

In situ characterisation of catalysts without compromising process conditions

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Reactor engineering is an integrated part of applied catalysis research and should go hand in hand with catalyst development. However, when combining experiments for simultaneous acquisition of *in situ* characterisation and kinetic data, several compromises in reaction cell design and reaction conditions have to be made in order to meet the minimum requirements for both the reaction and the characterisation technique(s). Whereas good experimental practice guidelines are well established for catalyst testing,ⁱ it is often challenging to fulfil these when performing *in situ* experiments.

The design of *in situ/operando* synchrotron X-ray experiments for combined characterisation and kinetic studies is frequently optimised towards the characterisation perspective, while the reactor optimisation is commonly ignored.ⁱⁱ The need for intrinsic kinetic information dictates that combined studies should be designed to eliminate heat and mass transfer limitations (differential reactor approach), and to include accurate temperature determination. The design is further complicated when the reaction, due to experimental restrictions, has to be downscaled into low-volume *in situ* cells and thus interfering with reactor design. In particular, wall effects, pressure drop, dead volumes, and flow characteristics should be taken into account. The frequent use of integral fixed-bed reactors (FBR) usually introduce gradients along and in the transverse of the reactor and create spatial distribution of reactants, products and intermediates as well as temperature gradients. Validation of the kinetic data obtained in miniaturised systems should be a compulsory part of *in situ/operando* characterisation studies.^{iii,iv,v}

There are ways to ensure that meaningful kinetic data are being collected. In this talk the most common diagnostic tools and guidelines for experimental catalyst testing practice will be presented. Various aspects of beamline development in connection with *in situ* catalyst studies will also be discussed, and examples from a combined *in situ* XAS/XRD/Raman set-up at the Swiss-Norwegian Beamlines (SNBL) designed to operate at 20 bar pressure and high temperatures, while simultaneously monitoring catalyst activity, will be used to highlight the need for good kinetic experimental practise.^{vi,vii}

The information obtained from combined XAS-XRD-Raman experiments on Fischer-Tropsch synthesis catalysts and other reactions will be used as examples. Experimental challenges and data acquisition and analysis strategies to enhance sensitivity and to minimise compromises will be discussed. The *in situ* set-up has for example been used for modulation enhanced XAS where the catalysts are being exposed to periodic changes in reaction environment. Such *in situ* experiments enhance the sensitivity of the technique, but generate large amounts of data which require new strategies for data analysis. The application of multivariate curve resolution (MCR) applied to large data sets from *in situ* X-ray absorption spectroscopy experiments. The results show that the information extracted from MCR goes well beyond the information from conventional XAS experiments. A rapid 2D CMOS detector allows for XRD acquisition on the same time-scale as for XAS (5-10 sec). Additional measurements using *in situ* ASAXS and

FT-IR on the same catalysts at similar conditions provide comprehensive information on the state of catalysts during Fischer-Tropsch synthesis. The combination of techniques allows all involved catalyst phases to be monitored at the different stages of the process at industrially relevant conditions.

References

- ⁱ C. Perego, S. Peratello, *Catalysis Today* 52 (1999) 133-145
- ⁱⁱ N.E. Tsakoumis, A.P.E. York, D. Chen, M. Rønning, *Catal. Sci. Technol.* 5 (2015) 4859-4883
- ⁱⁱⁱ F. C. Meunier, *Chem. Soc. Rev.*, 2010, 39, 4602–4614
- ^{iv} J.-D. Grunwaldt, J. B. Wagner and R. E. Dunin-Borkowski, *ChemCatChem*, (2012) 62–80
- ^v B. M. Weckhuysen, *Chem. Commun.* (2002) 97–110
- ^{vi} W. Van Beek, O.V. Safonova, G. Wiker, H. Emerich, *Phase Transitions*, 84, 8, 726-732, 2011
- ^{vii} M. Rønning, N.E. Tsakoumis, A. Voronov, R.E. Johnsen, P. Norby, W. van Beek, Ø. Borg, E. Rytter, A. Holmen, *Catal. Today*, 155 (2010) 289-295