PhD project proposals to the Einstein Center of Catalysis (EC^2) for a PhD start in Oct. 2023

Title of Project: **New Strategies for efficient Design-of-Experiments for material selection in Heterogeneous Catalysis Research**

Co-supervisor 1: **Prof. Dr.-Ing. Jens-Uwe Repke**
Dynamik & Betrieb techn. Anlagen, TU Berlin

Co-supervisor 2: **Dr. Frank Rosowski**
BasCat, TU Berlin

Abstract:

Research in heterogeneous catalysis relies on a systematic planning to maximize the information derived from a limited number of experiments. Efficient search strategies rely on the so-called Design-of-Experiments (DOE). Aim of the proposed work is the development of new methods for the efficient Design-of-Experiments (DOE) for (A) improved catalyst materials as well as (B) optimal reaction conditions. The proposed DOEs will combine data-driven modelling with micro-kinetic approaches and numerical optimization to incorporate pre-existing chemical knowledge into the planning of experiments. The resulting model-guided search strategies will not only improve the efficiency of catalytic experiments, but provide also data of higher quality and relevance for both research and practical applications.

Extended description version of the project:

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1. Overall goal of the project

The goal of this project is to develop a method for improved Design-of-Experiments, where online predictions of the next best set-points in terms of maximum sensitivity of testing conditions are enabled. Thereby, the experimental effort shall be minimized and the information of the gathered data maximized. This will be done by employing both Machine Learning models as well as theoretically sounder makrokinetic models. Both approaches shall be compared regarding computational efficiency and the quality of their predictions. At first, the development will be carried out for single functional catalyst systems (CZA for CO_2 hydrogenation) using data from a Berty reactor. In a second step, the methodology will be also applied to tandem catalysis systems (CO_2 hydrogenation with methanol dehydration to DME). In a third step, tandem systems for the direct conversion of CO_2 to platform chemicals (e.g., ethanol) will be tested and the developed framework applied to identify promising tandem catalysts.

2. State of the art

Developing new improved catalytic systems for coupled chemo-catalytic reactions faces significant challenges due to inherently high system complexity. Planning experiments that deliver a maximum of information at minimum cost can be guided by appropriate search strategies. So-called Design-of-Experiments (DOE) are formalized ways to formulate these search strategies.
Common DOEs are based on statistical considerations. However, heterogeneous catalysis and the interaction between different active sites are governed by a multitude of complex and often nonlinear relations between material composition, structure, surface dynamics, chemical kinetics, and transport processes. Literature, prior experience and experimental data exist for many reactions and materials of interest. This information can be used to focus the experimental effort. Including domain-specific knowledge is essential in order to do the DOE on regions of interest and highest gain in knowledge in the underlying multi-dimensional search spaces.
The Repke group has built up expertise in the generation and optimization of data driven models [1,2], experimental approaches to study catalytic systems and the analysis of coupled chemical reactions (EC² project “Fundamental experimental investigations on mass transfer between different catalytic centers situated in porous matrices”). Further experience includes data driven models for optimization [3] and the online model-based optimal experimental design [1]. Recent projects pioneer the use of machine learning in chemical engineering (SPP 2331, Co-initiated by Prof. Repke).

BasCat develops catalytic systems for the selective conversion of carbon dioxide (CO_2 + H_2) into valuable chemical feedstock, e.g., ethanol. Related catalysts represent prime examples of complex systems with coupled active sites [4]. Different data-driven workflows were established [5,6]. They can connect information from structure data bases with DFT and machine learning to guide the identification of improved catalysts.

[1] Chemie Ingenieur Technik 92, 2020, 1247-1247. [2] Computer Aided Chemical Engineering 48, 2020, 1189-1194. [3] Computer Aided Chemical Engineering 47, 2019, 311-316. [4] ACS Catalysis 7(11), 2021, 4047-4060. [5] Nature Communications 10, 2019, article # 441. [6] arXiv:2102.08269 [cond-mat.mtrl-sci].

3. Specific aims and how they may be reached:

i) Identify and train ML-models on existing data: In this work-package, the identified approaches from a thorough literature review will be trained to existing data from experiments on CZA catalyst for CO_2 hydrogenation in a Berty reactor. In parallel, makrokinetic approaches will be evaluated on their predictive behavior on the data and if necessary, parameters will be guessed new for the given data, since the original sets of parameters were taken from kinetic studies in a fixed bed reactor in comparison to the data from an ideally mixed Berty here. The two approaches will be compared in terms of CPU-time and interpolation capability.

ii) Develop online implementation on Berty reactor: The development for the online optimal experimental design approach will be carried out on a single reactor system (Berty) at the dbta. Next to the modeling and optimization algorithms, the main challenge will be to create concise data transfer between the process control and the ODE-framework. Moreover, the ODE-framework needs to be CPU-efficient and robust in terms of the results. Also, a strategy for bounding the testing conditions to safe operation windows of the facility needs to be implemented. For the implementation, the inhouse modeling toolbox *MosaicModeling* will be used, preferably utilizing a user-defined language specificator, which embeds analytical model formulations into code, towards python.

iii) CZA doping and screening: In this project, we will want to explore new catalysts for the direct conversion of CO_2 to ethanol by dry impregnation of CZA catalyst material with alkali metals. Wang et al. [7] for example used potassium-doped methanol synthesis CuZnAl catalyst together with an alkene synthesis Na-Fe@C catalyst for the direct synthesis route of ethanol from CO_2. In this project, dry impregnation of commercial CZA will be tried and different designs will be tested. The catalyst will be prepared by members of the BasCat laboratory. The decision which materials should be prepared and if it might be necessary to functionalize the CZA with another site (e.g., Fe colloids) will be based on the literature review. Preliminary screening will be carried out in a 4-fold parallel setup at BasCat.

iv) Test implementation on new catalyst data on 4-fold parallel reactor at BasCat: After the base development for single functional catalysts, the framework also shall be enabled to work for tandem catalyst systems. Here, one big challenge is to characterize promising candidates quickly and also get information on how the design could be changed. Also, an open question is how the framework can handle different catalyst samples in a parallel reactor testing facility. Here, two new strategies will be compared and held against a "traditional" DOE approach. In a parallel testing reactor, the reaction conditions (i.e., feed composition, temperature and pressure) are the same for all samples. The question is, whether it is better to individually test optimal conditions for one sample (and gain non optimal data points for the others) or weigh between all samples and have a trade-off as a next data point.

[7] ACS Catalysis, 11(18): 11742–11753, sep 2021.