

# Dennis Dowden Commemoration: Catalysis – from Fundamentals to Application

Catalyst characterisation, design and applications highlighted in a commemorative symposium to appreciate an outstanding scientist

<http://dx.doi.org/10.1595/147106714X679999>

<http://www.platinummetalsreview.com/>

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## Introduction

A commemorative symposium was held at the University of Durham, UK, on 3rd–4th April 2013 to celebrate the career of Professor Dennis Albert Dowden (1914–2012). The meeting was organised by the Royal Society of Chemistry (RSC) Applied Catalysis Group (ACG) and the RSC Surface Reactivity and Catalysis Group (SURCAT) and sponsored by Johnson Matthey. The meeting was attended by approximately 100 attendees from industry and academia and consisted of a series of oral and poster presentations.

## An Appreciation

'Dennis A. Dowden – An Appreciation of a Life in Catalysis' was presented by Martyn V. Twigg (formerly Johnson Matthey). Dennis Dowden was born in 1914, shortly after the direct catalytic synthesis of ammonia had begun on an industrial scale. Dowden won a scholarship to Merrywood School and afterwards to Bristol University, UK, where he obtained a first class degree in chemistry. He carried out some research with Professor William E. Garner at Bristol on heats of adsorption of gases on solids before moving to Amherst College, Massachusetts, USA, to continue his work with Professor Ralph Beebe. In a year, his careful study extended knowledge on the nature of adsorption processes and was published in the *Journal of the American Chemical Society* in 1938 (1). With the likelihood of war with Germany, he returned to the UK and joined ICI. He worked for ICI for his entire career, mostly at Billingham, until he retired aged 62 in 1977.

During this period he brought together empirical information and used concepts such as the band structure of semiconductors to develop theories of catalysis, at a time when catalysis was considered more 'black art' than science. He regularly lectured at catalysis conferences and was awarded the Chemical Society Industrial Medal in 1973 and a

Frank G. Ciappeta National Lecturer of the American Catalysis Society in 1974. In 1996 Dowden was awarded the International Congress on Catalysis Diploma in recognition of a lifetime service to the community of catalytic scientists (2). After retiring from ICI, he continued lecturing at Imperial College London, UK, and became a research fellow at Edinburgh University, UK. Dowden continued to work into his late seventies as a consultant and expert witness in industrial patent litigation. A fuller treatment of his life and work will appear in a forthcoming issue of this Journal.

### Electronic Structure of Catalysts

Long before modern methods of catalyst characterisation were commonplace, Dowden emphasised the importance of metal particle size, shape and electronic structure in determining catalyst performance. Professor Peter Wells (Cardiff University, UK) presented seven snapshots of work carried out at the University of Hull, UK, that were inspired by Dowden's ideas in a talk entitled 'Morphology and Selectivity in Catalysis by Metals'.

The influence of electronic structure on activity was illustrated by the correlation of the rate coefficients for  $C_6H_6/C_6D_6$  exchange with densities of states at the Fermi level ( $E_F$ ) for the majority of the transition elements, whilst the correlation of 1-butene yields in butadiene hydrogenation with Pauling electronegativity for the transition elements demonstrated the importance of electronic structure on selectivity (Figure 1). The role of bulk structure was considered using the examples of butadiene hydrogenation over rhombic and hexagonal forms of molybdenum disulfide ( $MoS_2$ ) and the selectivity patterns observed in the hydrogenation of di-unsaturated aliphatic hydrocarbons over the platinum group metals (pgms). Examples were also given that showed the importance of site congestion on selectivity (isopentene isomerisation), the impact of metal support interactions on crystal structure (unfolding of  $Os_6(CO)_{18}$  adsorbed on alumina using Fourier transform infrared spectroscopy (FTIR) and extended X-ray absorption fine structure spectroscopy (EXAFS)) and the role of edge and terrace sites (the enantioselectivity of a Pt catalyst in the hydrogenation of  $MeCOCOOEt$ ).

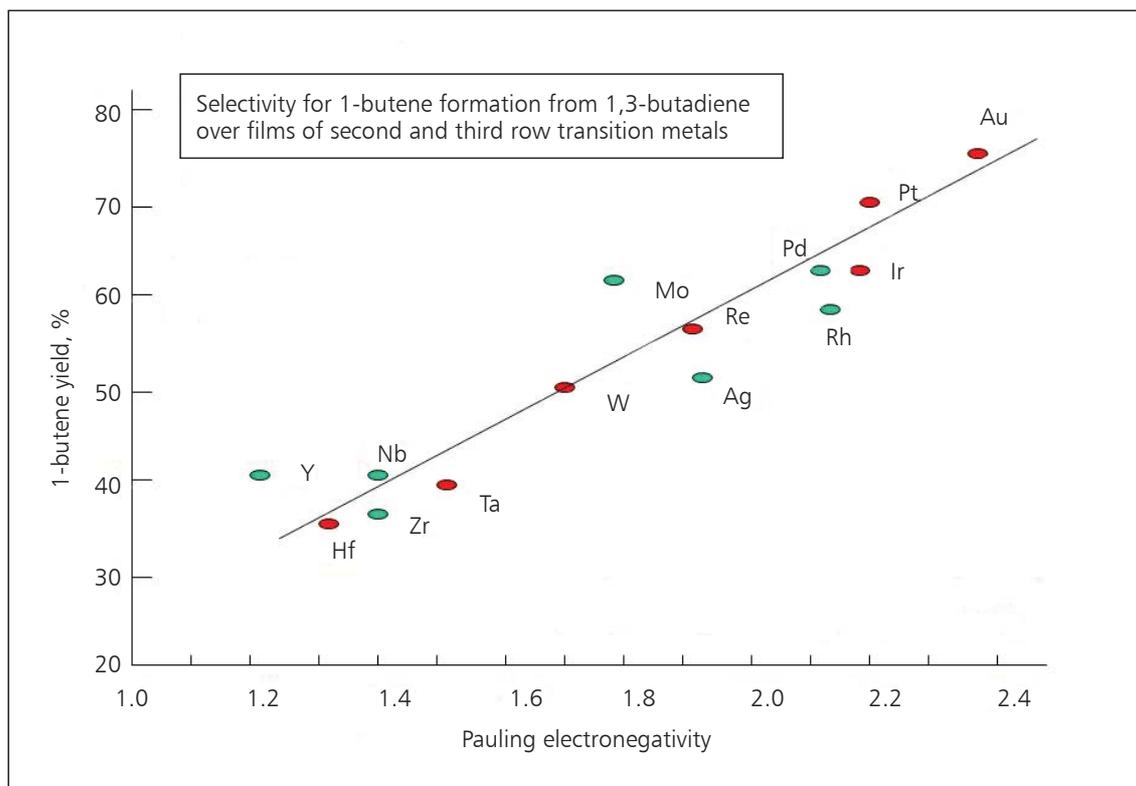


Fig. 1. Correlation of selectivity during hydrogenation reaction and Pauling electronegativity for transition elements (Adapted from (2) and reproduced with kind permission from Professor Peter Wells, Cardiff University, UK)

The theme of electronic structure in alloys was developed further by Professor Michael Bowker (Cardiff University, UK). In a talk entitled 'Catalytic Reactivity of Single Crystal Cu-Pd Alloys and the *d*-band Theory' he used the decomposition reaction of formic acid and ethanol on copper-palladium alloys to interrogate local electronic *vs.* non-local ensemble effects on reactivity. Ultraviolet photoelectron spectroscopy (UPS) shows that the *d*-band of Cu-Pd is shifted below the  $E_F$  and for formic acid decomposition the alloy appears more 'Group 11 like' with the decomposition energy intermediate between the two metals, i.e. there is evidence of non-local electronic effects. However, for ethanol decomposition, the reactivity patterns for both Cu metal and Pd metal are observed, suggesting that it is localised electronic structure that dominates reactivity notwithstanding the apparent *d*-band shift. Thus for Cu-Pd alloys, any theory that related reactivity to *d*-band position is apparently disproved.

Professor Richard Catlow (University College London, UK) described the application of computer modelling methods based on both interatomic potentials and density functional theory (DFT) to the determination of crystal, surface and active site structures in a range of oxide and microporous catalysts.

### Catalyst Design

Dowden's methodology for catalyst design viewed different forms of lattice and chemisorbed oxygen as possible selective or unselective species in partial oxidation reactions. Professor Ken Waugh (University of Manchester, UK) reviewed the role of oxygen species in maleic anhydride production from butane using a vanadium pyrophosphate ( $(VO)_2P_2O_7$ ) catalyst and ethylene oxide production from ethylene over a silver/alumina catalyst using temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) studies.

Professor Graham Hutchings (Cardiff University), in his talk 'Alkane Activation by Selective Oxidation', discussed alternative approaches to methane activation and highlighted a patent published in 1971 by Dowden and Walker which used a  $Fe_2O_3(MoO_3)_3$  catalyst for the direct synthesis of methanol (4). The group at Cardiff Catalysis Institute have shown that AuPd supported nanoparticles can activate  $CH_4$  with hydrogen peroxide for the production of methanol. By 'confining' any radical intermediates and by introducing acidic functionality, zeolites and

especially ZSM-5 promoted with Fe and Cu are shown to be very effective for methane activation. However,  $H_2O_2$  is a more expensive chemical than methanol and so oxygen is preferred as an oxidant. AuPd can convert toluene almost exclusively to benzoyl benzoate and is suggested as a model for selective C–H bond activation by  $O_2$  without the stoichiometric use of  $H_2O_2$  (or other terminal oxidants).

The performance of gold catalysts supported on carbon for reactions such as hydrochlorination of ethylene and  $H_2O_2$  synthesis is known to be strongly dependent on the pretreatment of the support – in particular the process of acid washing before the addition of the active component. The fundamental changes that occur at the nanoscale during these processes have been studied using atomic force microscopy (AFM), scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) on a highly ordered graphite sheet by Phillip Davies (Cardiff University). Mild acid treatment of the graphite sheet results in local delamination that resembles a 'surface bubble' in the AFM (Figure 2).  $Au^0$  nucleation then occurs at defect sites at the edge of the bubble. Hydrochloric acid pretreatment enhances Au nucleation and deposition, whilst nitric acid pretreatment produced larger particles. When the Au was deposited in the acid,  $HNO_3$  treatment led to larger particles compared to HCl.

Professor Jim Anderson (University of Aberdeen, UK) described how photocatalytic treatment of water pollutants produces minimal undesired byproducts and also overcomes the need for substantial quantities of hydrogen in catalytic hydrogenation in his paper 'Simultaneous Removal of Organics and Nitrates from Aqueous Environments using Photocatalysis'. Metal doped titania (Ag, Au) shows enhanced photocatalytic reactivity and selectivity compared to titania alone. In this study, the enhanced textural properties of sol-gel produced tin doped titania was studied by porosimetry and by high-resolution transmission electron microscopy (HR-TEM). FTIR was used to probe surface hydroxylation and CO adsorption and the band gap determined by ultraviolet-visible (UV-vis) spectroscopy. High Sn loadings enhance UV photocatalytic performance whilst low loadings enhance the visible photocatalytic performance for nitrate depletion. The addition of a hole scavenger (such as oxalic acid) enabled the simultaneous removal of organic and nitrate components from aqueous feeds.

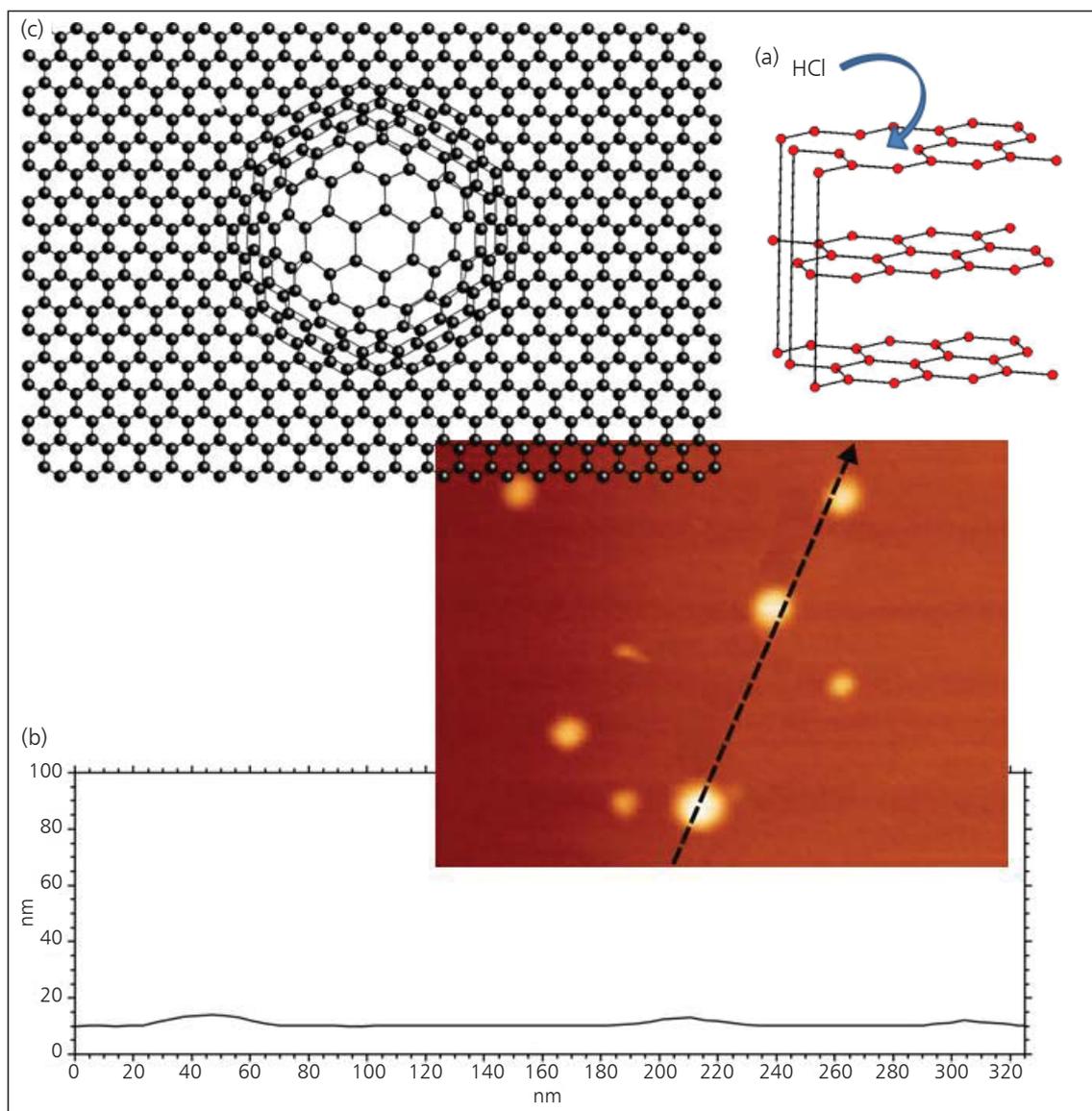


Fig. 2. Local delamination caused by acid treatment of a highly ordered graphite sheet observed using AFM: (a) attack by acid leads to local delamination; (b) surface contours detected by AFM; (c) schematics showing graphite lattice extending over feature (Reproduced with kind permission from Phillip Davies, Cardiff University, UK)

### Hydrogen Production and Storage

Dowden published a patent claiming the use of pgms and other modifiers for the production of hydrogen by the steam reforming of naphtha in 1966 (5). Today hydrogen is produced by the steam reforming of natural gas, and in the future biomass may become an important source. Some of the challenges associated with these alternative feedstocks were addressed in a paper by Professor David Jackson (University of

Glasgow, UK), entitled 'Steam Reforming of Ethane and Ethanol over Rh/Alumina: a Comparative Study', that examined activity, selectivity and deactivation during the steam reforming of two apparently simple and similar molecules, ethane and ethanol, over Rh/alumina, under similar conditions. No significant deactivation of catalysts was observed at 873 K although carbon filaments were formed during ethanol reforming (Figure 3).

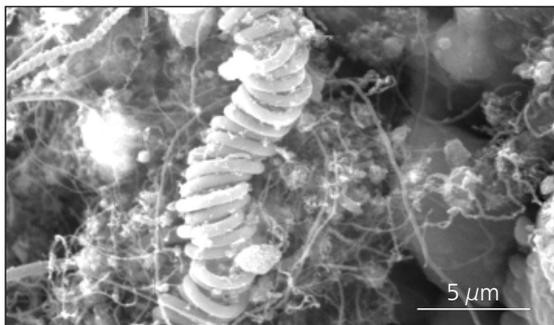


Fig. 3. Carbon filament formation during ethanol steam reforming over a  $Rh/Al_2O_3$  catalyst (Reproduced with kind permission from Professor David Jackson, University of Glasgow, UK)

For ethane, steam reforming and hydrogenolysis are the primary reactions and a high methane selectivity was observed, whilst the reaction of ethanol is much more complex involving a number of pathways including steam reforming and ethanol dehydration and dehydrogenation reactions. High hydrogen selectivity was observed.

Professor Julian Ross (University of Limerick, Ireland) described his recent work, 'Formic Acid Decomposition over Pd/C Catalysts: Promotion and Change of Mechanism caused by Doping with Alkali Metals Ions'. Formic acid has been proposed as a medium for storing hydrogen. K/Pd/C is a highly active and selective catalyst for the decomposition of formic acid to hydrogen and  $CO_2$ . Energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and carbon monoxide chemisorption results showed that mobile K species were uniformly distributed over both Pd and C while TEM did not show any noticeable change of the Pd particle size upon alkali doping. Catalyst activation experiments suggest that the formation of potassium formate species occurs, possibly in the liquid phase containing formic acid, within the pores of the C support. Pd appears essential for this process to occur. The reaction occurs on both alumina and silica supports.

### Industrial Applications

A number of industrial contributions were given that demonstrated the need for both fundamental and applied science for the successful development and application of new technology. Martin Hanton (Sasol Technology UK Ltd) gave a perspective on how

fundamental science and exploration is a requisite for the creation of robust new industrial processes. Using the example of selective ethylene tetramerisation the research and development (R&D) path was traced from initial discovery and patent filing in 2003 to operating plant in 2013. David Johnson (Lucite International, UK) gave a presentation entitled 'Commercialisation of a Novel Methyl Methacrylate Process – Catalyst Design and Development'. The talk described the development of a novel palladium phosphine catalyst which gives methyl propionate in 99.9+% selectivity and a caesium/zirconia/silica catalyst that reacts methyl propionate with formaldehyde. The key to the success of the condensation reaction was an understanding of the reaction mechanism and achieving the right balance of acidity and basicity in the catalyst to minimise byproduct formation. Chris Mitchell (Huntsman Polyurethanes, Belgium) described an approach for the evaluation of catalyst for phosgene manufacture. Gas phase reaction of chlorine with an excess of CO over an activated carbon catalyst produces peak temperatures of over  $500^\circ C$  which makes this reaction very difficult to study in the laboratory. Comparison of the performance of full size catalyst pellets *vs.* crushed catalyst allowed catalyst effectiveness factors and therefore effective gas diffusivities to be estimated. These data have been combined in a two-dimensional (2D) reaction engineering model incorporating a description of heat and mass transfer to predict catalyst performance in industrial scale phosgene reactors. The reactor model was used to help improve catalyst lifetimes. Finally Rob Parry (BASF Catalysts, UK) gave a marketing perspective on the challenges for catalysis associated with the shift from non-renewable to renewable feedstock in the fuels and energy industries.

### Summary

This was a very successful meeting, that brought together both young researchers and contemporaries of Dennis Dowden. As an industrial chemist, Dowden knew the importance of both fundamental understanding and the challenges of taking science through to industrial implementation. The range of contributions at the meeting demonstrated the breadth of these requirements well. Whilst modern methods have subsequently contradicted Dowden's hypothesis that bond formation during chemisorption at metal

surfaces occurs by ionisation or electron transfer, the importance of his ideas and the depth of thinking and insight that he showed for all aspects of catalysis were emphasised in the meeting by all who knew his work or had the fortune to work with him.

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### References

- 1 R. A. Beebe and D. A. Dowden, *J. Am. Chem. Soc.*, 1938, **60**, (12), 2912
- 2 M. S. Spencer and M. V. Twigg, *Appl. Catal. A: Gen.*, 2014, **473**, 146
- 3 R. B. Moyes, P. B. Wells, J. Grant and N. Y. Salman, *Appl. Catal. A: Gen.*, 2002, **229**, (1–2), 251

- 4 D. A. Dowden and G. T. Walker, Imperial Chemical Industries Ltd, 'Oxygenated Hydrocarbons Production', *British Patent* 1,244,001; 1971
- 5 D. A. Dowden and P. Davies, ICI Ltd, 'Improvements in or Relating to the Steam Reforming Hydrocarbons and Catalyst therefor', *British Patent* 1,032,754; 1966

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### The Reviewer

*Martin Fowles obtained a DPhil at University of Oxford, UK, in the area of gas phase kinetics. He joined Johnson Matthey (formerly ICI) in the Research and Technology department at Billingham in 1984 and has worked in a number of areas of high temperature catalysis, developing catalysts and innovative reactor concepts in the field of steam reforming and catalytic combustion. His current role is Research Associate, with interests in new opportunities for syngas developments.*