CSC-RUB PhD Project Proposal

Title: Activity and Selectivity of Transition Metal Oxides in Different Oxidation Reactions

Sector of research: Industrial Chemistry, Heterogeneous Catalysis

Degree awarded: PhD

Keywords: Heterogeneous catalysis, nanoparticles, transition metal oxides, oxidation

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: Liquid-phase oxidation reactions are traditionally performed with high-valent metal oxides as stoichiometric oxidants, leading to large amounts of metal-contaminated wastes. In the search for oxidation reactions with less ecological impact, catalytic processes using O_2 or peroxides have been intensely investigated in the past decades, relying mostly on noble metals such as Au, Pd, and Pt. Although these metals remain unchallenged in catalytic performance, the scarcity of noble metals makes the catalytic use of first-row transition metal oxides an attractive alternative. The applicability of metal oxides for liquid-phase oxidation was demonstrated for selective oxidation reactions to form aldehydes, ketones, esters, and nitriles from alcohols or alkanes.

Study objective: The aim is to develop efficient oxidation 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 liquid phase oxidation 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), autoclave, flow set-up, reactions under high pressure

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.