

Transient kinetics of the fischer-tropsch reaction on cobalt catalysts

Citation for published version (APA):

Chen, W., Pestman, R., & Hensen, E. J. M. (2019). *Transient kinetics of the fischer-tropsch reaction on cobalt catalysts*. 154-157. Abstract from 12th Natural Gas Conversion Symposium 2019, San Antonio, United States.

Document status and date:

Published: 01/01/2019

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

12TH NATURAL GAS CONVERSION SYMPOSIUM

June 2-6, 2019 • Grand Hyatt • San Antonio, TX



The Global Home of Chemical Engineers

Start

544359 Transient Kinetics of the Fischer-Tropsch Reaction on Cobalt Catalysts

At-A-Glance

Wednesday, June 5, 2019: 10:30 AM

Browse by Day

Texas Ballroom EF (Grand Hyatt San Antonio)

Browse by Topics

Wei Chen, Robert Pestman and Emiel Hensen, Schuit Institute of Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands

Author Index

Keyword Index

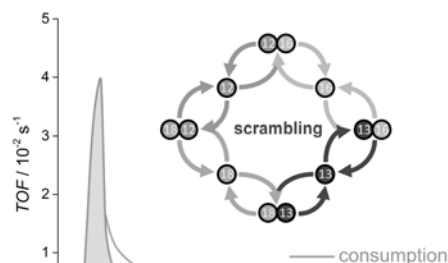
Transient Kinetics of the Fischer-Tropsch reaction on Cobalt Catalysts

Wei Chen, Robert Pestman, Emiel J.M. Hensen

Schuit Institute of Catalysis, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Fischer-Tropsch (FT) synthesis continues to expand in importance as an effective route to convert natural gas into liquid fuels and chemicals. Although the industrial application of the FT reaction preceded its scientific understanding, there remains a strong desire to understand the underlying reaction mechanism in order to develop better catalysts. In this context, the use of transient kinetics provides a unique method to furnish mechanistic information in a less ambiguous way than conventional steady-state kinetics. In this contribution, we provide novel insights into three topics of the kinetics and mechanism of cobalt-catalyzed FT reaction by combining transient kinetics with other techniques.

1) CO dissociation on Co/SiO₂ catalyst was probed by ¹²C¹⁶O/¹³C¹⁸O scrambling in the absence and presence of H₂ (Fig. 1). The initial scrambling rate without H₂ ($TOF = 1.6 \times 10^{-2} \text{ s}^{-1}$) is significantly higher than the rate of CO consumption under CO hydrogenation condition in steady state ($TOF = 3.0 \times 10^{-3} \text{ s}^{-1}$), meaning the surface contains sites sufficiently reactive to dissociate CO without the assistance of H atoms. Quantitative study reveals that only less than 20% of the cobalt metal surface, likely coordinatively unsaturated sites, is involved in CO scrambling. A minor influence of CO scrambling and CO residence time (by SSITKA) on H₂ partial pressure suggests that CO dissociation is only weakly affected by the presence of H₂. An additional proof of this conclusion was obtained by temperature-programmed in situ CO-IR studies on Co/SiO₂. With increasing temperature, the CO band shifts to higher wave number (from 2025 cm⁻¹ to 2060 cm⁻¹) at approximately 150 °C. As confirmed by supplementary IR experiments and DFT calculations, this blue-shift of CO band was correlated to the lateral C-CO and O-CO interaction resulted from CO dissociation on cobalt surface. We observed that the onset temperature of the CO dissociation was independent of the H₂ pressure. This further underpins the conclusion that H₂ is not involved in CO dissociation on cobalt surface.



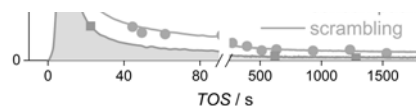


Fig.1. Dependence of CO scrambling (red) and consumption (blue) rate in the absence of H₂ on time-on-stream. Lines correspond to on-line MS measurement and points to GC-MS data. Condition: 220 °C, $p(^{12}\text{C}^{16}\text{O}) = p(^{13}\text{C}^{18}\text{O}) = 45$ mbar. The inset schematically presents the $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{18}\text{O}$ scrambling.

2) The mechanism of CO methanation at 260 °C was studied by using steady-state isotopic transient kinetic analysis (SSITKA) and backward and forward chemical transient kinetic analysis (CTKA) (Fig. 2) [2]. It was figured out that C and O hydrogenation are relatively slow compared to CO dissociation, and that the overall barrier for CO hydrogenation to CH₄ is lower than the CO adsorption energy. The combined transient kinetic data were used to fit an explicit micro-kinetic model for the methanation reaction. Micro-kinetics simulations based on the fitted parameters confirms that under methanation conditions the overall CO consumption rate is mainly controlled by C hydrogenation and to a smaller degree by O hydrogenation and CO dissociation. Under FT synthesis conditions, a model-based approach of SSITKA measurements involving hydrocarbon products containing up to five carbon atoms was employed to gain deeper insight into the relation between the kinetics and the composition of the surface adsorbed layer [3]. SSITKA data show that the rates of chain growth and chain decoupling are much higher than the rates of monomer formation and chain termination. An important corollary is that the fraction of free sites, which is mainly determined by CO pressure, has opposing effects on CO consumption rate and chain-growth probability. Lower CO pressure and more free sites leads to increased CO consumption rate but decreases chain-growth probability because of an increasing ratio of chain decoupling over chain growth (schematically presented in Fig. 3). The preferred FT condition involves high CO pressure in which chain growth probability is increased at the expense of the CO consumption rate. Degree of rate control analysis suggests that CO dissociation under FT condition controls the overall rate more significantly than that under methanation condition. The shift in rate-controlling steps relates to increased surface coverage at lower temperature.

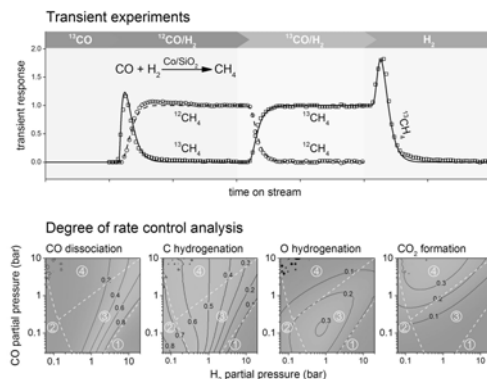


Fig.2. Combined transient experiments (top) and degree of rate control analysis based on model fitting (bottom). Condition: 260 °C, $p(\text{CO}) = 30$ mbar, $p(\text{H}_2) = 450$ mbar.

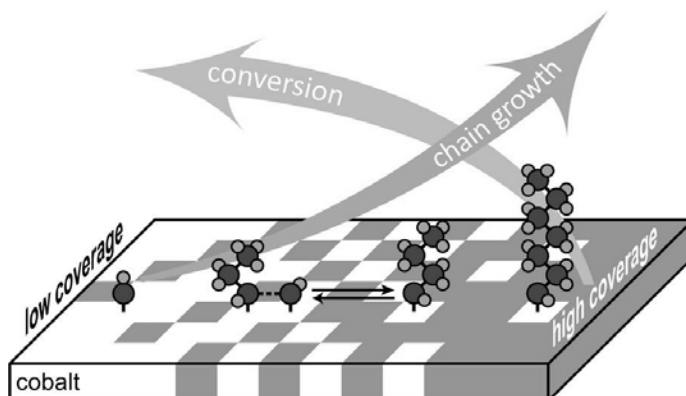


Fig.3. Schematic presentation of the influence of surface coverage on CO conversion and chain growth.

3) Effects of graphitic carbon deposits on FT performance is explained by a two-site model on the

basis of the structure-sensitivity of the elementary steps [4]. Depositing graphitic carbon via the Boudouard reaction on cobalt catalyst strongly suppresses the non-ASF CH_4 , while the formation of higher hydrocarbons is much less affected. We provide the evidence that the amorphous carbon does not influence the FT reaction as it can be easily hydrogenated under reaction conditions, and that the graphitic carbon cannot be removed under the CO hydrogenation condition. This unreactive form of carbon is located on terrace sites and mainly decreases the CO conversion by limiting CH_4 formation. Despite nearly unchanged higher hydrocarbon yield, the presence of graphitic carbon enhances the chain-growth probability and strongly suppresses olefin hydrogenation. We demonstrate the graphitic carbon slowly deposited on cobalt catalyst during the reaction influences the CO conversion and products distribution in a similar way to that for pre-deposited graphitic carbon. We present that the buildup of graphitic carbon by ^{13}CO facilitates the rate of C–C coupling in terms of the chain-growth probability during the $^{12}\text{C}_3\text{H}_6$ hydrogenation reaction, whose products follow an ASF-type product distribution of the FT reaction. We explain these results by a two-site model on the basis of structure sensitivity of the underlying reaction steps in the FT mechanism: step-edge sites catalyze CO dissociation and chain growth; carbon formed on step-edge sites is either involved in chain growth or migrate to terrace sites, where it is predominately hydrogenated to CH_4 (schematically presented in Fig. 4). Covering the terraces by graphitic carbon also increases the residence time of CH_x intermediates, therefor enhances the chain-growth probability. The occurrence of non-ASF is therefore attributed to the terrace sites that favor CH_4 formation. This two-site model is also demonstrated on silver-promoted Co/SiO₂ catalysts [5]. Characterization shows that mainly coordinatively unsaturated cobalt atoms are substituted at low silver content. Adding more silver results in replacement of both coordinatively unsaturated sites and planar sites, therefore affecting both structure-sensitive CO dissociation and structure-insensitive hydrogenation reactions. Transient experiments reveal that silver addition can accelerate oxygen-removal steps, compensating the negative effect on CO conversion. Our finding presents a possibility of improving the FT performance in terms of long-chain hydrocarbons production without much loss in activity toward CO conversion.

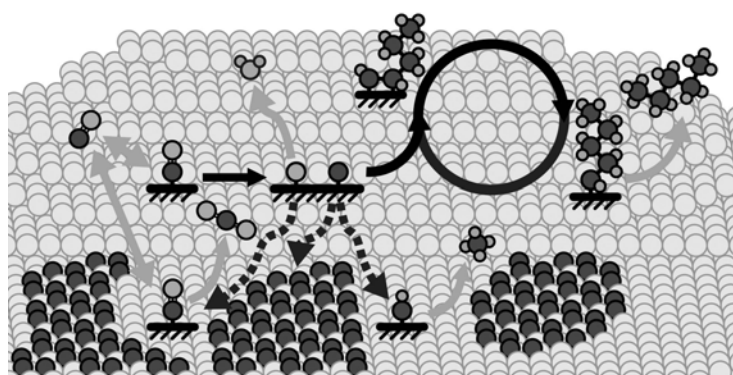


Fig.4. Schematic presentation of the effects of graphitic carbon on cobalt catalyst

These novel observations and the ensuing discussion will sharpen our thoughts on the extremely complex area of Fischer-Tropsch synthesis. We emphasize that the understanding in structure sensitivity of the elementary steps of the FT can help to design improved catalysts.

[1] W. Chen, B. Zijlstra, I.A.W. Filot, R. Pestman, E.J.M. Hensen, *ChemCatChem*, **2018**, 10 (1), 136–140.

[2] W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen, *ACS Catalysis*, **2017**, 7 (12), 8050–8060.

[3] W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, *ACS Catalysis*, 2017, 7 (12), 8061–8071.

[4] W. Chen, T.F. Kimpel, Y. Song, F.-K. Chiang, B. Zijlstra, R. Pestman, P. Wang, E.J.M. Hensen, *ACS Catalysis*, **2018**, 8 (2), 1580-1590.

[5] W. Chen, R. Pestman, F.-K. Chiang, E.J.M. Hensen, *Journal of Catalysis*, **2018**, 366, 107-114.

Extended Abstract: File Not Uploaded

See more of this Session: CO Activation I
See more of this Group/Topical: General Submissions

Follow Us

[LinkedIn](#)

[Twitter](#)

[Facebook](#)

[YouTube](#)

[Flickr](#)

[Slide Share](#)

[About](#) | [Join AIChE](#) | [Global](#) | [Contact](#) | [Advertise](#) | [Tools](#) | [Press](#) | [Privacy & Security](#) | [Code of Ethics](#) | [Sitemap](#) |

Copyright © American Institute of Chemical Engineers. All rights reserved.