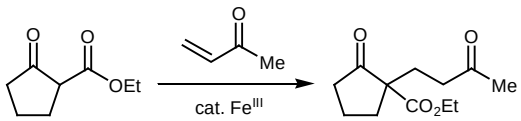
The combination of EXAFS, UV-Vis and Raman spectroscopy for investigations of Homogeneous reactions

M. Bauer, H. Bertagnolli

Although XAFS spectroscopy can presently be almost considered as standard method for structural characterization in solution, its use for the investigation of homogeneous metal catalyzed reactions is limited. Its property of averaging over all present species makes the identification of different compounds in catalytic solutions difficult. Especially such of small concentrations can not be detected due to this effect, although they might present the catalytically active species. Nevertheless, the structural information provided by XAFS spectroscopy is needed to achieve a detailed picture of catalytic systems. Thus a combination of XAFS UV-Vis and Raman spectroscopy can be used to obtain complementary information about the compounds present in the reaction mixture.

As an example of this combination, the Iron(III) catalyzed Michael addition reaction was studied and the results will be presented. In this reaction, a β-dicarbonyl compound (DC) is added to a α,β-unsaturated ketone catalyzed by Iron(III) salts. The overall reaction is shown below:



With $Fe^{III}(ClO_4)_3$ instead of $Fe^{III}Cl_3$ as catalyst an increased reaction rate is found. With XAFS spectroscopy, this fact was found to be due to the formation of complex $[Fe^{III}Cl_4]^-[Fe^{III}(DC)_2(H_2O)_2]^+$. Both parts of the complex could be identified with UV-Vis and Raman spectroscopy and prove the results of the EXAFS investigation.

The results of this study stimulated the construction of a cell for *in-operando* investigations of reactions under real conditions. Here, the simultaneous recording of XAFS and UV-Vis spectra offers two advantages: additional information on the structure of the present compounds can be obtained and the chemical stability of the solution during longer EXAFS scans can be monitored by UV-Vis spectroscopy. For this purpose, a energy dispersive UV-Vis spectrometer with an acquisition time of milliseconds is used. The ecological important hydroxylation reaction of diketones with molecular oxygen catalyzed by Cerium(III) serves as a model reaction to demonstrate the potential of the setup.