Catalysis seen in action

Moniek Tromp†

Characterisation in Catalysis, Department of Chemistry, Catalysis Research Center, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching bei München, Germany

Synchrotron radiation techniques are widely applied in materials research and heterogeneous catalysis. In homogeneous catalysis, its use so far is rather limited despite its high potential. Here, insights in the strengths and limitations of X-ray spectroscopy technique in the field of homogeneous catalysis are given, including new technique developments. A relevant homogeneous catalyst, used in the industrially important selective oligomerization of ethene, is taken as a worked-out example. Emphasis is placed on time-resolved operando X-ray absorption spectroscopy with outlooks to novel high energy resolution and emission techniques. All experiments described have been or can be done at the Diamond Light Source Ltd (Didcot, UK).

1. Introduction

(a) Catalysis

A catalyst is a material which increases the rate, by lowering the activation energy barrier, of a chemical reaction without being consumed itself (e.g. [1]) (e.g. https://www.youtube.com/watch?v=UxEnhPdHipU). It can change the reaction mechanism and can direct the reaction to form desired products specifically. Our daily life as it is now, with the products and materials we use, would not exist without catalysis. In fact, over 90–95% of all commercial chemical processes use one or more catalysts. Perhaps the most well-known catalyst example is the catalyst in our car: it converts toxic exhaust gases from the engine into more environmentally friendly gases. Large industrial processes for bulk chemicals use heterogeneous catalysts to, for example, synthesize nitric and sulfuric acids. The fine chemical industry, like the pharmaceutical, fragrance and flavour industry, uses highly specialized homogeneous catalysts to produce the required medicines or perfumes. A small deviation in the product contents (molecular formula)
or structure can result in the production of toxic rather than healing compounds or stinking rather than nice-smelling liquids, emphasizing the importance of catalytic selectivity. And of course also in our own body many catalysts are at work, the so-called enzymes.

Different types of catalysts are distinguished. First of all, a distinction is made based on aggregation state/phase of the reactants and the catalyst. In homogeneous catalysis, the reactant and catalyst are in the same phase, for example, liquid. In heterogeneous catalysis the reactant and catalyst are in different phases, e.g. solid and gas, or solid and liquid, etc. Further catalyst groupings are based on specific types of catalysis, like biocatalysis (mostly enzymes), organo-catalysis (no metal site present) and electrocatalysis (redox catalysts in battery and fuel cell applications).

(b) Characterization

In order to understand the specific catalyst properties, i.e. their detailed structure and electronics, and how they change during reaction are required to understand their exact functionality and derive reaction mechanisms. Only a full understanding of these parameters allows the further rational development of catalysts and process conditions in order to make them more environmentally sustainable. Many characterization techniques are possible, depending on the system under investigation. To allow information to be obtained under realistic conditions, during their function, operando approaches are required, preferably time-resolved to probe (catalytic) reaction intermediates. These require development of appropriate techniques and instrumentation. Here, the focus is on spectroscopic techniques, to make ‘pictures and movies of catalysts and chemical systems’. In principle, the entire energy spectrum available can be used.

A synchrotron, like the Diamond Light Source Ltd (Didcot, UK), provides a wide energy range, enabling different system properties to be investigated: all the way from photon energies of $10^{-3}$ eV (corresponding to wavelengths of approx. $10^{-3}$ m, which is similar to the dimensions of a biological cell) to approximately $10^{5}$ eV (wavelength of approx. $10^{-11}$ m, i.e. the atom size ranges). The advantage of doing spectroscopies at a synchrotron is the high beam intensity, flux and the tunability of the beam (energy, size and polarization).

Characterization of the active metal site or reaction intermediates is often limited by the properties of the complex or technique, providing only ex situ information or on selected parts of the molecule only. For example, nuclear magnetic resonance (NMR) can provide structural and electronic information, but only ex situ on reaction quenched samples, with its complex in certain geometries, and are difficult/impossible in the case of paramagnetic compounds. Infrared and UV–visible (UV–Vis) spectroscopy can give time resolved in situ information, but only on specific vibrations or electronic transitions, respectively. Especially in catalysis, X-ray absorption spectroscopy (XAS) techniques (e.g. [2]) are of great interest as they can provide detailed structural and electronic information on a system, without requiring long-range ordering of the system (crystal structures), hence amorphous powders as well as liquids/solutions can be measured. Moreover, synchrotron X-ray beam properties allow in situ/operando, i.e. at real catalytic conditions (variable temperature and pressure) in its application in, for example, industry, and time-resolved experiments to be performed. As with any other techniques, XAS has a disadvantage in that it is a macroscopic technique, providing an average of all structures in the sample under investigation, which of course complicates the analysis and interpretation. Therefore, complementary techniques are often applied simultaneously. At the same time, developments making XAS more selective are underway (vide infra).

While XAS and related techniques are used extensively in the field of heterogeneous catalysis [3], its application in homogeneous catalysis is still very limited, despite its high potential. In this contribution, we will focus on a few selected examples in homogeneous (liquid phase) catalysis, showing the promise of the techniques in this field. The homogeneous catalysts are preferred, from a spectroscopic point of view, because all catalyst molecules are the same at the start of the reaction, with one single well-defined catalytically active site. The molecules can be synthesized in a controlled manner and the structural and electronic properties of the active centre modified...
by changing the type of atoms and the overall structure around it, i.e. ligand modification. This allows these catalysts to be very selective towards desired products and hence find most of their use in the fine chemical or specialty chemicals industry. Here, we will present recent examples of new XAS techniques applied in homogeneous catalysis.

2. X-ray absorption spectroscopy

A characterization technique that provides detailed structural and electronic information on the working catalytic system during the catalytic reaction, i.e. in situ/operando and in a time-resolved mode, is XAS. The extended X-ray absorption fine structure (EXAFS) part provides the structural information (local geometry; type and number of neighbours, distance and disorder). The electronic information is reflected in the X-ray absorption near edge structure (XANES) part of the spectrum, which directly probes the unoccupied density of states of the sample under investigation.

EXAFS spectroscopy is powerful in determining the local structure of compounds including amorphous materials and solutions, as long-range order is not required. Detailed information about the catalysts in their dynamic chemical active environment can thus be obtained and structure–performance relationships and reaction mechanisms can be derived. Moreover, a combination of spectroscopic techniques (e.g. with NMR, UV–Vis, IR) gives complementary information about the system under investigation. The combination is attractive experimentally, and sometimes essential, as XAS, in general, is a macroscopic technique, probing an average of all structures in the sample (and thus actor and spectator species). Despite its strengths as a characterization technique, its use in homogeneous catalysis so far has been very limited, possibly due to the difficulties in data analysis [4].

(a) Time-resolved X-ray absorption spectroscopy

In a conventional scanning transmission or fluorescence data acquisition set-up, the data acquisition times for a full XAS (XANES and EXAFS) scan range from seconds to hours, depending on the element and concentration under investigation. Time-resolved XAS can be performed using two different acquisition methods, i.e. using a fast moving monochromator scanning through the energy range (QEXAFS) or an energy dispersive mode (EDXAS) [5]. The first can be used for either transmission or fluorescence detection, while the latter is limited to transmission, which requires higher concentrations of reactants, but enables faster time resolution. Over the last years, a few different approaches have been reported. Our group has developed stopped-flow methodologies allowing simultaneous time-resolved UV–Vis/XAS experimentation on liquid systems down to the millisecond (ms) time resolution [6].

The stopped-flow set-up is based on a commercially available stopped-flow system (SFM400/QS, Biologic, France). A schematic, including the XAS and UV–Vis techniques, is given in figure 1. The four syringes can be filled with solvents and solutions which, using the computer controlled motors, inject these via delay lines and mixers into an observation cuvette. Depending on the element and its concentration, different cuvettes with different path length are used (also the path lengths for the XAS and UV–Vis techniques are different because of their differing sensitivity). The overall dead time of the system (from syringe to observation cuvette) is approximately 3 ms. The standard instrument allows experiments at ambient conditions. For air and moisture sensitive systems, such as the Mo and Cr which are described below, the entire stopped flow can be connected to a Schlenk line under an argon atmosphere.

While the time-resolved X-ray transmission method has been proven for homogeneous Ni and Cu systems, elements with lower mass have even lower K-edge XAS energies at which the solvent, reactants (and even air) are highly absorbing and complicate or prevent the transmission experiment. For these low X-ray energy systems 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 [7]. This methodology maintains the time resolution of the
stopped flow (ms), but freeze-quenching reaction intermediates (in less than 1 s) to allow long fluorescence EXAFS data to be collected. The freeze-quench method is based on a freeze-quench XAS measurement cell, i.e. a Kapton capillary, attached to the stopped flow. The capillary is mounted into a custom holder attached to the BioLogic freeze-quench accessory and allows direct injection of the reaction mixture into the tube, which is sealed at one end and immersed into liquid nitrogen (before and during injection), directly freezing the mixture at 77 K. Different delays in the stopped flow allow the accurate timing of reaction intermediates. For the XAS measurement, the tube with frozen sample is transferred to a holder in the X-ray beam and cooled throughout the experiment using a Cryostream (100 K). Both the time-resolved and the freeze-quench methods have been successfully applied to 3d as well as 4d and 5d transition metal (TM) systems (Pd [8], Cu [6], Re [9], Mo [7], Sc [10] and Cr [11]).

3. Selective oligomerization

Most oligomerization processes produce a mathematical distribution of polymer lengths, a so-called Schulz–Flory distribution (typical chain lengths between C4 and C40). The industrial demand for C4, C6 and C8 is however growing more rapidly than for other polymer length chains. Selective processes, producing only these polymers or the polymer of interest, are therefore required. The selective trimerization and tetramerization of ethene to produce the linear alpha-olefins (LAOs) 1-hexene and 1-octene, respectively, are of major significance due to the importance of these co-monomers in the production of linear low-density polyethylene, which accounts for approximately 50% of the LAO co-monomers produced industrially (see [12] and references therein). A variety of TM catalysts, most of which are based on early TMs such as titanium, tantalum or, most importantly, chromium, can facilitate this type of selective oligomerization. By using a Cr(III) pre-catalyst with ethene in the presence of methylaluminoxane (MAO) as co-catalyst, an extremely high selectivity can be obtained (see [12] and references therein).

Chromium forms the basis of several key industrial catalysts for the trimerization of ethene, including the Phillips pyrrolide system, the Sasol mixed heteroatom systems and the BP diphosphine systems. The extremely high selectivity for 1-hexene is thought to occur via a mechanism based upon a metallocyclic intermediate [13] formed through reaction of Cr(III) pre-catalysts with ethene in the presence of a MAO co-catalyst. Although there are a lot of studies in the literature on the mechanism and possible intermediates, there is no proof for the cycle and especially the oxidation state of the activated Cr species. The cycle is proposed to go via a Cr(II)–Cr(IV) or a Cr(III)–Cr(I) catalyst reaction pair [12,14,15] (figure 2).
Further investigations by different groups around the world have also suggested the reaction to proceed via dimeric Cr species. For example, Gambarotta and co-workers [16,17] suggest that the industrially applied $[\text{CrCl}_3(\text{SNS})]$ with various alkylating agents at low Cr:Al ratios forms Cl-bridged dimers, including $[(\text{SNS})\text{CrMe}_2(\mu-\text{Cl})_2]^{2+}$. Also Braunstein and co-workers [18] have shown that for the industrial tetramerization catalyst $[\text{CrCl}_3(\text{NPN})]$ ($\text{NPN} = \text{bis(2-picolyl)phenylphosphine}$), chloro-bridged dimers, as well as mononuclear clusters with a mixture of alkyl and halide ligands can be formed, depending on the alkylating agent and reaction conditions. It is however, important to note that the ratio of Cr:MAO in the industrially operating catalyst system is significantly higher than used in the studies mentioned above.

The pursuit for higher performance catalysts as well as possibly replacing Cr by other 3d TMs, which are more abundant, cheaper and have less toxicity issues, e.g. Fe, requires a detailed understanding of the individual stages of the catalytic cycle, and their dependence upon metal, promoter and/or co-catalyst. However, developing such catalyst systems is hindered by characterization difficulties due to the paramagnetism of the majority of the Cr (and many 3d TM) complexes.

4. Results

(a) Experimental approaches

To tackle the characterization of the low X-ray energy Cr catalysts in detail, two different approaches have been pursued: (i) substitution of Cr(III) for the heavier 4d Mo(III) with subsequently higher X-ray energy (20 keV) to allow the time-resolved XAS/UV–Vis stopped-flow techniques [7] and (ii) using the stopped-flow/freeze-quench method as discussed above to trap reactive intermediates at short time scales (less than 1 s), to allow the long XAS data acquisition as required for the lower energy (approx. 6 keV) Cr catalysis [11]. Here, the initial activation of the Cr(III) pre-catalyst with aluminium reagent is studied in order to obtain insights in the actual active Cr catalyst formed, a Cr(III) or Cr(II) species, and provide proof towards the neutral or cationic reaction pathway as proposed.

All experiments were performed using AlMe$_3$ while the structures of MAO and MMAO as used in industry are unknown, complicating the analysis and interpretation, and a similar catalytic behaviour is observed with this aluminium co-catalyst for this specific reaction.
Figure 3. Combined time-resolved QEXAFS (a) and UV–Vis data (b) on the reaction of [MoCl₃(SNS)] (25 mM in toluene) with 20 equivalents of AlMe₃ at $t = 0$ (black), $t = 1$ min (red), $t = 2.5$ min (blue), $t = 7$ min (green), $t = 18$ min (orange) and $t = 19$ min (pink). Note that the EXAFS is not displayed beyond 7 min, since the edge step diminishes significantly due to loss of Mo out of solution and the EXAFS signal is too noisy to process. From approximately 18 min no signal is visible in either XAS or UV–Vis. Reprinted from Bartlett et al. [7]. Copyright 2011, with permission from Elsevier. (Online version in colour.)

Figure 4. Schematic of the proposed Mo complexes formed after activation with AlMe₃ ($E = N$ with $R = CH_2C_6H_4–p$–C(CH₃)₃).

(b) Mo polymerization

We prepared the Mo(III) trichloro SNS complex, [MoCl₃(SNS)] (SNS = RS(CH₂)₂NH(CH₂)₂SR) [7], analogous to the highly selective industrial CrCl₃(SNS), as a model system for the Cr catalyst and its reactivity. The complexes show little catalytic activity towards ethene oligomerization [19]. It is however reasonable, with Mo directly underneath Cr in the periodic table, that the Mo system will undergo similar chemistry in the initial stages of activation. The likely slower kinetics at Mo will aid the identification of the different species throughout the reaction.

Time-resolved XAS/UV–Vis reactions were performed at room temperature using the stopped-flow instrument. The combined time-resolved XAS and UV–Vis data for the reaction of [MoCl₃(SNS)] with AlMe₃ (ratio Mo:AlMe₃ is 1 : 20) are displayed in figure 3. QEXAFS spectra and time-resolved UV–Vis spectra were obtained every 20 s (only a selection is presented for clarity reasons).

The EXAFS clearly shows an overall loss in intensity, which, by EXAFS analysis, is attributed to the loss of chloride ligand and its replacement by carbon, i.e. methyl groups. The time-resolved data show that this replacement proceeds in a step-wise manner. The SNS ligand remains intact (figure 4). After approximately 18 min of reaction in the stopped-flow, the Mo K-edge XAS signal, as well as the UV–Vis signal, are lost completely, indicating the precipitation of Mo (which is confirmed after inspection of the cell and which is shown to be irrespective of the X-ray beam).

Dinuclear or halide-brigded dimers [18] have not been observed under the conditions investigated. At the high AlMe₃ ratios used, the activation reaction of the MoCl₃(SNS) is shown to be in competition with the deactivation reaction (forming eventually metallic Mo), which provides insights in the low overall catalytic activity and deactivation as was reported for these systems under real catalytic conditions [19].
(c) Cr oligomerization

In a next step, the industrially important CrCl₃(SNS) selective trimerization catalyst itself has been investigated [11]. The system was initially studied in a standard XAS solution cell [20] at room temperature, with fluorescence XAS data acquisition times of over 2 h (figure 5, blue solid and red dotted lines). The results obtained suggested, similar to the Mo analogue (as described above), the methylation of the Cr complex, forming a Cr(III)(SNS)(CH₃)₃ complex. In addition, some Cr metal was formed at the bottom of the cell. The catalyst, however, is known to deactivate in this time frame (typically less than 1 h), hence it is doubtful that this is the Cr intermediate responsible for the trimerization activity, but rather a (possibly deactivated) end-state.

The Cr catalyst activation has subsequently been studied using the stopped-flow freeze-quench methodology, freezing reaction intermediates at different reaction times, from 1 s up to 5 min. Whereas a significant change from the starting Cr(III) complex is observed, no further differences are visible between the Cr complexes after 1 s of reaction, hence just the 1 s spectrum is displayed and discussed here (figure 5, green dashed line). The frozen Cr intermediate is determined to be a four-coordinate Cr(II)(SNS)Cl complex, based on EXAFS analysis and advanced XANES simulations using the FEFF9 program [21,22]. Simulations show that a step-wise methylation of the complex would lead to an upward shift of the absorption edge energy as expected [23], whereas a downward shift as observed for the frozen reaction intermediate can be explained by the change in geometry from a six-coordinate to a four-coordinate square planar species, with the retention of one chlorine. The Cr(II) intermediate and corresponding bond lengths suggest the Cr–N is deprotonated in the process.

Again, as for the Mo systems, for this Cr system, at the high Al:Cr ratios measured, no evidence for directly bonded Cr–Cr or halide-bridged dimers is obtained. The Cr(II) intermediate as proposed here is in fact similar to an isolated species [Cr(Cl-AlEtCl₂)(R-SN(H)S)]AlEtCl₃.₅ as reported in the literature [17]. However, this is the first time that the activated Cr species has been measured in situ, at the relevant time scales, at the relevant Cr : Al ratios, and supports a Cr(II)-led reaction mechanism. Further experiments, to provide further insights into the high trimerization selectivity as displayed by this catalyst, including ethene, are now underway.

(d) Conclusions: oligomerization and time-resolved X-ray absorption spectroscopy

The different stopped-flow procedures, i.e. time-resolved and freeze-quench, have been shown to provide unprecedented insights in the formation of activated catalytic intermediates at real conditions and time scales and thereby new insights into their mechanisms. The limited activity and fast deactivation of the Mo systems were confirmed by the structural analysis of the
complexes in time, with the complex activation being in competition with the deactivation. The Cr-activated species was found to be a four-coordinated Cr(II) species, supporting a Cr(II) led reaction mechanism.

The time resolution of the stopped-flow XAS experiments is in the range of seconds down to milliseconds [6]. This is a time scale in which new reaction intermediates have been identified and new catalytic cycles could be proposed. These are, however, longer lived intermediates, resting states, and very reactive and short-lived intermediates, with lifetimes of pico- to nanoseconds, remain undetected. Further instrumentation as well as technique developments are required to probe these. Whereas light induced reactions in the field of photochemistry have been characterized with these time resolutions [24], this is much more difficult to achieve using liquid reactants. Different strategies are currently being pursued by us to enable this.

5. Further and novel X-ray spectroscopy developments

In this contribution, we have provided an extensive example into the characterization of homogeneous reaction intermediates using time-resolved XAS methodologies, providing mainly structure–performance relationships. Electronic information, i.e. on the oxidation state of the metal, was obtained from the XANES part of the spectrum. This part of the spectrum is however much less understood and often just used as a fingerprint of certain geometries and oxidation states. While the XANES directly probed the unoccupied molecular orbitals, there is however much more information present. Tuning the electronic properties of the catalytically active metal via ligand modification in homogeneous catalysis (or via support interactions in heterogeneous catalysis) is very important to influence the catalytic performance (activity and selectivity). Hence, more insights in the detailed electronics will help unravel and subsequently optimize many catalytic systems.

Detailed XANES studies on TM complexes have demonstrated the sensitivity of X-ray absorption K edges and their (pre)edge features to their chemical environment, e.g. oxidation state, site symmetry, crystal field splitting [23]. Careful analysis in combination with theoretical calculations methods can provide detailed electronic and structural information, for example the amount of charge redistribution and thus covalent interaction between catalyst and substrate, as we have shown for organometallic Pd complexes [25], as well as the Re MTO catalyst [9]. Making XAS more selective and providing chemical speciation would clearly be of benefit for studies of catalysis, which is currently being pursued by several groups.

Developments in XAS using new instrumentation and data acquisition methods while selecting specific X-ray energies provide this more detailed electronic information [26]. The developments are based upon a secondary spectrometer scanning the energies of the fluorescence (rather than measuring the transmission or total fluorescence as done routinely). In this case, the instrumental energy broadening is below the spectral line broadening due to the core-hole lifetime. It is then possible to scan either the intensity of a single emission line as a function of incident energy or, alternatively, the emission energy at fixed incident energy.

In the first case, the core-hole broadening observed in a ‘normal’ transmission or total fluorescence detected absorption spectrum is replaced by a modulated lifetime broadening (of the single emission line) that is considerably sharper than the broadening owing to the core-hole lifetime, the so-called high-energy resolution fluorescence detection (HERFD) XAS [27]. The multiple pre-edge features and shoulders present in the XANES region are thus better resolved and easier to separate and analyse.

While in an XAS spectrum (XANES), the spectrum provides information on the empty/unoccupied molecular orbitals, the X-ray emission spectrum provides information on the filled molecular orbitals. Non-resonant or valence-to-core X-ray emission spectroscopy (XES) with emission energies close to the Fermi level can map the density of occupied states in the valence orbitals of the metal under investigation. The spectra are very sensitive to the type of ligand enabling one to distinguish between, for example, OH$^-$ and H$_2$O, while keeping the advantage of element selectivity [28]. XES can thus amend one of the major shortcomings of
EXAFS, i.e. insensitivity to ligands with similar atomic number, which can be very important in catalysis, especially homogeneous, where the changes in ligand and substrate coordination are often between N, C and O.

In resonant inelastic X-ray scattering (RIXS) spectroscopy, the emitted energy is measured as a function of the incident energy, thus yielding two-dimensional (2D) X-ray information. The incident energy is close to the absorption edge, i.e. the electron is excited to a bound state. In the secondary process either the excited electron remains in the bound, previously unfilled, state and an electron from a filled orbital decays to fill the core hole (also called core-to-core RIXS), or the photo-excited electron decays to fill the core hole (also valence-to-core or valence band RIXS).

The 2D RIXS has been shown to resolve pre-edge features unobserved in transmission or total fluorescence detection mode. The two-dimensional picture is crucial to identify the correlation between the incident and emitted energies and gives information on the electronic density of states of the system. The energies of fluorescence emission are very sensitive to the chemical environment. When different emission lines can be resolved and assigned to specific chemical environments, selective XAFS can be performed. This allows a characterization of individual components in chemical mixtures. Valence band RIXS (absorption and emission energies around the absorption edge energy) was shown to provide detailed insight in the molecular $d$ density of states (for extended structures) and molecular orbitals (for organometallic structures) [29,30]. Several applications have recently been demonstrated, such as spin-selective XAS, valence-selective extended XAFS, and range extended XAFS using detection channels for a certain edge, valence and/or spin state. For example in the case of iron, recent RIXS experiments have shown that unequivocal information on the presence or the absence of Fe$^{4+}$ in a system with a mixture of Fe compounds with a mixture of oxidation states can be obtained [31]. Again, this is clearly important in catalysis, where when investigating full catalytic systems often a mixture of reaction intermediates with different oxidation states can be present.

The increase of information density is especially clear in 2p4d Mo RIXS, as measured for a series of reference compounds [32]. Whereas in the direct Mo L$_3$ edge XAS, in which a double white line is observed and is interpreted in terms of metal geometry, the 2D RIXS image consists of four isolated high-energy resolved features, giving a more detailed orbital picture, highlighting...
the strength of the technique (figure 6). All features could be reproduced and assigned using theoretical FEFF methods (figure 6). A recent example where the techniques have been used is in the characterization of Cr organometallic salen compounds, used for the epoxidation of alkenes. The complexes, as well as a series of Cr references in different oxidation states and geometries, were studied in detail using ‘direct’ Cr K and L edge XAS, as well as 1s3p (core-to-core) RIXS as a function of differing ligand electronics (different electron donating and withdrawing groups attached to the salen ligand) [33,34] (figure 6).

Unfortunately, the energy resolution of the high-energy RIXS (approx. 0.5 eV) did not allow us to distinguish the electronic properties between different Cr complexes, whereas the direct L edge (with an energy resolution of about 0.05 eV) did indicate changes. However, operando 2D RIXS identified additional features, unobserved in normal XANES and HERFD, indicative for mixed Cr(III)/Cr(V) oxidation state species, which could be related to electron paramagnetic resonance and EXAFS results, providing new insights in the reaction mechanism [33,34]. Applications of HERFD and valence band RIXS in heterogeneous catalysis, probing supported metal nanoparticles, provide fundamental insights, for example, in metal-support and metal-adsorbate interaction [35,36].

Application of these new high-energy resolution XAS and XES methods, albeit still under development, are appealing for homogeneous catalysis, as it will give detailed insights in electronic and geometric properties of the structures under investigation. In some cases, oxidation state and spin-selective XAS might be feasible, enabling one to identify and characterize selected catalytic intermediates only (rather than the macroscopic approach of normal XAS) and provide ligand specificity (some of which are not feasible in normal EXAFS). The reasons that these techniques have not been used more widely in catalysis is that the interpretation of the extensive datasets, i.e. the assignment of all features, is not straightforward and more theoretical developments are required (which are pursued by different group across the world [21,22,37,38]). All these experiments, time-resolved and high-energy resolution are possible at the Diamond Light Source.

Acknowledgements. Many people have of course contributed to the work described here, who are all mentioned as authors in the references provided. Special thanks go to Dr Stuart A. Bartlett and Dr Peter Wells, whose Mo and Cr PhD and post-doc work was mainly reviewed here. The work presented in this contribution has been executed at several beamlines at several synchrotrons across Europe: the Diamond Light Source—beamline I06, I18 and B18; the European Synchrotron Radiation Facility—beamline BM26A, ID26; the Swiss Light Source—SuperXAS beamline. The synchrotrons and their staff are gratefully acknowledged for provision of beamtime as well as their assistance during experiments. Sasol Technology Pty is thanked for useful interactions and collaborations.

Funding statement. The EPSRC is gratefully acknowledged for funding of the different projects (EP/E060404/1, EP/F032463/1).

References


34. Hobbs S *et al.* Submitted. *In situ* XAS and XES techniques revealing important insights in Cr(salen) catalysed epoxidation reaction performances.


