Summary & Future Work

POSSIBILITIES AND LIMITATIONS OF *IN SITU* X-RAY ABSORPTION SPECTROSCOPIC STUDIES OF CATALYSTS BY TEY DETECTION

Most of the work described in this thesis has dealt with technical aspects faced by the experimentalist employing gas-flow TEY detection. It is hoped that this thesis will therefore provide an entry point to the present state-of-the-art of a previously almost unexplored experimental technique. It should be borne in mind, however, that the development of TEY XAS should not be considered completely finished. Particularly two areas require further attention in the future. Firstly, the formation of the TEY signal in small particles and thin overlayers with size parameters comparable to the Auger electron penetration range must be investigated. A linear relation between the TEY current and the X-ray absorption coefficient has so far only been ascertained for bulk samples. Secondly, the work described in this thesis has not employed any gas-analysis techniques to monitor reaction rates under *in situ* conditions. Current efforts by the author focus on the construction and characterisation of *in situ* TEY cells for catalysis studies that will provide meaningful on-line information on reaction rates and reaction kinetics.

Despite the mentioned shortcomings in our understanding, the studies reported in this

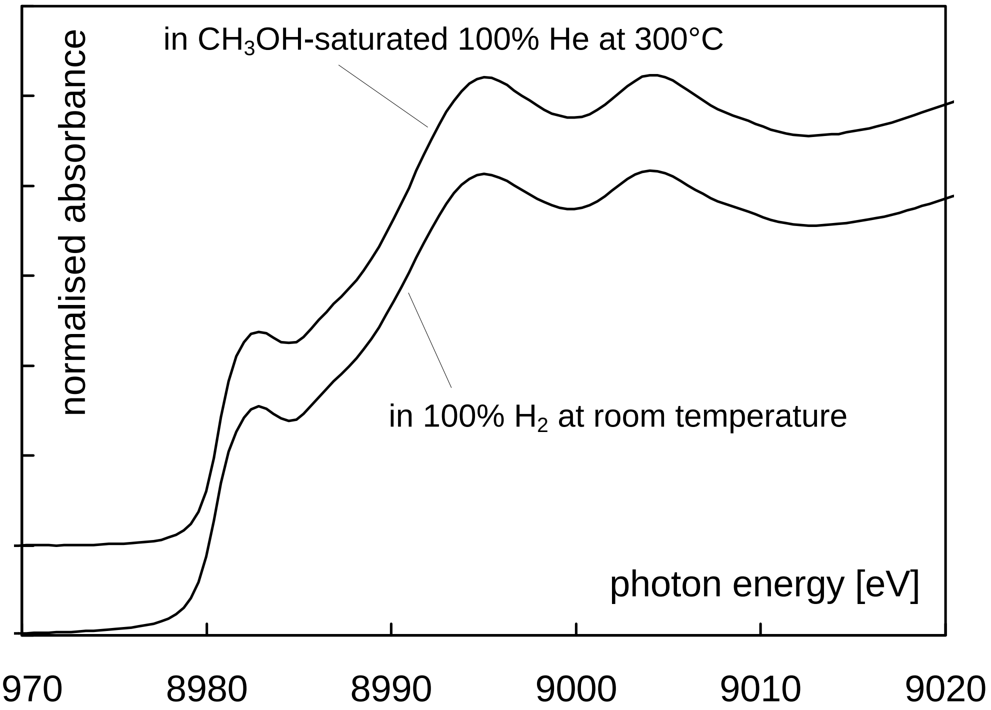

Fig. 7.1. Near-edge spectra of dispersed Cu collected in hydrogen (lower spectrum) and in a methanol-saturated stream of He (upper spectrum) at 300°C.

thesis have very clearly indicated that meaningful XAFS studies can be performed. Certainly, it emerged that, as with other XAFS detection techniques, care must be taken to identify possible artefacts intrinsic to TEY detection (c.f., chapter 4). However, it is important to remember that TEY detection is comparatively much less susceptible to these problems than FY and transmission detection. Gas-flow TEY detection thus opens up new possibilities for XAS investigations of a class of samples which was hitherto difficult, if not impossible, to study by other detection methods: namely specimens containing X-ray absorbers in high concentration and/or in an undispersed form.

Especially the spectra presented in chapter 5 have also illustrated a range of *in situ* conditions compatible with TEY detection of direct relevance to catalytic studies. In addition to the gas compositions referred to in this thesis the author has also performed measurements in air, in He-based mixtures containing N_2O, CO_2 and alkanes, as well as in moist environments such as a methanol saturated stream of He (fig. 7.1). Given the variety of gas compositions investigated, it appears now unlikely that there are gas environments which are entirely unsuitable to TEY detection. Of course, in moist gas environments the possibility exists that condensation occurs in the vicinity of the TEY detection electrodes. It was observed repeatedly that moisture from a methanol saturated atmosphere at room temperature caused a fluctuating DC current between sample and biased collector which was approximately two orders of magnitude larger (10^{-7} A) than typical TEY sample currents. This short-circuit current disappeared entirely upon heating the detector to temperatures above the evaporation point of the condensate.

The work presented in chapter 3 has shown that the depth probed by TEY detection is a strong function of absorption edge energy, sample composition and density. The probing depth varies between a few 10 Å at sub-keV energies and several 1000 Å for X-ray energies above 10 keV. Gas-flow TEY detection is therefore best categorised as a bulk probe with enhanced near-surface sensitivity. For gas-solid reactions which involve changes in the subsurface region of the sample, the TEY technique could yield information on the structural changes in the near-surface region. An alternative way to obtain true surface information by gas-flow TEY detection is to study thin and ultrathin films of X-ray absorbers adsorbed on a support containing different atomic species - in analogy to traditional SEXAFS experiments [1-3].

Chapter 4 has demonstrated that its near-surface sensitivity makes the TEY technique much less susceptible, albeit not entirely immune, to spectral distortions due to the ‘self-absorption’ and ‘thickness’ effects than FY and transmission detection of data from non-dispersed, concentrated and/or macroscopically heterogeneous samples [4].

All spectra in chapters 5 and 6 could not have been acquired by FY or transmission detection without destroying the integrity of the original samples by extensive grinding or milling, and dilution in a matrix to achieve the required low absorber concentrations. Moreover, even if transmission and FY samples are carefully prepared, the successful collection of accurate data is not guaranteed. This is illustrated for a particularly severe case in Appendix B which contains the near-edge transmission spectrum of CuO (99.9% pure, JM Chemicals, U.K.) which had been carefully ground in a mortar and dispersed in boron nitride to achieve an edge step height of $\Delta\mu(E_0)\cdot x = 0.5$. The distorted transmission spectrum shows that the heterogeneity of the diluted sample was still large enough to result in a strong 'thickness' effect. Similar problems were encountered by the author with samples of NiO, Cu_2O and pure transition metal powders. TEY detection circumvents these problems readily, as the pure sample is simply placed on the conducting sample support. Indications for small 'self-absorption' distortions, as observed in the TEY spectra of metallic samples (chapter 4), have so far not been identified in any TEY spectrum of a compound. Note also that the conductivity of the sample is not essential for TEY measurements because charge neutrality can be maintained by the secondary gas phase charges excited by energetic electrons. The TEY spectra of macroscopically thick coatings of insulators such as Cr_2O_3 have been obtained by the author without encountering any charging problems. Note that TEY data from the front surface of a *0.5 cm thick* sample of pure ZnO supported on a Ta foil were presented in chapter 4.

A remarkable feature of gas-flow TEY detection is the high signal-to-noise quality of the spectra which is routinely achieved when care is taken to shield detector and connections to the signal preamplifier from environmental electromagnetic noise. The most common problem is electromagnetic interference from resistive heaters in the *in situ* cell. Their effect is seen particularly in the spectra of fig. 5.21 which were acquired at elevated pessures. In the absence of electromagnetic noise, data collection times with a stepper motor driven monochromator are of the order of 30 min or less if the absorber concentration in the sample is higher than approximately 20at% - 30at%. Generally, for X-ray fluxes of the order of 10^{11} photons/s the noise level in the data is limited by spectrometer- or detector circuit noise, but not by the counting statistics. However, it should be borne in mind, that the signal quality deteriorates rapidly when the concentration of the element of interest decreases below 5at%-10at%, especially when the absorption edge of the minor component 'rides' on the absorption edge spectrum of the major sample constituent. This is illustrated in fig. 7.2. which contains raw TEY data for the calcined precursor of the unsupported Cu/Ni alloy particles containing 95at% Ni and 5at% Cu. The strong background absorption due to the Ni K-edge on the pre-edge region of the Cu K-edge amplifies all spectrometer noise considerably. Particularly pronounced are Bragg diffraction glitches (indicated by black arrows) in the monochromator transmission function, which are sustainably small relative to the intensity of the Ni XAFS features, but large compared to the small Cu edge step (see inset of fig. 7.2). However, even when a second absorption edge is absent from the pre-edge region of a small edge of interest, the background signal due to ionization events in loosely bound orbitals of the sample can be substantial. For small concentrations of absorbers, FY detection is the preferred detection mode because of its better counting statistics [5].

Finally, the spectral region accessible by *in situ* TEY XAS is limited only at lower energies, mostly by the transmission of the X-ray window materials and the lengths of the gas paths which the incident X-ray beam has to traverse to reach the sample. How such design choices determine the performance of the cell is illustrated in fig. 7.3. In the left diagram, the transmission characteristics of two window materials used in the author’s work are compared as a function of material thickness. It is seen

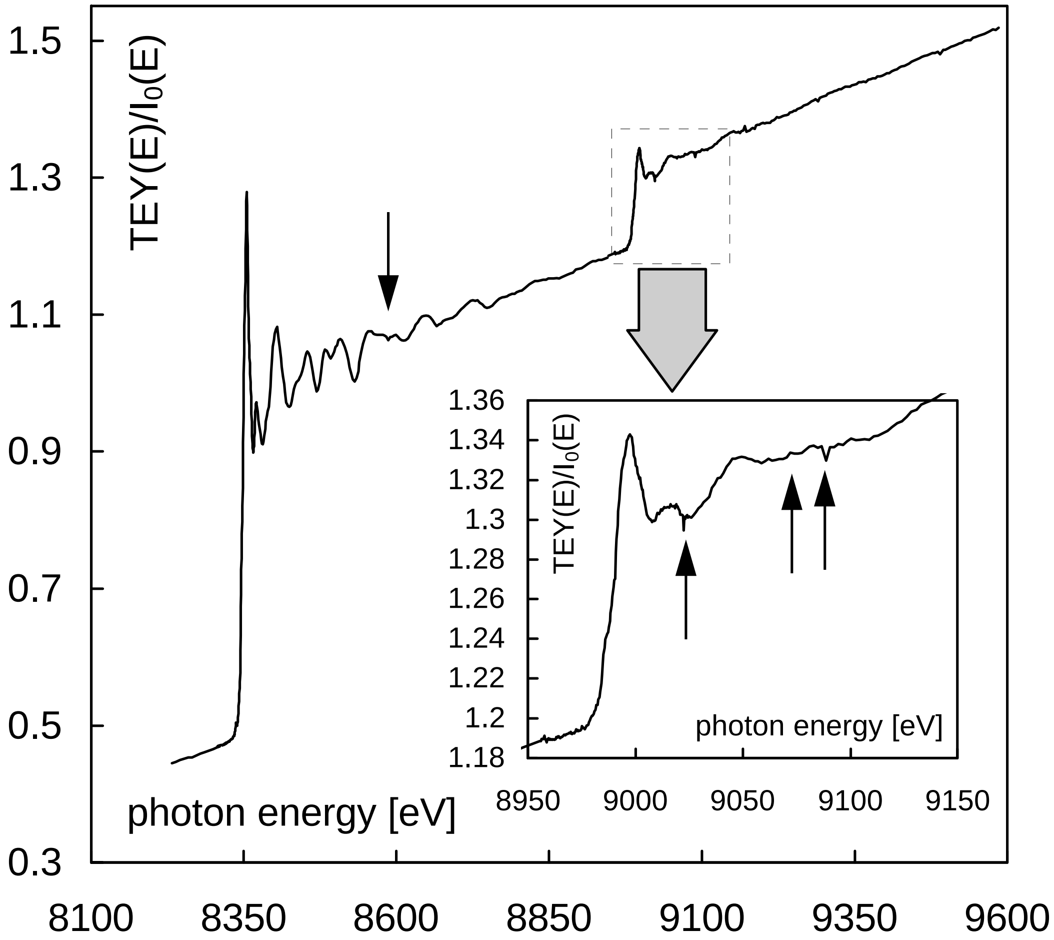

Figure 7.2. Raw TEY data for the calcined precursor to an unsupported Cu/Ni model catalyst containing 95at% Ni and 5at% Cu.

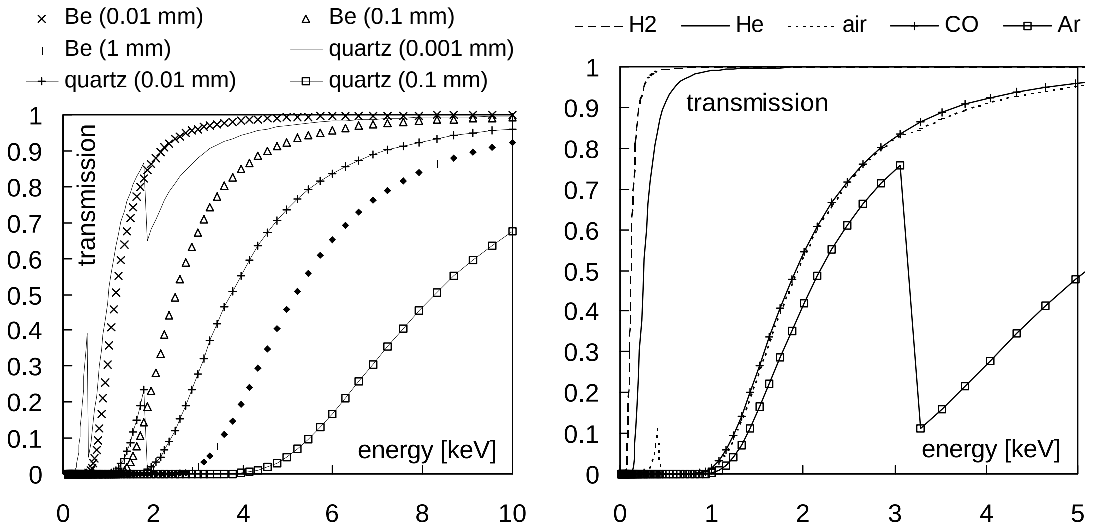

Figure 7.3. Left diagram: transmission of Be (0.01 mm, 0.1 mm, 1 mm) and quartz (0.1 μm, 1 μm, 10 μm) as a function of photon energy. Right diagram: transmission of a pathlength of 1 cm filled with H_2, He, air, CO and Ar as a function of photon energy. Absorption coefficients taken from reference [6].

that quartz window thicknesses well below 0.01 mm and Be windows below 0.1 mm thickness are required to allow experiments with even moderately (E ≈ 1-2 keV) soft X-ray energies. Similarly, assuming a pressure of 1 atm and a gas path between window and sample of 1 cm, CO, Ar, and air would all be too absorbing to permit measurements at absorption edges below 1.5 keV. Considerable dilution of these gases with He or severe shortening of the gas path between window and sample to well below 1 mm would be necessary to achieve a good gas transmission. These considerations demonstrate how difficult the construction of an *in situ* TEY XAS cell for measurements in the soft and ultra-soft X-ray region would be. However, the development of such equipment is nevertheless desirable because it would permit the study of adsorbed low-Z atoms under reaction conditions. The FY setup developed at Brookhaven over the last decade has been a first step in this direction [7-9]. In the meantime, the practical low-energy limit to the application of gas-flow detection is mainly determined by the availability of XAFS beamlines to which an *in situ* gas-flow TEY cell can be attached: in most cases, this limit is close to photon energies in the range between 2 keV and 4 keV.

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