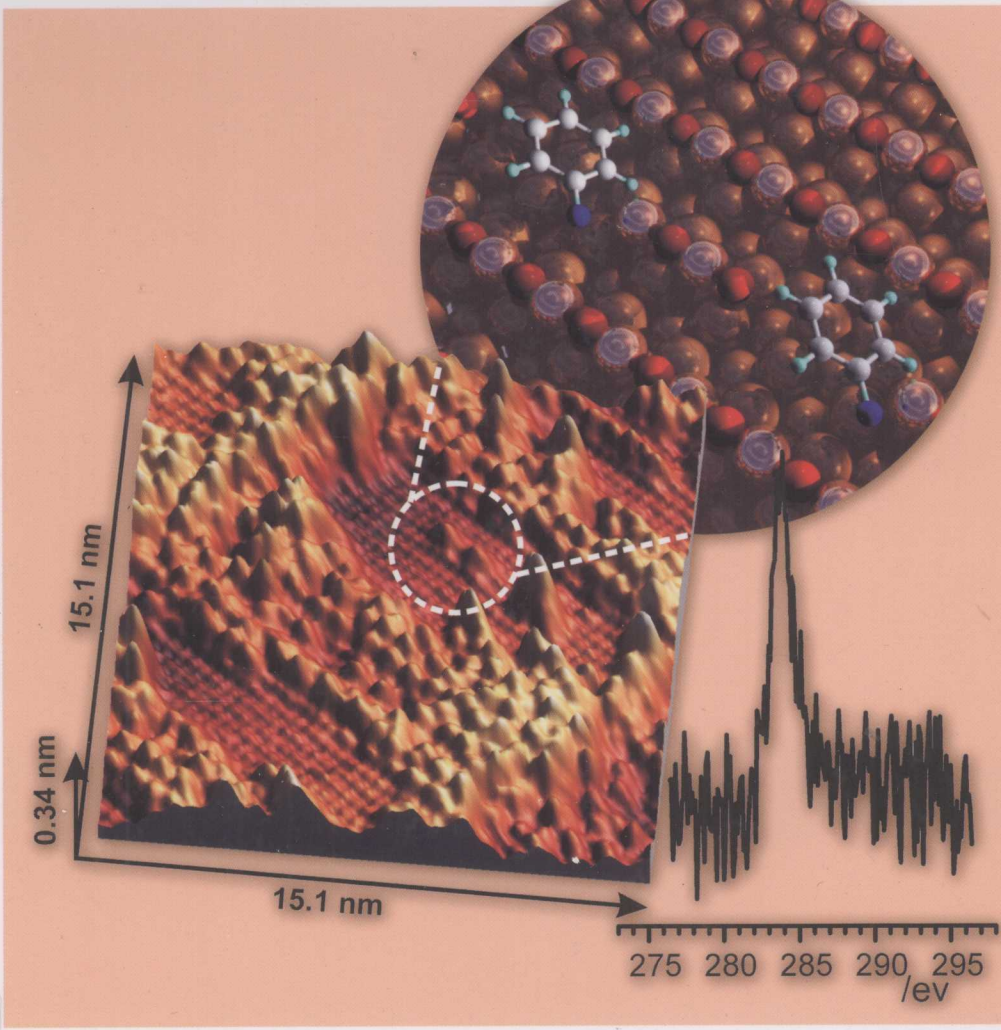
RSC Nanoscience & Nanotechnology

P. R. Davies and M. W. Roberts

Atom Resolved Surface Reactions

Nanocatalysis



RSC Publishing

Atom Resolved Surface Reactions
Nanocatalysis

P.R. Davies and M.W. Roberts
School of Chemistry, Cardiff University, Cardiff, UK

RSC Publishing

ISBN: 978-0-85404-269-2

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Atom Resolved Surface Reactions
Nanocatalysis

RSC Nanoscience & Nanotechnology

Series Editors

Professor Paul O'Brien, *University of Manchester, UK*
Professor Sir Harry Kroto FRS, *University of Sussex, UK*
Professor Harold Craighead, *Cornell University, USA*

This series will cover the wide ranging areas of Nanoscience and Nanotechnology. In particular, the series will provide a comprehensive source of information on research associated with nanostructured materials and miniaturised lab on a chip technologies.

Topics covered will include the characterisation, performance and properties of materials and technologies associated with miniaturised lab on a chip systems. The books will also focus on potential applications and future developments of the materials and devices discussed.

Ideal as an accessible reference and guide to investigations at the interface of chemistry with subjects such as materials science, engineering, biology, physics and electronics for professionals and researchers in academia and industry.

Titles in the Series:

Nanotubes and Nanowires

C.N.R. Rao, FRS and A. Govindaraj, *Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India*

Nanocharacterisation

Edited by A.I. Kirkland and J.L. Hutchison, *Department of Materials, Oxford University, Oxford, UK*

Atom Resolved Surface Reactions: Nanocatalysis

P.R. Davies and M.W. Roberts, *School of Chemistry, Cardiff University, Cardiff, UK*

Visit our website at www.rsc.org/nanoscience

For further information please contact:
Sales and Customer Care, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK
Telephone +44 (0)1223 432360, Fax +44 (0)1223 426017, Email: sales@rsc.org

"It is not the critic who counts, not the man who points how the strong man stumbled or where the doer of deeds could have done better. The credit belongs to the man that is actually in the arena whose face is marred by dust, sweat and blood, who strives valiantly, who errs and comes short again and again, who knows the great enthusiasm, the great devotions and spends himself in a worthy cause, who at the best knows in the end the triumph of high achievement and who at the worst, if he fails, at least fails while daring, so that his place shall never be with these cold timid sorts, who know neither victory nor defeat."

Theodore Roosevelt

Preface

"We build too many walls and not enough bridges"

Isaac Newton

Since the earliest days of scanning tunnelling microscopy (STM) and the award of the Nobel Prize to Binnig and Rohrer in 1986, it was evident that a powerful approach had become available for the study of structural aspects of solid surfaces. The technique provided a surface probe with atomic resolution with initial emphasis being given to semiconductors, Binnig and Rohrer being at IBM. It was clear, however, that it would be applicable for the study of surfaces over a wide range of scientific disciplines with nanotechnology, over the last decade, developing into a "stand-alone" discipline with far-reaching implications in many areas of science and technology and with significant financial investment in both academic and industrial laboratories. Matthew Nordon of Lux Research, a nanotechnology consultancy in New York, suggested in *The Economist*, 1 January 2005, that in 2004 the American government spent $1.6 billion on nanotechnology, more than twice as much as it did on the Human Genome Project. Also that IBM had in 2005 more lawyers than engineers working in the field of nanotechnology relating particularly to patent rights. However, at that time there had been no law suits as no real money had been made from the nanoparticles – mainly carbon nanotubes.

Much of the early STM studies of metals was focused on surface restructuring, particularly adsorbate-induced changes. Interpretation of adsorbate images was initially by simple inspection but it became clear that information from other experimental techniques would be required for particle identification. *In situ* chemical information, to complement structural information, was generally lacking until the mid-1990s and this was a serious disadvantage if we were to probe the details of molecular events associated with a surface-catalysed reaction. There was also a tendency in surface science to study either single adsorbate systems or to carry out experiments where two adsorbates were introduced to the solid surface sequentially rather than simultaneously. The latter coadsorption approach could be argued to simulate more closely a "real catalytic reaction" than the former; it was an approach we had adopted at

Cardiff using surface-sensitive spectroscopies and which provided a different insight into surface reactivity, particularly of the role of transient and precursor states in the dynamics of surface-catalysed reactions.

Although this book is research oriented, we have attempted to relate the information and concepts gleaned from STM to the more established and accepted views from the classical macroscopic (kinetic, spectroscopic) approach. How do well-established models stand up to scrutiny at the atom resolved level and do they need to be modified? We have, therefore, included a chapter where classical experimental methods provided data which could profit from examination by STM.

In taking this approach, someone new to the field of surface chemistry and catalysis can hopefully obtain a perspective on how more recent atom resolved information confirms or questions long-standing tenets. There is, therefore, a historical flavour to the book, with the first chapter dealing briefly with "how did we get to where we are now?". This inevitably means that the views expressed reflect personal perspectives but are very much influenced by the outstanding contributions from those who have pioneered the development of STM in surface chemistry and catalysis, of which groups at the Fritz-Haber Institut in Berlin and the universities at Aahrus, Berkeley and Stanford have been at the forefront.

Thirty years ago, one of us (M.W.R.) set out with Clive McKee to write the book *Chemistry of the Metal–Gas Interface* (Oxford University Press, 1979; Russian translation, Moscow, 1981). This was prompted by the then rapid developments in surface-sensitive spectroscopies – infrared, photoelectron and Auger – and structural information from low-energy electron diffraction. The present book represents a step-change in the quest to understand surface phenomena through the wealth of information now becoming available from STM. The atom resolved evidence brings into focus the limitations of long-held views in surface chemistry and, where appropriate, we have given some hints as to what questions should be addressed when formulating reaction mechanisms and the challenge of providing meaningful kinetic expressions for surface reactions.

J.W. Mellor, in his book *Modern Inorganic Chemistry*, published by Longman Green and Co., made the following interesting observation:

> "*The word catalysis itself explains nothing. To think otherwise would lay us open to Mephistopholes' gibe: A pompous word will stand you instead for that which will not go into the head.*"

He then goes on to state that there is no difficulty in covering an obscure idea so that the word appears to explain the idea. This, written in 1920, still has a ring of authenticity nearly 100 years later, with Mephitopholes' gibe having a much wider relevance than being confined just to the word *catalysis*.

There is good evidence that STM has already and will continue to have a significant and far-reaching impact on our understanding at the molecular level of the dynamics and structural aspects of adsorption processes and their role in

surface-catalysed reactions. There has, however, been only limited evidence on STM's impact in industrial or applied catalysis, the evidence being more obvious in materials science with atomic force microscopy (AFM) being used to greater advantage. There is indeed the view that the development of catalysts in the chemical industry has and will continue to rely very much on empirical skills in catalyst preparation, where nanoscale particles have been central to the control of both activity and selectivity. A knowledge of the development of principles and concepts which emerge from fundamental studies will, however, undoubtedly continue to influence thinking in industrial laboratories.

We hope that the book will appeal not only to those who wish to become familiar with the contribution that STM has made to the understanding of the field of surface chemistry and heterogeneous catalysis, but also to those who are new to catalysis, a fascinating and important area of chemistry and where so much has still to be achieved. Chapters have, where appropriate, suggestions for further reading where topics have been considered in more depth by others in both original papers and monographs. In addition to the references included with each chapter, dates are occasionally mentioned in the text to enable the reader to glean the time scale on which the science, concepts and experimental data first became available, then established and possibly modified.

About the Authors

Wyn Roberts, a student of the Amman Valley Grammar School, studied chemistry at University College Swansea where, after graduation, he pursued postgraduate studies investigating the role of sulfur as a catalyst in the formation of nickel carbonyl under the supervision of Keble Sykes. After being awarded his PhD, he was first appointed to a United Kingdom Atomic Energy Research Fellowship at Imperial College of Science and Technology, London, and then as a Senior Scientific Officer at the National Chemical Laboratory, Teddington. His first academic post was a lectureship at the Queen's University, Belfast, before in 1966 being appointed to the Foundation Chair of Physical Chemistry at the University of Bradford, where he also had periods as Head of Department and Dean of Physical Science.

In 1979 he moved to University College, Cardiff, where he was Head of Department (1987–1997), a Deputy Principal (1990–1992) and is currently a Research Professor. He was invited to be World Bank Visiting Professor in China in 1985, a Visiting Professor at Berkeley and is an Honorary Fellow of the University of Wales, Swansea. He was the first Chairman of the Surface Reactivity and Catalysis Group (SURCAT) of the RSC.

His research interests are in the application of surface-sensitive experimental methods in surface chemistry and catalysis and he has supervised over 80 PhD students, his co-author being one of them. He has received three National Awards, the Tilden Lectureship and Medal of the RSC, the Royal Society of Chemistry Award in Surface Chemistry and the John Yarwood Prize and Medal of the British Vacuum Society. He has also held appointments with the

University Grants Committee, the Science Research Council and the Ministry of Defence.

Phil Davies, a student of Blythe Bridge High School, Stoke-on-Trent, studied chemistry and mathematics in Southampton University. An undergraduate project on modelling of adsorption at fractal surfaces led to an interest in surface phenomena and, after graduating with double honours in 1986, he moved to Cardiff to study reactions at surfaces with surface-sensitive spectroscopy. After being awarded a PhD, he was appointed to a lectureship in the Department of Chemistry at Cardiff. His main research interests are studying reaction mechanisms at surfaces primarily through the use of surface sensitive spectroscopy but he also spent a short period of time with Professor Rutger van Santen in Eindhoven, studying adsorption and reaction using *ab initio* calculations on clusters. Since 1997, his interests have centred largely on the influence of local atomic structure on reaction mechanisms studied with scanning probe microscopies.

Between them, Davies and Roberts have published over 400 scientific papers and a number of books.

Acknowledgements

This book could not have been contemplated without the contributions that our graduate students have made to the understanding of molecular processes at metal surfaces, with Martin Quinn and Brian Wells providing early evidence from work function and photoemission studies of oxygen-induced surface reconstruction, Clive McKee and Richard Joyner of surface dynamics and structure, Julian Ross of "real" catalysis, Albert Carley and Paul Chalker in photoelectron spectroscopy and Chak-Tang (Peter) Au of surface transients in oxidation catalysis. These were studies that provided the science and impetus which led to the EPRSC funding an STM–XPS project in which Albert Carley, Giri Kulkarni, K.R. Harikumar and Rhys Jones were prominent. One of us (M.W.R.) has also enjoyed discussions over a wide range of surface chemistry with Ron Mason for some 30 years, exemplified by his prompting of a recent paper describing a novel approach to synthesising silica overlayers by nanocasting (Chapter 11).

We are also grateful for the permission we received from a number of groups to make reference (with figures) to their data, including Gerhard Ertl, Jost Wintterlin and Hajo Freund a the Fritz-Haber Institut, Bob Madix at Stanford, Gabor Somorjai and Miquel Salmeron at Berkely, the group of Besenbacker at Aahrus and Tøpsoe, John Thomas at Cambridge and Richard Palmer in Birmingham.

We also acknowledge the Institute of Physics' permission to make reference to quotations which appeared in *The Harvest of a Quiet Eye*, by Alan C. Mackey, Ed. M. Ebison, Institute of Physics, 1977.

Finally, we are indebted to Terrie Dumelow for her patience in preparing the manuscript and our families for their long-suffering support.

Some Relevant Units – SI and Derived Units

Physical quantity	**Name of unit**	**Symbol and definition**
Length	metre	m
Length	ångstrom, nanometre	$1\,\text{Å} \equiv 10^{-10}\,\text{m} \equiv 0.1\,\text{nm}$
		$1\,\text{nm} \equiv 10^{-9}\,\text{m} \equiv 10\,\text{Å}$
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Frequency	hertz	$\text{Hz} \equiv \text{s}^{-1}$
Energy	calorie	$1\,\text{cal} = 4.184\,\text{J}$

Pressure Conversion Factors

1 atm	101325 Pa
1 atm	1.01325 bar
1 bar	10^5 Pa
1 mbar	10^2 Pa
1 Torr	1.332 mbar
1 Torr	133.32 Pa

Gas Exposure 1 L (langmuir) $= 1 \times 10^{-6}$ Torr s

Abbreviations

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
DFT	Density Function Theory
EELS	Electron Energy Loss Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
ESR	Electron Spin Resonance
EXAFS	Extended X-ray Absorption Fine Structure
FEEM	Field Electron Emission Microscopy
FIM	Field Ion Microscopy
FTIR	Fourier-Transform Infrared
HAADF	High-Angle Annular Dark Field
HREELS	High-resolution Electron Energy Loss Spectroscopy
HRTEM	High-resolution Transmission Electron Microscopy
IETS	Inelastic Electron Tunnelling Spectroscopy
IRAS	Infrared Reflection Absorption Spectroscopy
L	Langmuir (exposure of 1 Torr s)
LEED	Low-energy Electron Diffraction
ML	Monolayer
NEXAFS	Near Edge X-ray Absorption Fine Structure
PIS	Penning Ionisation Spectroscopy
RAIRS	Reflection Absorption Infrared Spectroscopy
SEM	Scanning Electron Microscopy
SEXAFS	Surface Extended X-ray Absorption Fine Structure
SNOM	Scanning Near-field Optical Microscopy
SPM	Scanning Probe Microscopy
STEM	Scanning Transmission Electron Microscopy
STM	Scanning Tunnelling Microscopy
STS	Scanning Tunnelling Spectroscopy
SXRD	Surface X-ray Diffraction
TPD	Temperature-programmed Desorption
TPR	Temperature-programmed Reaction
UHV	Ultra-high Vacuum
UPS	Ultraviolet Photoelectron Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Contents

Chapter 2 Experimental Methods in Surface Science Relevant to STM

Chapter 3 Scanning Tunnelling Microscopy: Theory and Experiment

Chapter 4 Dynamics of Surface Reactions and Oxygen Chemisorption

Chapter 5 Catalytic Oxidation at Metal Surfaces: Atom Resolved Evidence

Chapter 6 Surface Modification by Alkali Metals

Chapter 7 STM at High Pressure