CSC-RUB PhD Project Proposal

Title: Synthesis and characterization of supported metal catalysts applied in catalytic hydrogenation for the synthesis of biofuel and high value chemicals

Sector of research: Industrial Chemistry, Heterogeneous Catalysis

Degree awarded: PhD

Keywords: Heterogeneous catalysis, nanoparticles, hydrogenation

Supervisors of PhD project:

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Research focus of supervisor:

The Laboratory of Industrial Chemistry performs fundamental research in heterogeneous catalysis. The scientific challenge is the elucidation of the reactions on the atomic level and their interplay with the complex surface chemistry of catalytically active solids. The investigated reactions belong to industrial redox chemistry. Reduction catalysis comprises methanol, Fischer-Tropsch and higher alcohol synthesis using syngas (CO, CO_2, H_2) under high-pressure conditions, and the hydrogenation of unsaturated organic molecules. Oxidation catalysis focuses on the selective oxidation of alcohols in the gas phase and in the liquid phase. Recently, we entered the fields of electrocatalysis using carbon-based materials, heterogeneous photocatalysis, and plasma catalysis. Liquid-phase oxidation and electrocatalysis require a deeper understanding of solvation-related phenomena. For the synthesis of catalysts, a large repertoire of methods is available including precipitation, spray drying and chemical vapor deposition. All the necessary routine techniques for bulk and surface characterization are available with a strong focus on sorption techniques including calorimetry. For improving the catalysts, we first study steady-state kinetics. Numerous continuously operated flow set-ups with online GC and FTIR analytics are available, which allow to screen the parameter space efficiently. The role of the various elementary steps is investigated by applying transient kinetic methods such as temperature-programmed reactor operation, dosing pulses and concentration steps, and using isotopes. For these methods we strongly rely on fast online mass spectrometry. In addition, we try to gain as much spectroscopic information as possible using mainly FTIR, Raman and photoelectron spectroscopy.

Publications:

(1) S. Kundu, W. Xia, W. Busser, M. Becker, D.A. Schmidt, M. Havenith, M. Muhler, The Formation of Nitrogen-Containing Functional Groups on Carbon Nanotubes Surfaces: A quantitative XPS and TPD Study, Phys. Chem. Chem. Phys. 12 (2010) 4351-4359.

(2) K. Kähler, M.C. Holz, M. Rohe, A.C. van Veen, M. Muhler, Methanol oxidation as probe reaction for active sites in Au/ZnO and Au/TiO2 catalysts, J. Catal. 299 (2013) 162-170.
(3) Zhao, J. Masa, W. Xia, A. Maljusch, M.-G. Willinger, G. Clavel, K. Xie, R. Schlögl, W. Schuhmann, M. Muhler, Spinel Mn-Co oxide in N-Doped carbon nanotubes as a bifunctional electrocatalyst synthesized by oxidative cutting, J. Am. Chem. Soc. 136 (2014) 7551-7554.
(4) F. Yang, B. Hu, W. Xia, B. Peng, J. Shen, M. Muhler, On the nature of spillover hydrogen species on platinum/nitrogen-doped mesoporous carbon composites: A temperature-programmed nitrobenzene desorption study, J. Catal. 365 (2018) 55-62.
(5) D. Laudenschleger, H. Ruland, M. Muhler, Identifying the nature of the active sites in methanol synthesis over Cu/ZnO/Al2O3 catalysts, Nature Commun. 11 (2020) 3898.

Summary of research plan

Background: Biofuels and chemicals can be synthesized through the hydrogenation of biomass-derived platform molecules using transition metal-based catalysts like Pd. A high atomic efficiency and uniform active sites are essential for the conversion and selectivity of the hydrogenation reactions. Instead of molecular H_2, formic acid can be used as alternative hydrogen donors. Various synthesis parameters can be varied to tune the structure and property of the catalysts, which can subsequently be used to tailor the conversion and selectivity of desired products. Reaction kinetics plays an important role in the industrial application of the catalysts. Various in-situ and operando techniques can be employed in these studies.

Study objective: The aim is to develop efficient hydrogenation catalysts and understand their functioning mechanism as well as reaction kinetics.

Expected Results: The concerned catalysts will be thoroughly investigated from atomic level to textual properties. The performance of the catalysts in hydrogenation will be studied in detail and thus a fundamental understanding of the system can be achieved.

Methods: XPS, TPD/TPR/TPO, in-situ and operando techniques (IR, Raman XRD), flow set-up

Candidate Requirements:

- an excellent master's degree in chemistry or chemical engineering
- solid knowledge of physical chemistry, familiar with catalysis
- a high level of spoken and written English (IELTS band score of 6.5 or higher)

Motivation for CSC application: The successful candidate will be working in a diverse team with all aspect of knowledges from characterizations to kinetic studies in the field of catalysis and material science. Various advanced equipment is available in the lab including NAP-XPS, HRTEM, TPD/TPR/TPO/TPSR, in-situ spectroscopy (IR, Raman), XRD, TG, and various flow setups. We aim to provide students with an international and interdisciplinary platform to conduct high-level scientific research with close cooperation with our industry partners.