Institution: University College London (UCL)

Unit of Assessment: 8 – Chemistry

Title of case study: Industrial application of computational models and experimental techniques for catalyst development and optimisation

1. Summary of the impact

The development and application, by a UCL and Royal Institution (UCL/RI) team, of a powerful range of computational and experimental techniques has had a major impact on understanding of catalysis at the molecular level. The translation of these approaches to industry – achieved through fellowships, collaborations and employment of trained UCL/RI scientists – has had substantial impact on the development and optimisation of key catalytic systems used in energy, environmental, bulk and fine chemicals production. Computational modelling software has been commercialised by Accelrys following interaction with the UCL/RI team. Products and processes at Johnson Matthey have been developed and enhanced over a shorter timescale, ultimately leading to good returns and a sustained market position. The approaches also provided evidence that platinum-containing vehicle emission catalysts are not a source of chloroplatinates in the environment and can therefore continue to be used.

2. Underpinning research

Research teams at UCL and the Royal Institution (RI) – which is affiliated with UCL and was returned jointly with UCL in previous RAE exercises – have for over two decades pursued major programmes exploiting the concerted use of computation and experiment in catalytic science. The aim of this work has been to develop detailed models of catalytic structures and processes at the molecular level. The synergistic computational and experimental exploration of catalysts has elucidated and probed the structures, properties and reactivities of these complex materials, helping to develop and direct the design of industrially relevant catalysts. The application of both computational models and experimental techniques has generated a significant body of work, and the UCL/RI team has published over 500 outputs in the field of catalytic science that have provided the underpinning research for industry.

The computational expertise developed has employed both force field and quantum mechanical techniques; for example, in 1996 the ZEBEDDE (ZEolites By Evolutionary *De novo* DEsign) code was developed by UCL/RI in collaboration with the University of Liverpool, primarily to support the synthesis and development of microporous materials. This code provides a method for the *de novo* design of template molecules, thus avoiding long and exhaustive searches and trial-and-error modifications of known templates in order to identify new structure-directing agents [1]. The UCL/RI team was also an integral part of the EU project QUASI (Quantum Simulation in Industry) that aimed to encourage and facilitate the adoption and implementation of simulation programs. In this project, in collaboration with the other project partners, UCL/RI researchers investigated robust QM/MM (quantum mechanics/molecular mechanics) procedures for modelling active sites and reaction mechanisms in catalytic processes, in turn demonstrating the wide applicability of QM/MM procedures to industrial modelling problems [2].

Complementary to the development and exploitation of advanced computational models, the UCL/RI team concurrently conducted experimental research on microporous catalyst structure determination using X-ray diffraction (XRD) and absorption spectroscopic (XAS) techniques, employing both laboratory and synchrotron radiation sources. In particular, UCL/RI researchers have pioneered the use of powder diffraction and X-ray absorption fine structure spectroscopy (XAFS) for the simultaneous elucidation of local and long-range structure [3, 4]. The combined use of these techniques offers a viable, atom-specific analysis of non-crystalline gels and crystalline solids when other techniques, such as DAFS (diffraction anomalous fine structure), are inapplicable. Furthermore, it enables a greater understanding of the formation of, and specific environment at, the active sites of microporous catalysts [3, 4]. Additionally, XAS techniques have been used to assess the environmental impact of platinum catalysts [5]. It was found that the use of platinum in vehicle emission catalysts is not likely to generate chloroplatinate species, which are of environmental concern; rather it was shown that Pt is coordinated to oxygen atoms.

A significant amount of research has been conducted in collaboration with industry, in particular with Johnson Matthey. For example, investigations into the solubility of metal ions in known catalysts for industrially relevant reactions, including the partial oxidation of methane and high-temperature catalytic oxidation processes, have been performed [3, 6]. Such studies are important because the size and morphology of metal particles (like Ni and Ce) supported on inorganic oxides impact upon the catalytic activity of the material for a specific reaction. A comprehensive understanding of how a synthetic route influences the size of a metal dopant and its most favourable conformation within a host lattice informs on both catalytic performance and lifetime.

Overall, this combined computational and experimental approach has enabled an increasingly detailed understanding at the molecular level of the synthesis and catalytic operation of oxide and microporous catalysts.

Key UCL researchers: Richard Catlow (Professor 1993-present), Gopinathan Sankar (Professor, RI 2004-2007; Professor, UCL 2007-present), Nora de Leeuw (Reader, Computational Materials Science 2004-2007; Professor 2007-present) and Dewi Lewis (Lecturer 1998-2003; Senior Lecturer 2003-present).

3. References to the research

[1] *De novo* design of structure-directing agents for the synthesis of microporous solids, D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas and G. J. Hutchings, *Nature*, 382, 604-606 (1996) doi.org/dqqdhf (In collaboration with the University of Liverpool)

[2] QUASI: A general purpose implementation of the QM/MM approach and its application to problems in catalysis, P. Sherwood, A. H. de Vries, M. F. Guest, G. Schreckenbach, C. R. A. Catlow, et al., *J. Mol. Str. Theochem.*, 632, 1-28 (2003) doi.org/fgjpj7 (In collaboration with the CLRC Daresbury Laboratory, Max-Planck-Institut Mulheim, ICI, Synetix, Norsk Hydro Oil and Energy Research Centre and BASF)

[3] Combined experimental and computational modelling studies of the solubility of nickel in strontium titanate, A. M. Beale, M. Paul, G. Sankar, R. J. Oldman, C. R. A. Catlow, S. French and M. Fowles, *J. Mater. Chem.*, 19, 4391-4400 (2009) doi.org/bz76g3 (In collaboration with Johnson Matthey)

[4] Probing the onset of crystallization of a microporous catalyst by combined X-ray absorption spectroscopy and X-ray diffraction, G. Sankar, J. M. Thomas, F. Rey and G. N. Greaves, *J. Chem. Soc., Chem. Commun.*, 2549-2550 (1995) doi.org/drt8zz (In collaboration with the CCLRC Daresbury Laboratory)

[5] X-ray absorption spectroscopic studies of platinum speciation in fresh and road aged light-duty diesel vehicle emission control catalysts, T. I. Hyde, P. W. Ash, D. A. Boyd, G. Randlshofer, K. Rothenbacher and G. Sankar *Platinum Met. Rev.*, 55(4), 233-245 (2011) doi.org/d9h9gs (In collaboration with Johnson Matthey, International Platinum Group Metals Association and European Precious Metals Federation)

[6] Computational modeling study of the solubility of cerium at $LaCoO_3$ perovskite surfaces, S. Khan, R. J. Oldman, C. R. A. Catlow, S. A. French and S. A. Axon, *J. Phys. Chem. C*, 112(32), 12310–12320 (2008) doi.org/cvr8qb (In collaboration with Johnson Matthey)

References [1], [3] and [4] best indicate the quality of the underpinning research.

4. Details of the impact

Catalytic processes underpin production in the chemicals and pharmaceuticals industries; as such, the value of the goods and products manufactured by catalysts is estimated at $15 trillion worldwide[1]. It is well recognised that improvements in the efficiency of catalytic processes – resulting in added value of the products manufactured and minimisation of environmental impact – require a science-led approach. The UCL/RI team has made significant contributions to development processes and products globally, fostered through deep and long-standing interactions with UK and international industry. These relationships have enabled the translation of

the pioneered techniques and their subsequent application in product and process optimisation.

Contribution to commercial software development: The translation to industry of QM/MM techniques has been realised through commercial software development. Professor Catlow was one of the lead scientific advisors to the Catalysis and Sorption Consortium and subsequently, between 2008 and 2011, advisor to the Nanotechnology Consortium. This latter consortium, in collaboration with the STFC, developed a QM/MM module (QMERA) for Accelrys' Materials Studio® modelling and simulation environment software [A]. Materials Studio enables investigators to relate product performance with material properties and behaviour at the molecular, atomic, and meso scales. QMERA was first included in Materials Studio 4.3 in 2008 [A]. In 2011, Accelrys released a new version of this software – Materials Studio® 6.0 [B] – that included a significantly enhanced QMERA module [A]. [text removed for publication]

Knowledge transfer of techniques and highly skilled specialists: At Johnson Matthey (JM), adoption of new techniques developed by UCL/RI and integration of UCL/RI-trained scientists has **shortened research projects, aided understanding and improved the company's competitiveness** [C]. Transfer of synchrotron radiation-based techniques to industry has been facilitated through Royal Society industrial fellowships, such as the secondment of Professor Sankar from UCL to JM between 2007 and 2011. During this period, Sankar shared his significant experimental know-how of diffraction and synchrotron radiation (SR) techniques with JM research and development (R&D), enabling the implementation of these techniques across a range of catalysts, from zeolite-based systems to supported oxide materials. The introduction of SR techniques at JM has been **invaluable to the company's catalytic technology and materials processing** [C]. Furthermore, a range of *in situ* methodologies has been designed and developed for JM, which has helped make its analytical science and technology **highly competitive with other similar chemical companies** around the world [text removed for publication] [C]. The relationship with Sankar has continued through a consultancy arrangement. Alongside this, JM has **recruited seven UCL/RI-trained scientists** over the last 10 years; one is now in a senior management role and **three were hired in the REF impact period**. Of the latter group, one is now managing projects incorporating modelling, while the other two are full-time practitioners [D].

New product development: Collaborative projects with JM – for example, those described in outputs [3] and [6], above – have led to commercial benefits for the company. Here, work has primarily focused on applying the techniques developed by the UCL/RI team to the field of bulk industrial chemical production, particularly in the development of inorganic oxides. These are important industrial catalysts used in the annual worldwide production of 130 million tonnes of ammonia, 50 million tonnes of hydrogen, 60 million tonnes of nitric acid and 100 million tonnes of methanol [E]. Catalyst development is a continuous process aimed at enhancing operational efficiency and in turn resulting in major financial benefits for the end users. Historically, the approach was mainly empirical, but new computational and experimental tools have provided major opportunities to enhance understanding and suggest new avenues for research. Computational modelling, backed by access to advanced X-ray techniques such as X-ray absorption spectroscopy (XAS) at SR sources, has been applied to a range of doped and defect-containing catalytic inorganic oxide materials of relevance to the bulk chemical interests of JM (including the former ICI Katalco) [E]. In turn, this work has contributed to **novel materials design, cost-effective synthesis of catalysts and understanding of their application** under aggressive chemical process conditions [E]. [text removed for publication]

[text removed for publication]

Impact on environmental policy: In 2011, in collaboration with JM and other international organisations, the application of XAS techniques (e.g. output [5] above) provided essential learning for members of the International Platinum Group Metals Association (IPA) who were seeking evidence to retain the use of platinum as the active component in vehicle emission catalysts. [text removed for publication] the global emission control catalyst market reached $6.7 billion in 2012 [C]. These catalysts, and platinum-containing systems in particular, were under scrutiny by the United States Environmental Protection Agency (EPA) as a potential source of chloroplatinates in the environment [G]. The work was used in 2012 as part of the science case that demonstrated that the major industrial use of platinum in the catalysts was not a direct source of chloroplatinates;

in turn, the work recommended a prospective, evidence-based approach to both occupational and public exposure assessment to legislators in Europe and North America [C].

1. *Topics in Catalysis* 52(8), 924-934 (2009) http://doi.org/cd2hgx

5. Sources to corroborate the impact

[A] Supporting correspondence from Senior Product Manager, Accelrys Ltd. – corroborates the contribution of UCL's Prof Catlow to software development at Accelrys [text removed for publication]. Available on request.

[B] Accelrys press release: http://ir.accelrys.com/releasedetail.cfm?ReleaseID=627761 – corroborates the release of the new Materials Studio® 6.0 software in 2011.

[C] Supporting correspondence from Technology Manager, Johnson Matthey PLC – corroborates the contribution that Prof Sankar and the UCL/RI team have made to the programs of work at JM. Available on request.

[D] Supporting statement from Technology Manager, Emissions Control Research, Johnson Matthey PLC – corroborates the recruitment of the UCL/RI-trained scientists by JM. Available on request.

[E] Supporting correspondence from Catalyst Research Associate, Johnson Matthey PLC – corroborates the contribution that the UCL team has made to the development of inorganic oxides and the impact that the UCL/RI team has had at JM. Available on request.

[text removed for publication]

[G] IRIS Toxicological Review of Halogenated Platinum Salts and Platinum Compounds (External Review Draft) http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=513625 by the US Environmental Protection Agency.