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A Career in Catalysis: Graham J. Hutchings

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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

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3 internationally, his work has influenced many in the discipline of heterogeneous
4 catalysis.
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7 8 9 10 11 12 **Introduction** 13

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16 Graham Hutchings has had a memorable career working on heterogeneous catalysis,
17 and we are sure he will continue to do so for years to come. Collectively the authors
18 have worked closely with Graham for a combined total of over 120 person years,
19 providing a lot of good times and fun, whilst undertaking some interesting science and
20 making some important discoveries and creating new fundamental understanding.
21
22 Graham has published more than 800 papers, and although it is not possible to cover
23 all of his work in this short article, we would like to present a more personal view of
24 our time, experience and achievements whilst working with Graham.
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39 Graham Hutchings made a rather unconventional entrance into the field of
40 heterogeneous catalysis. After completing his PhD in biological chemistry on *in vivo*
41 ATP synthesis at University College London, he was recruited by ICI to work on
42 biological chemistry projects. However, these projects were scrapped before he even
43 started the job, and he had to agree to switch to work on heterogeneous catalysis
44 projects if he wanted to remain with the company. He worked for ICI for 9 years, in
45 research, production and production support managerial positions in the UK, being
46 seconded to ICI South Africa in 1981, where he eventually became Chief Research
47 Officer.
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3 Graham then decided to end his industrial career and joined the academic staff in the
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5 Department of Chemistry at University of the Witwatersrand in 1984. There he quickly
6
7 established himself in the world of academia, where he has remained ever since.
8
9 Some of his early academic work focussed on Fischer-Tropsch chemistry¹⁻³ and at the
10
11 same time he was also very active in working on methanol conversion to hydrocarbons
12
13 using zeolites, with a particular emphasis on mechanistic studies. In a very short time
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15 span he and co-workers published a series of Chemical Communications around the
16
17 topic of methanol to hydrocarbons⁴⁻⁸, subsequently publishing many more in the
18
19 following years, earning him the admiring title of “*Chem Comm Hutchings*” from his
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21 growing research group and colleagues.
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28 One of the first projects Graham worked on when he joined ICI was the selective
29
30 oxidation of butane to maleic anhydride and the following year the first in a series of
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32 patents were filed on the synthesis of vanadium phosphate catalysts for this process,
33
34 with Raymond Higgins as co-inventor.⁹⁻¹³ These patents were Graham’s first
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36 publications, and he has carried on filing IP on his discoveries made in academia and
37
38 with many industrial collaborators throughout his career.
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43 In 1987 Graham left South Africa and joined the Leverhulme Centre for Innovative
44
45 Catalysis at Liverpool University (Figure 1). During his decade there, he graduated
46
47 many PhD students and wrote numerous papers and cemented his reputation as a
48
49 leading scientist in the field of heterogeneous catalysis. In 1997 he accepted the Chair
50
51 of Physical Chemistry at Cardiff University and from 1997-2006 Graham served as the
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53 Head of Chemistry at Cardiff University, and built up what is still the largest research
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55 group in the Department. In 2008 the Cardiff Catalysis Institute (CCI) was formed
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57 which Graham directed until 2019. Under his astute and inspiring leadership, the CCI
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3 developed a world-class reputation for catalysis research. Graham has received many
4 well-deserved honours over his career including most notably being elected a Fellow
5 of the Royal Society in 2009, being named Regius Professor of Chemistry at Cardiff
6 in 2016 as the inaugural Regius Chair in Wales and becoming a Commander of the
7 British Empire (CBE) in the 2018 Queen's Birthday Honours.
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54 **Figure 1.** Graham at the time he joined the University of Liverpool in 1987.

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57 The following sections highlight some of the areas in which Graham has worked.. The
58 coverage is by no means exhaustive as he has investigated so many topics, but the
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3 selection provides an insight to just some of the areas that have been important in his
4 career and ones where his work has made a significant impact. It is also well worth
5 highlighting his influence on the destiny of many people, over his long career he has
6 supervised many, helping to launch their careers in academia, industry and a wide
7 range of professions. His engaging approach, enthusiasm and creativity has been very
8 widely appreciated.
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16 17 18 19 20 21 22 **Gold catalysis**

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25 In the early 1980s while in AECL, Modderfontein, South Africa, Graham was
26 researching new Hg-based catalysts for the acetylene hydrochlorination reaction to
27 form vinyl chloride monomer (VCM). He was intrigued by Shinoda's¹⁴ attempt to
28 correlate the activity of dozens of metal/carbon supported VCM catalysts with the
29 metal cation electron affinity. Graham re-analysed the data taking into account the
30 metal standard electrode potential for the 2-electron process ($M^{2+} + 2e \rightarrow M$) and
31 produced a predictive model hypothesising that metals with high standard electrode
32 potentials would show greater catalytic activity for the VCM reaction (Figure 2)¹⁵. He
33 used this hypothesis to convince his management to let him construct a reactor to
34 successfully validate the prediction. In 1985 when he had moved to academia, he was
35 allowed to publish the prediction¹⁵ and immediately embarked on a more detailed study
36 of gold catalysts for this reaction. In 1988, he published more detailed experimental
37 work to validate this prediction (Figure 2b)^{16, 17}. Adsorption of $H AuCl_4$ in *aqua regia*
38 onto activated carbon resulted in a catalyst with superior VCM synthesis activity to the
39 standard industrial $HgCl_2/C$ catalyst. Given the toxicity and safety concerns of $HgCl_2$
40 and the scale of operation involved in VCM synthesis plants,
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Graham very quickly realised the huge positive environmental impact that substituting Au/C could have on this process.

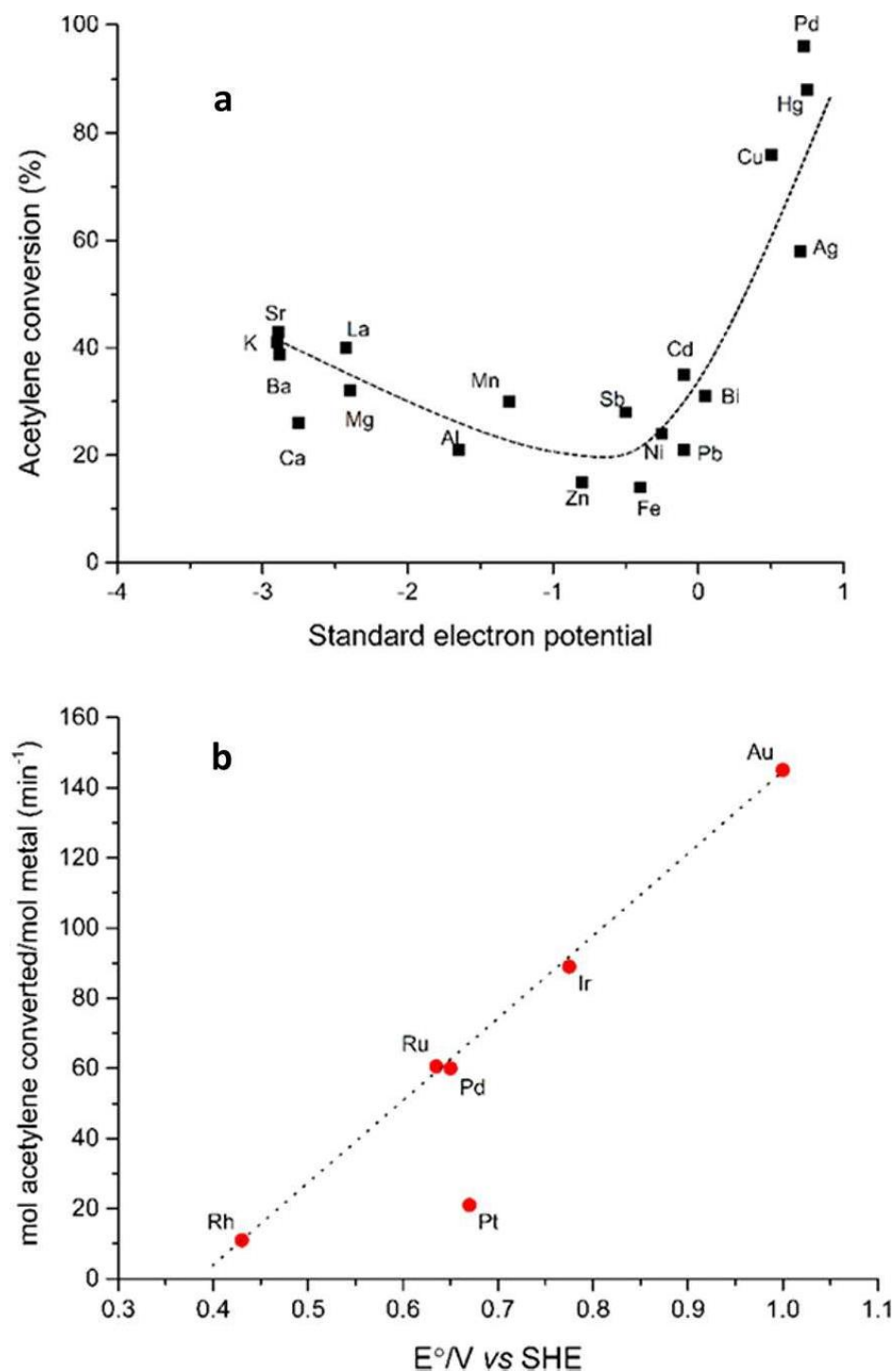


Figure 2 (a) Correlation of activity for acetylene hydrochlorination of carbon-supported metal chloride catalysts with the standard electrode potential. Reproduced with Permission

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3 from Ref 15. Copyright 1985, Elsevier. (b) Correlation of initial acetylene hydrochlorination
4 activity of supported metal chloride catalysts with the standard electrode potential of
5 metal chloride salts. Reproduced with Permission from Ref 18. Copyright 2017, Royal Society of
6 Chemistry.
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13 However, it was not until much later when China began to manufacture vinyl chloride
14 via acetylene hydrochlorination that the full potential of this new discovery of catalysis
15 by gold could be realised (as will be described later). These first papers sparked a
16 career long fascination with Au catalysis. His research, and that of his great friend
17 Professor Masatake Haruta, opened-up a field of heterogenous catalysts that had long
18 been under-explored due to the supposed chemical inertness of this 'uninteresting'
19 noble metal. To date, Graham has published over 400 articles showcasing the efficacy
20 of Au catalysts and their high activity for a number of selective oxidation reactions.
21 One of the key metrics for a successful catalyst is high product selectivity, which is
22 particularly challenging when the desired product is highly reactive and tends to react
23 quickly to form deeper oxidation products. The formation of epoxides from alkenes is
24 a good example of such a reaction and is usually achieved using hydrogen peroxide
25 or stoichiometric oxygen donors. Graham found that a high partial oxygenate
26 selectivity could be achieved when supported gold catalysts were employed for the
27 reaction at moderate reaction temperatures (60 °C) in the presence of air and a
28 catalytic amount of a radical initiator¹⁹. The oxidation of cyclohexene using 1,2,3,5-
29 tetramethylbenzene as a solvent afforded a 50% selectivity towards cyclohexene
30 oxide in the presence of a Au/C catalyst prepared by chemical reduction. When the
31 same optimised reaction conditions were investigated for styrene, *cis*-stilbene and *cis*-
32 cyclooctene, even greater selectivities towards the corresponding epoxide were
33 observed (80-98%), while retaining reasonable conversion levels (7-30%).
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56 Bulk gold is relatively unreactive and very resistant to oxidation and is often referred
57 to as the most noble metal, which presents a paradox to experimental Au catalysis
58 researchers. From the early days, the high activity of Au catalysts was thought to be
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4 a size effect as strikingly demonstrated by Professor Masatake Haruta's research in
5 Japan in the 1980s. Haruta found that Au/Fe₂O₃ catalysts prepared by co-precipitation
6 were exceptionally active for the aerobic oxidation of CO to CO₂ at sub-ambient
7 temperatures; oxidation with bulk gold powder required temperatures higher than 280
8 °C²⁰. Transmission electron microscopy measurements showed that the Au/Fe₂O₃
9 catalyst contained 2-4 nm sized gold nanoparticles supported on the Fe₂O₃ surface
10 that were somehow related to the active site.
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18 Subsequent advances in the imaging capability of electron microscopy via aberration
19 correction and high angle annular dark field (HAADF) STEM imaging allowed
20 Graham's team to develop an even deeper understanding of the active form of Au in
21 heterogenous catalysts. It is now known that the Au can potentially co-exist in several
22 different forms: namely FCC nanoparticles, sub-nm clusters, 2-D rafts and atomically
23 dispersed species depending on the exact preparation method used and the identity
24 of the support ^{20,21}. Co-precipitation or deposition precipitation methods on a support
25 such as Fe₂O₃ tends to produce a mixture of nanoparticles, sub-nm clusters and
26 atomically dispersed Au species. By careful correlation of the relative proportions of
27 each of these species present in Au/Fe₂O₃ catalysts, displaying different levels of
28 activity for the low temperature CO oxidation reaction, it was possible to deduce that
29 the sub-nm clusters were the most desirable species, closely followed by the Au
30 nanoparticles, whereas the atomically dispersed species were essentially inactive
31 (Figure 3) ²¹.
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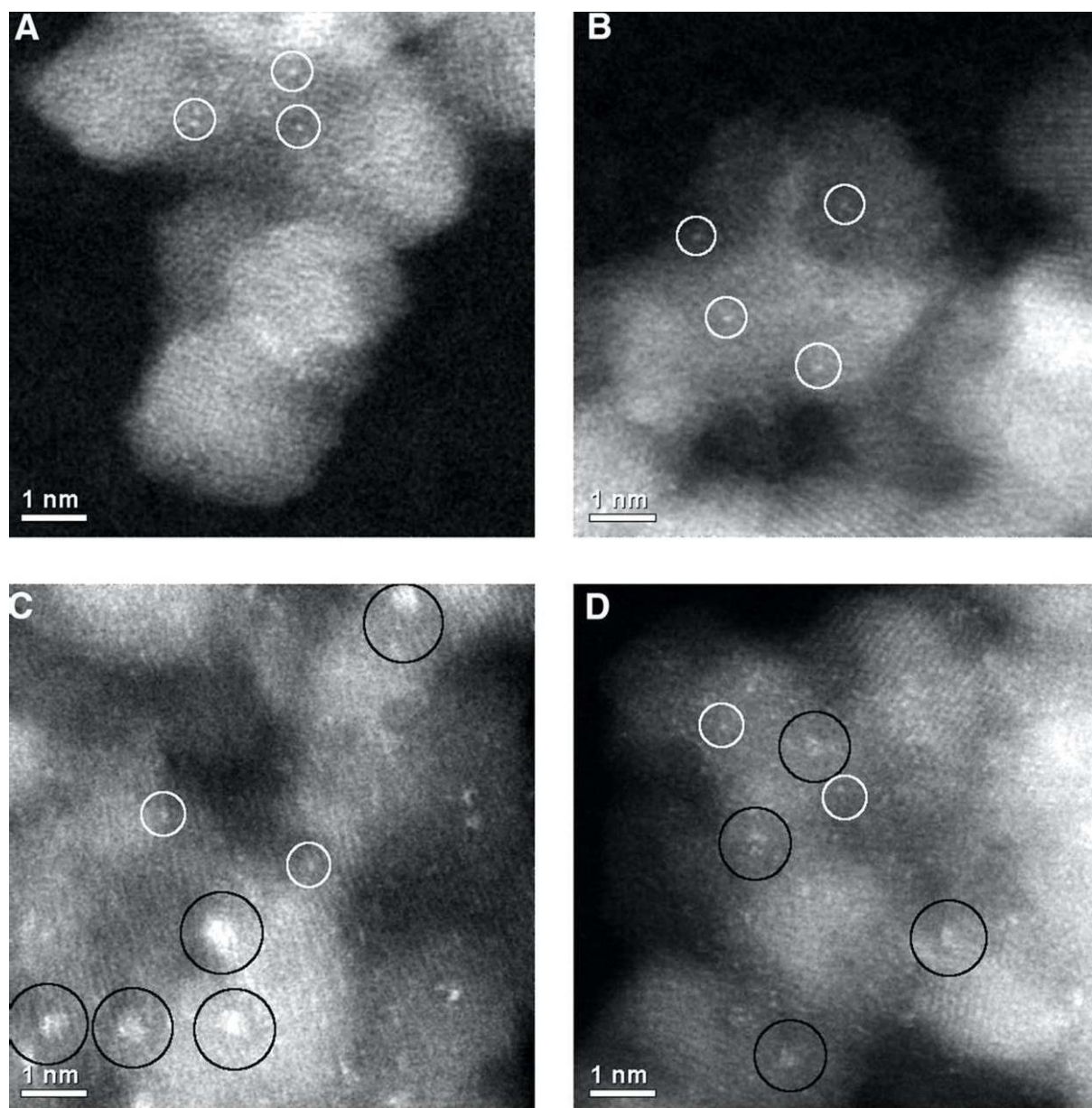


Figure 3. High-magnification aberration-corrected HAADF-STEM images of (A and B) the inactive (sample 1) and (C and D) the active (sample 2) Au/FeO_x catalysts acquired on the aberration-corrected JEOL 2200FS electron microscope. Note the presence of sub-nm bilayer structures present (circled in black) 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

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4 to maximise the amount of the desirable active Au component, and hence further
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6 optimise the catalytic performance.
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11 In contrast to the low temperature CO oxidation catalysts, the optimum Au morphology
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13 needed for acetylene hydrochlorination to form vinyl chloride monomer (VCM) is very
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15 different. The Hutchings group conclusively showed, using a combination of *in-situ*
16
17 EXAFS/XANES, aberration corrected electron microscopy and theoretical modelling,
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19 that a mixture of atomically dispersed cationic Au^I and Au^{III} species were the active
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21 components in the Au/C catalyst for the acetylene hydrochlorination reaction, while
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23 the nanoparticles and sub-nm clusters were essentially spectators.²² This study also
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25 confirmed his initial prediction that gold cations would be the most active catalysts.¹⁵
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27 This study was part of a long term collaboration with Peter Johnston at Johnson
28
29 Matthey. Peter was one of Graham's first PhD students at the University of
30
31 Witwatersrand and was involved with the initial work in South Africa. In 2007 Peter,
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33 now working for Johnson Matthey, approached Graham to work together to get an
34
35 improved Au catalyst for acetylene hydrochlorination. The initial work carried out in
36
37 South Africa and industry used catalysts containing 2% Au made using *aqua regia* as
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39 solvent. It was necessary to find a water-based route with very low levels of gold. This
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41 was successfully achieved and was followed by plant and full scale reactor trials.^{23, 24}
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43 The Johnson Matthey optimized Au/C catalyst (called Pricat MFC) is now being
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45 commercialized for VCM production in China as a replacement for the environmentally
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47 unfriendly HgCl₂ catalyst.²⁵ As a follow on to this, the Hutchings group have developed
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49 new improved and simple methods for synthesising atomically dispersed Au
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51 catalysts.²⁶ The discovery of a non-mercury catalyst has enabled the Minimata
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53 Convention to become international law, since the mercury-based VCM catalyst
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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.

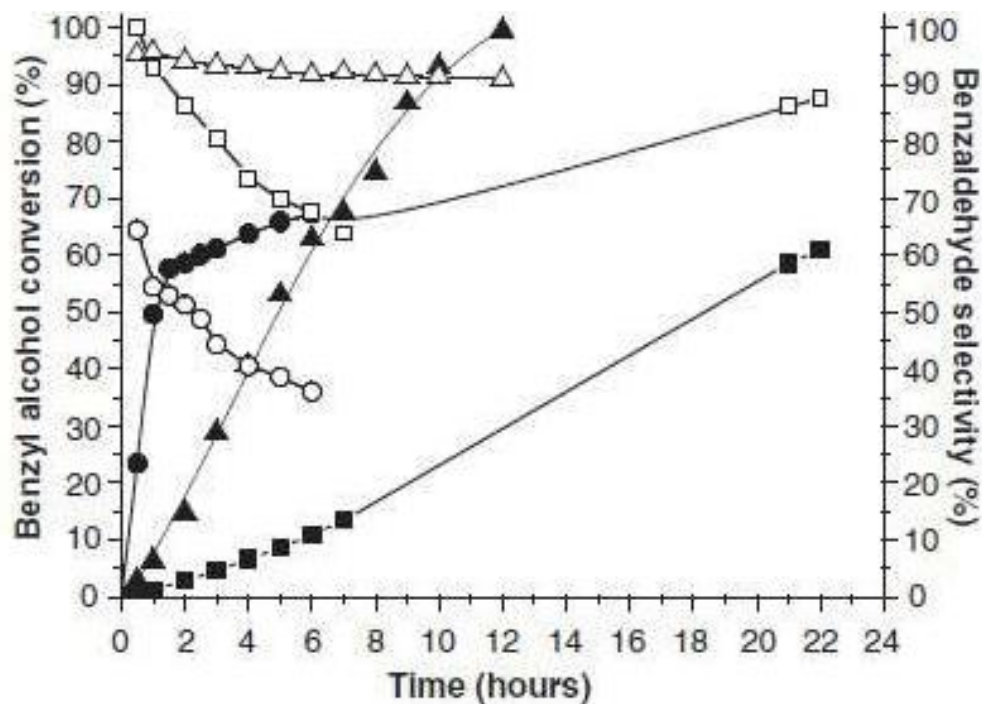


Figure 4 Benzyl alcohol conversion and selectivity to benzaldehyde as a function of reaction time (at 100 °C and 0.1 MPa) for Au/TiO₂ (squares), Pd/TiO₂ (circles), AuPd/TiO₂ (triangles) catalysts. Solid symbols indicate conversion, and open symbols indicate selectivity. Reproduced with Permission from Ref 28. Copyright 2006, American Association for the Advancement of Science.

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 TiO₂ with an aqueous solution containing HAuCl₄ and PdCl₂ with a total metal loading of 5 wt%. This method of preparation gave a very broad size

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3 distribution of nanoparticles ranging from 4 to 50 nm. Nevertheless, the nanoparticles
4 were all alloys, but with varying compositions²⁷. This particular catalyst formulation
5 proved to be very useful for catalyst discovery precisely because it contained such a
6 broad range of nanoparticle morphologies and compositions, and as such, it was an
7 ideal material to use as a starting point for catalyst design. This catalyst was found to
8 be very active for the direct synthesis of hydrogen peroxide (see later) and the
9 selective oxidation of benzyl alcohol (Figure 4).²⁸ The AuPd alloy was both active and
10 selective to benzaldehyde. Forming an alloy of AuPd typically gave catalysts that were
11 more active than their monometallic counterparts and this synergistic effect has been
12 a subject of intense research interest. This seminal work published in 2006 kick-started
13 many studies using AuPd alloys as redox catalysts and to this day remains a highly
14 active area of research in catalysis.

31 **Au-based catalysts for hydrogen peroxide synthesis**

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33
34 The supported AuPd alloy catalysts made by incipient wetness impregnation were
35 found to be very effective for the direct synthesis (DS) of hydrogen peroxide from
36 molecular hydrogen and oxygen. This reaction can provide a green alternative for
37 H₂O₂ production, especially for small scale local synthesis at the intended point-of-
38 use. Most H₂O₂ is manufactured *via* the commercial anthraquinone auto-oxidation
39 (AO) process, a mega-tonne process involving the sequential oxidation then reduction
40 of a substituted alkyl anthraquinone (AQ) over a Pd catalyst, producing H₂O₂ and
41 reforming the original anthraquinone. With complex distillations, high concentrations
42 of H₂O₂ (~70 wt%) are achieved and distributed globally, and subsequently in most
43 cases H₂O₂ then needs to be re-diluted to 1-8 wt.% for practical use. An ideal DS
44 process requires just H₂, O₂ and a solvent (with no acid or halide promoters, as
45 typically required with Pd catalysts²⁹), and if H₂O₂ concentrations in excess of 1wt%

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3 could be produced in flow and on-site as required, then energy costs associated with
4 the AO process such as H₂O₂ transportation and AQ replenishment could be greatly
5 reduced. This target has been a central aim for Graham's research in this area.
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10 In 1999 Graham was involved in a consortium funded by the Institute of Applied
11 Catalysis Foresight Challenge Research Programme. This collaboration between
12 industry and engineering partners was aimed at developing new, active commercial
13 catalysts for the DS process. Key metrics of a successful catalyst would be high H₂
14 selectivity (>90%), high catalyst productivity (>100 mol/kg_{cat}/h) and sufficient catalyst
15 longevity.
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25 The cohort's initial studies focussed on Au, AuPd and Pd nanoparticles supported on
26 ZnO prepared by co-precipitation and the materials were evaluated in a batch reactor
27 using supercritical CO₂ as the solvent³⁰. Very low levels of H₂O₂ were detected after
28 1h, and further tests indicated the relatively high reaction temperature of 35 °C was
29 responsible for facilitating the non-selective H₂O₂ decomposition reaction. Reducing
30 the temperature to 2 °C and using methanol as the solvent afforded higher H₂O₂ yields
31 for Al₂O₃ supported Au, Pd and AuPd catalysts, and indicated for the first time that
32 higher rates of H₂O₂ synthesis could be achieved when AuPd alloy catalysts were
33 used, compared to monometallic Au or Pd catalysts. The origins of this synergistic
34 effect were further investigated, and a wide range of Au, AuPd and Pd catalysts
35 supported on sulphonated carbon³¹, Al₂O₃³², Fe₂O₃³³ and TiO₂³⁴ were prepared by
36 simple wet impregnation, and in each study an increased yield or rate of H₂O₂
37 production was achieved when the catalysts comprising AuPd alloys were evaluated.
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55 In 2003, I (JKE) joined the group as a PhD student and, by what was essentially a flip
56 of a coin, joined the H₂O₂ team and thus began working on a research theme that is
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1
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3 still very much central to my research career today.. The target given for my PhD
4 research was to design a catalyst that could make hydrogen peroxide, but did not
5 decompose it. The calcination of a 2.5wt%Au-2.5wt%Pd/TiO₂ material at 400°C was
6 found to be a key step in synthesising a stable catalyst formulation. Catalysts calcined
7 below 400 °C were found to have very high activities in a single reaction cycle (>200
8 mol/kg_{cat}/h); however, this was not maintained when the catalyst was reused, and after
9
10 4 uses the activity of the catalyst dropped by 90% to only 20 mol/kg_{cat}/h³⁴. Atomic
11 absorption spectroscopy (AAS) performed on the used catalyst showed that 92% of
12 the Au and 95% of the Pd were being lost from a 2.5wt%Au-2.5wt%Pd/TiO₂ catalyst
13 dried at 25 °C, whereas none was lost from a catalyst calcined at 400 °C. In early
14
15 2000, advances in scanning transmission electron microscopy (STEM), coupled with
16
17 X-ray photoelectron spectroscopy (XPS) provided more insight into the nature of the
18
19 AuPd alloys, which were found to be below 10 nm in size³⁴. Comparative XPS analysis
20
21 of the 2.5wt%Au-2.5wt%Pd/TiO₂ catalyst calcined at 400 °C and dried at 25 °C showed
22
23 some striking differences, in that the dried sample exhibited both Au and Pd XPS
24
25 signals whereas the 400 °C calcined sample showed only the Pd XPS signal. Given
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27 that all the expected Au and Pd remained in the 400 °C sample after calcination, the
28
29 model of an Au-core/Pd-shell nanoparticle was postulated, where the photoelectrons
30
31 generated cannot escape from the Au core due to the presence of a Pd shell. STEM-
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33 XEDS mapping of the AuPd nanoparticles present in the 400 °C calcined sample
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35 showed this was indeed the case and elemental mapping clearly showed a PdO shell
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37 covering a Au-rich core (Figure 5). This model was presented at the World Congress
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39 in Oxidation Catalysis in Sapporo in 2005 and was the basis of some lively
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41 discussions.
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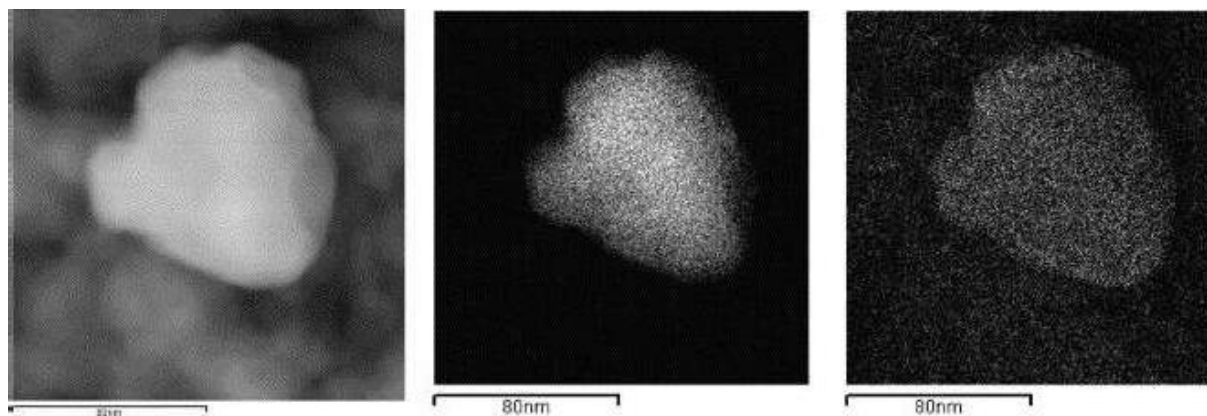


Figure 5 STEM-HAADF image of 2.5 wt.% Au–2.5 wt.% Pd/TiO₂ catalyst calcined at 400 °C, showing a large alloy particle (left), Au-M₂ STEM-XEDS map (centre), Pd-L1 STEM-XEDS map (right); note that the Pd signal appears to originate from a larger area than that of the Au signal. Reproduced with Permission 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 H₂O₂ synthesis recorded to date, with an H₂ selectivity > 95%³⁵. This was the first time such a high H₂ 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

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3 greater number of small (2-5 nm) Pd-rich (98%Pd-2%Au) particles, compared to the
4 non-acid-washed AuPd/G60 sample. These smaller particles have a surface capable
5 of synthesising H₂O₂ without over hydrogenation to water. The catalysis was validated
6 in the labs of industrial partners, and the catalyst preparation methodology was
7 eventually patented³⁶ and published.³⁵
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15 Graham has continued working in this area and set about designing catalysts that
16 could synthesis H₂O₂ without decomposing it. Realising that Pd was the active
17 component and that Au was acting as a modifier, several alternative less expensive
18 alloy components were considered. This led to a set of design principles identifying
19 PdSn alloys as being particularly interesting.³⁷
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26 27 28 29 30 **VPO catalysts for maleic anhydride production and catalyst preparation**

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34 While Graham was at the Leverhulme Centre for Innovative Catalysis in Liverpool
35 University, his interest in butane oxidation was re-kindled by an invitation to spend a
36 short sabbatical in Jean-Claude Volta's laboratories at the IRC, CNRS in Lyon in 1992.
37 This was a chance for Graham to return to the lab, and his first experiments were not
38 completely successful, resulting in a flask containing the reaction mixture breaking and
39 depositing hydrochloric acid into a hot isomantle creating quite a spectacular fire that
40 he immediately extinguished. However, despite this initial minor mishap, the visit
41 proved to be very productive, as it led to Graham's first peer reviewed publication on
42 vanadium phosphate catalysts appearing in Nature³⁸ in 1994, and more importantly,
43 sparking a 15-year collaboration with Jean-Claude based around their passion for
44 science and gastronomy in equal measures. As a PhD student, the group meetings in
45 Lyon were memorable experiences and I (JKB) fondly remember one particular event
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3 that was held in a mountain ski resort during the summer with particularly good
4 catering for breakfast, lunch and dinner.
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9 At the time there was considerable world-wide interest in butane oxidation partially
10 driven by the number of crystalline vanadium phosphate phases that had been
11 identified whose structure and catalytic properties have been well documented. Some
12 of the most widely studied are the V⁵⁺ vanadyl orthophosphates (α , α_1 , β , γ , δ and
13 ϵ -VOPO₄, and VOPO₄·2H₂O), the V⁴⁺ vanadyl hydrogen phosphates (VOHPO₄·4H₂O,
14 VOHPO₄·½H₂O, VO(H₂PO₄)₂), vanadyl pyrophosphate ((VO)₂P₂O₇)
15 and vanadyl metaphosphate (VO(PO₃)₂).
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27 Although a commercial process, the role and nature of the different phases identified
28 in the final catalyst was hotly debated in the scientific literature. The commercial
29 catalysts are derived from the *in-situ* activation of the hemihydrate precursor,
30 VOHPO₄·½H₂O, in *n*-butane/air. The presence of an oxidant and reductant in the feed
31 leads to a complex mixture of V⁴⁺ and V⁵⁺ phases, and some of Graham's early
32 collaborations in this field were aimed at developing characterisation techniques that
33 could be used to elucidate the nature of the active phase. This led to detailed
34 characterisation studies using *in-situ* Raman spectroscopy³⁸ and ³¹P NMR spin echo
35 mapping^{39, 40} with Jean-Claude Volta, detailed electron microscopy^{41, 42} studies of the
36 catalysts in collaboration with Chris Kiely, as well as XRD⁴³⁻⁴⁵ and XPS^{46, 47} studies in
37 collaboration with Robert Schlögl and co-workers at the Fritz Haber Institute of the
38 Max Planck Society in Berlin.
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55 The combination of these techniques identified the key role played by amorphous
56 vanadium phosphate phases in the final catalysts, although these were often
57 dismissed by other researchers. The interest in amorphous material was a result of an
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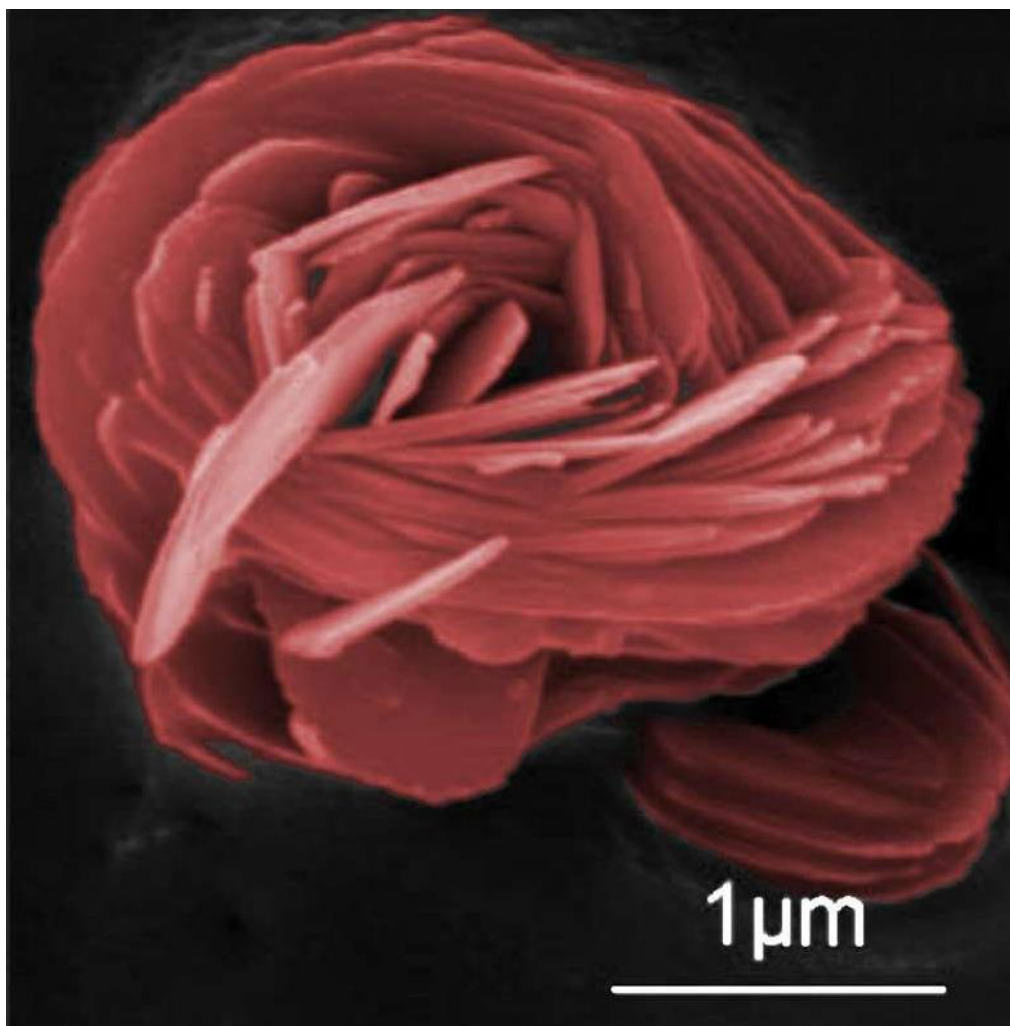
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3 *in-situ* Raman study into the transformation of $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ under reaction
4 conditions. They found that during the activation process, there is a structural
5 disordering at 370 °C, which corresponds to the appearance of maleic anhydride³⁸.
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7 The disordering was found to occur at a lower temperature (300 °C) when maleic
8 anhydride was added to the butane/air reaction mixture. The formation of the
9 disordered material was further studied using TEM in conjunction with XRD⁴⁸. This
10 demonstrated that $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ rapidly transformed into an amorphous material
11 under reaction conditions, before being further converted to a mixture of $(\text{VO})_2\text{P}_2\text{O}_7$
12 and δVOPO_4 . The δVOPO_4 phase was also shown to transform into $(\text{VO})_2\text{P}_2\text{O}_7$ with
13 time, clearly demonstrating the ability of the different phases to interconvert under the
14 reaction conditions and helping to explain why the commercial catalysts require a
15 considerable time (often >100 hours) before they are equilibrated.
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32 The other area that Graham made a significant contribution to in terms of vanadium
33 phosphate catalysis was in refining the synthesis methodology to improve
34 performance. Standard methods reacted vanadium(V) oxide with phosphoric acid in
35 the presence of a reducing agent to form $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and the activity of vanadium
36 phosphate catalysts was linearly dependent on the surface area⁴⁹. Hutchings, Volta
37 and Kiely identified that when precursors were synthesised *via* different methods, they
38 were found to have very different compositions. TEM studies indicated that the
39 common feature of these materials containing different phases was an amorphous
40 overlayer on the surface which could explain why the intrinsic activity of the different
41 catalysts was the same. This fitted with previous studies by Colston who identified a
42 phosphorus rich overlayer present on VPO catalyst surfaces by XPS.⁵⁰ The ³¹P NMR
43 studies added weight to the hypothesis that disordered materials were crucial
44 components of vanadium phosphate catalysts. Conventional NMR studies are
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3 hampered by the presence of paramagnetic vanadium ions in the catalysts. Spin echo
4 mapping uses the shift of the ^{31}P signals due to the paramagnetic ions, to gain
5 information about the oxidation state of the vanadium in the sample³⁹. The V^{3+} , V^{4+}
6 and V^{5+} ions are easily distinguishable using this technique, and the difference
7 between the spectra of V^{4+} compounds such as $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{VO}(\text{H}_2\text{PO}_4)_2$ and
8 $(\text{VO})_2\text{P}_2\text{O}_7$ enable easy identification. The VOPO_4 (V^{5+}) phases give spectra (with a
9 signal at 0 ppm), which are identical to the H_3PO_4 spectrum. Although polymorphs of
10 VOPO_4 phases can be distinguished using standard ^{31}P MAS NMR⁵¹, catalysts
11 prepared by different procedures were studied using this technique³⁹. The main
12 advantage of ^{31}P NMR spin echo mapping over other techniques, was found to be the
13 ability to detect low amounts of $(\text{VO})_2\text{P}_2\text{O}_7$, particularly in poorly crystalline materials,
14 and to distinguish between crystalline and disorganised $(\text{VO})_2\text{P}_2\text{O}_7$, to enable the
15 amount of amorphous material present in catalysts to be quantified.
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34 Graham investigated a number of different themes in the synthesis of vanadium
35 phosphate catalysts. These included studying the effect of dopants⁵²⁻⁵⁹, investigating
36 alternative precursor phases^{43, 60-62}, the role of the solvent⁶³⁻⁶⁶ and the use of structure
37 directing agents⁶⁷⁻⁷¹. However, one of the most significant contributions to the
38 synthesis was the discovery that new precursor morphologies could be accessed by
39 exploring new methodologies. This was first demonstrated exploring the reduction of
40 $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ using the two-step VPD route. The choice of alcohol was shown to be
41 crucial in determining the morphology of the $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ precursor.⁷² While
42 secondary alcohols were found to produce rhomboidal platelets, the use of primary
43 alcohols produced a very different morphology with only one major peak in the XRD
44 pattern and a high surface area, often described as a desert rose or rosette-type
45 structure (Figure 6)⁷³. In the same study, reduction with 3-octanol was found to
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3 produce an alternative precursor, $\text{VO}(\text{H}_2\text{PO}_4)_2$, which was a material I (JKB) became
4
5 well-acquainted with as the focus of my PhD research.
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43 **Figure 6.** SEM micrograph of the vanadium phosphate desert-rose morphology.
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50 Graham was also interested in exploring alternative methodologies for synthesising
51 catalysts. His early research in ICI had demonstrated that ball milling could have an
52 important influence on the catalyst performance, which he published 20 years after the
53 initial discovery⁷⁴, a research area he returned to periodically in academia^{75, 76}.
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59 Graham also investigated hydrothermal and solvothermal synthesis of vanadium
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3 phosphate catalysts^{59, 66, 77-79}. The most significant of these studies probed the
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5 reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with alcohols at elevated temperatures and pressures⁴³.
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7 Chemical reactions carried out under reflux conditions at atmospheric pressure provide
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9 access to a limited number of stable phases, typically $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in the absence of
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11 a reducing agent, $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ in the presence of a reducing agent with a
12
13 stoichiometric V:P ratio and $\text{VO}(\text{H}_2\text{PO}_4)_2$ in the presence of a reducing agent if there is
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15 an excess of the phosphorus source^{60, 61}. However, by exploring the solvothermal
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17 reaction at temperatures up to 400 °C and 150 bar in an autoclave, a number of new
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19 phases could be synthesised with interesting catalytic activity.^{43, 80} At low temperatures
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21 the $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was not reduced and the alcohol became intercalated between the
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23 vanadium phosphate layers replacing the water to give $\text{VOPO}_4 \cdot n\text{ROH}$. As the reaction
24
25 temperature was increased, reduction occurred to give $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at
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27 intermediate temperatures and pressures. However, as the temperature and pressure
28
29 were increased further, a new group of materials based on $\text{VPO}_4 \cdot \text{H}_2\text{O}$ polymorphs with
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31 varying stoichiometry were generated. As mentioned previously, vanadium phosphate
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33 activity is highly dependent on the surface area of the catalysts, but the surface area
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35 normalised activities are generally similar for vanadium phosphate catalysts, despite
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37 major differences in morphology or phases present⁴⁹. In this study, catalysts derived
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39 from the precursors synthesised under hydrothermal conditions were found to have
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41 higher intrinsic activity than those synthesised under ambient conditions,
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43 demonstrating the potential of this methodology to access more active catalysts.⁴³
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51 Another methodology that was pioneered for synthesising catalysts was supercritical
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53 antisolvent precipitation. Precursor solutions were pumped through a fine capillary
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55 contained within a co-axial nozzle into the precipitation vessel containing flowing CO_2 .
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3 The CO₂ was pumped through the outside of the co-axial nozzle and the temperature
4 and pressure controlled to maintain the vessel above the critical point of CO₂. As the
5 solution exits the nozzle the solvent diffuses into the CO₂, reducing the solvating power
6 and the solute is precipitated. One of the advantages of this technique is that it can
7 produce highly disordered materials during the precipitation process, with nucleation
8 occurring at a significantly faster rate than crystal growth. During my PhD, I (JKB) was
9 invited to visit Nottingham University by Steve Howdle and Martyn Poliakoff to
10 investigate this route for precipitating vanadium phosphates. The materials generated
11 using this methodology were proven to be amorphous by electron diffraction, but
12 displayed an intrinsic activity that was higher than conventionally prepared catalysts
13 and did not require a lengthy activation period to reach steady state.⁸¹ These findings
14 cast further doubt on the accepted wisdom that the crystalline phases in vanadium
15 phosphate catalysts were responsible for the activity and was the first clear and
16 definitive demonstration that a non-crystalline vanadium phosphate catalyst may be
17 the preferred material for the selective oxidation of butane to maleic anhydride. At the
18 time, this finding was controversial in the field, as I found out when Graham sent me
19 to give my first oral presentation at an international conference at the World Congress
20 on Oxidation Catalysis. During my presentation, a fairly lengthy queue of eminent
21 professors formed in front of the microphones in the aisles and during the questions
22 made it clear that they did not agree with our conclusions!⁸¹ However, we subsequently
23 showed using detailed *in-situ* studies that the surface of the catalyst can undergo rapid
24 transformations leading to metastable and disordered phases, demonstrating this
25 hypothesis was not as far-fetched as when first suggested.⁴⁵ The use of surface
26 sensitive characterisation techniques, such as low energy ion scattering (LEIS), have
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3 confirmed that surfaces are inherently different from bulk compositions, contributing to
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5 our hypothesis becoming accepted wisdom⁸².
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9 Realising that this methodology could provide a route to new catalyst compositions
10 and morphologies not readily available through other routes, we built our own
11 supercritical anti-solvent precipitation equipment and proceeded to investigate the
12 synthesis of other metal oxide catalysts using this methodology. It was demonstrated
13 that this new synthesis methodology could provide single oxides with improved
14 properties as catalysts⁸³⁻⁸⁶ and supports⁸⁷⁻⁸⁹, but the most interesting applications
15 involved mixed metal oxide catalysts⁹⁰⁻⁹⁸.
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26 Early studies were carried out on hopcalite, a mixed metal oxide of copper and
27 manganese, that is a catalyst that has been used for several different applications,
28 most notably in low temperature CO oxidation. Early studies showed that copper and
29 manganese acetates could be used to precipitate high surface area catalyst
30 precursors. Upon activation the catalysts were found to have a high intrinsic activity
31 which could be attributed to the homogeneous mixing of the components leading to
32 disordered CuMn_2O_4 catalysts, without producing any of the single component metal
33 oxide phases.⁹² However, the final catalysts were found to have a low surface area
34 due to the exothermic calcination of the acetates causing sintering. This led to a
35 modification of the precipitation process with the addition of water to the metal acetate
36 solution – a counter-intuitive step as water is considered insoluble in supercritical CO_2 .
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38 However, having water in the process enabled metal carbonates to be precipitated
39 which did not sinter upon calcination. This modification allowed hopcalite catalysts with
40 surface areas of up to $175 \text{ m}^2\text{g}^{-1}$ to be produced.⁹³ This improvement was attributed
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3 to the water reacting with CO₂ *in-situ* to produce carbonic acid, that could subsequently
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5 react with the precipitated acetates during an aging step.
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9 The antisolvent precipitation methodology was also applied to Cu/ZnO catalysts for
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11 methanol synthesis and the reverse water gas shift reaction.^{94, 95, 97, 99, 100} These are
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13 widely studied catalysts that are produced by co-precipitation. A number of hydroxy
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15 carbonate phases have been identified, but generally the best catalysts are derived
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17 from zincian malachite precursors. Georgeite is the least studied of the
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19 hydroxycarbonate phases as it is unstable, readily decomposing to malachite, and it
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21 is amorphous - being one of the few minerals to be classified from its infrared spectrum
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23 rather than X-ray diffraction data. Supercritical antisolvent precipitation was found to
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25 produce a stable zincian georgeite material, demonstrating again, the ability of this
26
27 synthesis technique to access materials and phases that cannot be readily produced
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29 by other methods. The Cu/ZnO catalysts derived from this precursor were found to be
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31 highly active methanol synthesis catalysts, as well as water gas shift catalysts that
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33 were resistant to deactivation.⁹⁷
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43 **Short chain alkane activation**

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47 Early in his career Graham developed a keen interest in alkane activation and
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49 conversion, especially around methane selective oxidation, and this has been a theme
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51 that has run throughout his research career. In the mid-1980s the process of oxidative
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53 methane coupling received a lot of research attention, as an alternative direct process
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55 for upgrading methane from natural gas reserves, and Graham contributed
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57 significantly to this topic ¹⁰¹.
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3 Ito and Lunsford showed that MgO was an effective catalyst for methane coupling¹⁰²,
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5 which sparked an avalanche of studies where a wide range of oxides were all
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7 compared to the best catalyst. It was not until three years later, that it was found that
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9 the role of the MgO catalyst was actually to produce gas phase methyl radicals.
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11 Graham was the first to publish this result (by a few days), as several groups had
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13 independently reached a similar conclusion.¹⁰³ This finding was initially considered
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15 extremely controversial, but was later accepted as being correct by the general
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20 community.

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23 Graham became deeply interested in the Lunsford MgO catalyst and a wider analysis
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25 of the corresponding literature revealed, that although all catalysts were described as
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27 MgO and had identical XRD patterns, they exhibited vastly varying catalytic
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29 performance¹⁰¹. MgO has a cubic structure, with exposed facets indexed as (100),
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31 (010) and (001)-type, and Graham and co-workers showed that activity differences
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33 were due to variations of morphology and related to the preparation procedure^{104, 105}.
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35 MgO catalysts were prepared by three different procedures, thermal decomposition of
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37 the hydroxide, burning Mg ribbon in air and thermal decomposition of the basic
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39 carbonate ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$). Transmission electron microscopy showed the
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41 ribbon residue MgO had a cubic morphology with a broad size distribution of
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43 crystallites (100-200 nm) with (100)-type surface termination planes. MgO from the
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45 hydroxide showed a similar cubic morphology and surface termination, but with much
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47 smaller crystallites in the size range 20-40 nm. The ex-basic carbonate MgO did not
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49 have the same cubic morphology. Instead it was much less regular and the surface
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51 was highly faceted, consisting of both pseudo-(111) and (110) facets, and it also had
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53 small particles (20–40 nm). By studying the effect of calcination temperature, it was
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55 possible to correlate the morphologies to the differences in catalyst activity and these
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3 studies helped to explain how different samples of MgO gave rise to different catalytic
4 performances for methane oxidative coupling.
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9 The formation of ethane and ethylene from oxidative methane coupling are important
10 products, but there is also a desire to produce oxygenates, like methanol and
11 formaldehyde directly from methane selective oxidation. Again, by using an MgO
12 catalyst it was shown that the product distribution could be switched from coupling
13 products to formaldehyde by modification of the reaction conditions ¹⁰⁶. On reducing
14 the catalyst contact time there was a dramatic switch from ethane and ethylene to
15 formaldehyde as the major product. This switch was rationalised by considering the
16 relative concentrations of methyl radicals and molecular oxygen in the gas phase. At
17 higher contact times the concentration of methyl radicals was relatively high, favouring
18 coupling to C₂ products. In contrast, at low contact times the methyl radical
19 concentration was lower and reaction with molecular oxygen is preferred, forming a
20 methyl peroxy species, a precursor to selective oxidation to formaldehyde. This study
21 helped to provide further mechanistic insight and reinforced the dominating role of gas
22 phase radical chemistry in high temperature gas phase catalytic methane selective
23 oxidation.
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44 Further studies targeted methane partial oxidation to oxygenates, and in particular a
45 pioneering design approach ^{107, 108}. Graham and his team hypothesised that simple
46 metal oxide components that activated methane and oxygen, but which did not over
47 oxidise methanol ¹⁰⁹, could be combined synergistically to produce an effective dual
48 component catalyst. Combining Ga₂O₃ and MoO₃ by physical mixing demonstrated
49 the validity of the design approach, producing significant activity for the direct partial
50 oxidation of methane to formaldehyde. Although progress and some understanding
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3 were achieved using metal oxide catalysts at high temperatures in the gas phase, it
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5 was clear that limits on oxygenate selectivity were constraining the yields in a direct
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7 conversion approach and that an alternative catalytic approach was required, which
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9 he later rigorously pursued.
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13 In 2008 Graham was successful as one of the winners of the Dow Methane Challenge,
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15 opening-up a new low temperature approach for methane selective oxidation in the
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17 liquid phase, resulting in a significant body of work. His idea was to use radical species
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19 in the liquid phase, initially derived from hydrogen peroxide, but eventually extended
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21 this to *in-situ* generation of activating species through co-feeding of molecular
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23 hydrogen and oxygen. He hypothesised that use of aqueous peroxide species would
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25 be an activated oxidant and hydrolyse intermediate species, closing the catalytic cycle
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27 that was not achieved in other low temperature approaches. Two distinctly different
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29 types of catalysts were successfully identified; namely those based on Fe-ZSM-5 and
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31 those using supported AuPd nanoparticles. A large team of PhD students and
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33 postdocs worked on this particular project, liaising closely with industry.
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40 The initial discovery was that commercial ZSM-5 was effective for the selective
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42 oxidation of methane to oxygenates at low temperatures in the aqueous phase with
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44 hydrogen peroxide¹¹⁰. Initially it appeared that the activity was dependent on the Si/Al
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46 ratio and the catalyst pre-treatment temperature, with 500°C being the best. Closer
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48 investigation using silicalite, and careful modification of the Al content by hydrothermal
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50 synthesis and post-treatment methods, identified that the Al content was not the critical
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52 parameter controlling activity. Elemental analysis of the active ZSM-5 zeolite showed
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54 low levels of Ti and Fe impurities. Subsequent studies using TS-1 under the same
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56 reaction conditions showed it was inactive, whilst introducing Fe into inactive silicalite
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3 by hydrothermal synthesis generated activity for selective methane oxidation. There
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5 was a linear relationship between the amount of Fe introduced and activity, confirming
6
7 the key role played by the Fe species. The increase of activity with heat treatment
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9 correlated with an increase of extra-framework Fe, as it migrated from tetrahedral
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11 framework sites to octahedral extra-framework sites. A combination of EXAFS and
12
13 DFT modelling studies allowed identification of the resting state of the active site as a
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15 di-iron complex $[\text{Fe}_2(\mu_2\text{-OH})_2(\text{OH})_2(\text{H}_2\text{O})_2]^{2+}$, containing antiferromagnetically coupled
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17 high-spin octahedral Fe^{3+} centres. EPR studies established that hydroxyl radicals
18
19 were responsible for over-oxidation of the desired methanol product and limiting such
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21 radical chemistry should allow high methanol yields. The addition of Cu^{2+} had an
22
23 important role, incorporating it to the Fe-ZSM-5, or as a heterogeneous or
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25 homogeneous additive to the reaction media, significantly increased methanol
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27 selectivity. Cu largely switched-off methanol over-oxidation, as hydroxyl radicals were
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29 no longer detected, whilst it had no effect on conversion. A methanol selectivity of 93%
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31 at 10% methane conversion was achieved, giving TOFs considerably greater than
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33 other reported catalysts.
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41 More detailed studies of the basic reaction mechanism and the reaction network
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43 focused on the most active 0.014 wt.% Fe-ZSM-5 catalyst, identifying that it exhibited
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45 the most efficient use of H_2O_2 , had no induction period and gave a very high initial
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47 TOF of $14,200 \text{ h}^{-1}$ ¹¹¹. Methyl hydroperoxide was confirmed as the primary product,
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49 whilst it was possible that some formic acid was also present at very low levels. Methyl
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51 hydroperoxide was subsequently oxidised to methanol and then to formic acid, and in
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53 stark contrast to gas phase oxidation, no formaldehyde was produced. Comparison of
54
55 the mechanism of Fe-ZSM-5 with homogeneous Fenton's reagent using radical
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57 scavengers clarified that the reaction mechanisms were different. Experimental
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3 observations supported the hypothesis that the heterogeneously catalysed Fe-ZSM-5
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5 reaction does not rely on homolytic cleavage of the H_2O_2 , and a subsequent free-
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7 radical chain mechanism involving highly reactive methyl, hydroxyl and hydroperoxyl
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9 radicals. Methane selective oxidation was at least heterogeneously initiated, with
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11 removal of the catalyst totally switching-off the reaction. Extended work elucidated
12
13 how the Fe active sites evolved¹¹² and established that isomorphous substitution of
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15 the trivalent cations Al^{3+} and Ga^{3+} into the ZSM-5 catalyst promoted the activity of the
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17 Fe-based catalyst¹¹³. The extra-framework Fe sites remained the catalytically active
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19 sites, but promotion occurred through facilitating the extraction of Fe from the
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21 framework, increasing the concentration of the active sites. Secondly, isomorphous
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23 substitution provided a negatively charged framework facilitating dispersion and
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25 stabilisation of the cationic active sites. This understanding led to further rational
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27 improvements of the catalyst performance.
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34 The direct selective oxidation of other short chain hydrocarbons also posed a
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36 challenge, and Graham's work identified that the Cu-Fe-ZSM-5 catalyst was also
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38 highly active and selective for ethane oxidation by aqueous hydrogen peroxide¹¹⁴.
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40 Ethane conversions of 56% with 70% selectivity to acetic acid was achieved, with a
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42 combined oxygenate selectivity > 95%. The reaction network was complex, forming a
43
44 broad range of C_2 oxygenated products, and some C-C bond scission was noted
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46 resulting in C_1 products. Ethene was also produced, which after undergoing further
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48 oxidation, gave ethanol as a primary product from ethane. In contrast to the
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50 mechanism proposed for methane oxidation over the same catalyst, ethane oxidation
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52 proceeded by carbon-based radicals, as opposed to oxygen-based radicals,
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54 explaining the higher conversion and more complex reaction network.
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3 A flow reactor was employed to demonstrate the efficacy of the Cu-Fe-ZSM-5 catalyst
4 for ethane selective oxidation¹¹⁵. Control over the catalyst contact time allowed a
5 significant reduction of C-C scission and formation of over-oxidation products.
6
7 Optimising the performance of the catalyst by modifying Fe and Cu content was
8 explored, as was investigating the influence of temperature, pressure and reactant
9 concentrations. In particular, varying pressure had a beneficial role, allowing us to
10 achieve 98% C₂ oxygenate selectivity, and high per-pass yields of acetic acid. Very
11 low levels of Fe leaching were observed, but there was no catalyst deactivation on
12 prolonged use, with conversion and selectivities remaining unaltered. Following this
13 demonstration with ethane, the same flow approach was also successfully employed
14 for continuous selective methane oxidation using Cu-Fe-ZSM-5, and a high
15 continuous selectivity towards methanol was achieved¹¹⁶.
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32 Indeed, the Cu-Fe-ZSM-5 catalyst with hydrogen peroxide in an aqueous solvent
33 proved to be a very effective selective oxidation system for a range of short chain
34 alkanes. Fe-ZSM-5 has also been applied for propane oxidation¹¹⁷. High oxygenate
35 yields were obtained, with the previously identified extra-framework active site being
36 responsible, showing that a relatively high proportion of Fe deposited on the zeolite
37 framework was an inactive spectator species and could be removed without
38 significantly reducing activity. The precise role of Cu in increasing oxygenate
39 selectivity is still under debate, however it is empirically clear that it is very effective
40 for limiting over-oxidation of partial oxidation products from methane, ethane and
41 propane¹¹⁸.
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56 The same low temperature aqueous hydrogen peroxide selective oxidation approach
57 was also pioneered by Graham using AuPd bimetallic nanoparticles supported on
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3 titania¹¹⁹. Initially the AuPd/TiO₂ catalysts were prepared using sol-immobilisation, but
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5 the metallic state and small nanoparticles showed high rates of hydrogen peroxide
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7 decomposition and the catalysts were not suitable. Instead, a catalyst prepared by
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9 incipient wetness impregnation was used, as previously this synthesis method was
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11 shown to be good for making highly effective catalysts for alcohol selective oxidation
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13 and direct hydrogen peroxide synthesis: both these reactions are linked by the
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15 involvement of hydroperoxy intermediates. When aqueous hydrogen peroxide was
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17 employed as the oxidant, appreciable yields of methanol were obtained under mild
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19 conditions, and analogously to the Fe-ZSM-5 catalyst, the primary reaction product
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21 was methyl hydroperoxide. The methyl hydroperoxide was sequentially oxidised to
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23 methanol, but unlike the situation for Fe-ZSM-5, no formic acid was produced,
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25 indicating that methanol was surprisingly stable over the AuPd/TiO₂ catalyst. Further
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27 studies of methanol oxidation demonstrated that around 29% of the CH₄ was
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29 converted, whilst oxidation of formaldehyde and formic acid to CO₂ were facile. The
30
31 AuPd nanoparticles were key in the oxidation of methane and methyl hydroperoxide
32
33 to methanol, whilst the TiO₂ support alone did not form any methanol. *In-situ* EPR
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35 studies identified that both methyl and hydroxyl radicals were produced during the
36
37 reaction, and the presence of the carbon-based radical was in clear contrast to the Fe-
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39 ZSM-5 catalyst for methane oxidation. It was further hypothesised that methyl radicals
40
41 can react with surface bound hydro-peroxy radical species, formed directly from
42
43 hydrogen peroxide decomposition, to generate the primary methyl-hydroperoxide
44
45 product. Consequently, Graham proposed that the surface hydroperoxy species could
46
47 be formed *in-situ* by feeding H₂ and O₂ instead of using pre-formed hydrogen peroxide.
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49 This hypothesis was supported by experimental evidence that showed co-feeding H₂
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51 and O₂ increased methanol selectivity and increased the activity three-fold.
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3 A more systematic study of the reaction conditions and catalyst parameters showed
4 that selective methane oxidation was possible using the AuPd/TiO₂ catalyst at 2 °C¹²⁰.
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6 Increasing the pressure of methane and hydrogen peroxide concentration increased
7 the productivity of oxygenates, and the reaction was first order with respect to
8 hydrogen peroxide. The combination of Au and Pd were required to optimise activity,
9 methanol selectivity and reduce excessive hydrogen peroxide decomposition, with a
10 1:1 molar ratio being the best. It was concluded that a core-shell nanostructure, with
11 a Au-core and a Pd-rich shell, was optimum for methane selective oxidation to
12 methanol. The addition of Cu species was found to be important for increasing
13 oxygenate selectivity with Fe-ZSM-5 catalysts¹¹⁰, so a similar approach was explored
14 with AuPd/TiO₂¹²¹. When compared to the bimetallic catalyst, the addition of Cu
15 increased productivity by a factor of five, with an associated increase of methanol
16 selectivity up to 83%. The Au and Pd remained present as core-shell nanoparticles,
17 whilst Cu was dispersed as 5 nm nanoparticles that were either Cu or Cu₂O. It is
18 interesting to note that Cu has the effect of increasing oxygenate selectivity for both
19 Fe-ZSM-5 and AuPd/TiO₂ catalysts, although they operate primarily through quite
20 different mechanisms.
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43 The development and refinement of synthesis methods for preparing bimetallic
44 supported nanoparticles with controlled morphological properties (e.g., particle size
45 and shape, oxidation state of metals and metal support interaction) and their
46 exploitation as potential catalysts for the transformation of organic compounds to
47 useful fine chemicals and fuels has been a major area of activity for Graham's research
48 group.^{122, 123} For the AuPd system, it should be noted that (i) Au and Pd can form a
49 continuous solid solution over the whole range of composition and (ii) the addition of
50 the second metal can alter the electronic and geometrical properties of the
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3 synthesized particles, positively affecting catalytic activity, catalyst stability and the
4 distribution of reaction products.
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8 Using colloidal methods for the preparation of highly active AuPd catalysts, Graham
9 demonstrated that the oxidation of methane to methanol was possible in the presence
10 of H₂O₂ as an initiator and molecular oxygen as the main oxidant under mild reaction
11 conditions¹²⁴⁻¹²⁶. The correct choice of stabiliser ligand for the colloidal AuPd
12 nanoparticle was found to be crucial for this reaction¹²⁴. By using polyvinylpyrrolidone
13 (PVP) instead of using the more commonly used polyvinylalcohol (PVA) stabiliser, it
14 was shown that unsupported AuPd-PVP colloidal nanoparticles could efficiently
15 transform methane to methanol with a selectivity of 90-92% while using a low amount
16 of H₂O₂ (50 μmol) in the presence of molecular oxygen at 50 °C. Moreover, for the
17 corresponding sol-immobilised 1 wt.% AuPd/TiO₂ material, the activity and selectivity
18 to methanol was low (26%). One of the major deductions of this work was that if the
19 AuPd colloidal nanoparticles were supported on TiO₂, the catalyst exhibited a much
20 higher rate of H₂O₂ degradation, suggesting that either the interfacial sites at the
21 support/metal interface or a change in the morphology of the colloidal nanoparticles
22 during the immobilisation step, led to the increase in H₂O₂ degradation. EPR spin-
23 trapping studies revealed the presence of both ·OH and ·CH₃ radicals during reactions
24 with a sol-immobilized AuPd catalyst, implying that the mechanism is radical-based.
25 The observation that the primary product was CH₃OOH implied that the primary
26 termination step is either between ·CH₃ and ·OOH radicals or from recombination of
27 ·CH₃ with dissolved O₂ in the solution, originating from the decomposition of H₂O₂. For
28 the unsupported colloidal catalyst which decomposes H₂O₂ at a much slower rate and
29 makes substantially more product, it was rationalized that ·CH₃ was being produced
30 over a longer time scale and by adding O₂ to the reaction mixture this would promote
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3 oxygen incorporation through the generation of $\text{CH}_3\text{OO}^\bullet$ radicals. The reaction of $^\bullet\text{CH}_3$
4 with O_2 has been reported to occur at high rates in gas-phase reactions¹²⁷, therefore
5 there was an indication that this could also be happening at low temperature with the
6 utilisation of H_2O_2 and O_2 as oxidants. The reaction mechanism was also investigated
7 by using isotopically labelled $^{13}\text{CH}_4$ which confirmed that the carbon source for the
8 product was CH_4 and not the PVP stabilizer ligand on the colloid. The incorporation of
9 O_2 into the primary products was also unequivocally confirmed via $^{18}\text{O}_2$ labelling
10 studies.
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26 **Selective oxidation using gold-based nanoparticles**

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29 Graham's early work using AuPd alloys utilised catalysts made by impregnation. As
30 part of the Auricat EU funded project he became interested in sol-immobilisation as a
31 preparation method. Graham and his co-workers have made extensive use of sol-
32 immobilisation methods for the synthesis of highly active bimetallic catalysts as it
33 provides an effective way to control particle morphology, size and composition on the
34 chosen support¹²⁸⁻¹³⁰. He showed that sol immobilized AuPd nanoparticles were active
35 for the oxidation of aromatic hydrocarbons, such as toluene, with molecular oxygen,
36 resulting in a high selectivity to benzyl benzoate (over 90%) under solvent-free
37 conditions (Figure 7).¹²⁸ Counterpart Au–Pd/ TiO_2 catalysts prepared by impregnation
38 were also investigated, but they were not particularly active for toluene oxidation.¹³¹
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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.

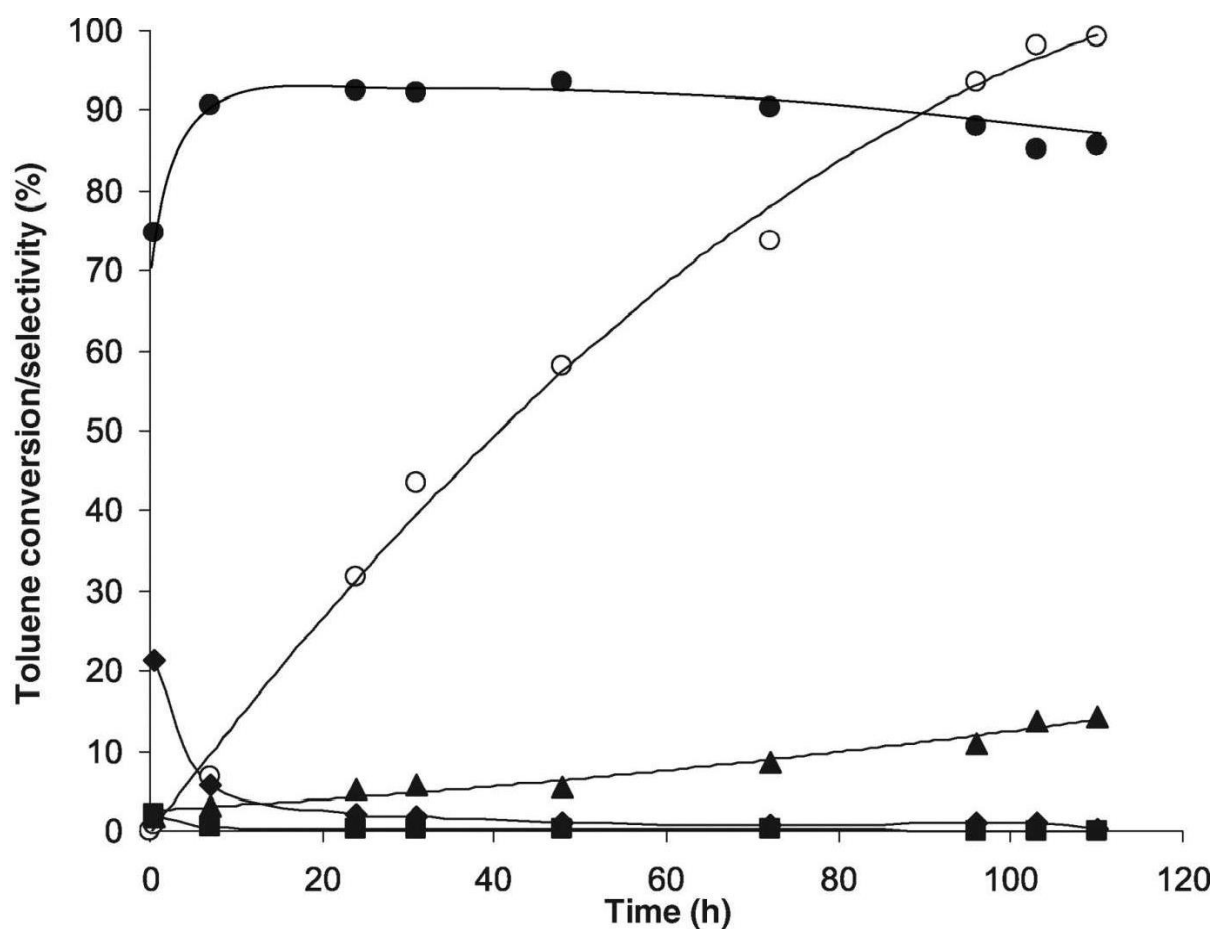


Figure 7. Toluene conversion and selectivity to benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate using 1 wt. % AuPd/C prepared by sol immobilization with a 1:1.85 Au/Pd ratio. Open circles indicate conversion, squares indicate selectivity to benzyl alcohol, diamonds indicate selectivity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

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5 Advancement of Science.
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11 Characterisation studies by HAADF-STEM analysis confirmed that any sintering or
12 structural modification of these highly active catalysts is minimal, and that the catalysts
13 are stable and reusable. The effect of the support on activity was important, and
14 carbon-supported catalysts gave improved performance when compared with titania.
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21 Graham has also extensively investigated the oxidation of alcohols for the production
22 of aldehydes and acids.¹³⁰ Specific focus was placed on the development of supported
23 bimetallic nanoparticles with controlled morphology using a range of preparation
24 methods. The effect of systematically changing parameters such as particle size,
25 elemental composition, oxidation state of the metal and formation of random alloy or
26 core-shell bimetallic nanoparticles was studied for the catalytic performance for model
27 reactions.^{132, 133}
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38 The morphology of the bimetallic particles made by sol-immobilisation could be
39 exquisitely controlled prior to the deposition of the pre-formed AuPd colloidal
40 nanoparticles on the support (Figure 8).^{132, 134}
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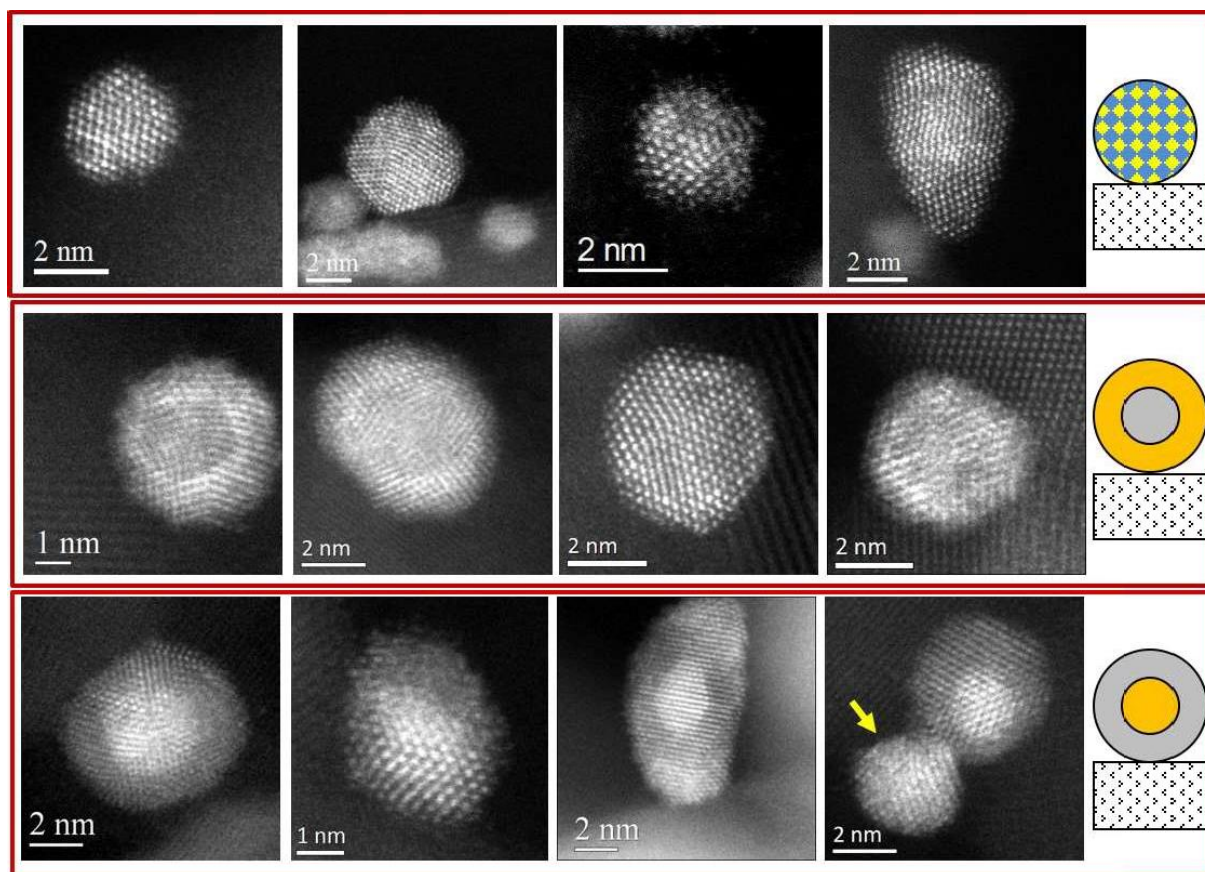


Figure 8. Representative STEM-HAADF images of individual sol-immobilized random AuPd alloy (top row) , Au shell-Pd core (middle row) and Pd shell-Au core (bottom row) nanoparticles on TiO₂ supports after drying at 120 °C for 16 h. The heavier metal (Au) shows much brighter mass contrast compared to the 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

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3 to highly active catalysts for the oxidation of benzyl alcohol under very mild conditions
4 (100–120 °C). The higher activity of the supported Au–Pd catalysts synthesised by the
5 sol-immobilization method in comparison to those made by the conventional
6 impregnation method, was attributed to the following parameters: (i) a smaller mean
7 particle size, (ii) a narrower particle size distribution, and (iii) a predominantly metallic
8 oxidation state of the AuPd supported colloidal nanoparticles.^{130, 132}
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12 Moreover, the effect of the nature of support (carbon versus metal oxide materials)
13 and heat treatment temperature was examined for the synthesised AuPd supported
14 nanoparticles. The choice of support (*i.e.*, carbon versus titania) was crucial in terms
15 of determining activity, with the AuPd nanoparticles supported on carbon showing a
16 higher activity (by a factor of 2) and a lower selectivity to benzaldehyde at iso-
17 conversion when compared to the corresponding AuPd nanoparticles supported on
18 TiO_2 ^{130, 135}
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34 Detailed studies were also carried out to identify general aspects of the reaction
35 mechanism and it was shown that the reaction was zero order with respect to
36 molecular oxygen concentration over 1 bar of O_2 . The oxidation of benzyl alcohol to
37 benzaldehyde was dependent on the concentration of oxygen at pressures below 1
38 bar of O_2 . Subsequent studies illuminated details of the mechanistic aspects of benzyl
39 alcohol oxidation and especially the formation of unwanted by-products such as
40 toluene.⁴ Two major reaction pathways were identified as the sources of the main
41 product, benzaldehyde. The first involved the direct catalytic oxidation of benzyl
42 alcohol to benzaldehyde by O_2 , while the second reaction pathway involved
43 disproportionation of two molecules of benzyl alcohol to produce equimolar
44 benzaldehyde and toluene.^{130 136}
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3 Therefore, the challenge was one of catalyst design and how to decrease and “switch-
4 off” the production of the unwanted toluene as a by-product. Graham made two
5 important advances to achieve this goal. Firstly, a basic support such as MgO was
6 required¹³⁷. Secondly, by substituting bimetallic AuPd with trimetallic AuPdPt
7 nanoparticles¹³³ it was found that the disproportionation reaction could be completely
8 “switched-off”, thereby significantly improving the selectivity to benzaldehyde to over
9 90% at a conversion of 40%.

23 **Environmental catalysis**

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27 Graham’s work has encompassed catalysis that is employed for environmental
28 protection, particularly on the abatement of atmospheric pollutants. Examples include
29 ambient temperature CO removal for respiratory protection using metal oxide
30 catalysts¹³⁸⁻¹⁴⁰ and metal-based catalysts,^{141, 142} and control of other gaseous
31 pollutants like carbonyl sulfide.^{143, 144}

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40 He has notably contributed to the subject of total oxidation, through the oxidative
41 destruction of Volatile Organic Compounds (VOCs), which is an important process for
42 pollution control and environmental protection. Based upon the ability of U₃O₈ to
43 accommodate non-stoichiometric phases with high defect concentrations and facile
44 redox behaviour of uranium cations, Graham hypothesised that this material could
45 potentially be an effective total oxidation catalyst and this started an area of research
46 that captured a lot of media attention. The hypothesis was proven to be correct and
47 U₃O₈ prepared in an appropriate manner was highly active for the total oxidation of a
48 wide range of chemically diverse VOCs¹⁴⁵. Comparison of the activity with Co₃O₄, a
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3 well-known highly active total oxidation catalyst, demonstrated that U_3O_8 was more
4 active for a range of VOCs, showing > 99% conversion, total CO_2 selectivity and long-
5 term stable activity. Catalyst performance could be further enhanced by supporting
6 U_3O_8 on high surface area silica, and low levels of a second component (e.g., Cu or
7 Co) increased activity even further. In particular, the U_3O_8 -based catalysts were very
8 active for the total oxidation of chlorinated VOCs. Mechanistic investigations using a
9 Temporal Analysis of Products (TAP) approach, pulsing the VOC in the presence and
10 absence of gas phase oxygen, confirmed that lattice oxygen from the U_3O_8 was the
11 active oxidising species¹⁴⁶. Further experiments using isotopically labelled gas phase
12 oxygen showed that the catalyst operated by a Mars-Van Krevelen mechanism.
13 Featured in the international press and media, the work raised many opinions and put
14 the spotlight on uranium oxide as a catalyst, initiating many lively debates when
15 presented at conferences.
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34 Graham has also recently focused on catalysis for water treatment, addressing one of
35 the major challenges we all face in securing future water supplies. By careful design,
36 a AuPd catalyst suitable for this purpose has been prepared by modified impregnation,
37 a synthesis method allowing for a homogeneous Au:Pd metal ratio independent of
38 alloy particle size¹⁴⁷. Careful tuning of the operating parameters meant that the
39 AuPd/ TiO_2 catalyst afforded a 100ppm yield of H_2O_2 in a flow reactor at ambient
40 temperatures in a water-only solvent.¹⁴⁸ This is an H_2O_2 concentration that is capable
41 of reducing a bacterial and viral load, forming the basis for a process of treating
42 greywater and increasing recycling.
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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 catalyst¹⁴⁹. 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 virus¹⁵⁰ 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

We would like to thank David Willock for his assistance with the table of contents graphic.

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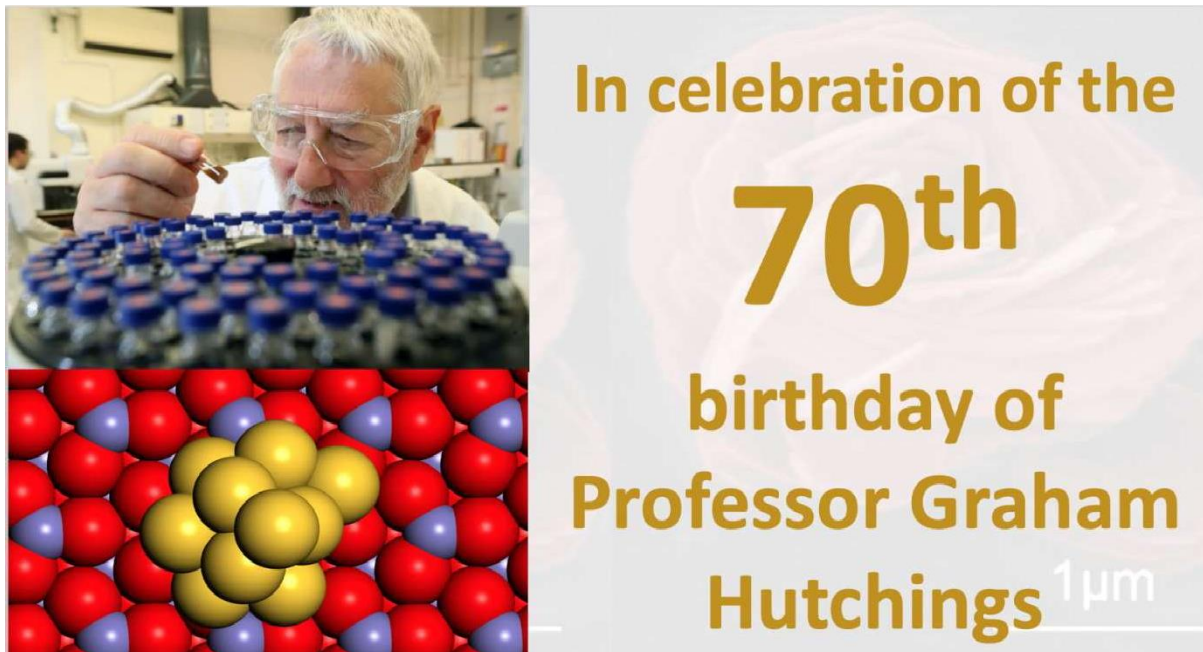
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