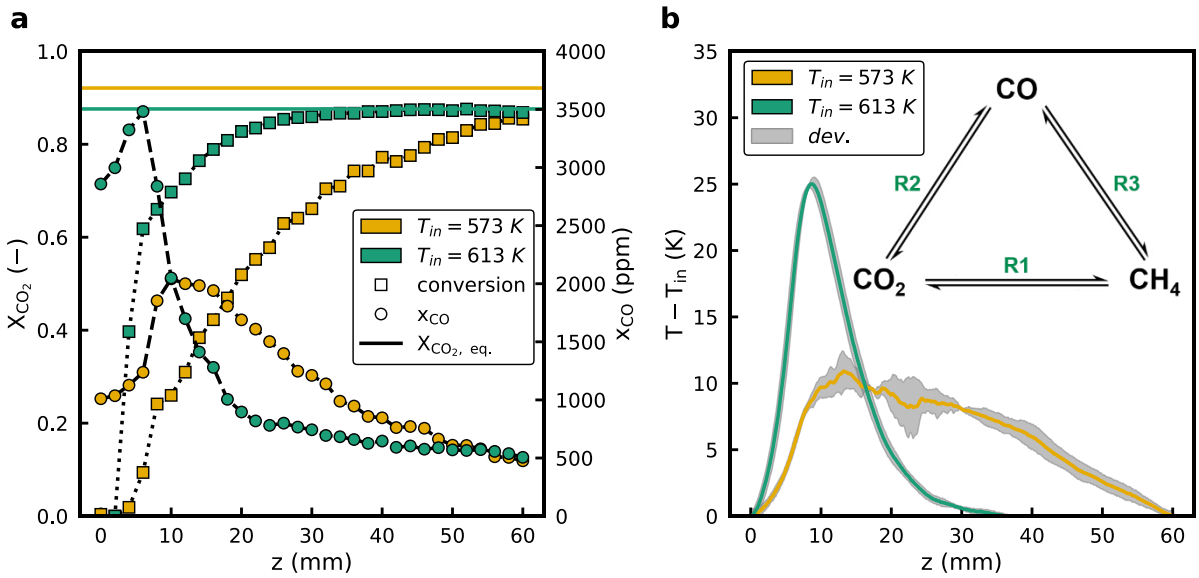

Figure 1. a) CO_2 conversion and CO intermediate product concentration for inlet temperatures of 573 K and 613 K with an axial resolution of 2 mm. **b)** The corresponding continuous temperature profiles. *Conditions*: Feed: 20 mol.-% H_2 and 5 mol.-% CO_2 in N_2, 0.8 g of 10 wt.-% Ni/Al_2O_3, d_p = 125-200 µm, $\dot{V}$ = 5 $L_N h^{-1}$, p = 2 bar, $T_{wall} = T_{in}$ = const. *Dimensions*: $d_{reactor}$ = 4 mm, $d_{capillary}$ = 0.7 mm, $L_{fixed\ bed}$ = 60 mm, *Insert*: Reaction network of CO_2 methanation (R1), reverse water gas shift reaction (R2, rWGS) and CO methanation (R3).

At lower inlet temperatures, the conversion steadily increases, but the equilibrium conversion is not reached. The maximum CO concentration, approximately 2000 ppm, occurs at an axial position of 11 mm. The location of the maximum is in line with the temperature hot spot. Considering the higher inlet temperature, full conversion is reached at a length of around 40 mm. Accordingly, the hot spot is more pronounced with slightly above 25 K. The CO concentration maximum occurs at a lower axial position with 3500 ppm. After the CO concentration maximum, the CO concentration decreases towards the reactor outlet at a length of 60 mm, what can be ascribed to the CO methanation reaction (R3), which is strongly exothermic and thus favored at the decreasing temperature after the hot spot. It has to be noted, that the CO is not fully converted and a significant amount of around 500 ppm remains at the reactor outlet.

4. Conclusions

The preliminary investigations reveal distinct temperature and concentration profiles. According to the assumed reaction network, CO appears as an intermediate product which gets largely converted further to the main product CH_4. The obtained results emphasize the benefits of axially-resolved measurements as a data basis for the development of reaction kinetics, as internal temperature and concentration profiles can be covered leading to a reduced reed for assumptions and lowered experimental limitations. These insights ultimately enable the derivation of sophisticated kinetics.

References

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Keywords
CO_2 methanation; axially-resolved concentration profiles; temperature profiles