Abstract:

Modeling of single and tandem reactions: from kinetic investigations to a general framework to understand catalytic systems

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This project aims to provide a methodology for the interpretation of experimental data of tandem catalytic systems. A mathematical model will be created integrating two single reactions based on kinetic data obtained experimentally over selected operating conditions. This model will aid in the interpretation of experimental catalytic data obtained within UniSysCat. Moreover, it will also serve to estimate the weight ratio of two catalyst functionalities, avoiding hundreds of hours of catalyst screening. The model will be thereafter improved to include (i) deactivation phenomena and (ii) mass transfer limitations of reaction intermediates between active sites. The mechanisms of deactivation will be understood by post-catalytic and in situ characterization performed in cooperation with other EC2 on-going projects. A general methodology to evaluate tandem systems will be constructed, which will guide experimental efforts and rational catalyst design in UniSysCat.

Extended description version of the project:

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1. Overall goal of the project

The main goal of this project is to provide a methodology for the interpretation of experimental data of tandem catalytic systems obtained with heterogeneous catalysts in tubular test reactors. Firstly, kinetic data for the single reactions will be obtained with specific catalysts operating at the kinetic regime over selected operating conditions. Secondly, a mathematical model will be created integrating the two single reactions to be able to predict the performance of a catalytic system. This model will be applied to experimental catalytic data of tandem systems to guide the interpretation of the results. The model will also be used to estimate the weight ratio of two catalyst functionalities, avoiding hundreds of hours of catalyst screening. The model will be thereafter improved to include (i) deactivation phenomena and (ii) mass transfer limitations of reaction intermediates between active sites. The mechanisms of deactivation will be understood by post-catalytic and in situ characterization performed in cooperation with other EC2 on-going projects.

2. State of the art

The coupling of catalytic reactions in a single reactor using more than one catalyst is called orthogonal tandem catalysis. Advantages compared to separated single reactions can be the increase in reaction rates, the improvement of selectivity and energy optimization. Focusing on carbon dioxide hydrogenation, two main routes exist: the CO-mediated [1] and the methanol-mediated routes [2]. Fine tuning of the interparticle distance [3] and use of well-defined nanostructured tandem catalysts [1] have been revealed as crucial factors. Further understanding of the fundamental mechanisms of interaction and deactivation of multi-metallic catalytic systems is necessary to further exploit such systems in heterogeneous catalysis [4].

Within the framework of UniSysCat, the application of tandem catalysts for CO_2 hydrogenation to olefins and paraffins has already yielded promising results. The challenge arises when interpreting the results: the complexity of stablishing the structure-activity correlations for a single reaction is exponentially increased for catalytic systems. A proper design of experiments for a catalytic system should be composed by hundreds of data points, resulting in prohibitive costs for catalyst research. It is mandatory to develop a model-based strategy to support the on-going research within UniSysCat and create a tool to aid researchers in the interpretation of catalytic tests and to enable the estimation of the weight ratio between functionalities.

3. Specific aims and how they may be reached

The objectives of the present project are: (i) to obtain robust kinetic data of the two single reactions that compose a tandem catalytic system and create a mathematical model that integrates the two reactions in a tandem system; (ii) to use the model to help comprehending tandem experimental data obtained within UniSysCat; (iii) to include catalyst deactivation and mass transfer limitations of the tandem system into the model; (iv) to discern the mechanisms of deactivation in cooperation with other EC2 projects; (v) to stablish a methodology to evaluate tandem catalytic data, based on indicators to allow comparison of the integration and the two separate consecutive reactions, and to guide catalyst design.

The working packages (WPs) of the present project are:

WP1. Construction of a mathematical model based on single-reaction kinetic data
WP1.1. Obtaining kinetic data for each single reaction.
Experimental reaction rates at kinetically relevant conditions will be obtained in a parallel 4-fold plug-flow reactor for two systems: (1), composed of (i) RWGS on a CeO_2 catalyst and (ii) FTS over a Co/Al_2O_3 catalyst; and system (2), composed of (i) $CuO/ZnO/ZrO_2$ for CO_2 hydrogenation to methanol and (ii) zeolite for methanol dehydration to DME. Catalysts will be studied at different T, P and reactant composition. Data acquisition will be started after long term equilibration of the catalyst systems. The data will be evaluated and the adequate rate expressions obtained.
WP1.2. Construction of a mathematical model to describe a tandem catalytic system.
The rate expressions for the formation of the relevant intermediates of the tandem reaction will be derived for each individual reaction and integrated into a single mathematical model to enable the prediction of tandem catalytic data. Experimental data obtained within research unit A of UniSysCat will be re-evaluated based on the model predictions. Deviations from the model prediction will be rationalized and the benefits of tandem catalysis compared to consecutive single reactions quantified. The model will further serve as basis to suggest weight ratio between two catalytic functionalities, preventing hours of catalyst screening.

WP2. Extension of the model to include catalyst interaction and mass transfer limitations
Building on the previous WP, the model will be extended taking into account phenomena arising from the interaction of individual functionalities with chemical compounds typically present in the other catalytic reaction or from the interaction of the two functionalities. To account for the first case, kinetic data will be obtained for single reactions co-feeding selected reaction products and intermediates of the system. Spent catalysts will be characterized within UniSysCat to reveal the mechanisms of deactivation. Mass transfer limitations might appear in tandem catalysis compared to single reactions and might explain deviances between tandem experimental data and the model created in WP1 under specific conditions. For these cases, intermediate mass transfer between the two functionalities will be modelled and incorporated into the model.

WP3. Formulation of a methodology to evaluate tandem catalysts.
A general framework to investigate tandem catalysts will be constructed, including a suggestion of DoE, a methodology to construct the kinetic model and a set of factors to aid in quantifying the benefits of integrating two chemical reactions in a catalytic system.

The objectives and methodology here described can be accomplished with the available equipment and expertise in the proposers' groups and the synergies already existing within research unit A: catalyst synthesis will benefit from Bischoff's project (Gurlo group), catalyst testing will be performed in a 4-fold parallel plug-flow reactor setup (BasCat/Rosowski) and operando and post catalytic characterization will be done within the cooperation Schomäcker/Gurlo/Kanngießer (synchrotron and lab-based in situ XRD and XAS) and ZELMI. Moreover, possible further collaborations of the present project are: (i) use of the generated kinetic data for reactor modeling and reactive CFD simulations (Repke group) (ii) generally, the methodology here described can benefit any other project attempting to apply tandem catalysis. Therefore, is of general interest for UniSysCat.

Project-relevant literature (max 5):
(1) Xie, C.; Chen, C.; Yu, Y.; Su, J.; Li, Y.; Somorjai, G. A.; Yang, P. Tandem Catalysis for CO_2 Hydrogenation to C_2-C_4 Hydrocarbons. *Nano letters* **2017**, *17* (6), 3798–3802.
(2) Gao, P.; Li, S.; Bu, X.; Dang, S.; Liu, Z.; Wang, H.; Zhong, L.; Qiu, M.; Yang, C.; Cai, J.; Wei, W.; Sun, Y. Direct conversion of CO_2 into liquid fuels with high selectivity over a bifunctional catalyst. *Nature chemistry* **2017**, *9* (10), 1019–1024.
(3) Mistry, H.; Behafarid, F.; Reske, R.; Varela, A. S.; Strasser, P.; Roldan Cuenya, B. Tuning Catalytic Selectivity at the Mesoscale via Interparticle Interactions. *ACS Catal.* **2016**, *6* (2), 1075–1080.
(4) Zečević, J.; Vanbutsele, G.; Jong, K. P. de; Martens, J. A. Nanoscale intimacy in bifunctional catalysts for selective conversion of hydrocarbons. *Nature* **2015**, *528* (7581), 245–248.