

Homogeneous catalysis and X-ray spectroscopy: Methods, timescales and perspectives

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Although not as prominent as investigations on heterogeneous catalytic systems, X-ray spectroscopy offers also many powerful techniques in order to study homogeneous systems, in particular with regard to *operando* combination with other spectroscopic methods. Such methodical combinations have several advantages: they allow to study different *spacial* regions of the system, like the catalytic metal center, its electronic and geometric structure as well as coordinating ligands and their time-dependent chemical changes.

But moreover they can provide complementary information in different *time* regions in the behaviour of the system. While for examples investigations of the geometric structure by extended X-ray absorption fine structure spectroscopy (EXAFS) require at least some minutes, product formation kinetics can be followed in course of the EXAFS measurements by Raman spectroscopy with a time resolution of some seconds.

Particularly, X-ray absorption spectroscopy (XAS) offers several experimental set-ups to approach the different time-scales needed to study homogeneous catalytic reactions of various experimental requirements. This will be demonstrated with the discussion of different reactions, starting from an iron-catalyzed Michael addition reaction, where static and *operando* EXAFS in combination with Raman spectroscopy allowed to identify details of the mechanistic cycle, as well as to explain the different reactivities of the pre-catalysts FeCl_3 and $\text{Fe}(\text{ClO}_4)_3$.^[1,2]

The investigation of the CeCl_3 -catalyzed hydroxylation of diketons with molecular oxygen by combined *operando* Quick-EXAFS/UV-Vis measurements required the design of a new set-up that allows experiments under a defined gas atmosphere. In contrast to the first example, different reaction pathways in dependence of the applied reactant could be identified and the role of Ce(IV) was elucidated by this spectroscopic combination.^[3,4]

Further reduction of the time scale was necessary to study the copper catalyzed Kharash-Sosnovsky reaction, in which hydrocarbons are oxidized to esters. The oxidation states of copper and their time-dependent fate were studied by stopped-flow dispersive-XAFS measurements at ID24, and first results will be presented here.^[5]

Finally, results of *in-situ* RIXS (Resonant Inelastic X-ray Scattering) and XES (X-ray Emission Spectroscopy) experiments of the mentioned reactions^[6] will be presented and the potential of these methods for investigations of homogeneous reactions and time-dependent studies will be critically discussed.

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