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MAX-PLANCK-INSTITUT
FOR DYNAMICS OF COMPLEX TECHNICAL SYSTEMS MAGDEBURG
PROCESS SYSTEMS ENGINEERING
Sandtorstrasse 1 I 39106 Magdeburg I Germany

Prof. Dr.-Ing. habil.
KAI SUNDMACHER
Director

Sandtorstraße 1
39106 Magdeburg
T +49 391 6110-351
F +49 391 6110-353
sundmacher@mpi-magdeburg.mpg.de
www.mpi-magdeburg.mpg.de

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Topic for a Master Thesis

Power-to-Methane: Derivation of a microkinetic model for the CO_2 methanation reaction

Motivation:
Due to the fluctuating availability of solar and wind power, efficient storage technologies are needed for saving surplus energy. For this purpose, one concept is Power-to-Methane. The key idea of Power-to-Methane is to use the surplus renewable energy in order to produce hydrogen via electrolysis of water. Together with carbon dioxide from technical exhaust gases, hydrogen is converted consecutively into methane. The heterogeneously catalyzed methanation reaction ($4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$) can be carried out in wall-cooled fixed-bed tubular reactors. However, due to the high heat release rate of the reaction, the optimal design of these reactors is still in the focus of current research.
For the optimization of fixed-bed reactors, a reliable kinetic model of the reaction is indispensable, like for example that of Koschany et al. [1]. However, due to the assumption of irreversible steps in the reaction network, this reaction kinetic model yields complex reaction rates ($r \in \mathbb{C}$), if conditions, which favor the backward reaction, are present. As a consequence, numerical stability issues are commonly encountered during reactor optimization, as most optimization solvers cannot handle complex numbers.

Problem definition:
The aim of this master thesis is the systematic derivation of a reaction kinetic model for a Ni/Al_2O_3 catalyst in collaboration with Prof. Yablonsky (Washington University in St. Louis and Ghent University). The model should be able to describe the methanation reaction rate for an arbitrary reactant composition in the technically relevant temperature range (250 – 450 °C). The kinetic model is checked for statistical significance and compared to published methanation reaction kinetic models. Based on the developed model, kinetic experiments both for forward and reverse methanation reaction are to be planned in accordance with the methodology described in [4] and [5].

In detail the following points are to be worked on:

- Derivation of a reaction kinetic model for the methanation reaction according to the principles shown in [2] and applied in [3]
- Fitting of the model to experimental data in the temperature range of 250 - 450 °C
- Checking of the model for statistical significance

- Comparison of the kinetic model to other methanation kinetics

Start: Summer / Autumn 2019

Duration: 4-5 months

1st reviewer: Prof. Dr.-Ing. Kai Sundmacher
2nd reviewer: Prof. Dr. Gregory S. Yablonsky
Supervisor: Ronny Zimmermann, M. Sc.

Prior knowledge:
- Basics of chemical kinetics and chemical reaction engineering
- Statistical analysis and optimization
- Dealing with a programming language (preferably Matlab)

Magdeburg, 20.06.2019

Prof. Dr.-Ing. Kai Sundmacher

Prof. Dr. Gregory S. Yablonsky
(Washington University in St. Louis; Ghent University)

References:

[1] Koschany F., Schlereth D., Hinrichsen O. (2016): On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)x, *Appl Catal B-Environ*, **181**, 504-516.
[2] Marin G. B., Yablonsky G. S., Constales D. (2019): *Kinetics of Chemical Reactions*, 2nd Edition, John Wiley & Sons, ISBN 978-3-527-34295-2.
[3] Yablonsky G. S., Pilasombat R., Breen J. P., Burch R., Hengrasmee S. (2010): Cycles across an equilibrium: a kinetic investigation of the reverse and forward WGS reaction over a 2% Pt/CeO_2 catalyst. Part I. Experimental data and qualitative interpretation, *Chem. Eng. Sci.*, **65**, 2325-2332.
[4] Yablonsky, G.S., Constales D., Marin G. (2011): Equilibrium relationships for non-equilibrium chemical dependences, *Chem. Eng. Sci.,* **66**, 111-114.
[5] Yablonsky, G.S., Gorban, A.N., Constales D., Galvita V., Marin G.B. (2011): Reciprocal relations between kinetic curves, *EuroPhysics Letters (EPL)*, **93***, 20004-20007.* http://arxiv.org/abs/1008.1056 [cond-mat.stat-mech].