XAS under real conditions: Two *in-situ* cells and their applications in homogeneous and heterogeneous catalysis

Roland Schoch, Matthias Bauer
roland.schoch@uni-paderborn.de, matthias.bauer@uni-paderborn.de
(Paderborn University, Inorganic Chemistry, Warburger Straße 100, 33098 Paderborn, Germany)

Introduction: The investigation of catalytic systems *in-situ* or *in-operando* are critical steps on the way to a fully understood catalytic system – not only in X-ray spectroscopy. In most cases, reaction conditions present in the laboratory have to be modified due to practical reasons to allow an implementation of spectroscopic methods like X-ray absorption (XAS). On the other hand, *in-situ* and *in-operando* investigations are indispensable to achieve a complete knowledge about the working principles and the active species of a catalyst. In our contribution, we will present two *in-situ* cells, which minimize deviations from laboratory conditions. One cell is derived from a Schlenk-tube and allows sample handling and reactions under inert atmosphere. The second cell imitates a conventional plug flow reactor, which is often used in heterogeneous catalysis. Usually, very thin glass tubes heated by a gas blower are applied for this purpose, which have significant differing dimensions from the laboratory setup. The dimensions of the cell, which will be presented, are inspired by a laboratory reactor tube. This allows the application of the same amount of catalyst and the same gas flow as apllied in a laboratory experiment.

Experimental methods: The liquid cell is predestinated for the investigation of air and moisture sensitive samples in solution and their reactions. Furthermore, a septum allows the addition of a reactant without injuring the inert conditions – if necessary using a syringe pump to control the addition during measurement. To minimize concentration inhomogeneities caused by reactant addition a magnetic stirring bar is implemented. The cell for heterogeneous catalysis imitates a macroscopic plugged flow reactor and can be heated up to 600°C using a heated filament. For a precise temperature measurement, two thermocouples in front and after the catalyst are placed. As X-ray permeable window a thin boron nitride plate is used. By application of a thermal shield the heat loss on the boron nitride window can be minimized to obtain a homogeneous temperature distribution in the catalyst.

Results: As examples for the applicability of our homogeneous catalysis cell, two systems will be presented. First, the photocatalytic reduction of CO_2 on a Cu-oxidic catalyst will be shown. In this case, the back-window of the cell was replaced, which allowed an illumination of the reaction mixture while XAS was measured in fluorescence mode through the front-window and enables an *in-situ* study of the reaction. Second, an iron catalyzed cross-coupling reaction was carried out. Here, the reactant was added by a syringe pump through the septum of the cell directly in advance of the measurements. This allowed a monitoring of the catalyst activation, which proceed on a very short time scale. The heterogeneous catalyst cell was tested in CO oxidation reaction over iron-based catalysts under reaction conditions. During the measurements, the catalytic performance of the catalyst obtained in laboratory experiments could be reproduced.

Conclusion: With the presented cell for homogeneous catalysis, it is possible to synthesize, handle and investigate air and moisture sensitive samples. Through the opportunity of stirring, the measurement of finely dispersed suspensions and homogeneous distribution of the sample are possible, even after addition of reactants. Through exchange of the backwindow, light-driven reaction can be followed. The cell for heterogeneous catalysis enables the same reaction conditions during the X-ray measurements as present in the laboratory, which allows a direct comparison.

Acknowledgement: SusChEmX FKZ 05K13UK1 (BMBF), BA 4467/5-1 (DFG)