Impact and Industrial Relevance of Catalysis Hub Projects

Impact Case Study: Direct fixation of CO_2 — Prof. Mike Bowker (Cardiff)

Global warming is a threat to the global environment and is a focus of a great deal of current social, political and scientific thinking due to the urgency of the problem.

A number of scenarios are in operation for the amelioration of this problem and one of them is to use renewable energy from (e.g.) wind and solar photovoltaic inputs to the grid.

However, the persistent problem with this idea is the great variability of these outputs (solar photovoltaic only daytime, and not every day, wind intermittent with sometimes long windless periods).

Hence, we need to store the energy during peak outputs, to be used during fallow periods. But how? A number of possibilities exist of which our work is one, that is, to store the energy at the peak in a chemical form to be used later. Ideally this could also be directly used as a fuel (e.g. to drive vehicles, or to drive turbines to regenerate electricity etc) or to recover the hydrogen in it for use in fuel cells.

So, our work is directed at methanol synthesis, using renewables. The renewable is solar-powered electrolysis of water to produce H_2 (and pure oxygen which has medical value), to react it with a hydrogen carrier (CO_2 from a coal-fired power station) and to make methanol, a storable, transportable form of solar energy.

So, we build a plant, for which there are several components. 1. CO_2 source (a working large-scale coal fired power plant in Germany) 2. CO_2 clean-up process 3. Hydrogen generator (electrolysis) 4. Methanol reactor/plant).

A crucial component of the latter, without which it would not work, is the methanol synthesis catalysts, and it is to this we have contributed our expertise. We have generated new types of catalyst (and have synthesised ~ 200 different types) and some of these are now patented for use in the plant.

The academic benefits including training for the postdoc on the work, including preparation of patent documentation. Collaboration with our European colleagues. Papers in the literature as described above, and publication of a paper related to the patent soon.

Impact Case Study: Development of XAFS methods for industrial applications — Dr. Peter Wells (Southampton)

A collaborative partnership between the UK Catalysis Hub, Diamond Light Source, partner universities (Southampton, QUB, Manchester, Glasgow, UCL), and Johnson Matthey Technology Centre (JMTC) have been working towards developing advanced reactor environments for the study of catalytic processes.

Led by Dr Peter Wells (Southampton, Diamond) and Prof. Alex Goguet (QUB), the endeavour behind these activities is to develop operando techniques that allow for precise, accurate, and reliable measurements regarding the evolving nature of catalysts under realistic conditions.

This work was funded through the UK Catalysis Hub – JMTC studentship call in 2014 and has focussed on developing a new approach to combining X-ray absorption fine structure (XAFS) and diffuse reflectance infrared Fourier transform (DRIFTS) spectroscopies.

This combination of techniques provides complementary information; XAFS provides structural and electronic information, whilst DRIFTS provides information on the nature of surface adsorbates. However, the current reported approaches in the literature are hindered by large reactor dead volumes and cannot provide any spatial information on the state of the catalyst; considering that in a fixed bed reactor there is a gradient between reactants and products, it is important to be able to capture these changes and understand the interplay between structure and the surface adsorbates at each position.

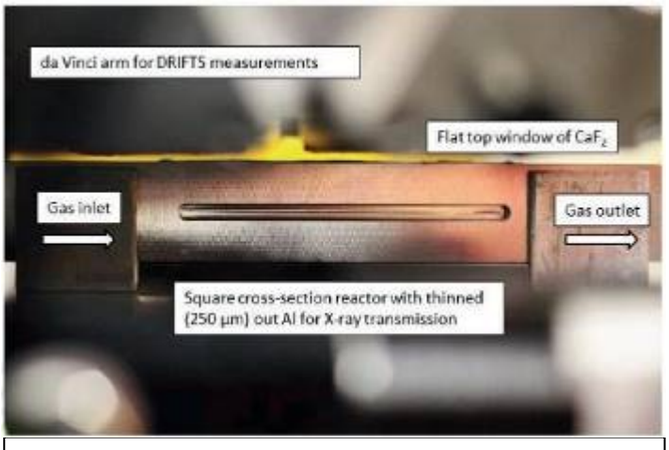

Figure x. New combined XAFS/DRIFTS reactor mounted on the I20 EDE beamline, Diamond Light Source.

This partnership has developed a reactor that solves both the problems linked to spatial analysis and large dead volumes (figure x) by moving away from typical 'dome' shaped sample chambers and exploiting a square cross-section reactor with axial windows for both XAFS and DRIFTS acquisition. The more conventional reactor geometry is not hindered by the dead volume of the dome and can collect data along the length of the fixed bed.

Furthermore, the cell has been recently integrated (April 2018) into the I20-EDE beamline at Diamond Light Source, which – in conjunction with a rapid scanning FTIR spectrometer – allows for ms time resolution of both the FTIR and XAFS data acquisition.

The success of this project is, in no small part, down to the determination and talent of the PhD student, Miss Ellie Dann, who has undertaken this work.

he first publication from this new development is currently under review and we look forward to updating Hub members further about these exciting developments.

Impact Case Study: Autonomous repair — Prof. Duncan Wass (Bristol)

Research funded by the EPSRC UK Catalysis Hub in the Wass research group at the University of Bristol has been developing catalyst systems to embed in carbon fibre composite materials to impart self-healing functionality.

This work has received wide media coverage (see www.epsrc.ac.uk/newsevents/news/selfhealingaircraftwings) and this attention has enabled engagement and materials exchange with industry across a range of sectors to develop real usable technology (for example, BMW; Maserati; C6n, a supplier of composite events pavilions; Dassi, a manufacturer of high performance road bikes; Acconia, who have wide interests in the use of composites for infrastructure projects; IHI, who have interest in the automotive supply chain; and GKN, a manufacturer of aerospace components.

Follow-on funding has been obtained from Innovate UK (administered by CPI) via two Materials Innovation Translation awards to develop this through technology readiness levels to the point where industry adoption is feasible; one project will focus on smart composite matrix materials, the other on using this technology for accelerated cure of composites.

Furthermore, this project has been widely disseminated for outreach activities, providing an inspirational and unusual example of catalysis in action. Wass has presented this science to over two hundred secondary teachers via the Prince's Teaching Institute, over a thousand secondary school children via various lecture tours, over two hundred senior industrials via a TTI Vanguard conference on 'Autonomy' in Brooklyn, N.Y. and more widely in the pan-European 'Science in Schools' journal.

INDEPENDENT

Lifestyle › Tech › News

Self-healing technology one step closer after scientists produce aircraft wings which fix themselves

The research is an important step in an emerging field which could soon produce self-healing nail polish and a cure for cracked mobile phone screens

Chris Green | @cghgreen | Saturday 6 June 2015 |

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The Airbus A380 passenger jet has a carbon fibre reinforced plastic fuselage for a lower fuel consumption

Impact Case Study: Biotechnology — Prof. Nigel Scrutton (Manchester)

Researchers from the Manchester Institute of Biotechnology (MIB) including five from the group of Prof. Nigel Scrutton attended the annual New Scientist Live event in London. The event attracted more than 30000 visitors from the general public with MIB researchers engaging the audience with hands-on activities about enzymes, DNA and highlighting current research in synthetic biology and biotechnology at the University of Manchester.

Legislations banning single-use plastics and consumers shifting towards sustainable products has led to the chemical industry seeking new ways to address market demands.

Biotechnology has emerged as a key technology towards the production of high-value fine chemicals used in flavours, fragrances, bio-polymers and pharmaceuticals.

The aim of the exhibition was to shift the poor perception of biotechnology by demonstrating the benefits and safety of this technology with case studies from MIB.

Attendees went away with a better understanding of biotechnology and how it is being used to sustainably produce commodity chemicals and strengthen the bio-economy of the UK.

Impact Case Study:Selective Polymerisation Charlotte Williams, Oxford

The research investigated using the Hub funding remains at an early stage as would be expected with EPSRC funded fundamental research. Nonetheless, the target area – making useful products from carbon dioxide, is one in which there is potential for both environmental and commercial impact. It is relevant to note that there is a UK based company, Econic technologies, formed on the basis of earlier catalytic science from C. K. Williams which has commercialized catalysts for carbon dioxide/epoxide copolymerization (http://www.econic-technologies.com/). The product polycarbonate polyols are attracting increasing industrial attention as components in polyurethanes, a large commodity sector of the polymer market. Thus, the discoveries of the EPSRC Catalysis Hub funding are relevant to an emerging sector in both the polymer and polymerization catalysis sectors. There is also a demonstrated environmental benefit to using carbon dioxide to make polymers – in effect there is a 'triple win' as for every tonne of carbon dioxide used to make polymers, there is a three-tonne saving in CO2 emissions. This arises because the carbon dioxide replaces epoxide in the conventional process and thus by avoiding petrochemical useage there are emissions savings also. The early-stage research in catalysis funded by the UK Catalysis Hub has allowed a broader range of polymers to be prepared from CO2. This is important because in future equivalent cost and environmental benefits could be envisaged in sectors beyond polyurethanes. For example, some of the polymers prepared using the switchable catalysis show good elastomeric behaviour so may be suitable as replacements for commodity materials like SBS (styrene-butadiene-styrene).

Another impact area that has been developed thanks to the Catalysis Hub funding has been the outreach and demonstration of the concept to the general public. The Imperial College London/Oxford team have participated in two large-scale outreach activities – the imperial College London Festival which attracted >10,000 members of the public in May 2015 and 2016. The Williams team presented the science behind carbon dioxide to polymers, including demonstrating a Co2-emittting 'factory' (a shoe box loaded with dry-ice and water) which was very popular, especially with families. It allowed the public to imagine the way that carbon dioxide emissions may one day be able to be transformed into useful products. The festival was held over two days and the group also participated in a schools outreach event each year. Furthermore, Charlotte Williams has presented the carbon dioxide catalysis on the *Radio 4* programme, 'Costing the earth' (http://www.bbc.co.uk/programmes/b081lkm1) which was broadcast in November 2016.

Impact Case Study: Neutrons in Catalysis (Hub Harwell), Johnson Matthey

In association with ISIS the Hub held a workshop on, "Neutron Techniques in Catalysis" in Nov 2014. There were a mix of delegates from industry and academia, with over fifty attendees. This helped to provide training and knowledge transfer to catalytic community who may previously not have used neutrons leading to a range of new users including Johnson Matthey, Academics from Southampton university and UCL. Following this workshop scientists from ISIS, The Catalysis Hub and Johnson Matthey proposed and led a special issue of PCCP edition, "Neutron scattering in catalysis and energy materials" (see Dissemination)

Industrial Importance: Use of Neutrons for catalysis research has led to industrial relevance

NO_x emissions from the energy and transport sectors represent a major hazard to human health and this has been the focus of significant industrial and academic research. One of the important processes in the armoury available for emissions control from vehicles, large and small, power stations, ships, trains and non-road machinery is the selective catalytic reduction reaction (SCR), in which a reductant such as ammonia, urea or hydrocarbon fuel, is injected into the exhaust to reduce the NO and NO_2 (NO_x) to harmless nitrogen. The use of urea (which is broken down to NH_3 under operating conditions) as a reductant in SCR is a key successful strategy in R&D in diesel emissions control R&D and is already used on modern vehicles, but will become much more prevalent in the near future.

Front Cover PCCP Themed issue

The typical catalysts used for urea (and ammonia) SCR include those based on vanadium oxide, iron supported on a zeolite, and copper supported on a zeolite (Cu/zeo). The Cu/zeo materials have proven to be extremely active for SCR, and also demonstrate excellent long-term stability, and are therefore often the prime choice for use in the catalytic SCR system. Research projects carried out at Johnson Matthey, as well

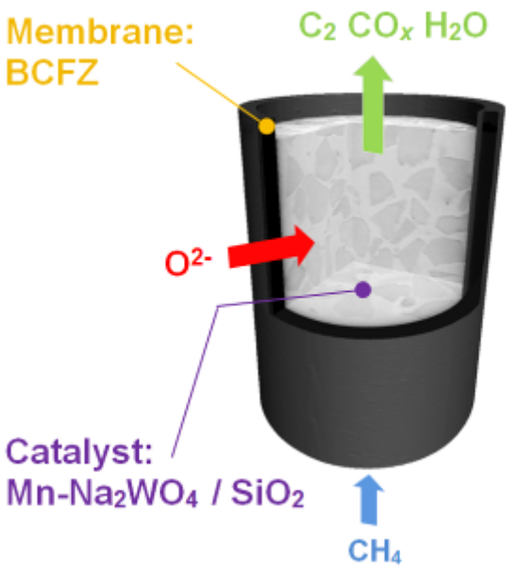
as elsewhere, have highlighted the excellent performance of small pore zeolites, such as chabazite (CHA) combined with Cu for the SCR reaction. With such small pore systems it is very important to understand not only the intrinsic NH_3-NO reaction kinetics and the chemistry of the active sites, but also the diffusion processes that might be important in the design of an optimum SCR catalyst.

Presented by Johnson Matthey: 14th International Conference on Applications of Quasielastic Neutron Scattering, 5-8th September, 2016, Potsdam, Germany (I. Hitchcock, Measuring diffusion of ammonia in zeolite NOx emissions control catalysts).

RCAH Impact Fellows Report, Dr Simon Jacques, Manchester

The RCaH Advanced Impact Position is an EPSRC scheme that encourages collaborative research between groups based at the Research Complex Harwell. I have been fortunate enough to have been awarded one of these fellowships. My project is a collaboration principally with Manchester X-ray Imaging Facility and the UK catalysis hub with the aim of developing methods to image the changing chemistry within working catalytic membrane reactors. These are a new breed of catalytic reactors and we are using these for the efficient and clean conversion of methane to industrially useful feedstock materials such as ethylene. Below is summary of the project and the progress made to date.

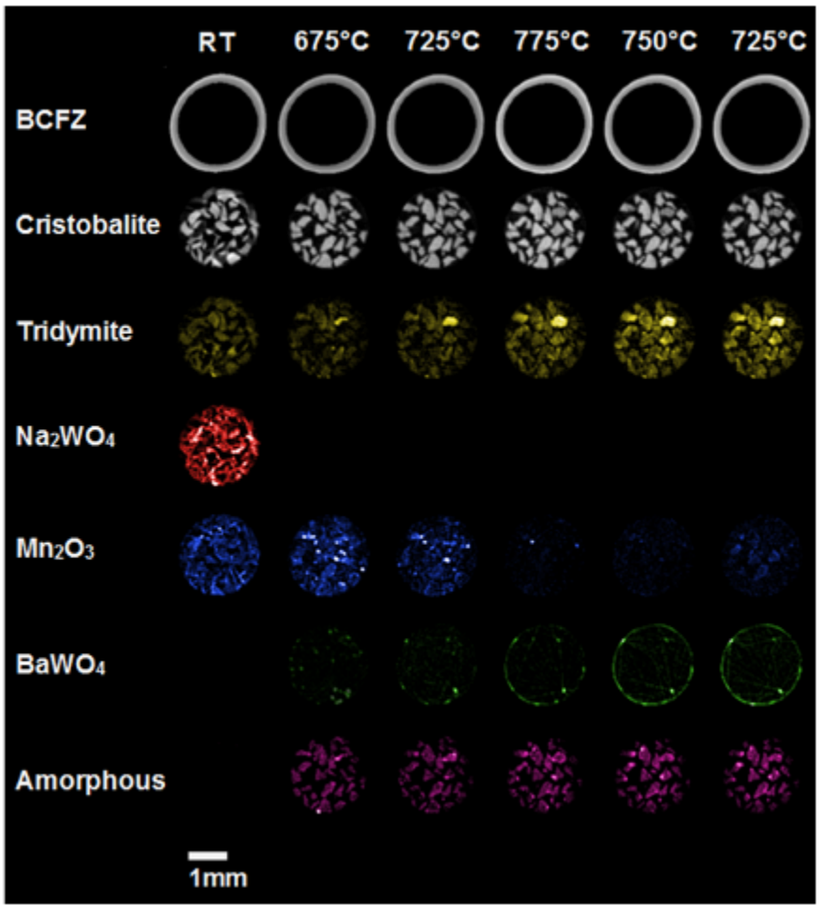
The imperative for efficient technologies to process methane: The continuous reduction of gas flaring and the exploitation of shale gas by hydraulic fracturing (fracking) has led to a dramatic increase in the availability of methane. Natural gas, whose main component is methane, is considered to be an abundant hydrocarbon source compared to crude oil and consequently there is much interest in producing higher value bulk chemicals from it. Environmentally-friendly and cost-effective processing technologies for direct conversion of methane to light olefins (e.g. ethylene) as an alternative to the highly energy-intensive cracking of crude oil are needed. The oxidative coupling of methane (OCM) can potentially provide an economically viable route for ethylene production. The application of catalytic membrane reactors (CMR) employing oxygen transport membranes can lead to a decrease of the cost of the overall process.



The reactor: Figure 1, left, shows the principle of operation of such a reactor. The membrane facilitates the transport of oxygen ions from surrounding air atmosphere to feed the catalytic bed with oxygen. Methane is fed into the base of the reactor and is oxidatively coupled by virtue of an OCM catalyst to produce ethylene product. This process is highly advantageous in that it does not need a source of pure oxygen *per se* or require separation of product from contaminating gasses such as nitrogen.
Whilst this technology is very promising, there is little known about the workings of membrane and catalyst candidate materials in combination.

Chemical Imaging: We have been developing a number of chemical imaging methods including X-ray diffraction computing tomography (XRD-CT) which we have used to image working CMR under operando conditions. XRD-CT is extremely powerful as it enables one to obtain images from bulk objects, where the composing pixels contain reconstructed diffraction patterns that themselves contain highly insightful physico-chemical information. Figure 2 below shows XRD-CT derived phase maps at a fixed height within a CMR under different applied conditions. The maps show that the position of the BCFZ membrane ($BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$), and the catalyst distribution within the catalyst particles within the hollow of the membrane, including the catalyst support phases (cristobalite, tridymite) and catalyst phases (Na_2WO_4 & Mn_2O_3) as a function of operating temperature. In this experiment we also see the evolution of $BaWO_4$ which is resulting from the interaction of the catalyst with the membrane. The formation of this phase is highly likely to be detrimental to the long-term

operation of the CMR. This phase would likely be unobservable by conventional single point measurements.



Phase maps for BCFZ, cristobalite and tridymite (SiO_2 polymorphs), Na_2WO_4, Mn_2O_3, Ba_2WO_4 and an amorphous phase as determined from the XRD-CT data. These maps have been obtained from the integrated intensities of the respective phases.

Current state of project: We are using XRD-CT and supporting measurements to look at a number of membrane catalyst combinations under intended industrial operating conditions. We have recently published a short paper reporting some initial findings and also a methods based paper [2] detailing some developed methods. We are currently preparing full papers on the membrane/catalyst combinations studied to date and also a second methods paper.

[1] *Real time chemical imaging of a working catalytic membrane reactor during oxidative coupling of methane.* Vamvakeros, A., Jacques, S. D. M., Middelkoop, V., Di Michiel, M., Egan, C. K., Ismagilov, I. Z., Vaughan, G. B. M., Gallucci, F., van Sint Annaland, M., Shearing, P. R., Cernik, R. J. & Beale, A. M. (2015). Chem. Commun. 51, 12752-12755. http://pubs.rsc.org/en/Content/ArticleLanding/2015/CC/c5cc03208c#!divAbstract

[2] *Removing multiple outliers and single crystal artefacts from X-ray diffraction computed tomography data.* Vamvakeros, A., Jacques, S. D. M., Middelkoop, V., Di Michiel, M., Egan, C.K., Cernik, R. J. & Beale, A. M. (2015). Accepted J. Appl. Cryst

Case Study: Development of an Ambient Pressure Microreactor for In Situ Soft XAS

Funding: UK Catalysis Hub, UCL, Diamond Light Source, Johnson Matthey

Aim

Building and commissioning of a high pressure (up to 3 bars) soft X-ray spectroscopy microreactor for industrial catalyst characterisation at the B07 beamline for identifying the nature of true active species during reaction.

New NEXAFS cell on the B07 beamline

Desired capabilities:

- pressure up to 3 bars
- Temperature range 273 - 773 K
- Presence of gases (tox, flam)
- In-line products analysis (MS, GC)
- NEXAFS compatibility (TEY)
- Energy range 250 to 2800 eV

Background

It is well known from ex situ structural characterisation that the morphology, composition and crystalline structure of the catalysts evolve during catalytic reactions. Undoubtedly significant progress has been made in using in situ X-ray diffraction (XRD), hard X-ray spectroscopy and computed tomography studies. However, taking into account that the metal active site loading in the sample is often only a few percent, the measured signal mainly originates from the bulk volume and not from the surface where the reaction takes place. Thus, the main scientific challenge for identifying the nature of true active species during reaction is the ability to accurately determine the behaviour/structure of the surface or species at the surface under operating conditions.

In situ soft X-ray absorption spectroscopy (NEXAFS) is capable of providing such data. Further to the surface sensitivity, spectra recorded at the L-edge offer 3-5 times greater energy resolution compared to those recorded at the K-edge, resulting in sharper spectral features. Transitions at the L-edge (2p-3d) are dipole-allowed, providing spectra that are more intense and structured than those from the dipole forbidden K-edge (1s-3d transitions). As a consequence, L-edge XAS spectra are more sensitive to oxidation and spin-states.

Outcomes

A new microreactor for the Ambient Pressure (AP) soft X-ray Absorption Spectroscopy (XAS) at the B07 VERSOX beamline at Diamond has been designed and commissioned. It has the volume of ~0.4 cm^3 and be operational at pressure 1-3 bars in the temperature range 273 - 650 K. The microreactor was tested using hydrogen, CO, helium gases and their mixture.

The new cell was used to study effect of poisoning on the performance of Co-based catalyst with titania support during industrially important processes like Fischer-Tropsch (FT) synthesis, converting syngas to liquid fuels, above ambient pressure operating conditions. The observed degree of catalyst reduction for 7h at 650 K was considerably better in comparison to the previous work reporting in situ NEXAFS of similar system reduced at 2 mbar pressure for 12h at 700 K.

The new cell has extended the in situ capability available for NEXAFS analysis at Diamond from 20 mbar to 1-3 bar pressure. The proof of principle experiments have been successfully performed using industrial catalysts for waste to energy conversion. Setup is suitable not only for model 2D catalysts (previously reported in the literature for the same system) but also for industrially relevant powdered catalysts. New microreactor will become a part of the standard beamline equipment and will be available to the broader scientific community providing access to measurements of major importance that are currently unavailable in the UK.

Johnson Matthey diamond CatalysisHub