Probing Active Species in Catalysis – Application of Advanced X-ray Techniques

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Detailed information on the structural and electronic properties of a catalyst or material and how they change during reaction is required to understand their reaction mechanism and performance. An experimental technique that can provide structural as well as electronic analysis and that can be applied in situ/operando and in a time-resolved mode, is X-ray spectroscopy. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is powerful in determining the local structure of compounds including amorphous materials and solutions, since long-range order is not required. Combined X-ray Absorption and X-ray Emission spectroscopy (XAS and XES resp.) provides detailed insights in the electronic properties of a material. Detailed information about the materials in their dynamic chemical active environment can thus be obtained and structure/electronic – performance relationships and reaction mechanisms derived. A combination of spectroscopic techniques (e.g. UV-Vis, IR) gives complementary information about the system under investigation.

Over the last years, different approaches have been reported to allow operando time resolved XAS on catalytic systems, mostly solid-gas. Our group has also developed stopped-flow methodologies allowing simultaneous time-resolved UV–Vis/XAS experimentation on liquid systems down to the millisecond (ms) time resolution [1]. Low X-ray energy systems (light elements) or for low concentrated systems, longer XAS data acquisition times in fluorescence detection are required and therefore a stopped flow freeze-quench procedure has been developed [2]. Pushing the time-resolution has been achieved by synchronizing the synchrotron bunches with an optical laser in order to perform fast pump-probe experiments [3].

Developments in XAS using new instrumentation and data acquisition methods while selecting specific X-ray energies provide this more detailed electronic information [4]. High energy resolution XAS, XES and Resonant Inelastic X-ray Scattering (RIXS) provide very detailed electronic information on the systems under investigation. The secondary spectrometer design also opens up lab based spectrometer designs as will be demonstrated.

The methodologies and instrumentation have been developed and applied to a wealth of materials science, for homogeneous and heterogeneous catalysis to batteries and fuel cells as well as art objects. In this lecture, several examples will be given with an emphasis on homogeneous and heterogeneous catalysis, providing insights in active/activated species and reaction mechanisms.

References

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