

Modelling the C₂₊ hydrocarbons during the Fischer-Tropsch synthesis using transient kinetics

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Introduction

Steady State Isotopic Transient Kinetic Analysis (SSITKA) is based upon a switch in isotopic labelled reactant species whilst maintaining steady-state conditions. The detection of this isotopic label is monitored on-line which allows for the determination of reaction kinetics and the identification of surface intermediates. SSITKA has been shown to be a valuable technique in elucidating the Fischer-Tropsch (FT) mechanism on a cobalt-based catalyst [1]. More recently [2], we have utilised SSITKA in the development of a mechanism for the methanation reaction under Fischer-Tropsch conditions.

In this study, we extend the methanation mechanisms [2] to account for the formation of higher hydrocarbons. Our approach is to model the C₂ and C₃ transients obtained from a ¹²CO → ¹³CO SSITKA experiment and then to use parameter estimation to discriminate between several rival models.

Experimental

A stainless steel tubular fixed bed reactor (I.D 7.0 mm, bed length 40 mm) is loaded with a precipitated Fe/K catalyst which is reduced with hydrogen at 420°C and 1.2 bar for 16 hrs. Thereafter the temperature is reduced to 330°C under a flow of argon. A mixture of hydrogen and carbon monoxide, typically with a H₂/CO ratio of 15, together with argon is fed into the reactor. An online gas chromatograph (GC), equipped with both a thermal conductivity detector and flame ionization detector is used to monitor the steady state performance of the catalyst. During the transient experiments one reactant is abruptly replaced by its labeled counterpart, while an inert tracer is abruptly removed from the feed. This labeled atom is monitored in time using either an online mass spectrometer (MS) for reactants and methane or an online GC-MS for the heavier hydrocarbons. For a ¹³C labeling experiment, the isotopic step-change is represented by H₂/¹²CO/Ar → H₂/¹³CO/Ar/Ne. A small amount of Ne replacing Ar during the switch takes into account the gas holdup in the reactor.

In the development of the C₂₊ model, the kinetic parameters for the methanation reaction pathway, obtained from our previous study [2] were kept constant in order to reduce the number of unknown model parameters. Details about the modelling procedure have been reported in the previous studies [1,2].

Results and Discussion

The lag in the ethene transient compared to the ethane transient observed on the Co-based catalyst [1] was not observed in this study for the Fe-based catalyst. Co-feeding ethene showed that direct hydrogenation of ethene to ethane was the main reaction. These two main results led us to the development of different C₂₊ model for the Fe-catalyst. This model (not shown) is similar to the model on the Co-based catalyst [1] containing olefin readsorption pathways but contains two surface intermediates for the C₂ hydrocarbons. The model predictions for the C₂ transients are shown in Fig. 1. Details on the development of this model and its comparison with rival models will be presented as well as the extended model accounting for the C₃₊ hydrocarbons.

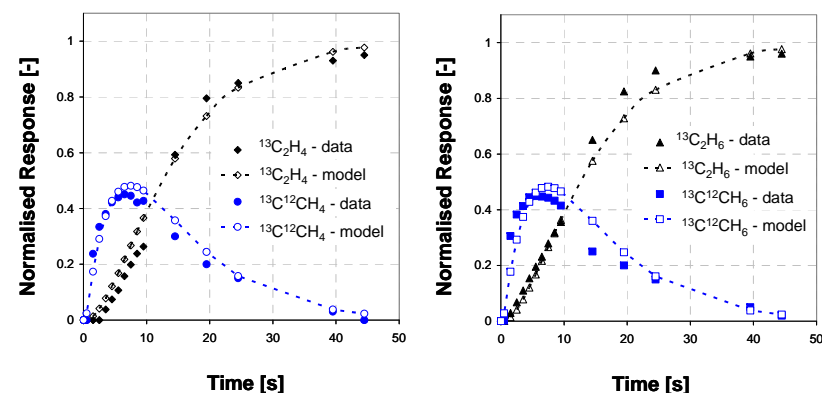


Figure 1. Normalised responses for ethene (left) and ethane (right). Data was obtained at 330°C, 1.2 bar and H₂/CO=15 and model predictions plotted using optimised parameters.

Significance

This paper should be of interest to a broad readership including those interested in Fischer-Tropsch synthesis, Gas-to-Liquids, Coal-to-Liquids, catalysis, CO hydrogenation and SSITKA. The information presented will contribute to a fundamental understanding of the Fischer-Tropsch mechanism on Fe-catalysts and allow for more robust kinetic and selectivity models.

References

1. Van Dijk, H. A. J., PhD thesis, Technische Universiteit Eindhoven, 2001.
2. Govender, N. S., Botes, F.G., De Croon, M.H.J.M., and Schouten, J.C., doi:10.1016/j.jcat.2008.10.008, in press.