Synchrotron radiation techniques in materials and environmental science

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1. Introduction and summary

Synchrotron-based techniques have had, over the last 30 years, a major and profound effect on the study of complex materials and on environmental science. Their ability to obtain accurate information at the atomic and molecular level on both local and long-range structures, together with the increasing ability to undertake time-resolved structural studies, has transformed our understanding of several key classes of functional material, while their power as analytical probes has a major influence on aspects of environmental science. Beamlines at the Diamond Light Source continue to make a major contribution to these fields, which are briefly reviewed in this article and which are clearly exemplified in the papers of Tromp [1] and Burke et al. [2].

2. Materials chemistry

The science of advanced functional materials is a rapidly growing area of current chemistry and physics and increasingly concerns complex and often multi-phase systems with extensive disorder, if crystalline, but which are also commonly amorphous. Knowledge of structure and structural changes during operation is increasingly necessary if materials performance is to be optimized. Synchrotron radiation (SR) techniques have played a pivotal role in this field over recent decades, where the following aspects have been particularly important:

(i) The ability of X-ray spectroscopy (XAS) to give accurate information about the local environment of specific atom types (often impurities/dopants)—now a major area in structural materials science and exemplified by early work on both crystalline [3] and amorphous systems [4].
Figure 1. Active site in iron molybdate catalyst. The left-hand side shows a side and top view of the $\alpha$-Fe$_2$O$_3$ (0001) surface. Different initial adsorption sites (from A to E) for the MoO$_3$ molecule are shown; the rhombohedron represents the surface unit cell. The drawn plane, on the side view and on the right-hand-side picture, marks the position of the semi-transparent oxygen ions shown in the left-hand picture. On the right-hand side is presented the relaxed structures for the different adsorption sites. Energies are based on DFT calculations on the relaxed surface for different absorption sites. Site D is not shown since it adopts either structure A or structure B. Red, brown and violet spheres denote oxygen, iron and molybdenum, respectively. Energies are in kJ mol$^{-1}$. The calculated structure accords well with EXAFS data. (Online version in colour.)

(ii) The role of SR-based diffraction, where powder techniques (XRD) are now used routinely in solving complex crystal structures using Rietveld refinement and where microcrystalline single crystal diffraction has allowed highly accurate structures to be obtained for samples which were previously inaccessible to single crystal techniques [5].

(iii) Stemming from the above developments, the combined use of XAS and XRD to obtain, simultaneously, both local and long-range structural information, which has had a major impact in several fields, especially catalytic science [6–8]. Multi-technique measurements have now been extended to include a variety of additional spectroscopies, especially IR and Raman [9–14].

(iv) The growing capability of time-resolved studies using all of the above techniques, with very rapid data collection being possible with energy dispersive XRD (EDXRD) [15,16].

(v) The use of ‘in situ’ and increasingly ‘in operando’ techniques to monitor structural and structural changes during the real operating environment of a material. These methods have again proved particularly effective and powerful in catalytic science [9,10,14].

(vi) The rapidly developing field of tomography, which allows compositional changes and movements to be monitored again increasingly with in situ techniques [9,10].

(vii) The use of small angle X-ray scattering (SAXS) techniques (frequently in conjunction with wide angle (WAXS) methods) in characterizing nanostructures and in following crystal nucleation and growth processes [17,18].

The field also benefits from many other SR techniques, including spectroscopic methods in elucidating electronic structure and the powerful battery of SR-based surface science techniques. The field has also profited from interaction with computational modelling whose increasing ability to develop accurate models of complex systems at the atomic and molecular levels is frequently of great assistance in interpreting experimental data.

As we have commented, SR techniques have proved especially powerful in catalytic science. The article of Tromp [1] gives a number of elegant examples of how XAS techniques, in conjunction with other spectroscopies, have given atomic-level insight into the operation of predominantly homogeneous, industrial catalytic systems. Recent examples of the power of these techniques are also shown by the work of Brookes et al. [19], who have used XAS to probe the widely used iron–molybdate heterogeneous catalyst (used in the selective oxidation of methanol to formaldehyde, which is of significant industrial importance) and with input from computational modelling have developed a model, shown in figure 1 for the active site of this widely studied system, which comprises an MoO$_3$ formula unit supported on Fe$_2$O$_3$. 
Recent years have also seen exciting developments relating to applications of imaging techniques in catalytic science. Indeed, the technological advances made in recent years at modern third-generation synchrotron sources regarding the delivery and detection of high-energy X-rays have resulted in nothing less than a revolution in terms of what is now achievable in terms of time and spatial resolution, and even the combination of the two. This has led to the realization of what has recently been termed five-dimensional imaging (i.e. following the changes in XRD patterns or XAS spectra from within the three spatial dimensions of a solid sample and time) of functional materials so as to be able to understand the significance of spatial variation (at the micrometre scale) in physico-chemical properties (composition) and how this impacts on the overall properties/sample performance [9]. While much of this research originates from the European Synchrotron Radiation Facility [9,20,21], there have been recent developments at the microfocus spectroscopy beamline I18 at the Diamond Light Source, which has the particular advantage in being able to record $\mu$-XAS/$\mu$-XRF and $\mu$-XRD (in principle simultaneously). This has been used, for example, to understand trace-metal poisoning by V and Ni leading to the selective destruction of the catalytically active crystalline zeolite component in an individual fluid catalytic-cracking catalyst particle and more recently the nature and distribution of Pt-clusters and Mo-promoters in catalysts used for liquid-phase hydrogenation [22,23], as illustrated in figure 2. Synchrotron-based techniques have also been able to contribute to our understanding of subtle structural changes taking place during the synthesis and preparation of catalytic systems. An interesting example is provided by the recent work of Martis et al. [24], who used both high-resolution powder diffraction (employing beamline I11 at the Diamond Light Source) and high-energy XRD, total scattering (using beamline BL04B2 at the Spring8 source) to examine the structural modifications taking place in micro-porous cobalt alumino-phosphate catalysts after synthesis. These catalysts are synthesized hydrothermally using organic templates which are occluded within their micro-pores. The organic material must be removed by calcination before

Figure 2. Chemical map of Pt species (coloured green at the sample periphery) and Mo species (coloured blue in the sample core). XANES measurements suggest the Pt species to be a mixture of fcc Pt clusters, PtO and PtCl2 while only one Mo species (Mo7O24 6+) is found. (Online version in colour.)
the catalyst can be used. This detailed study was able to follow the structural modifications taking place during the calcination and to show how these changes were affected by the distribution of transition metal ions in the framework of the material.

The capabilities exemplified by applications to catalytic systems are, of course, exploited in other areas of chemistry and materials science, including, for example, materials for applications in energy and electronics technologies. And the power of these techniques will continue to grow with new sources and developments in instrumentation.

3. Environmental science

The article of Burke et al. [2] very clearly shows the substantial and growing role of SR techniques—especially those available at the Diamond Light Source—on Earth and environmental science. The availability of X-ray microprobes to map the speciation of elements in the environment has had major impact. But the field makes use of a broad range of SR techniques and allows significant applications in investigating the distribution of toxic contaminants in mining waste and effluent and in monitoring radioactive elements in nuclear waste storage facilities. A broad range of environmental applications concerns the monitoring of trace element cycling in the environment and of processes including weathering and precipitation. The field has also embraced the exciting area of bio-mineralization of, for example, calcium carbonate. Rapid growth in the use of SR probes in environmental and Earth sciences can be anticipated in the future.

4. Perspective

Synchrotron-based experiments in general and the facilities developed at the Diamond Light Source in particular have had a major and increasing impact on a broad range of materials and environmental science, where their ability to probe complex systems under operating and often hostile conditions provides unique and crucial information. Future developments will lead to increases in the precision and focus of these probes and extension of their ability to operate under a wide variety of conditions. Combination of SR with other spectroscopic probes will also extend the power of this exciting field.

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References

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