Institution: University College London		
Unit of Assessment: 8 – Chemistry		
Title of case study: Application of experimental and computational methods for improved performance of industrial catalytic systems and processes		
Period when the underpinning research was undertaken: 2000 – 2020		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Andrew Beale	Professor of Inorganic Chemistry	2013 – present
Gopinathan Sankar	Professor of Solid State Chemistry	1999 – present
Richard Catlow	Professor	1971 – present
Period when the claimed impact occurred: August 2013 – 2020		
Is this case study continued from a case study submitted in 2014? Y		

1. Summary of the impact (indicative maximum 100 words)

UCL academics have been involved in the development and application of novel experimental approaches and computational methodology. This research has provided fundamental insight into the behaviour of catalytic materials, which in turn has translated into improved understanding and performance in the areas of energy, environment, bulk and fine chemicals production. Impact includes the creation of a start-up company Finden Ltd. (inc. 2012) whose novel analytical methods are the basis for annual turnover greater than GBP1,500,000 since 2014 and whose insights have enabled the redesign of industrial catalysts. Through sponsored research projects, industrial consultancy, and employment of trained UCL scientists, continued collaboration between UCL and industry leader Johnson Matthey plc (JM) has led to better understanding of catalyst properties and behaviour across multiple business divisions. [TEXT REMOVED FOR PUBLICATION].

2. Underpinning research (indicative maximum 500 words)

The academics involved at UCL (Catlow, Sankar, Beale) have a long history of research on the subject of heterogeneous catalysis with a significant number of outputs in the field (in excess of 160 publications) during this REF period. Pertinent to this case study has been research on the development of novel analytical techniques, methods, data handling and analysis procedures, for tracking the behaviour of catalytic materials often studied under real reaction conditions (**R1-6**). These data have been largely obtained from the Harwell campus which houses the UK's national capabilities for X-rays, Neutrons and Lasers. The insights obtained are unique, as they are obtained from UCL specific capability involving advanced characterisation methodology, often combined with novel computational methods.

The UCL team conducted experimental research on a series of heterogeneous catalytic materials (supported metals on powders to structured catalysts) using national facilities for X-rays, Neutrons and Lasers. In particular, UCL researchers have pioneered the development of multimodal X-ray tomography techniques, particularly the novel approach of '5D' X-ray diffraction computed tomography (XRD-CT) imaging, to study entire catalytic systems in real time, under real process conditions, non-invasively. This approach, now regularly exploited by Finden Ltd, yields a more holistic (spatial) characterisation of the evolving (i.e. during reaction) catalyst composition than more standard single point measurements. By using bright, hard X-rays, this work is particularly pertinent for the study of 'real' structured catalysts such as monoliths, enabling insight into industrial materials that has not been possible until recently (**R1, R2**).

The collaboration between UCL and JM, enabled through joint PhD research, collaborative and consultancy projects (in the areas of synthesis, advanced characterisation, computational methods and their application) underpinned research and development of catalytic technologies among a number of divisions in JM, in particular clean air, efficient natural resources (ENR) and energy generation and storage. Specifically, the continued application of *in situ* methods employing X-ray absorption spectroscopy (XAS), (which includes X-ray absorption near edge structure (XANES), high energy fluorescence detection of XANES (HERFD XANES), and extended X-ray absorption fine structure (EXAFS)) in addition to, increasingly, pair distribution function (PDF) methods, often in tandem, has proven powerful for differentiating between oxidation states and characterising short-range order in supported catalysts (**R3, R4**). Industrially-relevant materials that have been investigated during this REF period include mixed metal oxide shift systems for ENR and the energy sector, and microporous and supported catalysts for clean air (**R3, R4**).

Whilst experimental techniques provide insights into catalysts, discussed above, often the aid of computational methods are vital. To this end, the computational methods developed at UCL have been invaluable, as they employ both force field and quantum mechanical techniques for performing atomistic simulations. Notable developments include QM/MM (quantum mechanics/molecular mechanics) ChemShell procedures for modelling active sites and reaction mechanisms in catalytic processes, which has continued to the wide applicability of QM/MM procedures to industrial modelling problems (**R5**). Furthermore, a recent collaboration between UCL and JM using Quasi Elastic Neutron Scattering (QENS) and Molecular Dynamics (MD) simulations has provided valuable insight into diffusion mechanisms in zeolites used in selective catalytic reduction (SCR) to reduce emissions from diesel engines (**R6**).

3. References to the research (indicative maximum of six references)

R1. S.D.M. Jacques, M. Di Michiel, **A.M. Beale**, T. Sochi, M.G. O'Brien, L. Espinosa-Alonso, B.M. Weckhuysen, P. Barnes, Angew. 2011. "Dynamic x-ray diffraction computed tomography reveals real-time insight into catalyst active phase evolution," *Angewandte Chemie - International Edition,* 50 (43), 10148-10152. DOI: 10.1002/anie.201104604

R2. Vamvakeros, A., Jacques, S.D.M., Di Michiel, M., Matras, D., Middelkoop, V., Ismagilov, I.Z., Matus, E.V., Kuznetsov, V.V., Drnec, J., Senecal, P. and **Beale, A.M**., 2018. "5D operando tomographic diffraction imaging of a catalyst bed," *Nature communications*, 9(1), 4751. DOI: 10.1038/s41467-018-07046-8

R3. H. Marchbank, A.H. Clark, T.I. Hyde, H.Y. Playford, M.G. Tucker, D. Thompsett, J.M. Fisher, K.W. Chapman, K.A. Beyer, M. Monte, A. Longo, **G. Sankar**. 2016. "Structure of Nano-Sized CeO2Materials: Combined Scattering and Spectroscopic Investigations," *ChemPhysChem*, 17, 3494-3503. DOI: 10.1002/cphc.201600697.

R4. V. Martis, R. Oldman, R. Anderson, M. Fowles, T. Hyde, R. Smith, S. Nikitenko, W. Bras, **G. Sankar**, 2013. "Structure and Speciation of Chromium ions in Chromium doped Fe2O3 Catalyst," *Physical Chemistry Chemical Physics*, 15 (26), 168-175; Tahmiin Lais et al. 2021 DOI: 10.1039/D0CP06468H.

R5. S. Khan, R.J. Oldman, F. Cora, **C.R.A. Catlow**, S.A. French, S.A. Axon. 2006. "A computational modelling study of oxygen vacancies at LaCoO3 perovskite surfaces," *Physical Chemistry Chemical Physics*, 8 (44), 5207-5222. DOI: 10.1039/B602753A.

R6. A.J. O'Malley, I. Hitchcock, M. Sarwar, I.P. Silverwood, S. Hindocha, **C.R.A. Catlow**, A. P.E. York, P.J. Collier. 2016. "Ammonia mobility in chabazite: insight into the diffusion

component of the NH3-SCR process," *Physical Chemistry Chemical Physics*, 18 (26), 17159-17168. DOI: 10.1039/c6cp01160h

4. Details of the impact (indicative maximum 750 words)

Catalysis is estimated to be worth GBP50,000,000,000 and GBP1,500,000,000,000 per annum to the British and global economy respectively – 80% of every man-made chemical/product has encountered a heterogeneous catalyst in its lifetime. Improvements in catalyst performance can be realised via improved differential (activity) or integral (lifetime) yield, which leads to direct economic and environmental benefits (e.g. reduced unwanted products and lower energy costs) and indirect societal benefits (e.g. reduced NOx and CO_2). The close working relationships that the UCL team has developed with JM and Finden have been crucial in translating the expertise in advanced characterisation, using X-ray techniques (**R1-4**) and simulation (**R5**) in combination with advanced characterisation (**R6**) to obtain fundamental insight into a wide range of catalytic applications.

New product development and process improvements
Since Sankar and Catlow began their interactions with JM, realisation of the use of techniques such as PDF, XAFS, QENS (**R1-4**) and modelling methodologies (ChemShell) (**R5, R6**) has become an area of utmost importance in JM's strategy to develop "world class science and technology expertise" (**S1**). To this end, according to JM, the collaboration has had "a high and continuing impact across our [JM] businesses, brought about through advanced characterisation of model and industrial catalysts and materials" (**S1**).

Of particular note has been Sankar's collaboration with the Clean Air and ENR divisions using synchrotron radiation (SR) techniques, such as X-ray Absorption Spectroscopy (XAS, including XANES), to understand metal ion speciation within or at the surface of supported catalysts. This information has enabled JM to **prepare new products with improved performance that comply with current and future legislations.** The High Temperature Shift Technical Manager at JM, affirms that "JM High-Temperature Shift catalysts are sold across the globe to customers producing Hydrogen and Ammonia. [TEXT REMOVED FOR PUBLICATION]." The XAS study conducted by Sankar and the team has elucidated structural properties of the catalyst leading to enhanced understanding. (**S1**) The Global V-SCR Product Development Manager adds, "As part of improvement in NOx reduction technology for automotive emission control, it become critical to understand the oxidation states of new additives in JM catalysts after different ageing conditions. Sankar's expertise in XANES enabled this novel work with appropriate detection limit, and thus enabled industrialisation of the concept for customer sampling. [TEXT REMOVED FOR PUBLICATION]." (**S1**) In addition, Sankar's research in XAS "has sped up the commissioning process of electrochemical characterisation cells" (**S1**) which have an important role in the commercialisation of new battery cathode materials.

Catlow's collaboration with JM involved the application of a combination of neutron spectroscopy and computational methodologies (**R5, R6**) in "strategic areas," such as novel fuel cell formulations, sustainable hydrogen production and clean air applications. Most notably, computational modelling studies have "**provided unique and novel insight** [TEXT REMOVED FOR PUBLICATION]" in the ENR and the syngas catalyst, "where we [JM] have needed to go beyond intuition to make significant advances" (**S1**). Furthermore, the Chemshell procedures have allowed JM to model zeolites used in the selective catalytic reduction (SCR) reactions, which in turn enables JM to obtain its position as a market leader. The leading computational chemists at JM has said, "Fundamental understanding of zeolite catalysis using computational chemistry techniques, particularly Chemshell, in collaboration with Prof Catlow and his co-workers at UCL has helped guide the design of SCR catalysts with improved activity. [TEXT REMOVED FOR PUBLICATION]" (**S1**).

Finden Ltd, a UCL spinout established in 2012 with Beale as joint shareholder, has pioneered the application of the advanced X-ray methods for structure characterisation (**R1-**

2). In particular, the XRD-CT techniques developed at UCL provided Finden unique insight into the structure and performance of materials under operando conditions. This approach was, for example, successfully applied in collaboration with BASF in 2017 to study intact portions of [TEXT REMOVED FOR PUBLICATION]. The results from this study **enabled BASF to redesign their catalyst** to [TEXT REMOVED FOR PUBLICATION].

Knowledge transfer of techniques and highly skilled specialists
UCL-trained scientists have been employed by a number of industry partners including JM and Finden, where their knowledge on catalyst characterisation serves as a critical component of the success of the operation. At JM, the adoption of new X-ray techniques/analysis procedures developed by UCL (**R1-3**) and integration of UCL-trained scientists (6 FTE) has enhanced understanding, shortened research and development projects, and improved the company's competitiveness**.** At Finden, expertise on X-ray tomography (**R1, R2**) from UCL alumni (6 FTE) has enabled the expansion of the spinout to offer a wider variety of services, and it has driven an exponential growth in sales, particularly in the last three years (**S3**). By sharing technical expertise as part of a wider international collaboration, ex-UCL academics at Finden co-authored an academic output which became one of the primary motivations behind a GBP16,000,000 upgrade of two ESRF flagship materials science beamlines (ID15 & ID31@ESRF) and the *u*15 beamline at Diamond Light Source (**S4, S5**). The Diamond-II programme aims to enable unparalleled insight into industrial materials science problems spanning the fields of energy storage, manufacturing, pharmaceuticals and cultural heritage.

In addition to the employment of personnel from UCL trained researchers, transfer of SR and computational techniques facilitated through the continuous interaction with Sankar and Catlow has led to the development of major centres. [TEXT REMOVED FOR PUBLICATION]. Key examples include the creation of JM Research Centre in South Africa and the Electron Physical Science Imaging Centre (ePSIC) at the Diamond Light Source (Harwell Campus), both of which were initiated through UCL collaborations. The introduction of SR techniques at JM has been invaluable to the company's catalytic technology and materials processing. The senior JM microscopist at ePSIC, comments, "[TEXT REMOVED FOR PUBLICATION]. "The fact that Johnson Matthey, through Sankar's Fellowship, had an involvement with Diamond before the ePSIC initiative was an important part of our relationship building […]. I think more importantly our involvement with Sankar made us part of the industrial advisory group which made us aware of the bigger picture" (**S1**). [TEXT REMOVED FOR PUBLICATION] (**S1**). The computational research collaboration between UCL and JM led to the establishment of a Johnson Matthey Research Centre in computational chemistry located in Pretoria, South Africa in 2013. The centre has resulted in novel materials design, cost-effective synthesis of catalysts and a better understanding of catalyst application under aggressive chemical process conditions.

[TEXT REMOVED FOR PUBLICATION]

5. Sources to corroborate the impact (indicative maximum of 10 references)

S1. Colligated letter of support from Johnson Matthey (JM), dated 9th March 2021
S2. Letter of support from catalysts division, BASF Catalysts Germany GmbH
S3. Finden financial information available upon request
S4. Vaughan GBM, Baker R, Barret R, Bonnefoy J, Buslaps T, Checchia S, Duran D, Fihman F, Got P, Kieffer J, Kimber SAJ, Martel K, Morawe C, Mottin D, Papillon E, Petitdemange S, Vamvakeros A, Vieux J-P, Michiel MD. 2020. "ID15A at the ESRF – a beamline for high speed operando X-ray diffraction, diffraction tomography and total scattering," *Jour. Of Synchr. Radiation* https://journals.iucr.org/s/issues/2020/02/00/il5045/
S5. Diamond: Flagship Beamline Projects, access date: 12th March 2021
https://www.diamond.ac.uk/Home/About/Vision/Diamond-II/Flagship-Beamline-Projects.html