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A Career in Catalysis: Graham J. Hutchings

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Abstract

This article is to commemorate the 70th birthday of Graham Hutchings. He has a diverse and distinguished career in catalysis, working in industry and academia. The scope of his work is wide ranging, and he has contributed to many areas of catalysis, and has been a pioneer in several of them. Notable contributions to the discipline include novel methods of catalyst preparation for both metal oxides and supported nanoparticles, selective oxidation, acetylene hydrochlorination, direct hydrogen peroxide synthesis and he has played a central role in the discovery, application and understanding of gold-based catalysts. The aim of this article is to provide an outline of his career and highlight some of the contributions he has made to the field of catalysis. Successfully supervising over 190 PhD students, working directly with more than 90 postdoctoral researchers, and collaborating widely nationally and

internationally, his work has influenced many in the discipline of heterogeneous catalysis.

Introduction

Graham Hutchings has had a memorable career working on heterogeneous catalysis, and we are sure he will continue to do so for years to come. Collectively the authors have worked closely with Graham for a combined total of over 120 person years, providing a lot of good times and fun, whilst undertaking some interesting science and making some important discoveries and creating new fundamental understanding. Graham has published more than 800 papers, and although it is not possible to cover all of his work in this short article, we would like to present a more personal view of our time, experience and achievements whilst working with Graham.

Graham Hutchings made a rather unconventional entrance into the field of heterogeneous catalysis. After completing his PhD in biological chemistry on *in vivo* ATP synthesis at University College London, he was recruited by ICI to work on biological chemistry projects. However, these projects were scrapped before he even started the job, and he had to agree to switch to work on heterogeneous catalysis projects if he wanted to remain with the company. He worked for ICI for 9 years, in research, production and production support managerial positions in the UK, being seconded to ICI South Africa in 1981, where he eventually became Chief Research Officer.

Graham then decided to end his industrial career and joined the academic staff in the Department of Chemistry at University of the Witwatersrand in 1984. There he quickly established himself in the world of academia, where he has remained ever since. Some of his early academic work focussed on Fischer-Tropsch chemistry[1-3] and at the same time he was also very active in working on methanol conversion to hydrocarbons using zeolites, with a particular emphasis on mechanistic studies. In a very short time span he and co-workers published a series of Chemical Communications around the topic of methanol to hydrocarbons[4-8], subsequently publishing many more in the following years, earning him the admiring title of "*Chem Comm Hutchings*" from his growing research group and colleagues.

One of the first projects Graham worked on when he joined ICI was the selective oxidation of butane to maleic anhydride and the following year the first in a series of patents were filed on the synthesis of vanadium phosphate catalysts for this process, with Raymond Higgins as co-inventor.[9-13] These patents were Graham's first publications, and he has carried on filing IP on his discoveries made in academia and with many industrial collaborators throughout his career.

In 1987 Graham left South Africa and joined the Leverhulme Centre for Innovative Catalysis at Liverpool University (Figure 1). During his decade there, he graduated many PhD students and wrote numerous papers and cemented his reputation as a leading scientist in the field of heterogeneous catalysis. In 1997 he accepted the Chair of Physical Chemistry at Cardiff University and from 1997-2006 Graham served as the Head of Chemistry at Cardiff University, and built up what is still the largest research group in the Department. In 2008 the Cardiff Catalysis Institute (CCI) was formed which Graham directed until 2019. Under his astute and inspiring leadership, the CCI developed a world-class reputation for catalysis research. Graham has received many well-deserved honours over his career including most notably being elected a Fellow of the Royal Society in 2009, being named Regius Professor of Chemistry at Cardiff in 2016 as the inaugural Regius Chair in Wales and becoming a Commander of the British Empire (CBE) in the 2018 Queen’s Birthday Honours.

Figure 1. Graham at the time he joined the University of Liverpool in 1987.

The following sections highlight some of the areas in which Graham has worked.. The coverage is by no means exhaustive as he has investigated so many topics, but the selection provides an insight to just some of the areas that have been important in his career and ones where his work has made a significant impact. It is also well worth highlighting his influence on the destiny of many people, over his long career he has supervised many, helping to launch their careers in academia, industry and a wide range of professions. His engaging approach, enthusiasm and creativity has been very widely appreciated.

Gold catalysis

In the early 1980s while in AECI, Modderfontein, South Africa, Graham was researching new Hg-based catalysts for the acetylene hydrochlorination reaction to form vinyl chloride monomer (VCM). He was intrigued by Shinoda's[14] attempt to correlate the activity of dozens of metal/carbon supported VCM catalysts with the metal cation electron affinity. Graham re-analysed the data taking into account the metal standard electrode potential for the 2-electron process ($M^{2+} + 2e^{-} \rightarrow M$) and produced a predictive model hypothesising that metals with high standard electrode potentials would show greater catalytic activity for the VCM reaction (Figure 2)[15]. He used this hypothesis to convince his management to let him construct a reactor to successfully validate the prediction. In 1985 when he had moved to academia, he was allowed to publish the prediction[15] and immediately embarked on a more detailed study of gold catalysts for this reaction. In 1988, he published more detailed experimental work to validate this prediction (Figure 2b) [16, 17]. Adsorption of $HAuCl_4$ in *aqua regia* onto activated carbon resulted in a catalyst with superior VCM synthesis activity to the standard industrial $HgCl_2$/C catalyst. Given the toxicity and safety concerns of $HgCl_2$ and the scale of operation involved in VCM synthesis plants, Graham very quickly realised the huge positive environmental impact that substituting Au/C could have on this process.

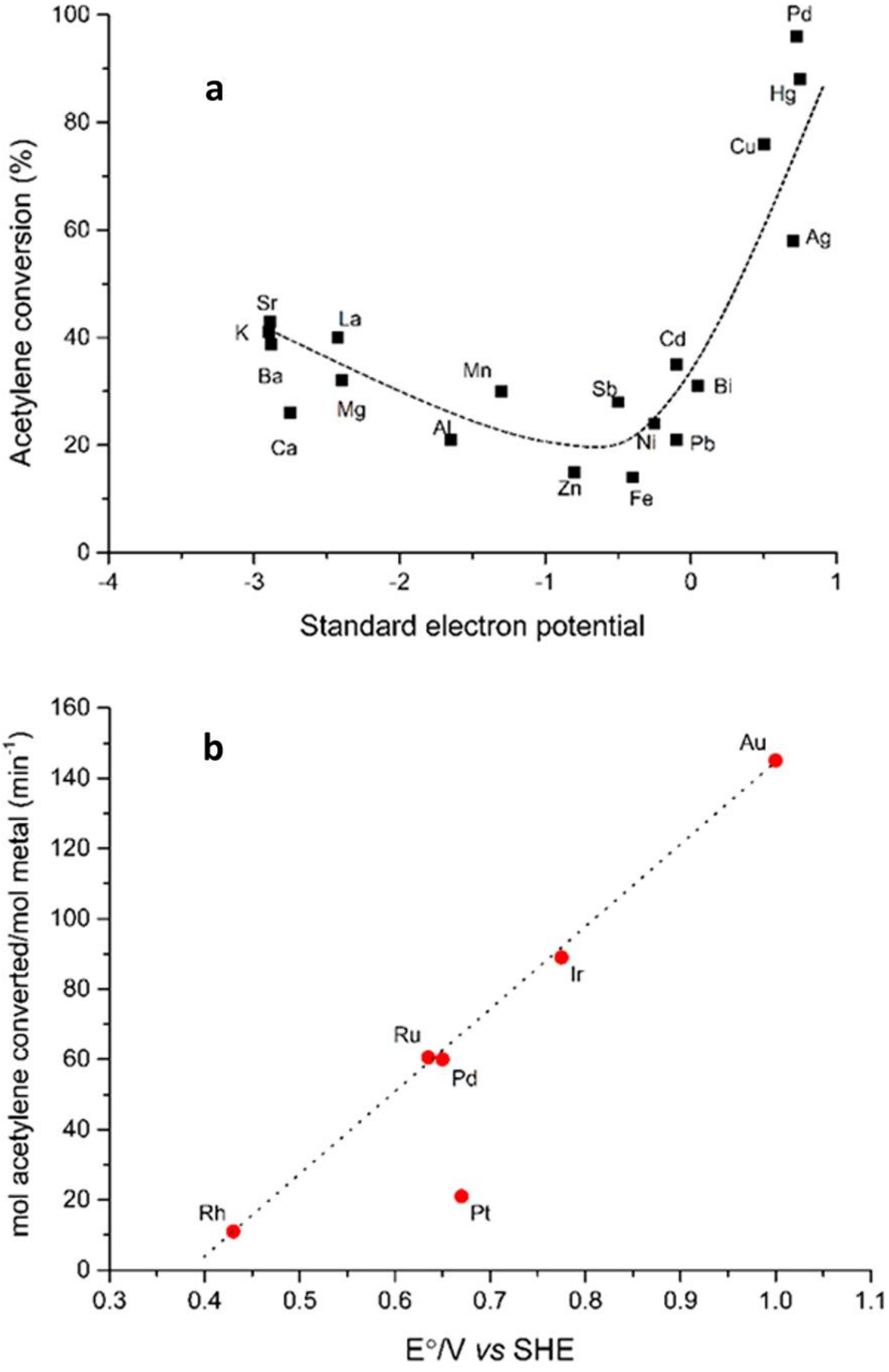

Figure 2 (a) Correlation of activity for acetylene hydrochlorination of carbon-supported metal chloride catalysts with the standard electrode potential. Reproduced with Permission

from Ref 15. Copyright 1985, Elsevier. (b) Correlation of initial acetylene hydrochlorination activity of supported metal chloride catalysts with the standard electrode potential of metal chloride salts. Reproduced with Permission from Ref 18. Copyright 2017, Royal Society of Chemistry.

However, it was not until much later when China began to manufacture vinyl chloride via acetylene hydrochlorination that the full potential of this new discovery of catalysis by gold could be realised (as will be described later). These first papers sparked a career long fascination with Au catalysis. His research, and that of his great friend Professor Masatake Haruta, opened-up a field of heterogenous catalysts that had long been under-explored due to the supposed chemical inertness of this 'uninteresting' noble metal. To date, Graham has published over 400 articles showcasing the efficacy of Au catalysts and their high activity for a number of selective oxidation reactions. One of the key metrics for a successful catalyst is high product selectivity, which is particularly challenging when the desired product is highly reactive and tends to react quickly to form deeper oxidation products. The formation of epoxides from alkenes is a good example of such a reaction and is usually achieved using hydrogen peroxide or stoichiometric oxygen donors. Graham found that a high partial oxygenate selectivity could be achieved when supported gold catalysts were employed for the reaction at moderate reaction temperatures (60 °C) in the presence of air and a catalytic amount of a radical initiator[19]. The oxidation of cyclohexene using 1,2,3,5-tetramethylbenzene as a solvent afforded a 50% selectivity towards cyclohexene oxide in the presence of a Au/C catalyst prepared by chemical reduction. When the same optimised reaction conditions were investigated for styrene, *cis*-stilbene and *cis*-cyclooctene, even greater selectivities towards the corresponding epoxide were observed (80-98%), while retaining reasonable conversion levels (7-30%).

Bulk gold is relatively unreactive and very resistant to oxidation and is often referred to as the most noble metal, which presents a paradox to experimental Au catalysis researchers. From the early days, the high activity of Au catalysts was thought to be a size effect as strikingly demonstrated by Professor Masatake Haruta's research in Japan in the 1980s. Haruta found that Au/Fe_2O_3 catalysts prepared by co-precipitation were exceptionally active for the aerobic oxidation of CO to CO_2 at sub-ambient temperatures; oxidation with bulk gold powder required temperatures higher than 280 °C[20]. Transmission electron microscopy measurements showed that the Au/Fe_2O_3 catalyst contained 2-4 nm sized gold nanoparticles supported on the Fe_2O_3 surface that were somehow related to the active site.

Subsequent advances in the imaging capability of electron microscopy via aberration correction and high angle annular dark field (HAADF) STEM imaging allowed Graham's team to develop an even deeper understanding of the active form of Au in heterogenous catalysts. It is now known that the Au can potentially co-exist in several different forms: namely FCC nanoparticles, sub-nm clusters, 2-D rafts and atomically dispersed species depending on the exact preparation method used and the identity of the support [20,21]. Co-precipitation or deposition precipitation methods on a support such as Fe_2O_3 tends to produce a mixture of nanoparticles, sub-nm clusters and atomically dispersed Au species. By careful correlation of the relative proportions of each of these species present in Au/Fe_2O_3 catalysts, displaying different levels of activity for the low temperature CO oxidation reaction, it was possible to deduce that the sub-nm clusters were the most desirable species, closely followed by the Au nanoparticles, whereas the atomically dispersed species were essentially inactive (Figure 3) [21] .

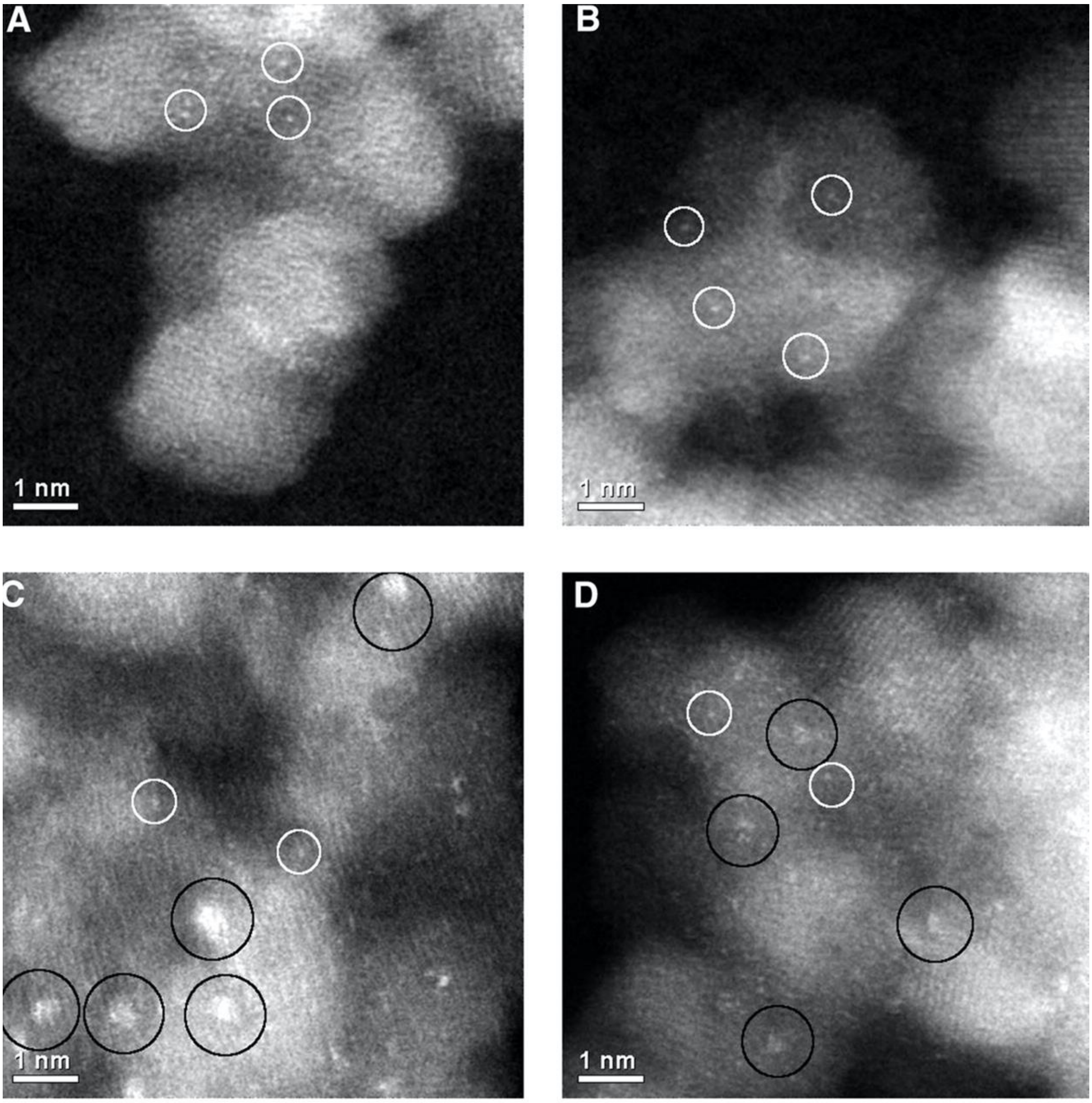

Figure 3. High-magnification aberration-corrected HAADF-STEM images of (A and B) the inactive (sample 1) and (C and D) the active (sample 2) Au/FeO$_x$ catalysts acquired an the aberration-corrected JEOL 2200FS electron microscope. Note the presence of sub-nm bilayer structures present (circled in black) in the active sample. Reproduced with Permission from Ref 21. Copyright 2008, American Association for the Advancement of Science.

Armed with this detailed knowledge of which particular gold morphology was preferred for specific reactions, synthesis and heat treatment protocols could then be designed to maximise the amount of the desirable active Au component, and hence further optimise the catalytic performance.

In contrast to the low temperature CO oxidation catalysts, the optimum Au morphology needed for acetylene hydrochlorination to form vinyl chloride monomer (VCM) is very different. The Hutchings group conclusively showed, using a combination of *in-situ* EXAFS/XANES, aberration corrected electron microscopy and theoretical modelling, that a mixture of atomically dispersed cationic Au^{I} and Au^{III} species were the active components in the Au/C catalyst for the acetylene hydrochlorination reaction, while the nanoparticles and sub-nm clusters were essentially spectators.[22] This study also confirmed his initial prediction that gold cations would be the most active catalysts.[15] This study was part of a long term collaboration with Peter Johnston at Johnson Matthey. Peter was one of Graham's first PhD students at the University of Witwatersrand and was involved with the initial work in South Africa. In 2007 Peter, now working for Johnson Matthey, approached Graham to work together to get an improved Au catalyst for acetylene hydrochlorination. The initial work carried out in South Africa and industry used catalysts containing 2% Au made using *aqua regia* as solvent. It was necessary to find a water-based route with very low levels of gold. This was successfully achieved and was followed by plant and full scale reactor trials.[23, 24] The Johnson Matthey optimized Au/C catalyst (called Pricat MFC) is now being commercialized for VCM production in China as a replacement for the environmentally unfriendly $HgCl_2$ catalyst.[25] As a follow on to this, the Hutchings group have developed new improved and simple methods for synthesising atomically dispersed Au catalysts.[26] The discovery of a non-mercury catalyst has enabled the Minimata Convention to become international law, since the mercury-based VCM catalyst represented the largest use of mercury in industry. This collaborative work has therefore been a great example of fundamental catalysis changing international law and improving the environment.

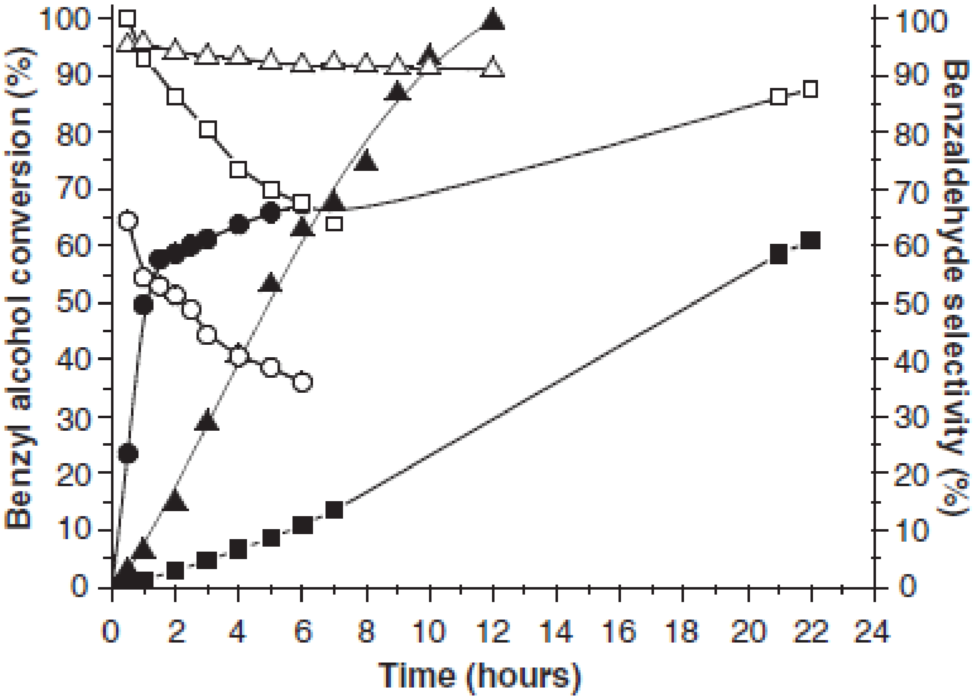

Figure 4 Benzyl alcohol conversion and selectivity to benzaldehyde as a function of reaction time (at 100 °C and 0.1 MPa) for Au/TiO_2 (squares), Pd/TiO_2 (circles), AuPd/TiO_2 (triangles) catalysts Solid symbols indicate conversion, and open symbols indicate selectivity. Reproduced with Permission from Ref 28. Copyright 2006, American Association for the Advancement of Science.

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Graham branched out from Au-only catalysts and pioneered the exploration of AuPd alloys as catalysts for redox reactions. The initial catalysts were based on co-impregnation of TiO_2 with an aqueous solution containing $HAuCl_4$ and $PdCl_2$ with a total metal loading of 5 wt%. This method of preparation gave a very broad size distribution of nanoparticles ranging from 4 to 50 nm. Nevertheless, the nanoparticles were all alloys, but with varying compositions[27]. This particular catalyst formulation proved to be very useful for catalyst discovery precisely because it contained such a broad range of nanoparticle morphologies and compositions, and as such, it was an ideal material to use as a starting point for catalyst design. This catalyst was found to be very active for the direct synthesis of hydrogen peroxide (seelater) and the selective oxidation of benzyl alcohol (Figure 4).[28]The AuPd alloy was both active and selective to benzaldehyde. Forming an alloy of AuPd typically gave catalysts that were more active than their monometallic counterparts and this synergistic effect has been t subject of intense research interest. This seminal work published in 2006 kick-started many studies using AuPd alloys as redox catalysts and to this day remains a highly active area of research in catalysis.

Au-based catalysts for hydrogen peroxide synthesis

The supported AuPd alloy catalysts made by incipient wetness impregnation were found to be very effective for the direct synthesis (DS) of hydrogen peroxide from molecular hydrogen and oxygen. This reaction can provide a green alternative for H_2O_2 production, especially for small scale local synthesis at the intended point-of-use. Most H_2O_2 is manufactured *via* the commercial anthraquinone auto-oxidation (AO) process, a mega-tonne process involving the sequential oxidation then reduction of a substituted alkyl anthraquinone (AQ) over a Pd catalyst, producing H_2O_2 and reforming the original anthraquinone. With complex distillations, high concentrations of H_2O_2 (~70 wt%) are achieved and distributed globally, and subsequently in most cases H_2O_2 then needs to be re-diluted to 1-8 wt.% for practical use. An ideal DS process requires just H_2, O_2 and a solvent (with no acid or halide promoters, as typically required with Pd catalysts[29]), and if H_2O_2 concentrations in excess of 1wt%

could be produced in flow and on-site as required, then energy costs associated with the AO process such as H_2O_2 transportation and AQ replenishment could be greatly reduced. This target has been a central aim for Graham's research in this area.

In 1999 Graham was involved in a consortium funded by the Institute of Applied Catalysis Foresight Challenge Research Programme. This collaboration between industry and engineering partners was aimed at developing new, active commercial catalysts for the DS process. Key metrics of a successful catalyst would be high H_2 selectivity (>90%), high catalyst productivity (>100 mol/kg_{cat}/h) and sufficient catalyst longevity.

The cohort's initial studies focussed on Au, AuPd and Pd nanoparticles supported on ZnO prepared by co-precipitation and the materials were evaluated in a batch reactor using supercritical CO_2 as the solvent[30]. Very low levels of H_2O_2 were detected after 1h, and further tests indicated the relatively high reaction temperature of 35 ˚C was responsible for facilitating the non-selective H_2O_2 decomposition reaction. Reducing the temperature to 2 ˚C and using methanol as the solvent afforded higher H_2O_2 yields for Al_2O_3 supported Au, Pd and AuPd catalysts, and indicated for the first time that higher rates of H_2O_2 synthesis could be achieved when AuPd alloy catalysts were used, compared to monometallic Au or Pd catalysts. The origins of this synergistic effect were further investigated, and a wide range of Au, AuPd and Pd catalysts supported on sulphonated carbon[31], Al_2O_3[32], Fe_2O_3[33] and TiO_2[34] were prepared by simple wet impregnation, and in each study an increased yield or rate of H_2O_2 production was achieved when the catalysts comprising AuPd alloys were evaluated.

In 2003, I (JKE) joined the group as a PhD student and, by what was essentially a flip of a coin, joined the H_2O_2 team and thus began working on a research theme that is still very much central to my research career today.. The target given for my PhD research was to design a catalyst that could make hydrogen peroxide, but did not decompose it. The calcination of a 2.5wt%Au-2.5wt%Pd/TiO_2 material at 400ºC was found to be a key step in synthesising a stable catalyst formulation. Catalysts calcined below 400 °C were found to have very high activities in a single reaction cycle (>200 mol/kg_{cat}/h); however, this was not maintained when the catalyst was reused, and after 4 uses the activity of the catalyst dropped by 90% to only 20 mol/kg_{cat}/h[34]. Atomic absorption spectroscopy (AAS) performed on the used catalyst showed that 92% of the Au and 95% of the Pd were being lost from a 2.5wt%Au-2.5wt%Pd/TiO_2 catalyst dried at 25 °C, whereas none was lost from a catalyst calcined at 400 °C. In early 2000, advances in scanning transmission electron microscopy (STEM), coupled with X-ray photoelectron spectroscopy (XPS) provided more insight into the nature of the AuPd alloys, which were found to be below 10 nm in size[34]. Comparative XPS analysis of the 2.5wt%Au-2.5wt%Pd/TiO_2 catalyst calcined at 400 °C and dried at 25 °C showed some striking differences, in that the dried sample exhibited both Au and Pd XPS signals whereas the 400 °C calcined sample showed only the Pd XPS signal. Given that all the expected Au and Pd remained in the 400 °C sample after calcination, the model of an Au-core/Pd-shell nanoparticle was postulated, where the photoelectrons generated cannot escape from the Au core due to the presence of a Pd shell. STEM-XEDS mapping of the AuPd nanoparticles present in the 400 °C calcined sample showed this was indeed the case and elemental mapping clearly showed a PdO shell covering a Au-rich core (Figure 5). This model was presented at the World Congress in Oxidation Catalysis in Sapporo in 2005 and was the basis of some lively discussions.

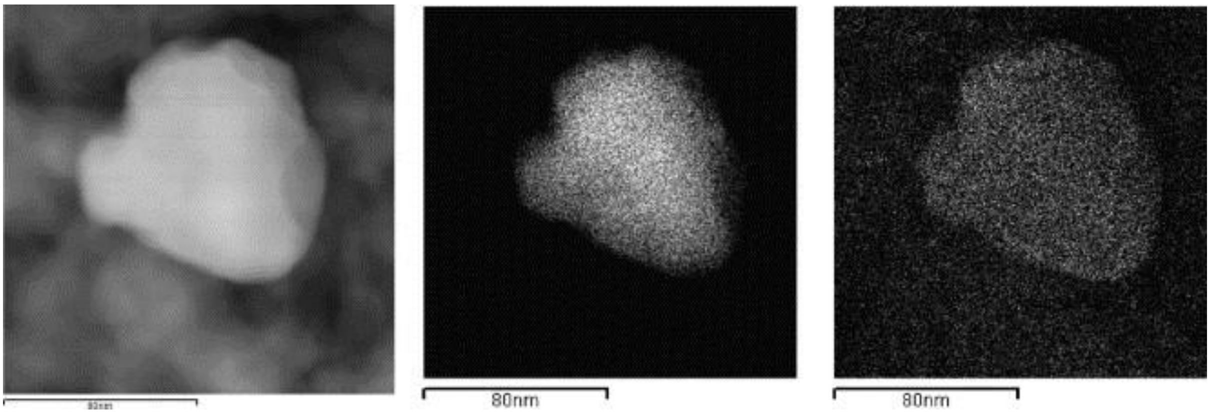

Figure 5 STEM-HAADF image of 2.5 wt.% Au–2.5 wt.% Pd/TiO_2 catalyst calcined at 400 °C, showing a large alloy particle (left), Au-M_2 STEM-XEDS map (centre), Pd-L1 STEM-XEDS map (right); note that the Pd signal appears to originate from a larger area than that of the Au signal. Reproduced with Permission from Ref 34. Copyright 2005, Elsevier.

Once the core-shell model of the AuPd nanoparticles was accepted, it became apparent that the catalyst support also plays a key role in the DS reaction; it was more than just simply providing an immobilising substrate for the Au-rich core-Pd shell nanoparticles. A series of activated carbons were readily available in the lab at the time and were evaluated as supports for AuPd catalysts prepared by wet impregnation. A G60 activated carbon was pre-treated with a dilute acid (either nitric or acetic acids) and then washed with water and dried. When impregnated with Au and Pd precursors, the acid washed G60 (AW-G60) showed the highest *stable* rate of H_2O_2 synthesis recorded to date, with an H_2 selectivity > 95%[35]. This was the first time such a high H_2 selectivity had been achieved in a batch reactor for the DS synthesis reaction in the absence of acid or halide promoters. Rigorous aberration corrected analytical microscopy analysis showed that the AuPd/AW-G60 catalyst contained a greater number of small (2-5 nm) Pd-rich (98%Pd-2%Au) particles, compared to the non-acid-washed AuPd/G60 sample. These smaller particles have a surface capable of synthesising H_2O_2 without over hydrogenation to water. The catalysis was validated in the labs of industrial partners, and the catalyst preparation methodology was eventually patented[36] and published.[35]

Graham has continued working in this area and set about designing catalysts that could synthesis H_2O_2 without decomposing it. Realising that Pd was the active component and that Au was acting as a modifier, several alternative less expensive alloy components were considered. This led to a set of design principles identifying PdSn alloys as being particularly interesting.[37]

VPO catalysts for maleic anhydride production and catalyst preparation

While Graham was at the Leverhulme Centre for Innovative Catalysis in Liverpool University, his interest in butane oxidation was re-kindled by an invitation to spend a short sabbatical in Jean-Claude Volta's laboratories at the IRC, CNRS in Lyon in 1992. This was a chance for Graham to return to the lab, and his first experiments were not completely successful, resulting in a flask containing the reaction mixture breaking and depositing hydrochloric acid into a hot isomantle creating quite a spectacular fire that he immediately extinguished. However, despite this initial minor mishap, the visit proved to be very productive, as it led to Graham's first peer reviewed publication on vanadium phosphate catalysts appearing in Nature[38] in 1994, and more importantly, sparking a 15-year collaboration with Jean-Claude based around their passion for science and gastronomy in equal measures. As a PhD student, the group meetings in Lyon were memorable experiences and I (JKB) fondly remember one particular event that was held in a mountain ski resort during the summer with particularly good catering for breakfast, lunch and dinner.

At the time there was considerable world-wide interest in butane oxidation partially driven by the number of crystalline vanadium phosphate phases that had been identified whose structure and catalytic properties have been well documented. Some of the most widely studied are the V^{5+} vanadyl orthophosphates (α_{I}-, α_{II}-,β-, γ-, δ-, ω- and ω'-$VOPO_4$, and $VOPO_4 \cdot 2H_2O$), the V^{4+} vanadyl hydrogen phosphates ($VOHPO_4 \cdot 4H_2O$, $VOHPO_4 \cdot \frac{1}{2}H_2O$, $VO(H_2PO_4)_2$), vanadyl pyrophosphate ($(VO)_2P_2O_7$) and vanadyl metaphosphate ($VO(PO_3)_2$).

Although a commercial process, the role and nature of the different phases identified in the final catalyst was hotly debated in the scientific literature. The commercial catalysts are derived from the *in-situ* activation of the hemihydrate precursor, $VOHPO_4 \cdot \frac{1}{2}H_2O$, in *n*-butane/air. The presence of an oxidant and reductant in the feed leads to a complex mixture of V^{4+} and V^{5+} phases, and some of Graham's early collaborations in this field were aimed at developing characterisation techniques that could be used to elucidate the nature of the active phase. This led to detailed characterisation studies using *in-situ* Raman spectroscopy[38] and ^{31}P NMR spin echo mapping[39, 40] with Jean-Claude Volta, detailed electron microscopy[41, 42] studies of the catalysts in collaboration with Chris Kiely, as well as XRD[43-45] and XPS[46, 47] studies in collaboration with Robert Schlögl and co-workers at the Fritz Haber Institute of the Max Planck Society in Berlin.

The combination of these techniques identified the key role played by amorphous vanadium phosphate phases in the final catalysts, although these were often dismissed by other researchers. The interest in amorphous material was a result of an *in-situ* Raman study into the transformation of $VOHPO_4 \cdot ½H_2O$ under reaction conditions. They found that during the activation process, there is a structural disordering at 370 °C, which corresponds to the appearance of maleic anhydride[38]. The disordering was found to occur at a lower temperature (300 °C) when maleic anhydride was added to the butane/air reaction mixture. The formation of the disordered material was further studied using TEM in conjunction with XRD[48]. This demonstrated that $VOHPO_4 \cdot ½H_2O$ rapidly transformed into an amorphous material under reaction conditions, before being further converted to a mixture of $(VO)_2P_2O_7$ and δ-$VOPO_4$. The δ-$VOPO_4$ phase was also shown to transform into $(VO)_2P_2O_7$ with time, clearly demonstrating the ability of the different phases to interconvert under the reaction conditions and helping to explain why the commercial catalysts require a considerable time (often >100 hours) before they are equilibrated.

The other area that Graham made a significant contribution to in terms of vanadium phosphate catalysis was in refining the synthesis methodology to improve performance. Standard methods reacted vanadium(V) oxide with phosphoric acid in the presence of a reducing agent to form $VOHPO_4 \cdot ½H_2O$ and the activity of vanadium phosphate catalysts was linearly dependent on the surface area[49]. Hutchings, Volta and Kiely identified that when precursors were synthesised *via* different methods, they were found to have very different compositions. TEM studies indicated that the common feature of these materials containing different phases was an amorphous overlayer on the surface which could explain why the intrinsic activity of the different catalysts was the same. This fitted with previous studies by Colston who identified a phosphorus rich overlayer present on VPO catalyst surfaces by XPS.[50] The ^{31}P NMR studies added weight to the hypothesis that disordered materials were crucial components of vanadium phosphate catalysts. Conventional NMR studies are hampered by the presence of paramagnetic vanadium ions in the catalysts. Spin echo mapping uses the shift of the ^{31}P signals due to the paramagnetic ions, to gain information about the oxidation state of the vanadium in the sample[39]. The V^{3+}, V^{4+} and V^{5+} ions are easily distinguishable using this technique, and the difference between the spectra of V^{4+} compounds such as $VOHPO_4·½H_2O$, $VO(H_2PO_4)_2$ and $(VO)_2P_2O_7$ enable easy identification. The $VOPO_4$ (V^{5+}) phases give spectra (with a signal at 0 ppm), which are identical to the H_3PO_4 spectrum. Although polymorphs of $VOPO_4$ phases can be distinguished using standard ^{31}P MAS NMR[51], catalysts prepared by different procedures were studied using this technique[39]. The main advantage of ^{31}P NMR spin echo mapping over other techniques, was found to be the ability to detect low amounts of $(VO)_2P_2O_7$, particularly in poorly crystalline materials, and to distinguish between crystalline and disorganised $(VO)_2P_2O_7$, to enable the amount of amorphous material present in catalysts to be quantified.

Graham investigated a number of different themes in the synthesis of vanadium phosphate catalysts. These included studying the effect of dopants[52-59], investigating alternative precursor phases[43, 60-62], the role of the solvent[63-66] and the use of structure directing agents[67-71]. However, one of the most significant contributions to the synthesis was the discovery that new precursor morphologies could be accessed by exploring new methodologies. This was first demonstrated exploring the reduction of $VOPO_4.2H_2O$ using the two-step VPD route. The choice of alcohol was shown to be crucial in determining the morphology of the $VOHPO_4·½H_2O$ precursor.[72] While secondary alcohols were found to produce rhomboidal platelets, the use of primary alcohols produced a very different morphology with only one major peak in the XRD pattern and a high surface area, often described as a desert rose or rosette-type structure (Figure 6)[73]. In the same study, reduction with 3-octanol was found to produce an alternative precursor, $VO(H_2PO_4)_2$, which was a material I (JKB) became well-acquainted with as the focus of my PhD research.

Figure 6. SEM micrograph of the vanadium phosphate desert-rose morphology.

Graham was also interested in exploring alternative methodologies for synthesising catalysts. His early research in ICI had demonstrated that ball milling could have an important influence on the catalyst performance, which he published 20 years after the initial discovery[74], a research area he returned to periodically in academia[75, 76]. Graham also investigated hydrothermal and solvothermal synthesis of vanadium phosphate catalysts[59, 66, 77-79]. The most significant of these studies probed the reduction of $VOPO_4 \cdot 2H_2O$ with alcohols at elevated temperatures and pressures[43]. Chemical reactions carried out under reflux conditions at atmospheric pressure provide access to a limited number of stable phases, typically $VOPO_4 \cdot 2H_2O$ in the absence of a reducing agent, $VOHPO_4 \cdot ½H_2O$ in the presence of a reducing agent with a stoichiometric V:P ratio and $VO(H_2PO_4)_2$ in the presence of a reducing agent if there is an excess of the phosphorus source[60, 61]. However, by exploring the solvothermal reaction at temperatures up to 400 °C and 150 bar in an autoclave, a number of new phases could be synthesised with interesting catalytic activity.[43, 80] At low temperatures the $VOPO_4.2H_2O$ was not reduced and the alcohol became intercalated between the vanadium phosphate layers replacing the water to give $VOPO_4 \cdot nROH$. As the reaction temperature was increased, reduction occurred to give $VOHPO_4 \cdot ½H_2O$ at intermediate temperatures and pressures. However, as the temperature and pressure were increased further, a new group of materials based on $VPO_4 \cdot H_2O$ polymorphs with varying stoichiometry were generated. As mentioned previously, vanadium phosphate activity is highly dependent on the surface area of the catalysts, but the surface area normalised activities are generally similar for vanadium phosphate catalysts, despite major differences in morphology or phases present[49]. In this study, catalysts derived from the precursors synthesised under hydrothermal conditions were found to have higher intrinsic activity than those synthesised under ambient conditions, demonstrating the potential of this methodology to access more active catalysts.[43]

Another methodology that was pioneered for synthesising catalysts was supercritical antisolvent precipitation. Precursor solutions were pumped through a fine capillary contained within a co-axial nozzle into the precipitation vessel containing flowing CO_2.

The CO_2 was pumped through the outside of the co-axial nozzle and the temperature and pressure controlled to maintain the vessel above the critical point of CO_2. As the solution exits the nozzle the solvent diffuses into the CO_2, reducing the solvating power and the solute is precipitated. One of the advantages of this technique is that it can produce highly disordered materials during the precipitation process, with nucleation occurring at a significantly faster rate than crystal growth. During my PhD, I (JKB) was invited to visit Nottingham University by Steve Howdle and Martyn Poliakoff to investigate this route for precipitating vanadium phosphates. The materials generated using this methodology were proven to be amorphous by electron diffraction, but displayed an intrinsic activity that was higher than conventionally prepared catalysts and did not require a lengthy activation period to reach steady state.[81] These findings cast further doubt on the accepted wisdom that the crystalline phases in vanadium phosphate catalysts were responsible for the activity and was the first clear and definitive demonstration that a non-crystalline vanadium phosphate catalyst may be the preferred material for the selective oxidation of butane to maleic anhydride. At the time, this finding was controversial in the field, as I found out when Graham sent me to give my first oral presentation at an international conference at the World Congress on Oxidation Catalysis. During my presentation, a fairly lengthy queue of eminent professors formed in front of the microphones in the aisles and during the questions made it clear that they did not agree with our conclusions! However, we subsequently showed using detailed *in-situ* studies that the surface of the catalyst can undergo rapid transformations leading to metastable and disordered phases, demonstrating this hypothesis was not as far-fetched as when first suggested.[45] The use of surface sensitive characterisation techniques, such as low energy ion scattering (LEIS), have confirmed that surfaces are inherently different from bulk compositions, contributing to our hypothesis becoming accepted wisdom[82].

Realising that this methodology could provide a route to new catalyst compositions and morphologies not readily available through other routes, we built our own supercritical anti-solvent precipitation equipment and proceeded to investigate the synthesis of other metal oxide catalysts using this methodology. It was demonstrated that this new synthesis methodology could provide single oxides with improved properties as catalysts[83-86] and supports[87-89], but the most interesting applications involved mixed metal oxide catalysts[90-98].

Early studies were carried out on hopcalite, a mixed metal oxide of copper and manganese, that is a catalyst that has been used for several different applications, most notably in low temperature CO oxidation. Early studies showed that copper and manganese acetates could be used to precipitate high surface area catalyst precursors. Upon activation the catalysts were found to have a high intrinsic activity which could be attributed to the homogeneous mixing of the components leading to disordered $CuMn_2O_4$ catalysts, without producing any of the single component metal oxide phases.[92] However, the final catalysts were found to have a low surface area due to the exothermic calcination of the acetates causing sintering. This led to a modification of the precipitation process with the addition of water to the metal acetate solution – a counter-intuitive step as water is considered insoluble in supercritical CO_2. However, having water in the process enabled metal carbonates to be precipitated which did not sinter upon calcination. This modification allowed hopcalite catalysts with surface areas of up to 175 m^2g^{-1} to be produced.[93] This improvement was attributed to the water reacting with CO_2 *in-situ* to produce carbonic acid, that could subsequently react with the precipitated acetates during an aging step.

The antisolvent precipitation methodology was also applied to Cu/ZnO catalysts for methanol synthesis and the reverse water gas shift reaction.[94, 95, 97, 99, 100] These are widely studied catalysts that are produced by co-precipitation. A number of hydroxy carbonate phases have been identified, but generally the best catalysts are derived from zincian malachite precursors. Georgeite is the least studied of the hydroxycarbonate phases as it is unstable, readily decomposing to malachite, and it is amorphous - being one of the few minerals to be classified from its infrared spectrum rather than X-ray diffraction data. Supercritical antisolvent precipitation was found to produce a stable zincian georgeite material, demonstrating again, the ability of this synthesis technique to access materials and phases that cannot be readily produced by other methods. The Cu/ZnO catalysts derived from this precursor were found to be highly active methanol synthesis catalysts, as well as water gas shift catalysts that were resistant to deactivation.[97]

Short chain alkane activation

Early in his career Graham developed a keen interest in alkane activation and conversion, especially around methane selective oxidation, and this has been a theme that has run throughout his research career. In the mid-1980s the process of oxidative methane coupling received a lot of research attention, as an alternative direct process for upgrading methane from natural gas reserves, and Graham contributed significantly to this topic [101].

Ito and Lunsford showed that MgO was an effective catalyst for methane coupling [102], which sparked an avalanche of studies where a wide range of oxides were all compared to the best catalyst. It was not until three years later, that it was found that the role of the MgO catalyst was actually to produce gas phase methyl radicals. Graham was the first to publish this result (by a few days), as several groups had independently reached a similar conclusion.[103] This finding was initially considered extremely controversial, but was later accepted as being correct by the general community.

Graham became deeply interested in the Lunsford MgO catalyst and a wider analysis of the corresponding literature revealed, that although all catalysts were described as MgO and had identical XRD patterns, they exhibited vastly varying catalytic performance[101]. MgO has a cubic structure, with exposed facets indexed as (100), (010) and (001)-type, and Graham and co-workers showed that activity differences were due to variations of morphology and related to the preparation procedure [104, 105]. MgO catalysts were prepared by three different procedures, thermal decomposition of the hydroxide, burning Mg ribbon in air and thermal decomposition of the basic carbonate ($3MgCO_3 \cdot Mg(OH)_3 \cdot 3H_2O$). Transmission electron microscopy showed the ribbon residue MgO had a cubic morphology with a broad size distribution of crystallites (100-200 nm) with (100)-type surface termination planes. MgO from the hydroxide showed a similar cubic morphology and surface termination, but with much smaller crystallites in the size range 20-40 nm. The ex-basic carbonate MgO did not have the same cubic morphology. Instead it was much less regular and the surface was highly facetted, consisting of both pseudo-(111) and (110) facets, and it also had small particles (20–40 nm). By studying the effect of calcination temperature, it was possible to correlate the morphologies to the differences in catalyst activity and these studies helped to explain how different samples of MgO gave rise to different catalytic performances for methane oxidative coupling.

The formation of ethane and ethylene from oxidative methane coupling are important products, but there is also a desire to produce oxygenates, like methanol and formaldehyde directly from methane selective oxidation. Again, by using an MgO catalyst it was shown that the product distribution could be switched from coupling products to formaldehyde by modification of the reaction conditions [106]. On reducing the catalyst contact time there was a dramatic switch from ethane and ethylene to formaldehyde as the major product. This switch was rationalised by considering the relative concentrations of methyl radicals and molecular oxygen in the gas phase. At higher contact times the concentration of methyl radicals was relatively high, favouring coupling to C_2 products. In contrast, at low contact times the methyl radical concentration was lower and reaction with molecular oxygen is preferred, forming a methyl peroxy species, a precursor to selective oxidation to formaldehyde. This study helped to provide further mechanistic insight and reinforced the dominating role of gas phase radical chemistry in high temperature gas phase catalytic methane selective oxidation.

Further studies targeted methane partial oxidation to oxygenates, and in particular a pioneering design approach [107, 108]. Graham and his team hypothesised that simple metal oxide components that activated methane and oxygen, but which did not over oxidise methanol [109], could be combined synergistically to produce an effective dual component catalyst. Combining Ga_2O_3 and MoO_3 by physical mixing demonstrated the validity of the design approach, producing significant activity for the direct partial oxidation of methane to formaldehyde. Although progress and some understanding were achieved using metal oxide catalysts at high temperatures in the gas phase, it was clear that limits on oxygenate selectivity were constraining the yields in a direct conversion approach and that an alternative catalytic approach was required, which he later rigorously pursued.

In 2008 Graham was successful as one of the winners of the Dow Methane Challenge, opening-up a new low temperature approach for methane selective oxidation in the liquid phase, resulting in a significant body of work. His idea was to use radical species in the liquid phase, initially derived from hydrogen peroxide, but eventually extended this to *in-situ* generation of activating species through co-feeding of molecular hydrogen and oxygen. He hypothesised that use of aqueous peroxide species would be an activated oxidant and hydrolyse intermediate species, closing the catalytic cycle that was not achieved in other low temperature approaches. Two distinctly different types of catalysts were successfully identified; namely those based on Fe-ZSM-5 and those using supported AuPd nanoparticles. A large team of PhD students and postdocs worked on this particular project, liaising closely with industry.

The initial discovery was that commercial ZSM-5 was effective for the selective oxidation of methane to oxygenates at low temperatures in the aqueous phase with hydrogen peroxide[110] . Initially it appeared that the activity was dependent on the Si/Al ratio and the catalyst pre-treatment temperature, with 500°C being the best. Closer investigation using silicalite, and careful modification of the Al content by hydrothermal synthesis and post-treatment methods, identified that the Al content was not the critical parameter controlling activity. Elemental analysis of the active ZSM-5 zeolite showed low levels of Ti and Fe impurities. Subsequent studies using TS-1 under the same reaction conditions showed it was inactive, whilst introducing Fe into inactive silicalite by hydrothermal synthesis generated activity for selective methane oxidation. There was a linear relationship between the amount of Fe introduced and activity, confirming the key role played by the Fe species. The increase of activity with heat treatment correlated with an increase of extra-framework Fe, as it migrated from tetrahedral framework sites to octahedral extra-framework sites. A combination of EXAFS and DFT modelling studies allowed identification of the resting state of the active site as a di-iron complex $[Fe_2(\mu_2\text{-}OH)_2(OH)_2(H_2O)_2]^{2+}$, containing antiferromagnetically coupled high-spin octahedral Fe^{3+} centres. EPR studies established that hydroxyl radicals were responsible for over-oxidation of the desired methanol product and limiting such radical chemistry should allow high methanol yields. The addition of Cu^{2+} had an important role, incorporating it to the Fe-ZSM-5, or as a heterogeneous or homogeneous additive to the reaction media, significantly increased methanol selectivity. Cu largely switched-off methanol over-oxidation, as hydroxyl radicals were no longer detected, whilst it had no effect on conversion. A methanol selectivity of 93% at 10% methane conversion was achieved, giving TOFs considerably greater than other reported catalysts.

More detailed studies of the basic reaction mechanism and the reaction network focused on the most active 0.014 wt.% Fe-ZSM-5 catalyst, identifying that it exhibited the most efficient use of H_2O_2, had no induction period and gave a very high initial TOF of 14,200 h^{-1} [111]. Methyl hydroperoxide was confirmed as the primary product, whilst it was possible that some formic acid was also present at very low levels. Methyl hydroperoxide was subsequently oxidised to methanol and then to formic acid, and in stark contrast to gas phase oxidation, no formaldehyde was produced. Comparison of the mechanism of Fe-ZSM-5 with homogeneous Fenton's reagent using radical scavengers clarified that the reaction mechanisms were different. Experimental observations supported the hypothesis that the heterogeneously catalysed Fe-ZSM-5 reaction does not rely on homolytic cleavage of the H_2O_2, and a subsequent free-radical chain mechanism involving highly reactive methyl, hydroxyl and hydroperoxyl radicals. Methane selective oxidation was at least heterogeneously initiated, with removal of the catalyst totally switching-off the reaction. Extended work elucidated how the Fe active sites evolved [112] and established that isomorphous substitution of the trivalent cations Al^{3+} and Ga^{3+} into the ZSM-5 catalyst promoted the activity of the Fe-based catalyst[113]. The extra-framework Fe sites remained the catalytically active sites, but promotion occurred through facilitating the extraction of Fe from the framework, increasing the concentration of the active sites. Secondly, isomorphous substitution provided a negatively charged framework facilitating dispersion and stabilisation of the cationic active sites. This understanding led to further rational improvements of the catalyst performance.

The direct selective oxidation of other short chain hydrocarbons also posed a challenge, and Graham's work identified that the Cu-Fe-ZSM-5 catalyst was also highly active and selective for ethane oxidation by aqueous hydrogen peroxide[114]. Ethane conversions of 56% with 70% selectivity to acetic acid was achieved, with a combined oxygenate selectivity > 95%. The reaction network was complex, forming a broad range of C_2 oxygenated products, and some C-C bond scission was noted resulting in C1 products. Ethene was also produced, which after undergoing further oxidation, gave ethanol as a primary product from ethane. In contrast to the mechanism proposed for methane oxidation over the same catalyst, ethane oxidation proceeded by carbon-based radicals, as opposed to oxygen-based radicals, explaining the higher conversion and more complex reaction network.

A flow reactor was employed to demonstrate the efficacy of the Cu-Fe-ZSM-5 catalyst for ethane selective oxidation[115]. Control over the catalyst contact time allowed a significant reduction of C-C scission and formation of over-oxidation products. Optimising the performance of the catalyst by modifying Fe and Cu content was explored, as was investigating the influence of temperature, pressure and reactant concentrations. In particular, varying pressure had a beneficial role, allowing us to achieve 98% C2 oxygenate selectivity, and high per-pass yields of acetic acid. Very low levels of Fe leaching were observed, but there was no catalyst deactivation on prolonged use, with conversion and selectivities remaining unaltered. Following this demonstration with ethane, the same flow approach was also successfully employed for continuous selective methane oxidation using Cu-Fe-ZSM-5, and a high continuous selectivity towards methanol was achieved[116].

Indeed, the Cu-Fe-ZSM-5 catalyst with hydrogen peroxide in an aqueous solvent proved to be a very effective selective oxidation system for a range of short chain alkanes. Fe-ZSM-5 has also been applied for propane oxidation[117]. High oxygenate yields were obtained, with the previously identified extra-framework active site being responsible, showing that a relatively high proportion of Fe deposited on the zeolite framework was an inactive spectator species and could be removed without significantly reducing activity. The precise role of Cu in increasing oxygenate selectivity is still under debate, however it is empirically clear that it is very effective for limiting over-oxidation of partial oxidation products from methane, ethane and propane[118].

The same low temperature aqueous hydrogen peroxide selective oxidation approach was also pioneered by Graham using AuPd bimetallic nanoparticles supported on titania[119]. Initially the AuPd/TiO_2 catalysts were prepared using sol-immobilisation, but the metallic state and small nanoparticles showed high rates of hydrogen peroxide decomposition and the catalysts were not suitable. Instead, a catalyst prepared by incipient wetness impregnation was used, as previously this synthesis method was shown to be good for making highly effective catalysts for alcohol selective oxidation and direct hydrogen peroxide synthesis: both these reactions are linked by the involvement of hydroperoxy intermediates. When aqueous hydrogen peroxide was employed as the oxidant, appreciable yields of methanol were obtained under mild conditions, and analogously to the Fe-ZSM-5 catalyst, the primary reaction product was methyl hydroperoxide. The methyl hydroperoxide was sequentially oxidised to methanol, but unlike the situation for Fe-ZSM-5, no formic acid was produced, indicating that methanol was surprisingly stable over the AuPd/TiO_2 catalyst. Further studies of methanol oxidation demonstrated that around 29% of the CH_4 was converted, whilst oxidation of formaldehyde and formic acid to CO_2 were facile. The AuPd nanoparticles were key in the oxidation of methane and methyl hydroperoxide to methanol, whilst the TiO_2 support alone did not form any methanol. *In-situ* EPR studies identified that both methyl and hydroxyl radicals were produced during the reaction, and the presence of the carbon-based radical was in clear contrast to the Fe-ZSM-5 catalyst for methane oxidation. It was further hypothesised that methyl radicals can react with surface bound hydro-peroxy radical species, formed directly from hydrogen peroxide decomposition, to generate the primary methyl-hydroperoxide product. Consequently, Graham proposed that the surface hydroperoxy species could be formed *in-situ* by feeding H_2 and O_2 instead of using pre-formed hydrogen peroxide. This hypothesis was supported by experimental evidence that showed co-feeding H_2 and O_2 increased methanol selectivity and increased the activity three-fold.

A more systematic study of the reaction conditions and catalyst parameters showed that selective methane oxidation was possible using the AuPd/TiO_2 catalyst at 2 °C[120]. Increasing the pressure of methane and hydrogen peroxide concentration increased the productivity of oxygenates, and the reaction was first order with respect to hydrogen peroxide. The combination of Au and Pd were required to optimise activity, methanol selectivity and reduce excessive hydrogen peroxide decomposition, with a 1:1 molar ratio being the best. It was concluded that a core-shell nanostructure, with a Au-core and a Pd-rich shell, was optimum for methane selective oxidation to methanol. The addition of Cu species was found to be important for increasing oxygenate selectivity with Fe-ZSM-5 catalysts[110], so a similar approach was explored with AuPd/TiO_2 [121]. When compared to the bimetallic catalyst, the addition of Cu increased productivity by a factor of five, with an associated increase of methanol selectivity up to 83%. The Au and Pd remained present as core-shell nanoparticles, whilst Cu was dispersed as 5 nm nanoparticles that were either Cu or Cu_2O. It is interesting to note that Cu has the effect of increasing oxygenate selectivity for both Fe-ZSM-5 and AuPd/TiO_2 catalysts, although they operate primarily through quite different mechanisms.

The development and refinement of synthesis methods for preparing bimetallic supported nanoparticles with controlled morphological properties (*e.g.,* particle size and shape, oxidation state of metals and metal support interaction) and their exploitation as potential catalysts for the transformation of organic compounds to useful fine chemicals and fuels has been a major area of activity for Graham's research group.[122, 123] For the AuPd system, it should be noted that (i) Au and Pd can form a continuous solid solution over the whole range of composition and (ii) the addition of the second metal can alter the electronic and geometrical properties of the synthesized particles, positively affecting catalytic activity, catalyst stability and the distribution of reaction products.

Using colloidal methods for the preparation of highly active AuPd catalysts, Graham demonstrated that the oxidation of methane to methanol was possible in the presence of H_2O_2 as an initiator and molecular oxygen as the main oxidant under mild reaction conditions[124-126] The correct choice of stabiliser ligand for the colloidal AuPd nanoparticle was found to be crucial for this reaction[124]. By using polyvinylpyrrolidone (PVP) instead of using the more commonly used polyvinylalcohol (PVA) stabiliser, it was shown that unsupported AuPd-PVP colloidal nanoparticles could efficiently transform methane to methanol with a selectivity of 90-92% while using a low amount of H_2O_2 (50 µmol) in the presence of molecular oxygen at 50 °C. Moreover, for the corresponding sol-immobilised 1 wt.% AuPd/TiO_2 material, the activity and selectivity to methanol was low (26%). One of the major deductions of this work was that if the AuPd colloidal nanoparticles were supported on TiO_2, the catalyst exhibited a much higher rate of H_2O_2 degradation, suggesting that either the interfacial sites at the support/metal interface or a change in the morphology of the colloidal nanoparticles during the immobilisation step, led to the increase in H_2O_2 degradation. EPR spin-trapping studies revealed the presence of both $^{\bullet}OH$ and $^{\bullet}CH_3$ radicals during reactions with a sol-immobilized AuPd catalyst, implying that the mechanism is radical-based. The observation that the primary product was CH_3OOH implied that the primary termination step is either between $^{\bullet}CH_3$ and $^{\bullet}OOH$ radicals or from recombination of $^{\bullet}CH_3$ with dissolved O_2 in the solution, originating from the decomposition of H_2O_2. For the unsupported colloidal catalyst which decomposes H_2O_2 at a much slower rate and makes substantially more product, it was rationalized that $^{\bullet}CH_3$ was being produced over a longer time scale and by adding O_2 to the reaction mixture this would promote oxygen incorporation through the generation of $CH_3OO^{\bullet}$ radicals. The reaction of $^{\bullet}CH_3$ with O_2 has been reported to occur at high rates in gas-phase reactions[127], therefore there was an indication that this could also be happening at low temperature with the utilisation of H_2O_2 and O_2 as oxidants. The reaction mechanism was also investigated by using isotopically labelled $^{13}CH_4$ which confirmed that the carbon source for the product was CH_4 and not the PVP stabilizer ligand on the colloid. The incorporation of O_2 into the primary products was also unequivocally confirmed via $^{18}O_2$ labelling studies.

Selective oxidation using gold-based nanoparticles

Graham's early work using AuPd alloys utilised catalysts made by impregnation. As part of the Auricat EU funded project he became interested in sol-immobilisation as a preparation method. Graham and his co-workers have made extensive use of sol-immobilisation methods for the synthesis of highly active bimetallic catalysts as it provides an effective way to control particle morphology, size and composition on the chosen support[128-130]. He showed that sol immobilized AuPd nanoparticles were active for the oxidation of aromatic hydrocarbons, such as toluene, with molecular oxygen, resulting in a high selectivity to benzyl benzoate (over 90%) under solvent-free conditions (Figure 7).[128] Counterpart Au–Pd/TiO_2 catalysts prepared by impregnation were also investigated, but they were not particularly active for toluene oxidation.[131] The corresponding AuPd catalysts prepared by sol-immobilisation on TiO_2, produced only benzyl alcohol, benzaldehyde, benzoic acid and benzyl benzoate. The monometallic Au catalyst was not active, but the addition of Pd increased conversion, and a clear synergistic effect was shown with the optimum catalyst formulation having a Au:Pd molar ratio of 1:2. To show general applicability, the selective oxidation of xylenes was studied, and the catalyst formed the aldehyde, acid, and esters, with the relative amounts being dependent on conversion. A key feature of this catalytic reaction is the high selectivity to benzyl benzoate and the absence of significant amounts of benzoic acid.

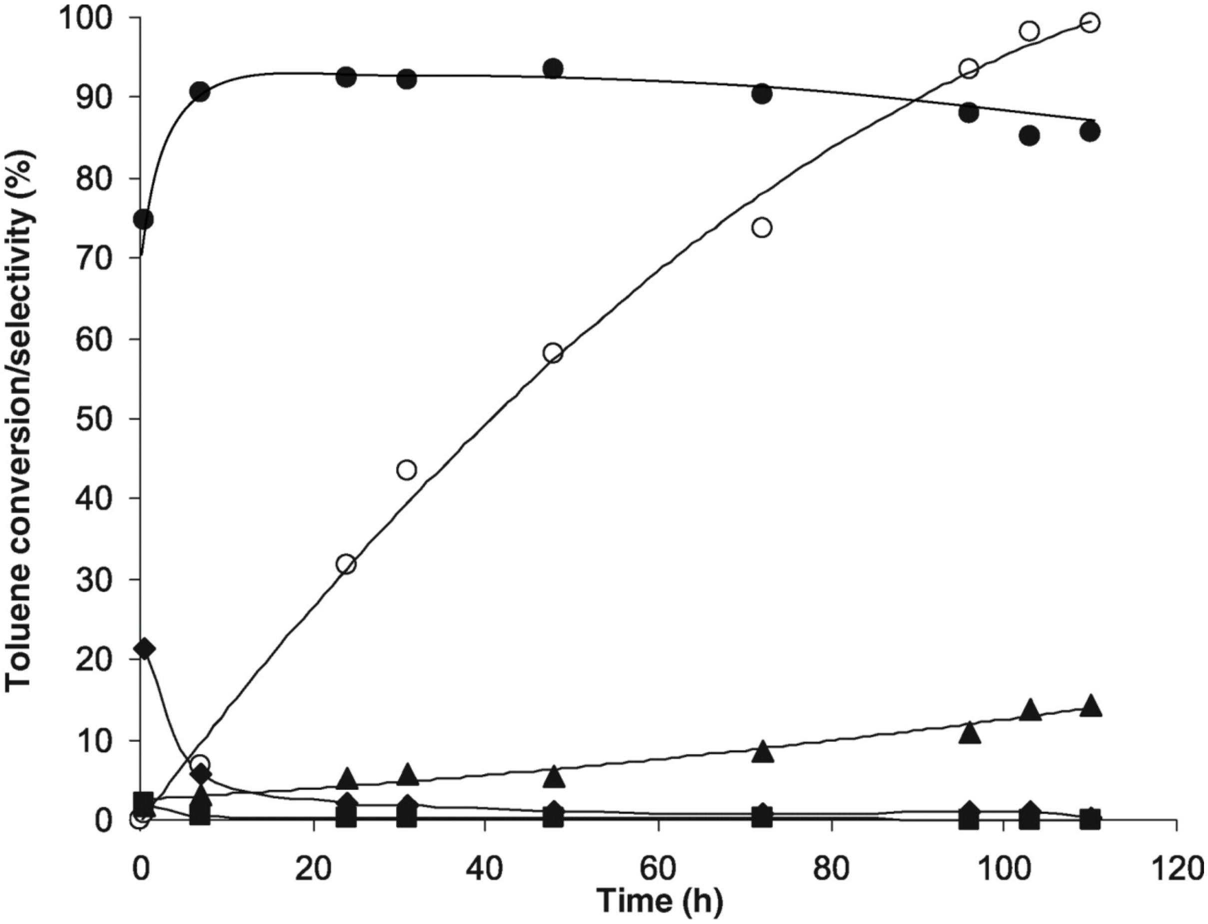

Figure 7. Toluene conversion and selectivity to benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate using 1wt. %\ AuPd/C prepared by sol immobilization with a 1:1.85 Au/Pd ratio. Open circles indicate conversion, squares indicate selectivity to benzyl alcohol, diamonds indicate selectivity to benzaldehyde, triangles indicate selectivity to benzoic acid, and solid circles indicate selectivity to benzyl benzoate.

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Characterisation studies by HAADF-STEM analysis confirmed that any sintering or structural modification of these highly active catalysts is minimal, and that the catalysts are stable and reusable. The effect of the support on activity was important, and carbon-supported catalysts gave improved performance when compared with titania.

Graham has also extensively investigated the oxidation of alcohols for the production of aldehydes and acids.[130] Specific focus was placed on the development of supported bimetallic nanoparticles with controlled morphology using a range of preparation methods. The effect of systematically changing parameters such as particle size, elemental composition, oxidation state of the metal and formation of random alloy or core-shell bimetallic nanoparticles was studied for the catalytic performance for model reactions.[132, 133]

The morphology of the bimetallic particles made by sol-immobilisation could be exquisitely controlled prior to the deposition of the pre-formed AuPd colloidal nanoparticles on the support (Figure 8).[132, 134]

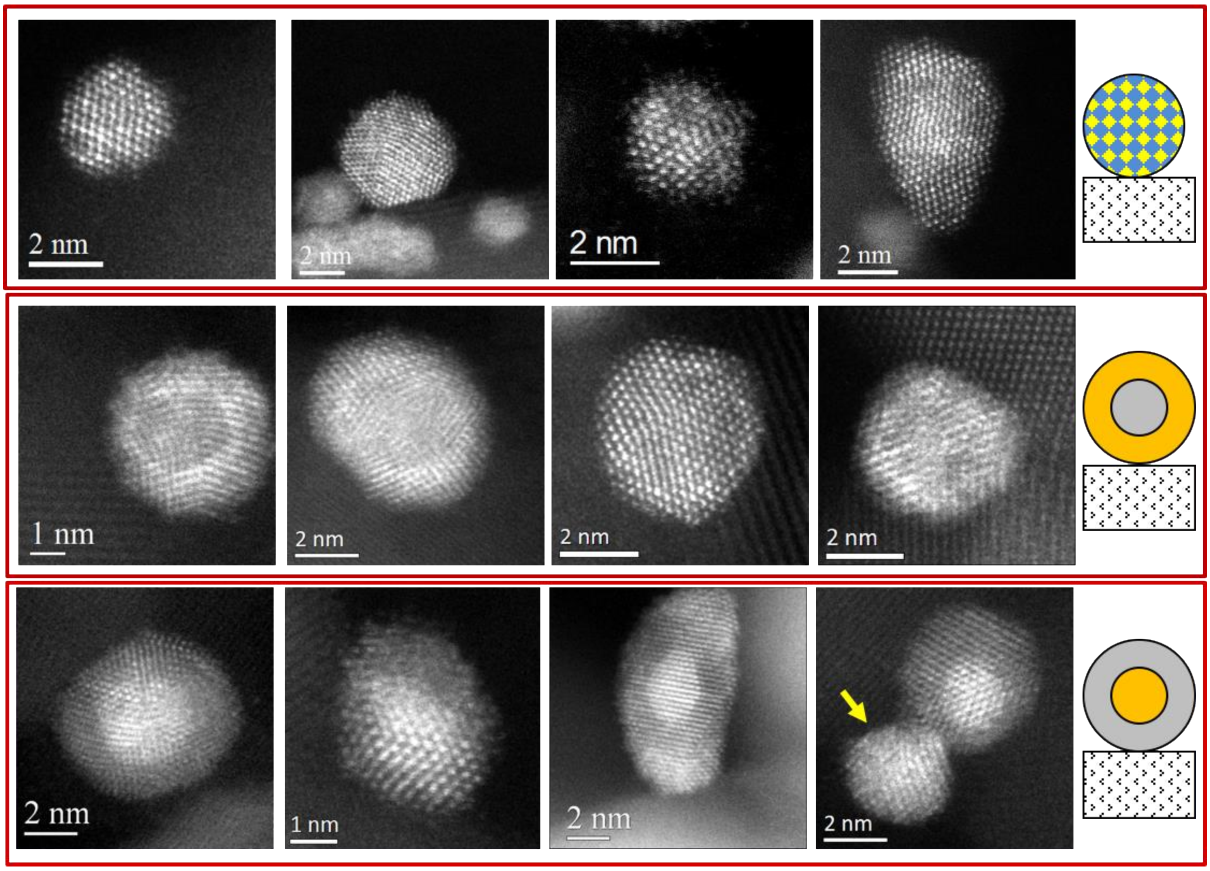

Figure 8. Representative STEM-HAADF images of individual sol-immobilized random AuPd alloy (top row) , Au shell-Pd core (middle row) and Pd shell-Au core (bottom row) nanoparticles on TiO_2 supports after drying at 120 °C for 16 h. The heavier metal (Au) shows much brighter mass contrast compared to the lighter (Pd) metal. Reproduced with Permission from Ref 132. Copyright 2011, Royal Society of Chemistry.

In addition to the support influence, the elemental composition of the AuPd particle and the effect of morphology (core–shell versus random alloy structure) was investigated by Graham's group, for a range of alcohol and polyol reactions. Specifically, for alcohol oxidation, the oxidation of benzyl alcohol was used as a model reaction, where it was demonstrated that the formation of small homogeneous random alloy particles (2-5 nm), in which the Au and Pd exhibited a metallic oxidation state led to highly active catalysts for the oxidation of benzyl alcohol under very mild conditions (100–120 °C). The higher activity of the supported Au–Pd catalysts synthesised by the sol-immobilization method in comparison to those made by the conventional impregnation method, was attributed to the following parameters: (i) a smaller mean particle size, (ii) a narrower particle size distribution, and (iii) a predominantly metallic oxidation state of the AuPd supported colloidal nanoparticles.[130, 132]

Moreover, the effect of the nature of support (carbon versus metal oxide materials) and heat treatment temperature was examined for the synthesised AuPd supported nanoparticles. The choice of support (*i.e.,* carbon versus titania) was crucial in terms of determining activity, with the AuPd nanoparticles supported on carbon showing a higher activity (by a factor of 2) and a lower selectivity to benzaldehyde at iso-conversion when compared to the corresponding AuPd nanoparticles supported on TiO_2[130, 135]

Detailed studies were also carried out to identify general aspects of the reaction mechanism and it was shown that the reaction was zero order with respect to molecular oxygen concentration over 1 bar of O_2. The oxidation of benzyl alcohol to benzaldehyde was dependent on the concentration of oxygen at pressures below 1 bar of O_2. Subsequent studies illuminated details of the mechanistic aspects of benzyl alcohol oxidation and especially the formation of unwanted by-products such as toluene.[4] Two major reaction pathways were identified as the sources of the main product, benzaldehyde. The first involved the direct catalytic oxidation of benzyl alcohol to benzaldehyde by O_2, while the second reaction pathway involved disproportionation of two molecules of benzyl alcohol to produce equimolar benzaldehyde and toluene.[130 136]

Therefore, the challenge was one of catalyst design and how to decrease and “switch-off” the production of the unwanted toluene as a by-product. Graham made two important advances to achieve this goal. Firstly, a basic support such as MgO was required[137]. Secondly, by substituting bimetallic AuPd with trimetallic AuPdPt nanoparticles[133] it was found that the disproportionation reaction could be completely ‘‘switched-off’’, thereby significantly improving the selectivity to benzaldehyde to over 90% at a conversion of 40%.

Environmental catalysis

Graham’s work has encompassed catalysis that is employed for environmental protection, particularly on the abatement of atmospheric pollutants. Examples include ambient temperature CO removal for respiratory protection using metal oxide catalysts[138-140] and metal-based catalysts,[141, 142]and control of other gaseous pollutants like carbonyl sulfide.[143, 144]

He has notably contributed to the subject of total oxidation, through the oxidative destruction of Volatile Organic Compounds (VOCs), which is an important process for pollution control and environmental protection. Based upon the ability of U_3O_8 to accommodate non-stoichiometric phases with high defect concentrations and facile redox behaviour of uranium cations, Graham hypothesised that this material could potentially be an effective total oxidation catalyst and this started an area of research that captured a lot of media attention. The hypothesis was proven to be correct and U_3O_8 prepared in an appropriate manner was highly active for the total oxidation of a wide range of chemically diverse VOCs [145]. Comparison of the activity with Co_3O_4, a well-known highly active total oxidation catalyst, demonstrated that U_3O_8 was more active for a range of VOCs, showing > 99% conversion, total CO_2 selectivity and long-term stable activity. Catalyst performance could be further enhanced by supporting U_3O_8 on high surface area silica, and low levels of a second component (*e.g.,* Cu or Co) increased activity even further. In particular, the U_3O_8-based catalysts were very active for the total oxidation of chlorinated VOCs. Mechanistic investigations using a Temporal Analysis of Products (TAP) approach, pulsing the VOC in the presence and absence of gas phase oxygen, confirmed that lattice oxygen from the U_3O_8 was the active oxidising species[146]. Further experiments using isotopically labelled gas phase oxygen showed that the catalyst operated by a Mars-Van Krevelen mechanism. Featured in the international press and media, the work raised many opinions and put the spotlight on uranium oxide as a catalyst, initiating many lively debates when presented at conferences.

Graham has also recently focused on catalysis for water treatment, addressing one of the major challenges we all face in securing future water supplies. By careful design, a AuPd catalyst suitable for this purpose has been prepared by modified impregnation, a synthesis method allowing for a homogeneous Au:Pd metal ratio independent of alloy particle size[147] . Careful tuning of the operating parameters meant that the AuPd/TiO_2 catalyst afforded a 100ppm yield of H_2O_2 in a flow reactor at ambient temperatures in a water-only solvent.[148] This is an H_2O_2 concentration that is capable of reducing a bacterial and viral load, forming the basis for a process of treating greywater and increasing recycling.

Concluding remarks

Those that have worked with Graham will know he is full of ideas and is very creative about thinking across areas of the discipline and more widely outside of the discipline (Figure 9). Undoubtedly Graham has contributed significantly to the fundamental understanding of heterogeneous catalysis, but for some time Graham has also been exploring ways in which his research could be translated and used to improve society's health and well-being. A notable example is how the reaction of H_2 and O_2 to form H_2O_2 could be used to remediate water in places of limited water supply or drought. In 2020/21 we are all aware that the world is in the grip of a global pandemic that is unprecedented in modern times. The rapid spread and devastation left in the wake of the SARS-CoV-2 virus led governments to call on and invest in research to combat this biological threat. Graham has collaborated with Selden, a company specialising in the development and production of cleaning and hygiene products for almost a decade. In a KTP funded joint project they have recently (2019) developed a new class of surface disinfectants activated using a simple copper based catalyst[149]. This new formulation allows facile surface decontamination, and work supported by funding from UKRI and Sêr Cymru is ongoing to evaluate the efficacy of the technology against the Sars-CoV-2 virus[150] This latest example is typical of Graham's approach throughout his career, demonstrating his great ability to see opportunities for catalysis, but at the same time to have the intellectual capacity and ideas for successful catalyst design.

Figure 9. Graham as he approached his 70th birthday writing with his favourite blue fountain pen, a gift from his wife Sally in 1994.

Acknowledgements

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