

Total Electron-Yield XAS as an *In Situ* Probe for Studies of Catalysts and Other Materials in Reactive Gas Environments

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DECLARATION

This dissertation is the result of my own work except where reference is made to other sources. Furthermore, except where explicitly stated, it includes nothing which is the outcome of work done in collaboration. It has not been submitted, in whole or in part, for a degree or any other qualification at another university. The scientific body of this work contains no more than 60000 words.

Sven Schröder

SUMMARY

This work explores for the first time the possibilities and limitations in applying the total electron-yield (TEY) detection mode of X-ray absorption spectroscopy (XAS) to *in situ* studies of catalysts and other materials in reactive gas environments. The main objectives of the work were

- to design, test and optimise a new apparatus for *in situ* studies of materials under gas-flow at elevated temperatures and pressures,
- to achieve a quantitative understanding of the TEY signal formation process, and especially the probing depth of the technique, as a function of experimental and sample specimen parameters,
- to examine whether and under which conditions the TEY signal is an accurate measure of the X-ray absorption coefficient,
- to carry out first *in situ* characterisations of catalytically relevant materials.

All these aims have been fulfilled and the results are presented in this thesis.

The thesis is organised as follows. In the first chapter, a summary of the most salient principles of X-ray absorption spectroscopy and relevant data analysis techniques is presented. The second chapter describes the development and characterisation of the new apparatus used for obtaining the experimental TEY XAS data presented in the remaining chapters of the thesis. Chapter 3 describes for the first time how fast Monte-Carlo algorithms for the simulation of electron trajectories can be employed to calculate the depth information carried by the TEY signal. An experimental study of NiO overlayers on Ni has been carried out to confirm the predictions of the Monte-Carlo simulation model. Data in chapter 4 demonstrate conclusively that the response of the TEY signal to the X-ray absorption coefficient becomes non-linear at grazing X-ray incidence (due to a non-linearity analogous to the well-known ‘self-absorption’ effect in fluorescence-yield XAS). Furthermore, it is shown that sample materials with high X-ray fluorescence yields exhibit a ‘self-absorption’ effect due to TEY contributions excited by fluorescent photons. It is shown that the magnitude of the expected spectral distortions can be calculated using simple recipes based on the simulation results obtained earlier in chapter 3. These results resolve some long-standing uncertainties in the literature. Chapter 5 describes an *in situ* XAS/XRD study of a commercial methanol synthesis catalyst (Cu/ZnO/Al₂O₃), and discusses mainly the relation between the Cu K-edge XAFS amplitudes and the oxidation state and the morphology of the Cu particles. The question whether the chemical state of

the active Cu surface under reaction conditions is characterised by a (sub)oxide layer is has been adressed *in situ*. No evidence for the dissociation of carbon dioxide on Cu was found. Chapter 6 describes *in situ* studies of unsupported Cu/Ni alloy particles by TEY XAS, XRD and XPS. This study was undertaken because Cu/Ni alloys are one of the best characterised catalytically active bimetallic systems, providing a benchmark against which TEY XAS results could be calibrated. Previous observations of Cu segregation from the bulk of these particles were confirmed by XPS. The presence of segregated layers provided a final test for the probing depth characteristics of TEY XAS.

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Synchrotron experiments last 24 hours a day and are therefore impossible to perform without a co-worker or two. Most of the time, Geoff Moggridge and Mark Ormerod played the keyboard and swung the mono for me when I was asleep. Thanks to both of you for your effort and for making the time at DL fun.

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GLOSSARY OF ACRONYMS

Within chapters and in major subsections I have tried to be consistent in avoiding acronyms without explaining their meaning first. As experimental solid-state science is studded with techniques named by three-, four- or more-letter words, I might have overlooked the explanations every now and then. For the sake of improved readability I am therefore providing a list of expansions which might be useful to the reader of the next 200 pages.

AES	Auger electron spectroscopy
AFM	Atomic force microscopy
ARSES	Angle-resolved secondary electron spectroscopy
ARUPS	Angle-resolved ultraviolet photoelectron spectroscopy
CEMS	Conversion electron Mössbauer spectroscopy
CEY	Conversion electron-yield (= TEY detected under gas-flow)
DAFS	Diffraction anomalous fine-structure
EDAX	Energy-dispersive analysis of X-ray fluorescence
EDX	Energy-dispersive X-ray fluorescence analysis
EELS	Electron energy loss spectroscopy
EXAFS	Extended X-ray absorption fine structure
FIM	Field ionisation microscopy
FY	Fluorescence-yield
FYNES	Fluorescence-yield near-edge spectroscopy/structure
LBA	Line-broadening analysis
LEED	Low-energy electron diffraction
MS	Multiple scattering
NEXAFS	Near-edge X-ray absorption fine-structure
PEY	Partial electron-yield
SAXS	Small-angle X-ray scattering
SEM	Scanning electron microscopy
SEXAFS	Surface extended X-ray absorption fine structure
SES	Secondary electron spectroscopy
SEY	Secondary electron-yield
SS	Single scattering
STM	Scanning tunneling microscopy
TDS	Thermal desorption spectroscopy
TEY	Total electron-yield
TEM	Transmission electron microscopy
TOF	Time-of-flight
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
TPRS	Temperature programmed reaction spectroscopy
UHV	Ultra-high vacuum
UPS	Ultraviolet photoelectron spectroscopy
WAXS	Wide angle X-ray scattering
XAFS	X-ray absorption fine-structure
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction