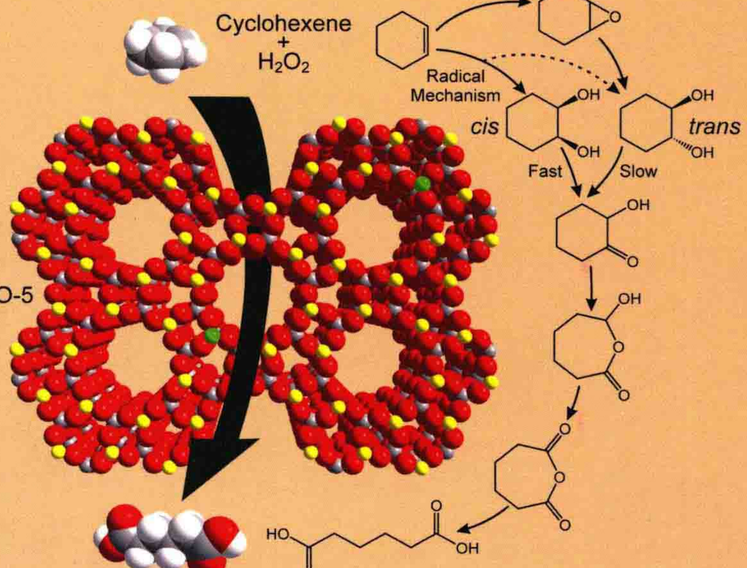
Design and Applications of Single-Site Heterogeneous Catalysts

Contributions to Green Chemistry, Clean Technology and Sustainability

Sir John Meurig Thomas



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FOR JEHANE

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FOREWORD

Homogeneous and enzymatic catalysis operate usually with well-defined molecular entities, and hence strategies for elucidation of the underlying elementary processes are quite straightforward. Quite in contrast, with heterogeneous catalysis the surface generally exposes sites with widely varying structure and composition, so that deeper understanding could only recently be reached along the "surface science" approach by using single crystal surfaces as model systems. However, a bridge between these two areas is offered by so-called single-site heterogeneous catalysts (SSHCs). These are porous inorganic solids with well-defined structures exposing inner surfaces with a high surface area in which the active centres are uniformly distributed without mutual interaction. Such systems gained considerable practical applications during the past years, and Sir John Meurig Thomas has been at the forefront of research in this area over many years. This monograph presents a concise comparison of these catalysts with enzymes and immobilised homogeneous catalysts, and then outlines in detail their structural and catalytic properties, as well as their application to clean and sustainable technologies. It will certainly become a milestone in the attempts to develop unifying concepts in catalysis.

Gerhard Ertl
August 2011

PREFACE

In December 2010, I was fortunate to be the recipient of the Gerhard Ertl Lecture Award, sponsored by the universities and Max Planck Institutes (MPIs) of Berlin as well as by the company BASF in Ludwigshafen. Conscious of the fact that, three years earlier, these universities and MPIs had set up what is arguably the largest group of academics in the world devoted to the study and application of catalysis — UniCat is the cluster of excellence which focuses on the pursuit of unifying concepts in catalysis — I chose as my topic "Unifying Concepts in Single-site Catalysis". In doing so, I knew that my audience would include many young students and post-doctoral researchers who might find it helpful if I were to trace both the emergence and the growth of this rapidly expanding field of study and application.

In order to comply with the limits imposed by a one-hour lecture, I concentrated overwhelmingly in my presentation on single-site heterogeneous catalysts (SSHCs), which has been my own field of speciality for over two decades. It was simply not possible to delve into the realm of single-site homogeneous catalysis, where the work of pioneers such as Grubbs, Schrock, Kaminsky, Britzinger, Noyori, Sharpless, Heck, Negishi, Suzuki, Stevens, Marks and others involving liquid-phase homogeneous catalysis, or the elegant gas-phase studies of Helmut Schwarz and his colleagues, stands supreme.

I attempted in my lecture to illustrate the way in which inorganic solid-state chemistry constitutes a powerful route to the design, preparation and characterization of new solid catalysts, especially those required for the era of sustainability, clean technology and green chemistry, all of which are key features of current science and the manner in which it is applied for the public good.[1]

This monograph includes several illustrations and sub-sections that could not be presented in my lecture, owing to the strictures of time. Some facets of SSHCs that are discussed rather fully here were alluded to almost subliminally during the lecture itself. The scientific principles of the various techniques used for the preparation, and especially for the *in situ* or *ex situ* characterization of new catalysts, were not covered in the lecture itself, and neither do they figure at all eminently in this monograph. We are more interested here in charting the fundamental aspects of, and the results that arise from, the design of new, potentially important and practical examples of heterogeneous catalysts, through the engineering of active sites. It has not been possible to do justice to all the active workers in this field, nor to the numerous relevant publications pertaining to it. Ever since I occupied the chair created for Michael Faraday (my scientific hero) and worked in his laboratory (and lived in his residence) at the Royal Institution (RI), London, I have felt that his practice of collecting many of his key papers and publishing them in a "united" text[2] was an admirable one. It is invidious even to suggest any comparisons with Faraday, whom Lord Rutherford described as "the greatest discoverer ever", but it is surely not ignoble to emulate him in the practice of collating and unifying one's thoughts on particularly important scientific topics. Whilst pursuing research at the Davy Faraday Research Laboratory of the RI (1986–2006), I also read with awe the publications of Faraday's friend, my fellow countryman, W. R. Grove, the inventor of the fuel cell. In his book *The Correlation of Physical Forces*,[3] Grove (who, with others, is accredited with the discovery of the first law of thermodynamics) writes: "Every one is but a poor judge where he is himself interested, and I therefore write with diffidence; but it would be affecting an indifference which I do not feel if I did not state that I believe myself to have been the first who introduced this subject as a general system…". The idea of pursuing single-site heterogeneous catalysis has occupied my mind with ever-growing intensity since I first started working at the RI.[4]

I am especially grateful for the encouragement given to me by members of my Berlin audience, particularly Professors Gerhard Ertl, Matthias Dries, Joachim Sauer and the following directors of the Fritz-Haber-Institute der Max-Planck-Gesellschaft, Professors Robert Schlögl, Hajo Freund and Gerard Meijer, to put into print an amplification of the quintessential features of my lecture. I make many other acknowledgements (see ensuing pages) to individuals who have collaborated with me in many ways. I particularly wish to single out Professor Kenneth Harris of Cardiff University for the enormous help he has provided in bringing this monograph to fruition. I am also deeply grateful to Mrs Linda Webb for her expert typing and Mr Nathan Pitt for invaluable help with the illustrations. I greatly appreciate the assistance of Professor Kenneth Harris and Ms Caroline Hancox for help with the cover. Ms Jacqueline Downs is thanked for her expert editorship. Professors Peter Edwards and Alan Windle are also thanked for their general support over many years. Last but not least, I thank my wife, Professor Jehane Ragai, for her constant help and understanding.

For convenience my text is divided into three parts. The first recalls the essence of SSHCs and why they offer a strategy for the design of new catalysts. The second describes microporous SSHCs and the third describes mesoporous ones. (In the IUPAC definitions, those nanoporous solids that have pore diameters up to 20 Å (2 nm) are microporous, whereas in mesoporous ones pore diameters exceed 20 Å.) I hope that readers will find it pedagogically and otherwise helpful that full titles are given of all the articles that appear in the references at the end of each chapter; titles are an important feature of all published work.

John Meurig Thomas, FRS, FREng.
Cambridge
June 2011

References

1. J. M. Thomas. The principles of solid state chemistry hold the key to the successful design of many heterogeneous catalysts for environmentally responsible processes. *Micropor. Mesopor. Mat.* **146**, 3 (2011).
2. Michael Faraday's *Experimental Researches in Chemistry and Physics.* Foreword to Bicentennial Edition (1991) by J. M. Thomas. Taylor and Francis, London (original publication: 1859).
3. W. R. Grove. *The Correlation of Physical Forces,* 5th ed., Longmans, Green & Co., London (1874).
4. J. M. Thomas. Uniform heterogeneous catalysts: the role of solid-state chemistry in their development and design, *Angew. Chem. Int. Ed.,* 27, 1673 (1988).

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Fig. 4.3	*PNAS,* **102,** 13732 (2005)

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Fig. 1.3	*Phys. Chem. Chem. Phys.,* **11,** 2799 (2008)
Fig. 3.3	*Chem. Commun.,* 2833 (2006)
Fig. 3.4	*Dalton Trans.,* 5498 (2007)
Fig. 3.20	*Faraday Disc.,* **105,** 1 (1996)
Figs 4.8 and 4.10	*Microporous Framework Solids* (by P. A. Wright) (2009)
Fig. 4.9	*JCS Faraday Trans.,* **91,** 3975 (1995)
Fig. 5.2	*Chem. Commun.,* 448 (2006)
Scheme 6.1	*Chem. Commun.,* 3350 (2007)
Schemes 6.4 and 6.5	*Green Chem.,* **9,** 731 (2007)
Figs 6.11, 6.12 and 6.13	*Turning Points in Solid-State Materials and Surface Chemistry* (ed. D. M. Harris & P. P. Edwards) (2007) p. 385
Scheme 6.11, Table 6.3 and Fig. 6.15	*Chem. Commun.,* 1340 (1984)
Fig. 7.4	*J. Mater. Chem.,* **18,** 4021 (2008)
Fig. 8.3	*Chem. Commun.,* 1126 (2003)
Figs 8.12 and 8.13	*Faraday Disc.,* **138,** 301 (2008)
Fig. 8.28	*Chem. Commun.,* 2653 (2003)

Wiley-VCH

Figs 1.1 and 3.15	*Angew. Chemie. Intl. Ed.*, **47,** 5627 (2008)
Figs 1.2, 3.18, 6.1 and 6.3	*Angew. Chemie. Intl. Ed.*, **44,** 6456 (2005)
Fig. 2.3	*Eur. J. Biochem.*, **270,** 4082 (2003)
Fig. 3.16	*Angew. Chemie. Intl. Ed.*, **37,** 2466 (1988)
Fig. 3.19(a)	*Angew. Chemie. Intl. Ed.*, **48,** 6543 (2009)
Fig. 4.2	*Angew. Chemie. Intl. Ed.*, **27,** 1673 (1988)
Fig. 4.4 and Scheme 4.1	*Handbook of Heterogeneous Catalysis,* **Vol 1** (ed. G Ertl *et al.*) (1997) p. 286
Fig. 4.7	*Angew. Chemie. Intl. Ed.*, **31,** 1472 (1992)
Fig. 4.12	*Angew. Chemie. Intl. Ed.*, **38,** 3588 (1999)
Scheme 4.2	*Green Chemistry and Catalysis* (by R. A. Sheldon & I. Arends) (2007)
Fig. 4.22	*Angew. Chemie. Intl. Ed.*, **47,** 5179 (2008)
Fig. 4.23	*Angew. Chemie. Intl. Ed.*, **50** (2011)
Fig. 4.24	*Chem. Cat. Chem.*, **2,** 1548 (2010)
Fig. 4.29	*Angew. Chemie. Intl. Ed.*, **42,** 1520 (2003)
Figs 4.31 and 4.34	*Chem. Euro. J.*, **7,** 2973 (2001)
Fig. 4.32	*Angew. Chemie. Intl. Ed.*, **39,** 2310 (2000)
Fig. 4.39	*Chem. Eur. J.*, **16,** 1368 (2010)
Fig. 4.42	*Chem. Cat. Chem.*, **3,** 95 (2011)
Fig. 5.1	*Chem. Europ. J.*, **14,** 2340 (2008)
Fig. 5.7	*Angew. Chemie.*, **37,** 1198 (1988)
Scheme 6.9	*Chem. Eur. J.*, **14,** 8098 (2008)
Figs 7.1 and 7.2	*Chem. Cat. Chem.*, **1,** 223 (2009)
Figs 7.6, 7.7 and 7.8	*Angew. Chemie. Intl. Ed.*, **46,** 1075 (2007)
Figs 8.5 and 8.6	*Angew. Chemie.*, **43,** 6745 (2004)
Fig. 8.10	*Chem. Cat. Chem.*, **2,** 402 (2010)
Fig. 8.14	*Angew. Chemie. Intl. Ed.*, **45,** 4782 (2006)
Fig. 8.25	*Chem. Cat. Chem.*, **2,** 403 (2010)

Nature (Macmillan)

Fig. 2.5	*Nature,* **309,** 589 (1984)
Fig. 3.19	*Nature,* **461,** 246 (2009)

Figs 4.6 and 4.19	*Nature*, **457,** 671 (2008)
Fig. 7.4	*Nature Chem.*, **2,** 353 (2010)

Science (AAAS)

Fig. 1.4	*Science*, **273,** 1688 (1996)
Fig. 3.9	*Science*, **317** (2007)
Fig. 5.3	*Science*, **331,** 195 (2011)
Fig. 5.7	*Science*, **328,** 602 (2010)
Fig. 8.7	*Science*, **280,** 705 (1998)
Figs 8.23 and 8.24	*Science*, **329,** 1633 (2010)

Elsevier

Fig. 2.4	*Micro. & Mesoporous Materials*, **118,** 334 (2009)
Fig. 4.13	*Micro. & Mesoporous Materials*, **146,** 1 (2011)
Scheme 4.3	*Catal. Today*, **60,** 227 (2000)
Fig. 4.30	*Appl. Catal. A*, **194,** 487 (2000)
Scheme 4.7 and Fig. 4.40	*Solid State Science*, **8,** 326 (2006)
Fig. 6.8	*J. Catal.*, **216,** 265 (2003)
Fig. 7.18	*J. Mol. Catal. A*, **139,** 253 (1999)
Figs 8.15, 8.16, 8.17 and 8.18	*Chem. Phys. Lett.*, **443,** 337 (2007)
Fig. 8.22	*J. Catal.*, **223,** 232 (2004)

American Chemical Society (ACS)

Fig. 2.2	*C&E News*, July 19 (2010)
Figs 3.7, 8.2 and 8.8 and Table 8.3	*Acc. Chem. Res.*, **36,** 20 (2003)
Fig. 3.17	*J. Am. Chem. Soc.*, **125,** 4325 (2003)
Schemes 3.1 and 3.2	*J. Am. Chem. Soc.*, **126,** 3052 (2004)
Fig. 4.1	*J. Phys. Chem.*, **B108,** 869 (2004)
Figs 4.35, 4.36, 4.37 and 4.38	*Acc. Chem Res.*, **34,** 191 (2001)

Fig. 4.41	*J. Am. Chem. Soc.*, **131,** 15887 (2009)
Fig. 6.7	*J. Phys. Chem. B,* **103,** 8809 (1999)
Fig. 6.10	*J. Phys. Chem. C,* **111,** 13 (2007)
Figs 7.9, 7.11, 7.12, 7.13, 7.16 and 7.17	*Accts. Chem. Rev.*, **41,** 708 (2008)
Table 8.2	*Ind. Eng. Chem.*, **42,** 1563 (2003)
Figs 8.26 and 8.27	*ACS Catalysis,* 1 (2011), DOI:10.1021/ CS100043

Springer

Fig. 3.11	*Topics in Catal.*, **40,** 65 (2006)
Fig. 3.21	*Topics in Catal.*, **53,** 859 (2010)
Fig. 4.20	*Topics in Catal.*, **52,** 1630 (2009)
Scheme 4.5	*Topics in Catal.*, **21,** 67 (2002)
Fig. 4.33	*Topics in Catal.*, **40,** 3 (2006)
Fig. 5.4	*Catal. Lett.*, **110,** 179 (2006)
Fig. 6.9	*Topics in Catal.*, **40,** 3 (2006)
Schemes 6.7 and 6.8	*Topics in Catal.*, **53,** 200 (2010)
Fig. 8.9	*Topics in Catal.*, **53,** 848 (2010)
Figs 8.29 and 8.30	*Topics in Catal.*, **54,** 588 (2011)

Blackwells Scientific Publishers

Fig. 3.8	*Perspectives in Catalysis* (ed. J. M. Thomas and K. I. Zamanaeu) (1992) p. 125
Figs 3.12 and 3.13	*Perspectives in Catalysis* (ed. J. M. Thomas and K. I. Zamanaeu) (1992) p. 147

Royal Society Publishing

Scheme 8.2	*Phil. Trans. R. Soc. A.*, **368,** 1473 (2010)

Taylor and Francis

Fig. 3.1	*Int. Rev. Phys. Chem.*, **8,** 207 (1989)
Fig. 5.8	*Catal. Rev.*, **46,** 369 (2004)

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Fig. 2.1	*Protein Structure and Function* (ed. G. A. Petsko and D.Ringe) (2004)