Bridging the “pressure gap” towards high pressures – Elastic neutron scattering for in-situ investigation of catalysts under industrial conditions

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Introduction

Catalyst characterization is usually performed in the pressure range from UHV to ambient depending on the methods used. Linear extrapolation of the catalytic properties over these several orders of magnitude in pressure is often not possible (“pressure gap”), which makes in-situ characterization necessary. Typically, only little information is available about structural dynamics of catalysts at pressures above atmospheric pressure, i.e. in the range, which is important for many industrial processes.

Neutron diffraction is uniquely suitable to close this gap, because thick metallic walls of tubular reactors are almost transparent for neutrons. Thus, such conventional reactors, which allow application of elevated pressures, can be used for characterization of the catalyst bed without the necessity of special beam transparent windows. Using neutrons, information on the crystalline phases present, the crystal structure, structural disorder, crystalline domain size and shape, lattice strain and defect structure of the working catalyst are available from diffraction experiments.

Experimental

For this purpose a continuous flow reactor was designed, which is suitable for reaction temperatures up to 300°C and pressures up to 60 bars (Fig. 1a). Preliminary experiments in the laboratory have shown that the reactor is suitable for catalyst pre-treatment, catalytic reactions and application of special types of specific surface area determination using e.g the reactive-frontal chromatography method (N_2O decomposition) for Cu. Preliminary diffraction experiments with the designed reactor setup were carried out at the high-resolution beamline E9 [1] at the research reactor BER II at Helmholtz-Centre Berlin (HZB).

Results

A prominent example of the aforementioned processes is the synthesis of methanol from syngas. $Cu/ZnO/Al_2O_3$ catalysts are employed in industry and such catalyst delivers stable methanol yield at 250°C and 60 bars for several days on stream also in our reactor. Powder patterns of a reduced $Cu/ZnO/Al_2O_3$ catalyst were acquired at 250°C

under ambient pressure and 50 bars static deuterium atmosphere. The diffraction pattern showed that the signature of the Cu-phase is strong enough to give detailed results required (Fig. 1b).

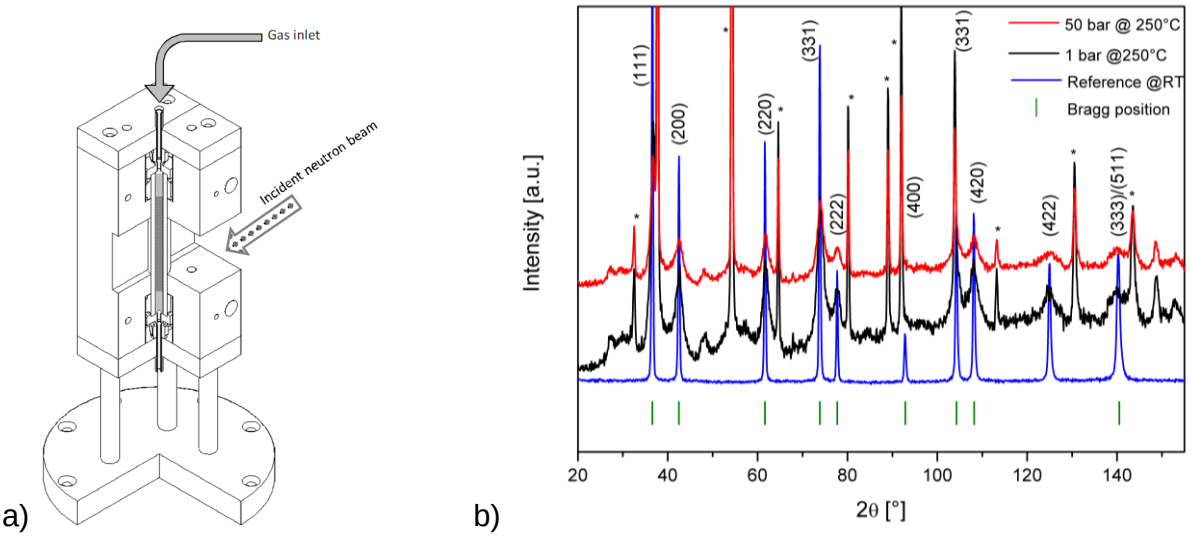

Figure 1**:** Pattern of $Cu/ZnO/Al_2O_3$ catalysts in 1 bar (black) and 50 bar (red) D_2 at 250°C. Copper reference (blue) was measured at ambient conditions in a non-scattering containment. Sharp reflections ‚*' are due to the crystalline Al reactor walls, non-marked peaks are due to ZnO.

Even though these catalysts have been used for a long time in industry, the nature of the Cu/ZnO "synergy" and structure-activity relationships in this system are still not fully understood. A dynamic wetting/de-wetting and alloying effect of Cu-ZnO is discussed to be responsible for formation of the active state of Cu under reaction conditions, i.e. in a strongly reducing atmosphere at high pressures [2]. Studying the evolution of structural (lattice constant, texture) and microstructural (domain size, lattice strain, defects) features [3] of active $Cu/ZnO/Al_2O_3$ catalysts with in situ experiments are essential to deconvolve static and dynamic effects which contribute to the activation and deactivation of the catalyst. The patterns in Fig. 1b show that enough Cu reflections are available for whole powder pattern fitting and line profile analysis of $Cu/ZnO/Al_2O_3$ catalysts under in-situ conditions. In our contribution, we will present first results of the in-situ methanol synthesis measurements scheduled for October/November 2010 at the high-flux beamline D1B [4] at Institute Laue-Langevin (ILL).

References

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