Surface Characterization

In Situ Investigations into Chemical Processes by Electron-Energy-Resolved X-Ray Absorption Spectroscopy**

*Antje Vollmer, John D. Lipp, Helmut Weiss, Rachel O'Malley, and Trevor Rayment**

Over the last 200 years industrial catalysis has become increasingly important so that currently more than 90% of the world's chemical manufacturing processes are controlled by catalysis.[1] Catalytic converters used in exhaust detoxication and for atom-economic processes are of comparable importance,[2,3] and yet the elementary steps and in particular the role of the support material are frequently unclear.[4,5]

Surface-sensitive analytical probes are highly desirable, but most of those in common use rely upon the low mean free path of electrons in materials and operate under ultrahigh-vacuum (UHV) conditions that are far from those under which the material functions. X-ray absorption spectroscopy (XAS) is an invaluable tool for the study of catalysts because it yields interatomic distances, coordination numbers, the identities of neighboring atoms, and details of electronic structure in the presence of short-range order.[6] It is also ideal for studies under normal operating conditions because X-rays will readily pass through the reactive gas atmospheres used in catalysis. Yet in this advantage lies also the greatest challenge to the use of X-rays in the study of catalysts: the penetrating nature of X-rays means that the surface sensitivity of XAS is low. Most XAS experiments provide no surface information. However, there is an alternative method for detecting XAS signals that offers some surface sensitivity. If the Auger emission arising from relaxation of the core hole is measured instead of the photon transmission or fluorescence emission, then only the region lying within the escape depth of the elastically and inelastically scattered Auger electrons contributes to the signal.[7] It has been shown that electron detection is possible in most gases, at elevated pressures and temperature.[8] Unfortunately, the total escape depth for Auger electrons in these circumstances is substantial: typically between 100 and a few 1000 Å.[9–11]

[*] Dr. A. Vollmer, R. O'Malley, Dr. T. Rayment
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB21EW (UK)
Fax: (+44) 1223-336-362
E-mail: tr22@cam.ac.uk
J. D. Lipp
CCLRC Rutherford Appleton Laboratory
Prof. H. Weiss
Otto-von-Guericke-Universität Magdeburg (Germany)

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Auger electrons lose energy as they move to the surface and the elastic mean free path is typically an order of magnitude smaller than the escape depth. Thus energy-selective detection radically improves the surface sensitivity that can be achieved by use of electrons. This fact is well known for UHV experiments, but it is only recently that a practical scheme for energy-resolved electron detection has been presented for use at ambient pressure.[12] This scheme uses a gas microstrip detector (GMSD) that functions as a very robust proportional counter. The key component shown in Figure 1a is a pattern of interleaved metallic strips

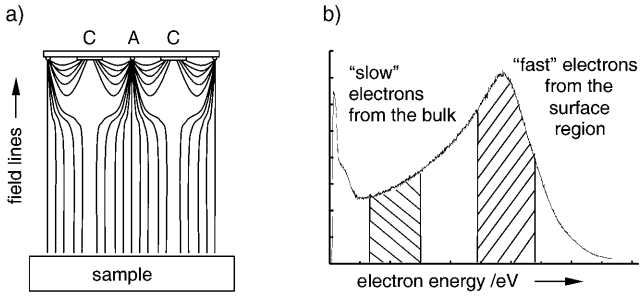

Figure 1. a) Schematic diagram of the GMSD detection showing the characteristic field line geometry. The sample is biased to high negative potentials creating a drift field to the detector plate that supports interleaved cathode (C) and anode (A) strips. An electron cascade caused by impact ionisation of the detector gas only micrometers away from the detector plate allows pulse-counting measurements. b) A typical pulse height distribution for a GMSD showing the relationship between electron energy and the depth of origin in the solid. (The vertical axis shows the number of events in a given energy range.)

deposited onto a semiconducting glass plate. In a suitable gas atmosphere, these strips function as the anodes, and the sample as the cathode, of an avalanching gas counter. The amplification is such that an Auger electron gives a measurable pulse, the amplitude of which is proportional to the initial energy of the electron. A typical pulse height distribution (PHD) is shown in Figure 1b in which the height of the pulse has been converted into electron energy. Since the depth from which an Auger electron originates increases as the energy of the emerging electron decreases, the PHD contains information about this depth.

The feasibility of nondestructive depth profiling at ambient pressure with energy-selective XAS had been demonstrated for a model system in a previous publication.[12] This system comprised overlayers of NiO on a polished nickel plate and the use of a standard detector gas mixture of isobutane and helium. In these experiments, X-ray spectra could be collected with just two electron-energy-detection windows: a high-energy window for electrons emerging close to the surface and a low-energy window for electrons that originated deep within the bulk as shown in Figure 1b. It is clear that the measurement of a full electron-energy spectrum at each incident photon energy would yield the maximum information on surface composition. Improved instrumentation now makes the collection of two-dimensional datasets a practical proposition: data for copper powder reduced in a hydrogen atmosphere are shown in Figure 2.

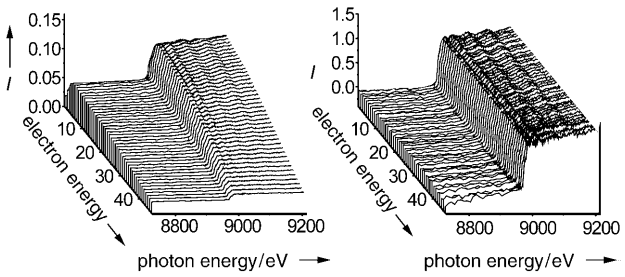

Figure 2. Typical data derived from powdered copper. a) A two-dimensional matrix of raw data showing a PHD at every photon energy step of the EXAFS scan. The labeling of the electron energy axis (pulse heights) corresponds to the pulse counting channels of the MCA electronics (see Supporting Information). b) Data normalized to a constant edge step.

Figure 2a shows raw data in which for each value of incident X-ray energy, the typical PHD can be seen. Consideration of the normalized data in Figure 2b indicates that the X-ray spectra display little dependence upon electron energy. The most simple (and correct) interpretation of these data is that the structure of this sample shows little depth dependence. Though not obvious, it is worth noting that constancy of these data also shows that the detection scheme is immune to the nonlinearities present in the use of fluorescent detection for concentrated samples.[8]

Despite this progress, if the technique is to move beyond from being a curiosity to become a useful tool for a wider community, it has to demonstrate three capabilities: operation with useful (reactive) gas mixtures, independence of sample form, and operation at non-ambient temperatures. Each of these criteria has now been satisfied. Gas microstrip detectors are not restricted to the standard gas mixture used in proportional counters (typically a mixture of a noble gas and a hydrocarbon) but will operate in reducing and oxidizing gas mixtures that are wet or dry and that may or may not contain hydrocarbons. Details of these investigations can be found elsewhere.[13] Fulfillment of the second and third criterion is described below. Results are presented herein upon a metal, semiconductor, and insulator in powdered form (data have also been collected for oils and liquids). The first results of a variable-temperature GMSD study of an in situ reduction process are described below, followed by preliminary results for an electrochemical system.

Experiments were carried out for temperatures up to 300 °C.[14] Copper oxide provides an ideal test system for variable-temperature GMSD studies, since it is readily reduced at modest temperatures, and since copper is both a key component of catalysts for methanol synthesis and is widely used in the purification of gases. The sequence of the experiment is best illustrated by considering the total electron-yield spectra (Figure 3) that give the structure averaged over a sampling depth of about 600 Å.

Three spectra (A) were collected at room temperature in a H_2/He gas mixture, during which time there was no discernable change. These spectra show a sharp feature at 8996 eV, which is highly characteristic of oxides (called the "white line" for historical reasons). After the third spectrum had been completed the temperature was raised to 170 °C

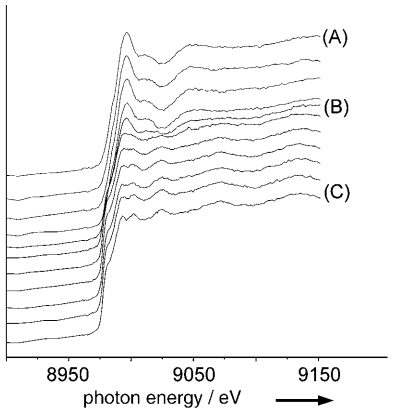

Figure 3. A time sequence of total electron yield spectra for the in situ reduction of copper oxide. A) Spectra 1–3, room temperature; spectrum 4, during heating to 170 °C. B) Spectra 5–10, 170 °C. C) Spectrum 11, 170 °C following complete reduction.

over the course of a single scan (11 min). It can be seen that during the next six scans (B) the intensity of the white line diminishes and the spectra gradually evolve to that characteristic of copper metal. After this time, no more changes in the spectra were seen (C).

The extent of the reaction in each spectrum was determined by fitting a linear combination of the spectra for pure Cu and CuO to it. Figure 4 shows zero-order reaction kinetics up to 80% conversion. This result suggests that reduction does not occur according to a core–shell model for which $\sqrt{t}$ dependence is predicted. Analysis of the structure as a function of depth from the surface as the reaction proceeds provides direct confirmation as shown in Figure 5.

The X-ray spectra for both the starting material and the product are independent of the electron-energy depth, which indicates a uniform structure throughout the sampling depth. However, during the process of reduction, a substantial core–shell structure might have been expected. The middle plot of Figure 5 shows the energy-resolved spectra for datasets in which the total electron yield (or average composition) spectra could be fitted by the spectrum of an about 50:50 mixture of CuO and Cu. To a first approximation, all spectra have the same shape in the vicinity of the edge, irrespective of the depth from which they originate. Pattern matching shows that the fraction of metallic Cu in each sample is in the range of 45 to 55%. Thus there is only a very small variation of composition throughout the outermost 60 nm of the material and certainly no discrete copper–copper oxide shell structure. This result is in agreement with the above conclusion that the progression of the reduction is not dominated by diffusion.

GMSDs function exceedingly well in the presence of water vapor.[13] This offers the possibility of conducting studies on wet surfaces. Figure 6 shows a schematic drawing of the simple three-electrode electrochemical cell that fits in place of the normal sample holder for investigations under ambient conditions. The key feature of the cell is the ability to flood the sample with electrolyte to undertake an electrochemical modification. The electrolyte is then drained away leaving a thin layer covering the sample that allows potential control to be maintained at all times.

Nickel oxides and hydroxides have been extensively studied previously by a range of spectroelectrochemical techniques because of their applications in batteries, capacitors, and electrochromic devices. The useful electrochemical

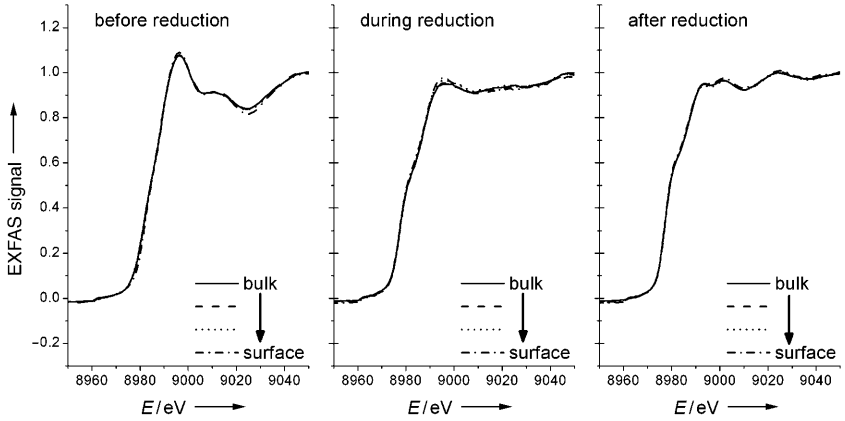

Figure 5. Energy-resolved EXAFS spectra of the initial CuO (left), a sample in the course of the reduction (middle) and the metallic copper product (right). Data have been summed within four electron energy ranges to improve statistics.

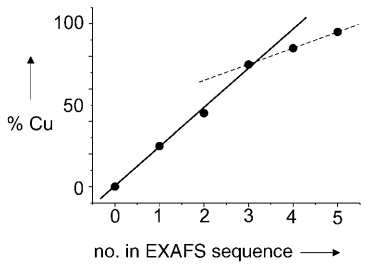

Figure 4. Dependence of the extent of reaction as a function of reduction time (expressed as number in the EXAFS sequence).

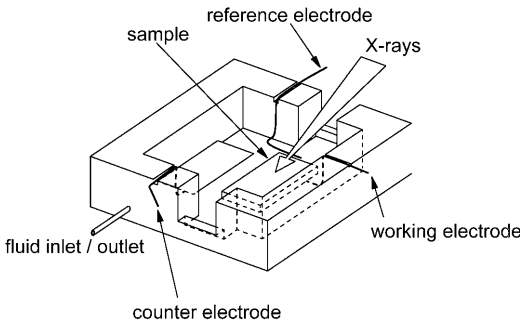

Figure 6. Schematic drawing of the in situ PTFE electrochemical cell. The grounded stainless steel frame of the cell to prevent its surface from charging when exposed to X-rays is not shown. The cell is made leak tight by two mylar windows clamped over its front and rear apertures (omitted for clarity). The sample acts as the working electrode, the counter electrode is a platinum foil of comparable area, and the reference electrode is a silver wire.

properties of nickel hydroxides arise from the facile and reversible oxidative conversion of $Ni(OH)_2$ to NiOOH. Both materials can exist in two phases, and the mechanism for the conversion is very complex, involving cation, anion, and solvent transfer both within the electrode and also between the electrode and the solution electrolyte.[15] The purpose of the experiments described here is to establish that it will be possible in future to investigate the evolution of structure and oxidation state of thin films under potential control, in the presence of a thin film of electrolyte.

It was convenient to deposit a nickel hydroxide film onto a nickel electrode. Figure 7 shows a set of electron-energy resolved extended X-ray absorption fine structure (EXAFS) spectra for the starting material. The spectra arising from low-energy electrons are identical to those obtained for nickel metal, but under ambient conditions polished nickel has a native oxide/hydroxide overlayer of about 2–5 nm thickness. In the spectra arising from the surface region, the intensity of the white line is substantially increased, thus confirming the presence of oxide species.[12]

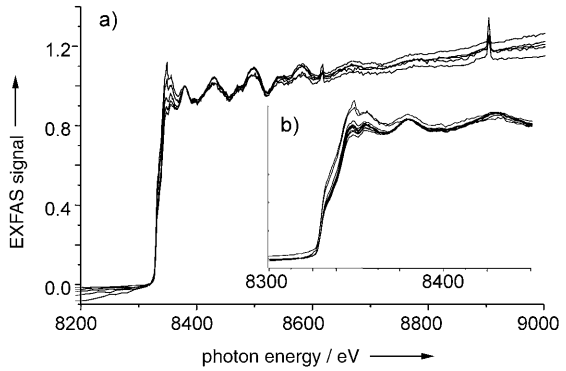

Figure 7. a) Depth-dependent EXAFS spectra of a Ni plate exposed to water vapor at room temperature in the detector cell. b) Zoom into the XANES region. The spectra are arranged vertically in order of increasing electron energy window. Thus the lowest and the uppermost spectra correspond to signals arising from the bulk and surface, respectively.

Figure 8 gives the spectra collected from a thick layer of electrochemically deposited nickel hydroxide and these show that there are marked differences in the X-ray absorption near-edge structure (XANES) region between signals emerging from the surface and the bulk of the electrode. A comparison of these data with the most recent data obtained by Hillman's group suggests that the outermost surface has retained the structure of Ni^{II} hydroxide but the deeper layers have been electrochemically charged to form NiOOH.[16] This proposal is somewhat speculative, but it does show that in future it will be possible to study electrochemical oxidations in conditions that are very close those found in situ and to be able to determine depth profiles of oxidation state without recourse to the use of invasive analytical tools of surface science.

The development of gas microstrip detectors has made it possible to perform energy-resolved Auger electron detection

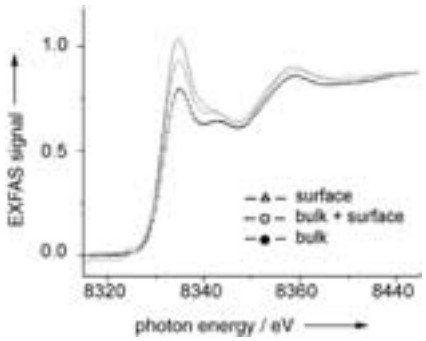

Figure 8. Electron-energy-resolved XANES spectra of $Ni(OH)_2$, electrochemically deposited onto a nickel plate from $Ni(NO_3)_2$.

under ambient conditions. The work described here shows that this technique is suitable for in situ studies in the field of heterogeneous catalysis and electrochemically modified surfaces. It could be argued that this technique represents a significant step forward in bridging the materials and pressure gap in analytical science. In these challenging experiments, the statistical quality has not yet reached the level at which a full EXAFS data analysis is possible at each electron energy, but improvements to the design of GMSD plates and the addition of more data channels will bring this about. A program of study is underway to build a suite of software tools that will permit quantitative deconvolution of the depth profile information contained in these data; the results of which will be reported elsewhere.

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