

Transient reaction kinetics for CO hydrogenation: Combining periodic experimentation with micro-kinetic modeling

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Highlights

- Transient periodic experimentation methods are applied to CO hydrogenation.
- Insights into transient formation kinetics of short-chain Fischer-Tropsch products derived.
- Micro-kinetic modelling considers the involved surface processes.
- Evidences for accumulation of surface carbon species of different reactivity found.

1. Introduction

The catalytic CO/CO₂ hydrogenation is a highly relevant research topic, due to the possible application in Power-to-X processes. However, kinetic and mechanistic aspects of the involved reactions are still under debate due to their complex nature. Hence, sophisticated methods are necessary to elucidate these as yet unresolved issues. Transient experimental methods have proven to be suitable to investigate kinetic and mechanistic effects on the catalyst surface [1-3].

2. Methods

In the present contribution, the periodic transient kinetics (PTK) method is employed, which is based on periodic switching between two feed gas mixtures and measuring the product gas compositions with high temporal resolution via a calibrated mass spectrometer (MS) [4,5]. Ar is fed into the reactor as internal standard, which allows the *in situ* measurement of the residence time distribution (RTD). Hence, transient effects originating from RTD and those caused by reaction under transient conditions can be distinguished. Consequently, the transient responses between the two steady-states induced by the step-change in reactant concentration can be traced back to the transient kinetics of surface reaction steps occurring during the reaction. The PTK technique is already demonstrated for the methanation reaction [5]. In the present work, the method is extended to Fischer-Tropsch (FT)-like conditions, in order to investigate the transient chain-growth during formation of short-chain hydrocarbons. Therefore, operating points are identified providing sufficient formation of short-chain hydrocarbons with negligible production of liquid compounds to ensure applicability of MS-based quantification. Emphasis is on analyzing the step responses of CH₄, C₂ and C₃₊ species, to draw conclusions about the transient kinetics and mechanism of chain-growth under FT-like conditions.

For kinetic analysis of the transient data, a model was developed considering the RTD in the reactor setup and comprising a micro-kinetic model for the surface reaction steps. The micro-kinetic model considers relevant ad- and desorption, as well as elementary surface reaction steps. Furthermore, surface species are implemented, which are most probably participating in the reaction mechanism. The underlying reaction mechanism was taken from literature [2].

3. Results and discussion

In Fig. 1, the step responses for CH₄, C₂ and C₃₊ formation rates normalized to their steady-state values are shown during build-up (switch from H₂ to syngas) and back-transient phase (switch back to H₂) together with the RTD. Here, an overshoot followed by a characteristic decrease for each species can be seen after both switching events. The deviations between the measured responses and those expected from RTD can be linked to surface reaction steps.

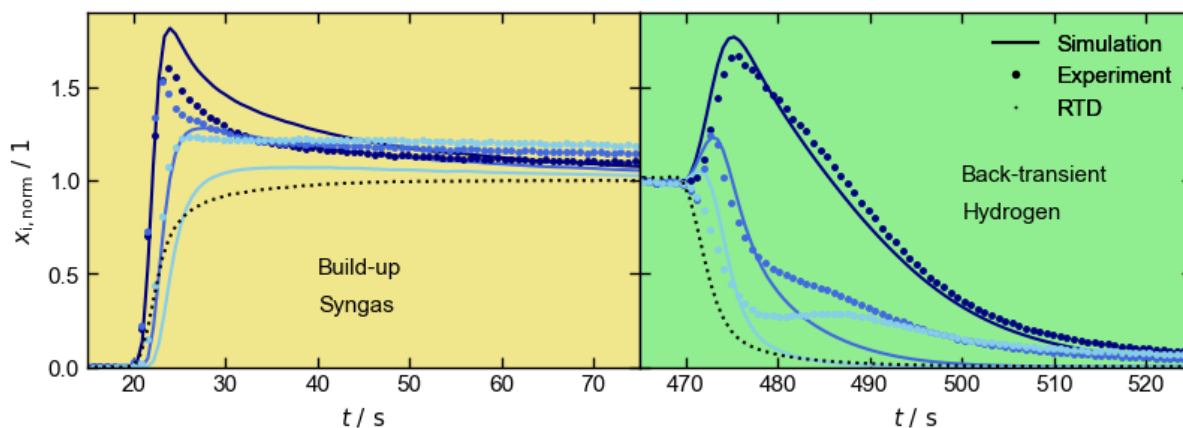


Figure 1. Measured and simulated normalized step response of CH₄ (dark blue), C₂ (blue), and C₃₊ (light blue) as well as the residence time distribution (RTD, black). Operating conditions: 280 °C, 4 bar, H₂:CO ratio of 4:1, 100 mg of 10 wt% Co/TiO₂ catalyst, 6 % CO conversion, 89 % CH₄ selectivity. Switch at $t = 0$ s and $t = 450$ s respectively

By fitting between the measured step response and the simulation results, the kinetic parameters of each reaction step are determined. Based on the remaining deviations, the presumed underlying reaction mechanism was extended systematically. Thereby, a mechanistic understanding of the transient formation of short-chain hydrocarbons under FT-like conditions is achieved. For instance, the pronounced tailing of the C₂ and C₃₊ signals in the back-transient phase indicate the presence of less reactive carbonaceous species, which are hydrogenated after more reactive surface species are consumed already. Furthermore, the overshoot in the back-transient phase clearly points at the substantial accumulation of surface carbonaceous species during the build-up phase. We have to emphasize that our experimental method provides species-resolved molar flow rates, which are used to determine the kinetic parameters using the transient reactor model based on (micro-)kinetic expressions.

4. Conclusions

We included step-wise the micro-kinetic mechanism from Chen et al. [2] in our model and found evidence for accumulation of a second, less active carbon species C_β on the catalyst surface as reported in literature [3]. On that basis, we obtained reasonable agreement between measured and simulated step-responses (Fig. 1). However, certain deviations remain, which require further extension of the micro-kinetic model. For instance, previous investigations showed that H₂O plays a major role in the dynamics of the reaction [4]. Therefore, modelling of the transient behaviour of H₂O was evaluated, as well. Consequently, the present contribution provides quantitative understanding on the transient reaction steps involved in CO hydrogenation and chain-growth under FT-like conditions.

References

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Keywords

CO hydrogenation, transient experimental methods, micro-kinetic modelling, Fischer-Tropsch synthesis