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Bridging the pressure gap: can we get local quantitative structural information at 'near-ambient' pressures?

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Abstract

In recent years there have been an increasing number of investigations aimed at 'bridging the pressure gap' between UHV surface science experiments on well-characterised single crystal surfaces and the much higher (ambient and above) pressures relevant to practical catalyst applications. By applying existing photon-in/photon-out methods and developing instrumentation to allow photoelectron emission to be measured in higher-pressure sample environments, it has proved possible to obtain surface compositions and spectroscopic fingerprinting of chemical and molecular states of adsorbed species at pressures up to a few mbar. None of these methods, however, provide quantitative structural information on the local adsorption sites of isolated atomic and molecular adsorbate species under these higher-pressure reaction conditions. Methods for gaining this information are reviewed and evaluated.

The 'surface science method' – the use of highly controlled experiments under ultra-high vacuum (UHV) conditions on well-characterised single crystal surfaces, exemplified by the work of Gerhard Ertl and his co-workers that led to the award of the Nobel Prize in Chemistry in 2007 [1], has led to major advances in our understanding of fundamental aspects of chemical processes at solid surfaces, and particularly those that underpin heterogeneous catalysis. The 'surface science method' typically involves the application of several different techniques to the same combination of solid surface and reactant species, specifically determining the surface composition, the chemical and molecular character of species at the surface, and the quantitative structure in the form of adsorption sites and bondlengths. Of course, practical heterogeneous catalysis typically operates at much higher pressures, and in recent years there has been an increased focus on extending the 'surface science method' to try to bridge this 'pressure gap' of typically more than 10 orders of magnitude. These studies have clearly identified some reaction systems in which fundamentally different processes occur at very different pressures, such as in the case of CO oxidation over certain metals, where at higher oxygen pressures surface oxide phases are formed that are far more reactive than chemisorbed oxygen that is present on the surface at much lower pressures.

The basic problem with applying many of the techniques of modern surface science to higher pressures is that they involve relatively low energy (no more than a few keV) electrons and ions that are strongly scattered by gas phase species at near-ambient pressures. The most obvious solution to this problem is to use photon-in/photon-out techniques that typically allow passage through higher-pressure gases with only modest absorption. Indeed, the use of infrared absorption spectroscopy to investigate molecular adsorption on supported metal particles following near-ambient pressure exposures predates the main developments of the modern 'surface science method' (e.g. [2]), and continues to be used to characterise the state of a surface during catalytic reactions in what are now referred to as *in operando* studies (e.g. [3, 4]). More recently, this capability to obtain vibrational spectroscopic information at higher pressures (also from single crystal surfaces, e.g. [5]) has been complemented by instrumental developments

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allowing X-ray photoelectron spectroscopy (XPS) to be used to obtain compositional and electronic structure information at higher pressures. Specifically, early attempts to extend the pressure range of XPS [6] using differential pumping have been advanced and combined with the use of synchrotron radiation. Although the accessible pressures of these low vacuum instruments fall short of those required for true *in operando* studies, these 'near-ambient pressure XPS' (NAP-XPS) studies have proved to be very fruitful [7, 8, 9, 10, 11]. The intermediate pressures accessible, typically up to ~10 mbar, are high enough to allow the surface species present during some steady-state catalytic reactions to be monitored, provided that their coverage under these conditions is sufficiently high. An important feature of all of these *in operando* studies, of course, is that one not only monitors the condition of the surface, but also correlates this with the reaction as reflected in changes in the gas phase monitored with mass spectrometry.

While these advances have certainly led to methods that can provide new insight into the different reaction mechanisms that may occur at higher pressures on a well-characterised single crystal surface during a surface reaction, none of them provide the quantitative structural information that is one of the key ingredients required for complete understanding of the surface chemistry. In particular, they do not provide quantitative identification of the 'active site' that is believed to be the key to the effectiveness of some heterogeneous catalysts. Vibrational spectroscopy such as infrared absorption (and sum-frequency) spectroscopy can provide a spectral signature of adsorption coordination sites, although even in the highly-investigated case of CO adsorption, longstanding misinterpretation of these data to identify the associated site can occur [12]. Moreover, the use of scanning tunnelling microscopy at ambient pressure can provide invaluable information on structural transformations that occur during reactions [13], but none of these methods provide quantitative structural information.

Under UHV conditions much the most widely-used method for obtaining quantitative surface structural information is low energy electron diffraction (LEED) [14], but the fact that this technique involves both incident and scattered electrons, over a wide angular range, with energies less than ~300 eV, seems to exclude its use at near-ambient

pressures, even with cleverly-designed differential pumping systems. Moreover, conventional LEED relies on long-range periodicity, and so cannot provide *local* structural information on adsorbate species that are not in well-defined ordered domains, as is likely to be the case in the steady-state situation of many surface reactions. Replacing the electrons by X-rays, leading to the technique of surface X-ray diffraction (SXRD) [15], does provide an effective route to obtain quantitative structural information on ordered surfaces at near-ambient (or higher) pressures. Indeed, despite the weak scattering cross-sections of X-rays for low atomic number elements, SXRD has been used to identify pressure-dependent modification of the ordered phases of CO on Ni(111) up to 1.2 bar [16]. More generally, however, SXRD (like LEED) relies on long-range order to produce the diffracted beams. As a result most of the reported high-pressure SXRD experiments have provided information on the modification of the structure of the underlying surface resulting from the presence of the gas phase species, such as oxide phase formation [17] or a modified morphology [18], rather than on the adsorption site of these species.
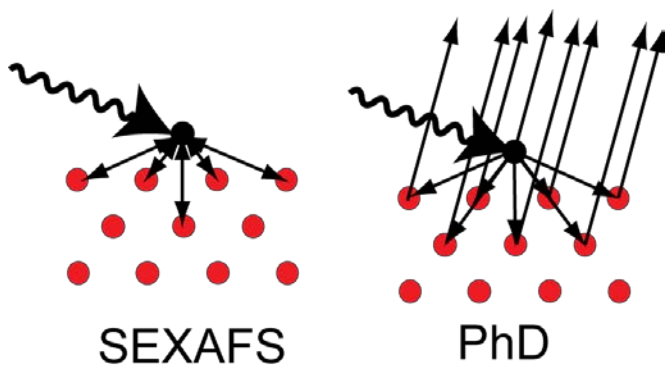

Fig. 1 Schematic diagram showing the single-scattering photoelectron paths in the SEXAFS and PhD techniques. Red circles denote substrate atoms, the black circle denotes an adsorbate atom.

These structural transformations of the surface have been shown to play a key role in surface chemical activity. However, obtaining quantitative structural information on transient adsorbed species, such as reaction intermediates present only under steady-state reaction conditions, requires the use of techniques that do not rely on long-range order. Two such techniques have proved effective in UHV surface science. One is a modification of the bulk technique of EXAFS (extended X-ray absorption fine structure), so-called surface EXAFS or SEXAFS [19], the other is photoelectron diffraction,

particularly in the scanned-energy mode (PhD) [20]. Both techniques exploit the coherent interference of the directly emitted component of a photoelectron wavefield, emerging from a core level of an adsorbate atom, with other components of the same wavefield elastically scattered by surrounding atoms. The dominant scattering paths relevant to the two techniques are shown schematically in Fig. 1. In EXAFS the interference occurs at the emitter atom centre, modulating the final-state photoionisation wavefunction and thus the total ionisation cross-section, while in PhD it occurs at the detector of the photoelectrons outside the surface and it is a partial, angle-derivative, cross-section that is measured. In both techniques the photon energy is scanned such that the photoelectron energy, and thus the photoelectron wavelength, is varied; this leads to modulations in the detected signal as scattering paths switch in and out of phase. Interpreting these modulations in terms of the scattering pathlengths allows the local structure to be determined.

Both techniques use incident X-rays, allowing penetration through higher gas pressures, but the ability to use these methods at higher pressures is limited by the method of detection. In conventional EXAFS the absorption is measured by monitoring the transmitted photons after passing through the sample, so these X-ray-in/X-ray-out experiments can to be performed at high gas pressures; *in situ* and *in operando* studies of dispersed catalysts have been studied extensively using this approach (e.g. [21]), but transmission detection is not possible (or would not be surface specific if the transmitted intensity could be detected) for single crystal samples. Surface specificity in SEXAFS from single crystal samples is achieved by detecting the photoabsorption indirectly, monitoring the results of the core hole refilling. Most commonly this is done by detecting the Auger electron emission, or the total or partial electron yield resulting from the inelastic cascade following the photoemission and Auger electron emission. The alternative hole refilling channel of X-ray fluorescence can also be detected, an approach that is not *intrinsically* surface specific, although if the energy of the detected fluorescent X-rays corresponds to that of an atomic species that is *only* on the surface, then in practice the information is surface specific. Evidently this variant of SEXAFS (also X-rays-in/X-rays-out) could be applied to higher-pressure surface science studies of well-

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characterised single crystal surfaces, but there do not appear to be any published reports of such studies. This may, in part, be due to the fact that the relatively poor signal-to-noise ratio of most published SEXAFS data means that the structural information is limited to a nearest-neighbour bondlength, and the angle of this bond relative to the surface normal.
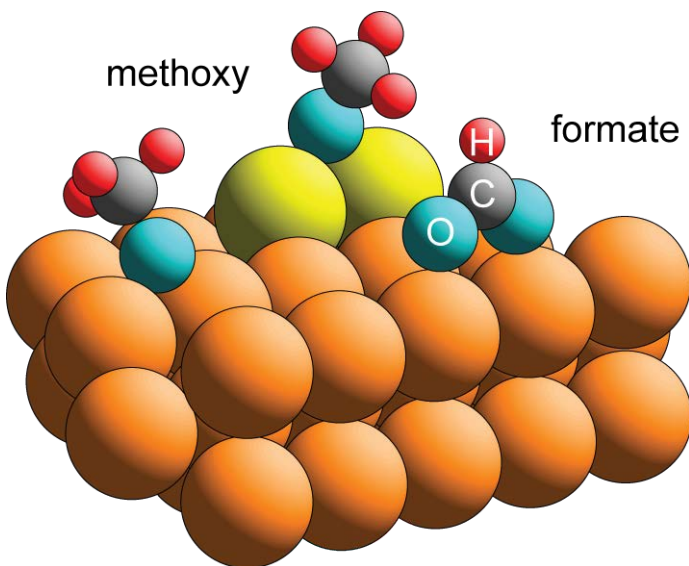

Fig. 2. Schematic diagram showing the local adsorption sites adopted by the methoxy and formate species on Cu(110) [23]. Under UHV conditions with an ordered phase methoxy occupies both the bridge site on the bare surface (left) and a bridge site on Cu adatoms (centre) but under reaction conditions the adatom structure is not seen.

The PhD technique, by contrast, can provide significantly more complete local structural information, and has led to successful determinations of more than 70 local molecular adsorption sites (e.g. [22]), including those of several surface reaction intermediates, under UHV conditions. The fact that the technique involves the detection of relatively low energy (≤~350 eV) electrons, however, means that it has been regarded a UHV-specific technique. However, the required measurement is basically angle-resolved XPS, so by using NAP-XPS instrumentation PhD data can be collected at higher pressures. So far only one proof-of-principle experiment of this kind has been performed [23], studying a Cu(110) surface during the steady-state oxidation of methanol in a mixed methanol/oxygen gas mixture. Two surface reaction intermediates occur on the surface during this reaction, namely methoxy (CH_3O) (the intermediate for formaldehyde production) and formate (HCOO) (the intermediate for combustion). The presence of these coexisting species can be identified through the O 1s and C 1s photoelectron

binding energies in a standard NAP-XPS experiment, but by recording the normal emission O 1s PhD data from these two chemically-shifted components under reaction conditions the local adsorption site and bondlength of both species could be determined. These sites are shown schematically in Fig. 2. These data were recorded with a sample temperature of 450 K at a rather low gas pressure of 10^{-5} mbar, chosen because at this pressure and temperature a steady-state reaction could be observed with formaldehyde production in the gas phase, and also with detectable amounts of the two species on the surface; this was not the case at significantly higher pressures. However, the methodology should be equally applicable to significantly higher pressures, as used in standard NAP-XPS.

A significant limitation of this first experiment is that it was only possible to measure the emitted photoelectrons in a single (normal emission) direction. As in the LEED technique [24], a very small data set (and specifically a PhD modulation spectrum measured in a single direction [25]) can lead to ambiguities in the structure determination. In the specific system studied in this first experiment, comparison of the data obtained with the results of more complete UHV PhD structure determinations of the same species allowed the structure to be determined with some confidence. More generally, a reliable structure determination would require modulation spectra recorded in a range of different emission directions. Newer designs of the electron energy analyser and associated electron optics in NAP-XPS instrumentation (e.g. [26]) offer a solution to this problem, as it is possible to collect a wide range of emission angles in parallel, also exploiting a 2D detector in the exit plane of the detector. This parallel detection also goes some way to ameliorating another problem with these experiments. Collecting these energy scan spectra typically takes tens of minutes, and for the data to be meaningful a steady-state reaction with constant surface coverages of the reactant species is required. If one could record many spectra simultaneously, the time required to collect the complete data set is significantly reduced, enhancing the probability that all data do correspond to the same surface condition. The successful demonstrations of the early NAP-XPS instruments at the ALS (Berkeley) and BESSY II (Berlin) synchrotron radiation facilities have led to an increasing number of these instruments being installed (or planned to be installed) at

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other new and existing facilities worldwide. The future prospects for exploiting the NAP-PhD technique as an essentially unique way of obtaining quantitative local structural information on molecular species on well-characterised single-crystal surfaces under higher-pressure reaction conditions therefore seem good.

However, it is, perhaps appropriate to mention a few general problems associated with these experiments and, indeed, with many existing attempts to extend the 'surface science method' to higher gas pressures. One problem is that already mentioned above, namely that meaningful data requires sufficiently stable steady-state reaction conditions to be established over the timescales of the measurement. This is evidently a more demanding requirement for NAP-PhD structural measurements than for some much more rapid spectroscopic fingerprinting. A second key requirement that is not always met is for the steady-state coverage of the species of interest to be sufficiently high to be measured; this may not be the case for very short-lived chemically-important reaction intermediates, and is likely to be strongly dependent on the surface temperature as well as the reactant pressures. Notice, incidentally, that the energy-dependent intensity modulations on PhD (and SEXAFS) are attenuated at higher temperatures by a Debye-Waller factor, limiting the useful temperature range of these methods. Finally, it is appropriate to note that as the gas pressure is increased, the possibility of contamination grows significantly. In UHV surface science, with a base pressure of $\sim 10^{-10}$ mbar, if adsorbing gases are introduced at a pressure of, say, 10^{-7} mbar, an impurity concentration in the gas of 1 ppm corresponds to a partial pressure of only 10^{-13} mbar, and is likely to have a negligible effect on the surface cleanliness unless the primary gas species has an exceptionally low sticking coefficient. However, if the adsorbing gas pressure is 1 mbar then a 1 ppm impurity corresponds to a partial pressure of 10^{-6} mbar, sufficient to produce ~ 1 ML of impurity adsorption in 1 second with unity sticking coefficient. These higher-pressure studies are therefore far more likely to be influence by surface contamination. Of course, the practical catalytic operating conditions will certainly have significant gas impurities too, but these may differ from those in the model surface studies.

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