Synchrotron Radiation and Catalytic Science

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Introduction

Techniques employing synchrotron radiation (SR) have had a major and growing impact on catalytic science. They have made key contribu-tions to our understanding of structural properties of catalytic systems and of structural changes during the operation of a catalytic process. They can also improve our understanding of electronic and vibrational properties, which can contribute to the understanding of mechanisms. SR techniques are now key components of the experimental tool box of the catalytic scientist.

The most widely used range of techniques in catalysis studies is possibly X-ray Absorption Fine Structure (XAFS), comprising both the near edge (XANES) and extended (EXAFS) regions of the X-ray absorption spectrum. Catalytic science benefits from the element-specific data that these techniques provide on oxidation state, coordina-tion number, and detailed local structure. As such, they provide unique information on active site structures and structural changes.

X-ray Powder Diffraction (XRPD), which with SR yields high-quality data that can be refined using profile refinement (Rietveld) techniques, enables the resolution of the crystal structures of complex catalytic materials, such as microporous catalysts, which are only available as powders, while the intensity of SR enables single crystal studies on microcrystals. Since the 1990s, it has also been possible to combine XAFS and XRPD, allowing local and long-range structure to be obtained simultaneously. Moreover, tomographic techniques based on both spectroscopic and diffraction data allow the development of detailed 3D structures of heterogeneous catalytic particles. Catalytic science also benefits from a range of surface sensitive techniques, including XPS and surface diffraction, while SR-based IR measure-ments are recently proving to be of growing value.

Catalytic science has profited hugely from the ability to undertake SR-based experiments in situ (while the catalyst is functioning) and in operando (as the product distribution is also monitored). The intensity of SR has also allowed increasingly fine time and spatial resolution, so that it is now possible, for example, to undertake kinetic in-situ structural studies, spatially resolved along a catalytic reactor. SR data may also be collected in combination with other experimental techniques, where combined XAFS/DRIFTS have proved to be particularly powerful.

Developments in sources, instrumentation, and data analysis techniques continue to extend the range and power of SR techniques in catalytic science. In this article, their growing impact is illustrated using a series of case studies based on work within the UK Catalysis Hub, a UK network of catalytic scientists, which has made extensive contributions to both the development and application of SR techniques in catalysis, especially using the facilities of the Diamond Light Source based on the UK Harwell Science and Innovation Campus.

Development of multimodal tomography for microscale chemical imaging of catalysts under operational conditions

By accident or by design, catalysts often possess a micro- and nano-structure that can influence performance, but which is rarely considered when correlating structure with function during in-situ and/or ope-rando studies. In recent years, we have developed chemical imaging approaches to better understand the importance of the distribution of these multi-scale structures and how they evolve [1]. For this purpose, at Diamond Light Source's beamline I18, we have developed a mul-timodal tomography approach that allows for simultaneous collection of X-ray fluorescence, diffraction, and absorption measurements on a functional material under operando conditions. In an exemplar study we characterized a packed bed micro-reactor (500 µm reactor contain-ing Co/SiO_2 Fischer Tropsch synthesis (FTS) catalysts), enabling iden-tification of the active species and correlation with performance [2, 3].

In Figure 1, we show the multimodal data acquired in one shot of the X-ray beam. The data (particularly the XRD) are of sufficiently high quality to extract detailed structural insight; for example, fitting of the XRD-CT patterns revealed no hexagonal close packed (HCP) cobalt but a mixture of cubic close packed (CCP) and intergrown Co (i.e., a random mixture of CCP and HCP layers). This degree of intergrowth can be directly correlated with the Ti modification on the silica support. When Ti is deposited before the Co, it crystallizes on the support as TiO_2 anatase, increasing the strength of the metal support interaction and resulting in smaller, strained Co nanoparticles (a result of a higher degree of intergrowth) that are prone to reoxidation under FTS con-ditions (Figure 1). The spatially resolved nature of the measurements reveals that this reoxidation occurs only in regions with a high concen-tration of this TiO_2.

When Ti is deposited after Co, anatase does not form, and the Co does not oxidize during FTS. In both cases, however, the degree of intergrowth (i.e., disorder) in the Co is linked to the concentration of Ti and not its crystallinity. The Co nanoparticles formed when Ti is deposited first are smaller and more active, yielding higher CO conver-sion, whereas when Ti is deposited second, the Co nanoparticles formed are larger and have greater selectivity towards the more desired longer-chain hydrocarbons.

The principal advantage of these tomographical approaches is their ability to provide information that spatially resolves signals concerning the microstructure of the sample that would otherwise be lost in a bulk measurement. Such local signals are simpler to interpret since they are likely to contain fewer phases. Furthermore, studying intact materials rather than idealized powders allows for behavior under industrially rel-evant conditions to be observed, mitigating some of the risk when trying

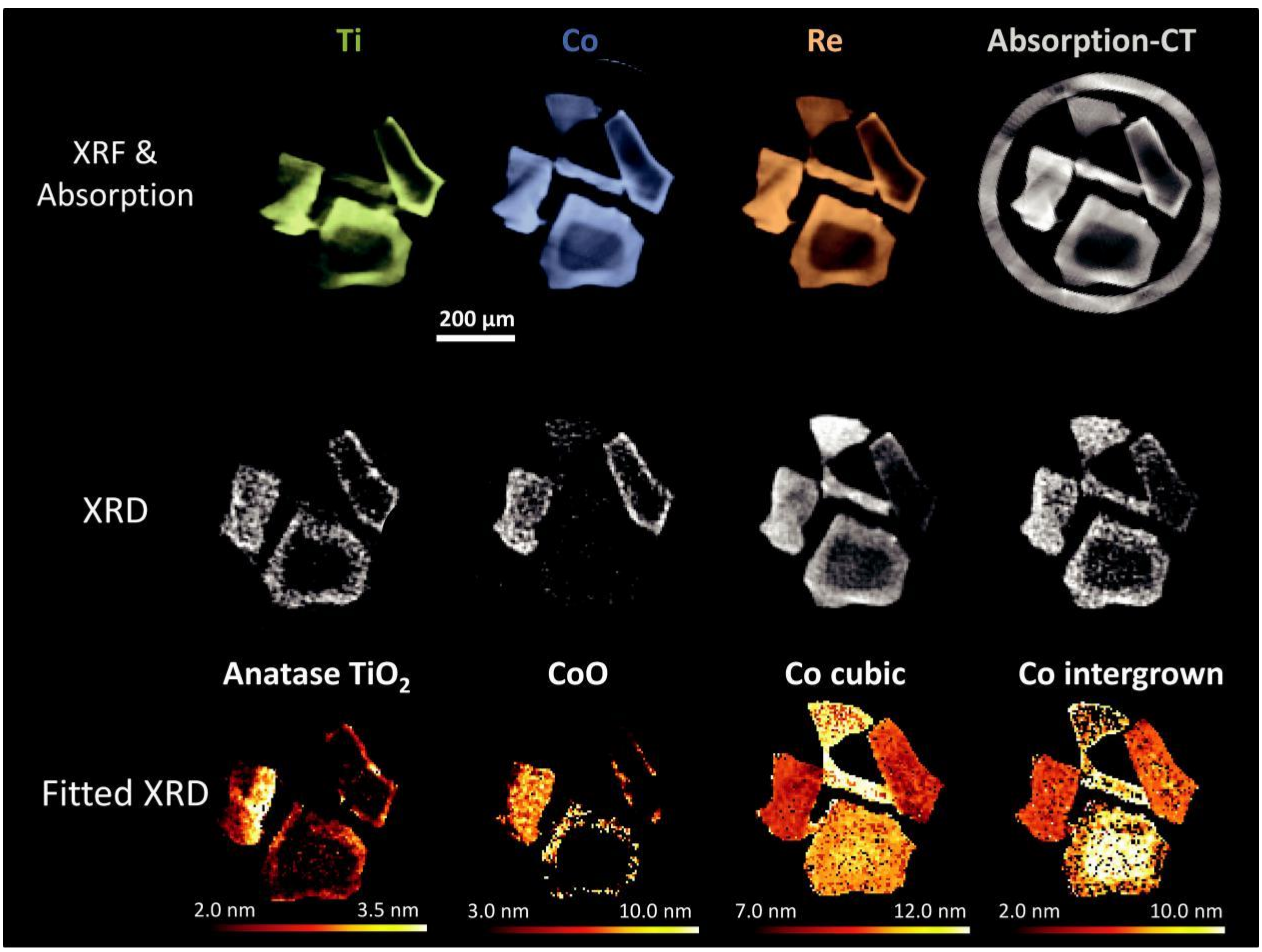

Figure 1: Co/SiO_2 catalyst structure during FTS. (Top) XRF-CT reconstructions showing elemental distributions during FTS at 2-bar pressure. Green, Ti; blue, Co; orange, Re. Absorption-CT reconstruction (grey) also shows the capillary wall surrounding the particles. (Middle) XRD-CT reconstructions of the catalyst revealing the phases present. (Bottom) Average crystallite size per pixel for each phase identified. Each pixel is 5 µm × 5 µm.

to translate results from the lab to the plant. In addition, the background signal from the apparatus/cell can be readily separated. Recent advances in data processing allow for this information to be visualized in near real-time during experiments, allowing for informed decisions on its progress, enabling treatments and measurements to be adapted accordingly [4].

UK Catalysis Hub Block Allocation Group (BAG) access to Diamond Light Source

Within the catalysis community, access to synchrotron radia-tion techniques has primarily been the preserve of the experienced user groups and their academic offspring. However, this model fails in fulfilling the potential of the methodology and scientific advances that these groups have pioneered for several decades. The impact of this work is more keenly realized when it is exposed to an increased breadth of scientific challenges. In 2011, a fledgling catalysis consortium within the UK was formed, which in 2013 became the UK Catalysis Hub. With a research base adjacent to Dia-mond Light Source, there was a determination to make better use of the central facilities. Discussions with Diamond led to the idea of a Block Allocation Group (BAG) for the new catalysis consor-tium on the core X-ray absorption beamline, B18. There was, how-ever, a key difference in how this BAG was to be administered. The BAG access had an internal panel that prioritized access not only on the excellence of the underpinning science, but also on bring-ing in new scientific challenges and user groups. Furthermore, the administrators of this access route—Peter Wells and Emma Gib-son—endeavored to see the potential of the scientific proposals and collaborated with user groups to design the most appropriate experi-ments for the scientific challenge at hand.

This approach has proved to be hugely successful and makes a sig-nificant contribution to the publication output of the beamline, beyond what would be expected based on the number of assigned days. A few highlights of this approach are detailed next.

Artificial rhodium hydroformylase for linear aldehydes

As part of this initiative, there was a concerted effort to broaden the uptake of synchrotron radiation methods beyond heterogeneous cataly-sis. This project harnessed the catalytic properties of transition metal complexes—in this case, Rh—and the specificity afforded through the development of artificial metalloenzymes (ArMs) for the selective hydroformylation of long-chain alkenes [5]. The design approach uti-lizes phosphine bioconjugation methods for anchoring of Rh complexes to protein scaffolds. The ArMs developed through this method demon-strated an activity 10^3 times higher than the conventional homogeneous Rh complex analogue. The unanswered question was the nature of the Rh center in the ArM and how it was interacting with the protein scaf-fold. The XAFS data suggested that the initial Rh complex, Rh(acac) $(CO)_2$, underwent loss of both CO ligands during the immobilization and was bound to two P environments as part of the phosphine bio-conjugation. However, these phosphine groups are particularly large and there would be significant steric hinderance with two bound to the Rh center. It was therefore postulated that, rather than P, there could be a bound S, from methionine, from the protein scaffold. To test this hypothesis, selenomethionine analogues were prepared, allowing for clear differentiation between Se and P coordination. There was a pro-found change in the XAFS between both samples, which were found to be consistent with Se coordination to the Rh center. This provided a unique insight in that the complex was not solely binding to the protein through the introduced phospine linkages, but to other functionalities on the protein scaffold itself. This structural level of understanding of the ArMs would not have been possible without both the UK Catalysis Hub network and the steering of the BAG administration.

Behavior of diphosphine ligands in iron-catalyzed Negishi cross-coupling

In promoting the uptake of XAFS amongst the UK homogeneous catalysis community, a collaboration with Robin Bedford's group was initiated on the use of Earth-abundant Fe complexes for cross-coupling reactions—a potential alternative to scarce and expensive Pd-based catalysts [6]. To provide information on the active catalytic species, as opposed to the end "resting state" complex, an operando continuous flow reactor was developed. In this approach, each spatial position becomes a static time point that allows the catalyst to be assessed under realistic concentrations and with a temporal resolution (determined by the length of the flow reactor) consistent with the whole breadth of the reaction pro-file. This study provided time-resolved changes in catalyst speciation that were entirely consistent with the reaction profile (measured both during the XAFS data acquisition and offline). The thrust of the work had been to build a library of diphosphine ligands that are crucial to catalytic activity. However, the XAFS investigations provided a very surprising insight—during catalysis, the diphosphine ligand does not reside on the Fe cen-ter. Instead, under reaction conditions, the diphosphine ligand resides on the Zn co-catalyst (confirmed subsequently with ^{31}P NMR). Indeed, the XAFS confirmed that the homogeneous Fe complexes formed Fe nanoparticles soon after the start of reaction, which subsequently formed a bromoferrate as the deactivation product. The exact nature of the active iron center is the subject of further investigations; however, it is proposed that the key role of the diphosphine ligand is to facilitate transmetallation between the Fe and Zn centers, which is an important step in understand-ing how Fe catalysts work for cross-coupling reactions and their future uptake as replacements for precious metals.

Single-site gold catalysts for the acetylene hydrochlorination reaction

A collaboration between several universities, industrial partners at Johnson Matthey, ISIS neutron source, and Diamond Light Source, through the UK Catalysis Hub, has resulted in significant advances in the understanding of industrially relevant gold catalysts used in the pro-duction of vinyl chloride monomer (VCM). VCM is the key material for the manufacture of polyvinyl chloride (PVC), with over 40 million tons produced annually. The project has been highly successful, with publications in *Science* [7] and *ACS Catalysis* [8] to date. Further, the findings were assisted through combined computational theoretical cal-culations enabled by the Catalysis Hub.

The main route for the VCM production in China is the hydrochlori-nation of acetylene, traditionally catalyzed by carbon-supported mercuric chloride. In 2013, the “Minamata Convention on Mercury” prohibited the use of mercury in VCM plants [9]. Following the pre-diction of Hutchings [10] that Au would be an effective catalyst for the VCM production, Johnson Matthey has recently validated an Au/C catalyst for this large-scale industrial process [11].

However, a full understanding of the nature of the gold during reaction has hindered catalyst design. Our study [7] reported the first detailed X-ray absorption spectroscopy (XAS) experiment at B18 Diamond Light Source, which followed the behavior of these catalysts during the reaction. Analysis of the Au L_3- edge XANES and EXAFS showed that the operating catalyst was comprised of atomically dispersed cationic gold in both Au(III) and Au(I) oxi-dation states (Figure 2a, b), showing analogies with the single-site homogeneous catalysis.

Follow-up work, published in *ACS Catalysis* [8], investigated the role of reactants in the deactivation and the reaction mechanism of these Au/C catalysts (Figure 2c), via in-situ XAS sequential gas flow experiments. Alternating between a reaction mixture of HCl/C_2H_2 and the single reactant, it was demonstrated that oxidative addition of HCl across an Au(I) chloride species requires concerted addition with C_2H_2, in accordance with the XAS measurements and the reaction kinetics. Exposure of the Au/C catalyst to only C_2H_2 changed Au speciation and resulted in the formation of oligomeric acetylene species, as detected by inelastic neutron scattering (INS).

Effect of NPT on low-temperature methane oxidation over a Pd/Al_2O_3 catalyst

Stringent incoming regulations on methane emissions are of major concern for the automotive sector. One of the investigated solutions is the coupling of supported metal catalysts for methane oxidation with

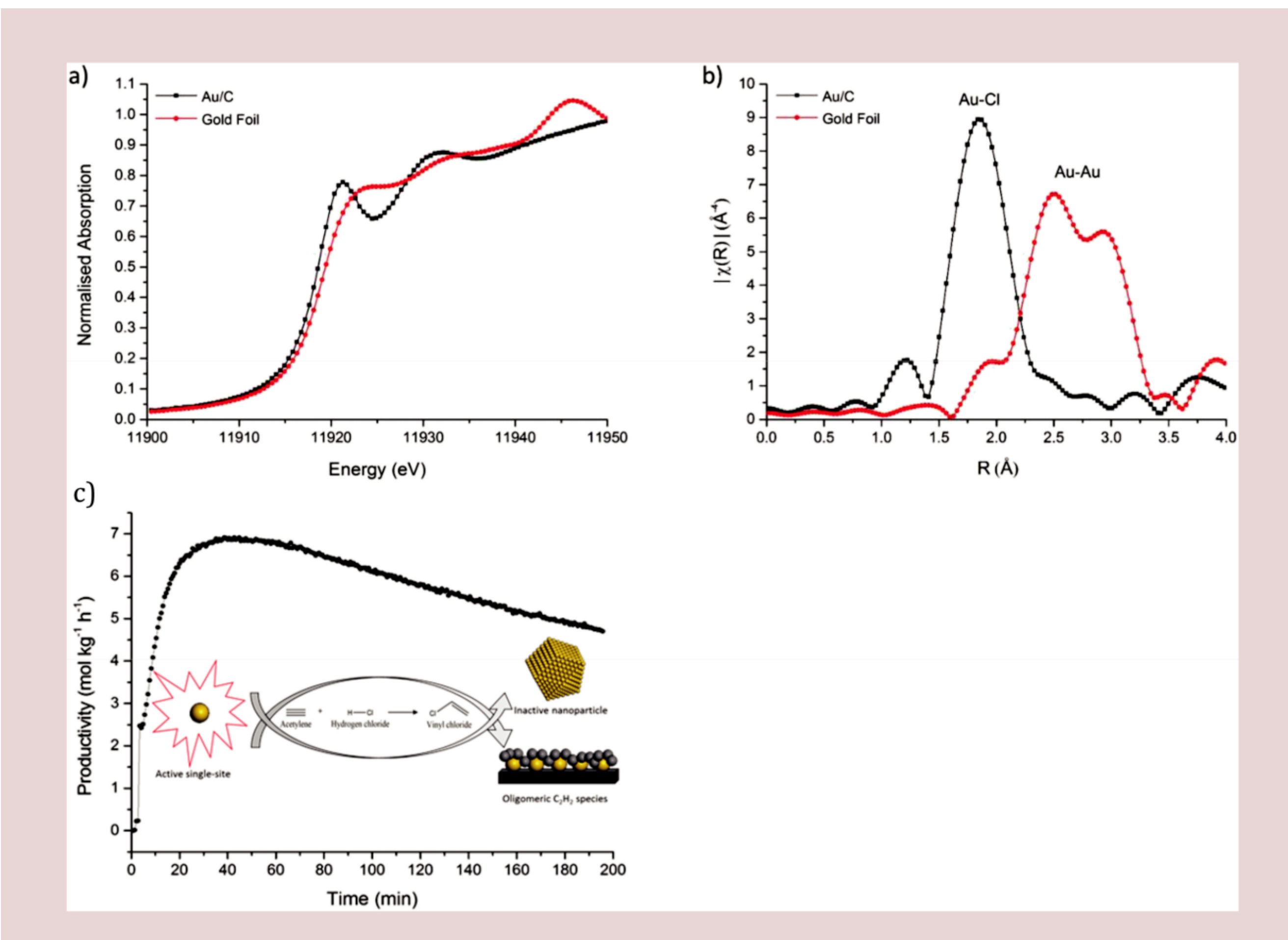

Figure 2: Au L_3-edge: (a) normalized XANES; (b) Fourier transform of k^3-weighted χ EXAFS spectra of the Au/C catalyst (black squares) and a gold foil reference material (red circle); (c) schematic representation of the deactivation pathways of single-site Au/C catalyst during the acetylene hydrochlorination reaction.

non-thermal plasma (NTP) to address the issue of low-temperature methane slip. Palladium-based catalysts are highly active for the oxidation of CH_4 to CO_2 and H_2O, but temperatures above 300 °C are required, which prevent them being effective under cold start conditions and operation with methane as the fuel. In contrast, high CH_4 conversions with high selectivity to CO_2 can be achieved when using a combined plasma-catalytic system. An in-depth understanding of what is happening in the plasma-catalyst system during real-time and realistic reaction conditions would offer valuable information to the industrial sector and academia, as very few in-situ studies are available to date for any plasma-catalytic systems. For the first time, a XAS investigation of a hybrid plasma-catalyst system was carried out by a consortium of researchers using the B18 beamline at Diamond Light Source (Figure 3).

The state-of-the-art technique was developed to facilitate the investigation of the gas-phase reaction environment during plasma opera-tion, while simultaneously allowing the recording of XAFS spectra, providing crucial insights into the impact of the plasma on the catalyst structure [12]. The study indicated a selective change in temperature for the Pd nanoparticles compared to the bulk of the catalyst, and no significant structural changes of the catalyst. Therefore, the high activ-ity was not due to a modification of the catalyst by the plasma under the reaction conditions investigated. Furthermore, the reported change in temperature was not sufficient to account for the observed methane conversion; therefore, the hypothesis that the role of the plasma for such a system was merely to provide heating to the catalyst could be ruled out. The most reasonable explanation for the high CH_4 conver-sions was attributed to the cleavage of the first C-H bond in the gas phase via electron impact reactions. Since this step is reported to be the rate-determining step for the methane oxidation reaction over the Pd/ Al_2O_3 catalyst, the NTP can be regarded as a “positive perturbation” of the catalytic system [13], which opens up alternative reaction pathways through a lower activation barrier than in the thermal catalytic systems.

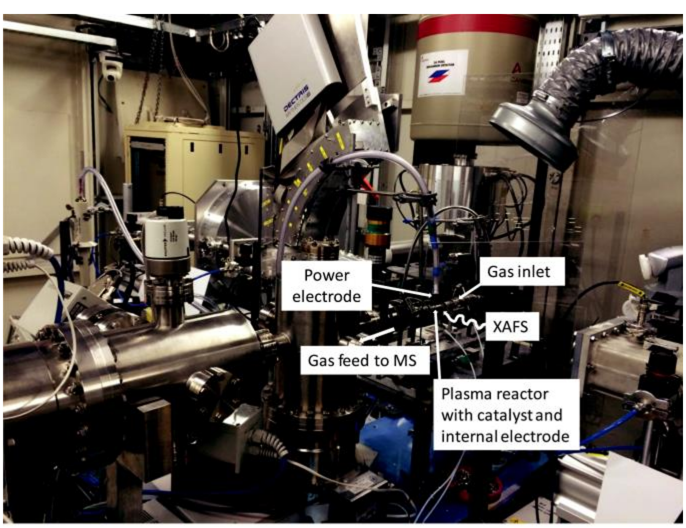

Figure 3: Setup for plasma-assisted gas phase measurements and XAFS spectroscopy.

This study demonstrated the value of combining the activity data with information on the catalyst structure and oxidation state during plasma operation in developing an understanding of the plasma effect on the catalyst and reaction. It highlighted the importance of in-situ studies in bridging the knowledge gap for plasma-catalytic systems.

Conclusions

We hope that this article has illustrated the range and power of synchrotron-based techniques in gaining detailed information at the molecular level of structure and processes in catalytic systems. New sources will open up new opportunities. In particular, the advent of the X-ray Free Electron Laser (XFEL) will offer exciting challenges and opportu-nities for catalytic science by giving direct information on mechanisms.

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