Catalysts in Action: Advances in X-ray Spectroscopy Providing New Insights Faster

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Introduction and Objectives

X-ray Absorption spectroscopy (XAS) is a technique for detailed structural and electronic characterisation of materials. Its strengths include the ability to perform experiments in situ/operando (variable temperature and pressure) and time-resolved. The technique is element specific and it does not require long-range order so amorphous systems and solutions can be studied, which makes it a powerful techniques in catalysis. New technique developments are centred on increased energy resolution and thereby increased information content as well as increased time-resolution. The techniques are developed as tools in single site and homogeneous catalysis, where the use of XAS is still very limited.

Results and Discussion

So far, XAS has been mainly used to obtain a structural picture whereas the electronic structure is often poorly understood. Moreover, the major disadvantage of XAS is that it determines an average of all the different structures present, as such complicating the analysis and interpretation. New developments in XAS using new instrumentation and data acquisition methods while selecting specific x-ray energies provide more detailed electronic information as has been feasible so far [1,2]. The charges on and bonding between atoms can now be visualised and their distribution and orientation studied, creating ultimately a 3-dimensional electronic picture or movie of the material. In catalysis insights in the changing electronics of active sites is obtained, which is not available from any other method (see figure 1). Theoretical simulations are currently being developed.

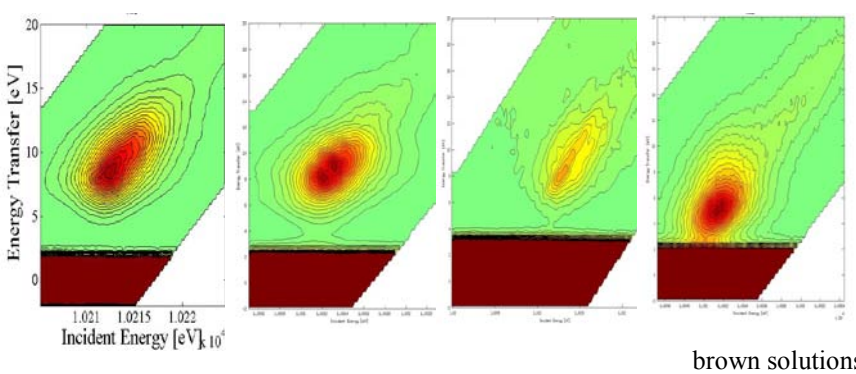

Figure 1. W L_3 Valence band RIXS on W organometallic systems during metathesis. Whereas only C and N atoms are interchanged, EXAFS provides limited information. UV-Vis is not accessible for these brown solutions.

At the same time, fast moving monochromators and energy dispersive acquisition methodologies have enabled the study of catalytic systems down to the millisecond time scales and reaction mechanisms have been obtained. For example, time-resolved XAFS in combination with UV-Vis has allowed detailed characterization of homogenous reaction intermediates in situ and time-resolved, making it a powerful tool in revealing reaction mechanisms [3,4]. For many catalytic systems, this time resolution is sufficient for the information required. However, an even higher time resolution is required when one wants to investigate photochemical or photocatalytic systems, as well as formation of some catalytic intermediates. The activated or intermediate states in general have life-times of picoseconds to nanoseconds. Using new detector developments in combination with an energy dispersive data acquisition approach, XAS spectra down to a time resolution of 10s of picoseconds have been obtained [5] (see figure 2).

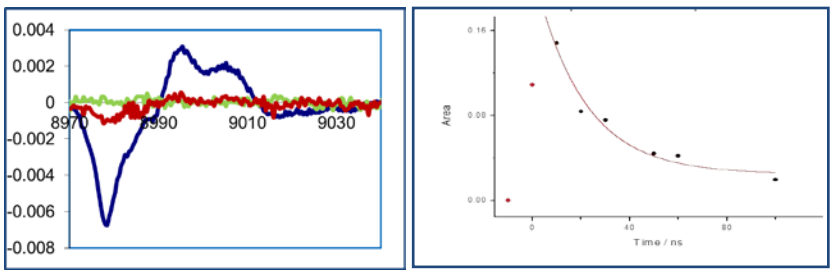

Figure 2. Differential Cu K edge XANES on photoactivated system (left) and decay activated state in time (right).

Conclusions

These novel XAS techniques, both theory and instrumentation, are currently being developed and applied to catalytic systems. The properties and catalytic performance of homogeneous (and heterogeneous) catalysts are studied during their synthesis and activity, with a combination of complementary (spectroscopic) techniques. The influences of different ligands and/or supports on the structural and electronic properties of the active site are investigated. Detailed insights in reaction mechanisms are obtained. Ultimately, a combination of fast time-resolved RIXS is pursued.

References

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