

EuropaCat X

Highlights of platinum group metal catalysis from biennial congress

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Introduction

Held under the auspices of European Federation of Catalysis Societies (EFCATS) the 10th EuropaCat Congress was held in Glasgow, UK, from 28th August to 2nd September, 2011 (1). EuropaCat is a highly regarded biennial congress which brings together researchers from across Europe and further afield for scientific dissemination in catalysis. EuropaCat X was a truly international congress with approximately 1200 delegates attending, representing some 44 countries. The theme of the Congress was 'catalysis across the disciplines' with an aim of delivering a unified conference covering all aspects of catalysis. The setting for the conference was the Glasgow University main building, a fine example of Gothic revival architecture and a prominent local landmark.

The programme included six plenary and 21 keynote lectures. The plenaries were presented by international leaders from a wide range of disciplines. In total over 210 oral presentations were given, representing the latest in scientific advances and successful commercial applications. Each day was split into five parallel sessions covering the following topics: Catalyst Preparation, Catalyst Characterisation, Kinetics and Mechanism, Theory and Modelling, Homogeneous Catalysis, Industrial Application, Catalyst Deactivation and Environmental Catalysis. In addition there were three poster sessions with approximately 900 posters. A parallel workshop on Selective Oxidation (ISO 2011, X European Workshop on Selective Oxidation) was organised independently with 17 oral presentations and 97 posters.

There was an excellent attendance from industrial attendees who accounted for approximately 15% of the delegates, representing over 90 companies. The exhibition space, with 24 companies represented, was also well attended throughout the conference.

A full social programme was organised for the attendees with a range of day trips available showcasing the best of Scotland. The conference dinner was held in the magnificent Kelvingrove Art Gallery and Museum and the final night's Céilidh was a popular and energetic event!

In terms of its original aims EuropaCat X was a huge success in delivering a unified conference covering all aspects of catalysis and highlighting the huge

breadth and depth of science and technology that is encompassed in the field. In terms of the impact of platinum group metals (pgms) in the conference, over 30% of the oral papers presented involved the use of pgms. A more detailed analysis shows the following split between the pgms: 32 platinum, 22 palladium, 13 ruthenium, 12 rhodium and 2 iridium papers respectively. The industrial applications sessions included 11 papers that incorporated pgms.

With such a range of oral presentations and parallel sessions to choose from, this conference review can only discuss a few highlights. Therefore, in this review only papers which made significant use of pgms have been included.

Fischer-Tropsch Synthesis

The influence of pgm promoters on cobalt-supported Fischer-Tropsch catalysts continues to be an area of interest. Eric Marceau (Université Pierre et Marie Curie/Centre National de la Recherche Scientifique (CNRS), France) presented a keynote paper characterising the impact of sorbitol and Ru promotion in the structure and performance of silica-supported cobalt catalysts. Addition of sorbitol to the impregnating solution was found to lead to a decrease in the size of the cobalt(II)(III) oxide (Co_3O_4) crystallites formed from 11 nm to 7 nm. Sorbitol was shown, by a combination of *in situ* quick-scanning X-ray absorption spectroscopy (Q-XAS), *in situ* UV-visible spectroscopy and thermal analysis to retard the decomposition of the cobalt precursor into Co_3O_4 . *In situ* Q-XAS and temperature-programmed reduction (TPR) showed that the Co_3O_4 particles first

reduced to cobalt(II) oxide (CoO). The reducibility of the Co-sorbitol/ SiO_2 catalyst was quite low due to the formation of cobalt silicate (2). The presence of Ru greatly enhanced the reducibility of the catalysts. Transmission electron microscopy (TEM) images of reduced catalysts demonstrate the homogeneous distribution of cobalt particles in the catalyst prepared with sorbitol (**Figure 1**).

Ru in its own right can, of course, be used as a Fischer-Tropsch catalyst. Although cobalt and iron are preferred for industrial application due to cost considerations, Ru continues to draw scientific interest due to its ability to produce high molecular weight hydrocarbons. Xian-Yang Quek (Schuit Institute of Catalysis, Eindhoven University, The Netherlands) presented a very interesting paper demonstrating unprecedented oxygenate selectivity during Fischer-Tropsch synthesis over Ru nanoparticles. The Ru nanoparticles, encapsulated and stabilised in polyvinylpyrrolidone (PVP), were prepared in a size range of between 1.3 and 3.3 nm. The product distribution formed depended strongly on temperature. An aldehyde selectivity as high as 70% was obtained over 2.2 nm Ru nanoparticles at 125°C. With increasing temperature the total oxygenate selectivity decreased and the amount of hydrocarbon produced was increased. Mechanistic consideration of the product chain lengths suggested that the hydrocarbons and the oxygenates were formed on different sites.

Michael Claeys (University of Cape Town, South Africa) presented an *in situ* magnetometer study on

Plenary Lectures

Professor Manfred Reetz (Max-Planck-Institut für Kohlenforschung, Mülheim, Germany), 'Tuning Monoxygenases by Genetic and Chemical Means'

Professor Istvan Horvath (City University of Hong Kong), 'Heterogenization of Homogeneous Catalytic System'

Professor Charles T. Campbell (University of Washington, USA), 'Thermodynamics and Kinetics of Elementary Reaction Steps on Late Transition Metal Catalysis, and in Their Sintering'

Professor Rutger van Santen (University of Eindhoven, The Netherlands), 'Structure Sensitivity and Unsensitivity in Heterogeneous Catalysis'

Professor Matthias Beller (Leibniz Institute for Catalysis, Rostock, Germany), 'Development of Practical Molecular-Defined Catalysts for Industrial Applications and Hydrogen Technology'

The 2011 Michel Boudart Award for Advances in Catalysis

This was awarded to **Professor James Dumesic** (University of Wisconsin-Madison, USA), who presented a plenary lecture on 'Routes for Production of Liquid Transport Fuels by Liquid-Phase Catalytic Processing'.

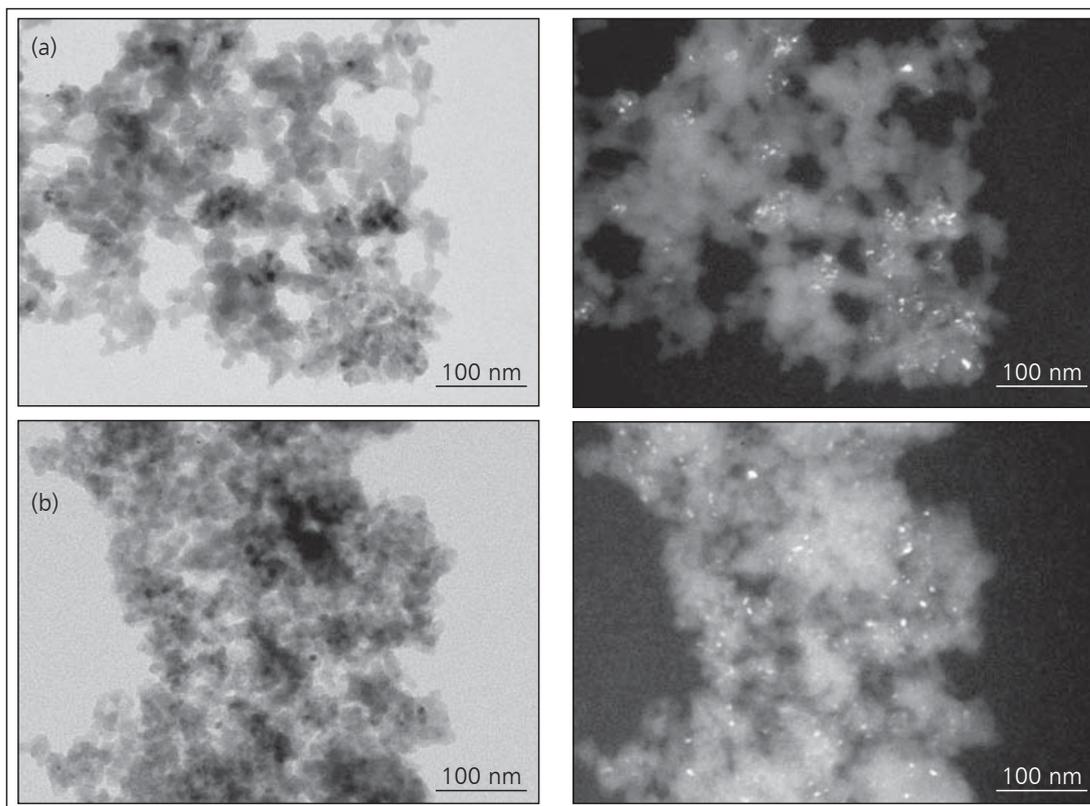


Fig. 1. Bright-field and dark-field high angle annular dark field (HAADF)-TEM images of: (a) CoRu/SiO₂; and (b) of CoRu-sorbitol/SiO₂ catalysts after reduction and passivation in He (Courtesy of Eric Marceau and Andrei Khodakov, Université Pierre et Marie Curie/Centre National de la Recherche Scientifique (CNRS), France)

the formation and stability of cobalt carbide during Fischer-Tropsch synthesis. Novel methods that yield different attributes of a catalytic system within the same measurement are both information rich and valuable from a research and development efficiency perspective. The application of magnetometry can reveal structural features of Co crystallites under authentic gas-to-liquid (GTL) process conditions. This study concentrated upon the formation and role of cobalt carbides during time on line of a simple Co-Pt/alumina catalyst operated under varying conditions typical of Fischer-Tropsch processes. The experimental approach made use of a fixed-bed reactor placed within the field supplied by a magnetometer, from which it was possible to infer the state of magnetisation of the catalyst at different times and subject to the influence of reaction condition changes. Changes in magnetisation could be correlated with the extent of carbide formation, as confirmed by *ex situ* X-ray diffraction (XRD) measurements, and with the degree

of reduction when the catalyst was treated under TPR conditions. Detailed analysis of magnetisation hysteresis allows modelling of Co crystallite size and some insight into active site mobility under reaction conditions.

When tested under Fischer-Tropsch conditions (230°C, 14 bar, H₂:CO = 2:1) a pre-carbided catalyst showed an increase of magnetisation during time on line, which is indicative of carbide decomposition to form the metallic state. However, this carbide decomposition took place slowly and remained incomplete even after an extended period of testing, suggesting that once carbides are formed, they will not decompose completely under typical Fischer-Tropsch conditions. The pre-carbided catalyst also displayed inferior Fischer-Tropsch performance (activity and methane selectivity) compared to a non-carbided catalyst. This performance was regained after hydrogen treatment, which also led to completely restored magnetisation (Figure 2).

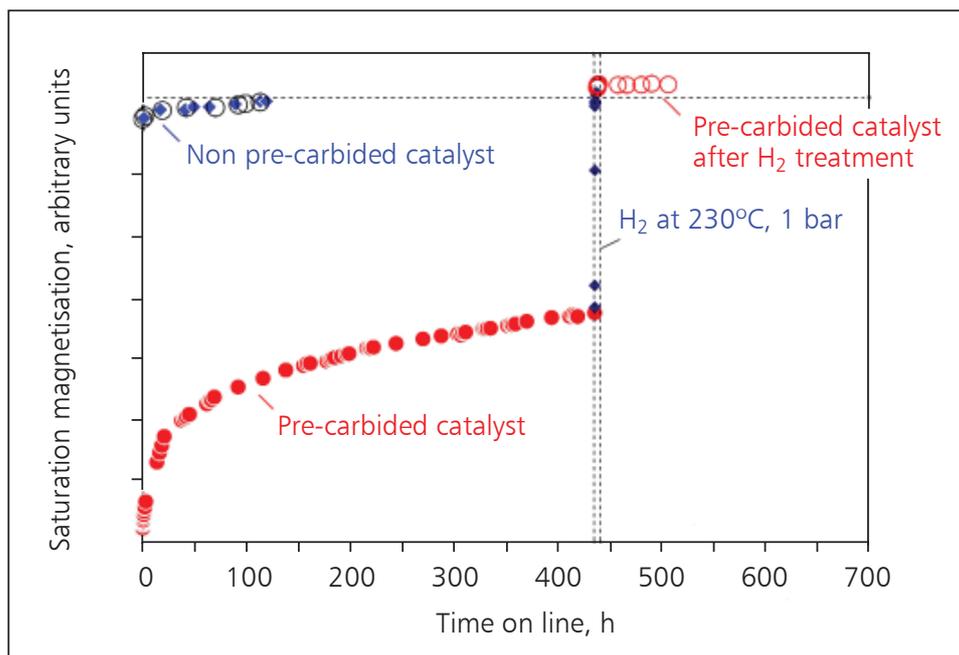


Fig. 2. Magnetisation of pre-carbided and non-carbided catalyst monitored during Fischer-Tropsch synthesis (Courtesy of Michael Claeys, University of Cape Town, South Africa)

Biomass Conversion

One of the Industrial Application sessions was devoted to the conversion of biomass into liquid fuels. In this session it was clear that the use of pgms was key in many of the processes described.

Two papers were presented on the use of supported Ru catalysts to convert cellulose to sugar alcohols. The first of these from Kameh Tajvidi (Max-Planck-Institut für Kohlenforschung, Germany) investigated alternatives to sulfuric acid in conjunction with a 5 wt% Ru/C catalyst for the hydrolytic hydrogenation of cellulose. Reactions in the presence of silicotungstic acid achieved almost full conversion of cellulose and a sugar alcohol yield of up to 80%. The concept was successfully transferred to the direct conversion of spruce wood fibres as a real feedstock again with an almost full conversion of the cellulose and hemicellulose content to sugar alcohols. An alternative approach, presented by Weiping Deng (Xiamen University, China), was to adsorb Ru nanoparticles onto caesium salts of tungstophosphate. This bifunctional catalyst contained both the acidity and hydrogenation activity required for the conversion of cellulose. A Ru/Cs₃PW₁₂O₄₀ material was stable in repeated use and sorbitol yields of ~75% could be

sustained after five recycling uses. The sorbitol yield increased with decreasing mean size of Ru particles from 10.8 to 1.6 nm.

Alexey Kirilin (Åbo Akademi University, Finland) investigated the use of a 5 wt% Pt/Al₂O₃ catalyst for the aqueous phase reforming (APR) of erythritol, xylitol and sorbitol as a means of producing hydrogen and components of liquid fuels. Sorbitol and xylitol were viewed as the most promising raw materials for the APR process due to the possibility of obtaining transportation fuel components (hexane etc.). No catalyst deactivation was observed after more than 140 h on line. Hydrogen yields for erythritol, xylitol and sorbitol under the same operating conditions were 48%, 28% and 22% respectively (Figure 3).

A series of supported 2 wt% Ru catalysts (Ru, ruthenium(IV) oxide, ruthenium(IV) sulfide) were investigated by Marcelo Kaufman-Rechulski (Paul Scherrer Institut, Villigen, Switzerland) as an alternative to the cold scrubbers that are currently used to remove tars and organic sulfur compounds during biomass gasification. The Ru catalysts were tested against commercially available NiMoS and CoMoS materials. The RuS₂ catalyst was active for all three of the reactions under investigation (sour water gas shift, sulfur

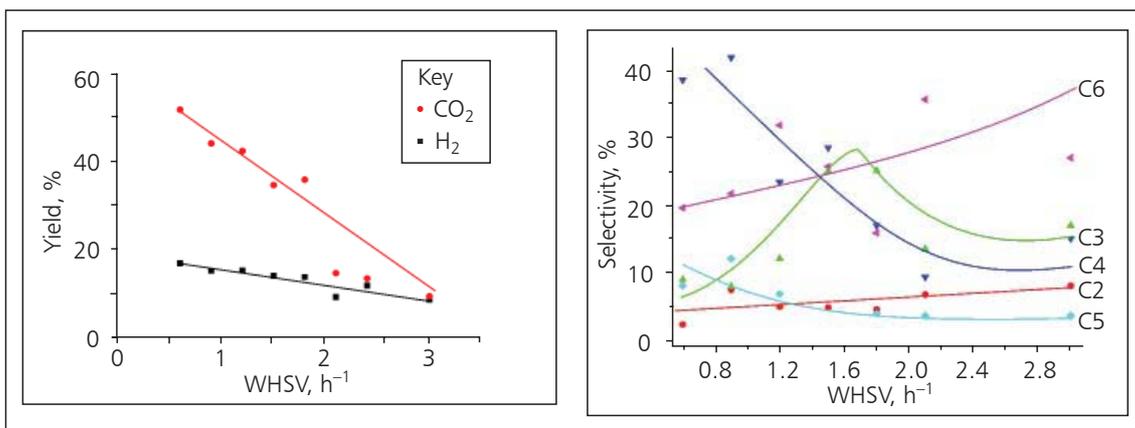


Fig. 3 (a) Yields of H₂ and CO₂ in APR as a function of WHSV; and (b) selectivity towards compounds presented in the liquid phase during APR of sorbitol as a function of space velocity (Courtesy of Alexey V. Kirilin, Åbo Akademi University, Finland)

resistant hydrogenation and hydrodesulfurisation of thiophene) and appeared to be more stable under real process conditions.

Chuan Wang (Institute of Materials Science and Engineering, Singapore) presented an interesting paper on low-temperature hydrogenation of furfural on Pt catalysts supported on a multiwall carbon nanotube (MWCNT) support. A 5 wt% Pt/MWCNT catalyst at 150°C and 20 bar H₂ achieved a furfural conversion of >95%. Both of the products formed, furfuryl alcohol (~90% selectivity) and 2-methylfuran, are more chemically stable than furfural, thereby facilitating further bio-oil upgrading at high temperature.

Aldehydes such as furfural are present in significant amounts in bio-oils obtained from the fast pyrolysis of biomass. Under typical conditions for bio-oil upgrading, these reactive aldehyde compounds can form tar-like black solids. This work demonstrated that a mild hydrogenation treatment can be used to remove reactive compounds in bio-oils, facilitating their storage and further high-temperature upgrading.

Methanol Reforming

Karin Föttinger (Vienna University of Technology, Austria) presented a paper investigating the use of *in situ* X-ray and vibrational spectroscopic studies on palladium/zinc(II) oxide and palladium/gallium(III) oxide as potential methanol steam reforming (MSR) catalysts. The localised generation of hydrogen as a fuel for proton exchange membrane (PEM) assemblies, is key to the successful design and deployment of fuel

cells intended to support initiatives for sustainable means of transportation. The paper sought to address, with some success, the issue of current steam reforming catalysts in which the conversion of methanol generally results in the co-production of carbon monoxide – a potent catalyst poison. Pd supported on ZnO and Ga₂O₃ had shown excellent activity and selectivity to the steam reforming reaction, yielding only H₂ and CO₂ (3). Experiments undertaken at the Swiss Light Source (superXAS beamline), made use of a catalytic reaction cell from which it was possible to study the system by extended X-ray absorption fine structure (EXAFS) and infrared (IR) techniques, along with gas chromatography-mass spectrometry (GC-MS) analysis of catalyst performance. Using time-resolved EXAFS, it was possible to follow, *in situ*, the formation of the active Pd-Zn alloy phase of a Pd/ZnO MSR catalyst, *via* spillover and reduction of the ZnO by H₂ generated in the reaction. With time-on-stream, the degree of alloying was observed to steadily increase and, in parallel, the reactivity changed from methanol decomposition (CO/H₂) to MSR (CO₂/H₂), confirming that the Pd-Zn alloy is the selective phase for MSR. Pd-Zn alloying was found to be reversible on contact with O₂, producing Pd metal and ZnO with a corresponding reversion of selectivity to CO/H₂. The corresponding surface state and available adsorption sites were studied by FTIR spectroscopy of CO adsorption. Pd-Zn alloy formation led to the disappearance of bridge-bonded CO and a shift of the on-top CO band from 2090 cm⁻¹ to 2070 cm⁻¹. Upon O₂ treatment the bands assigned to unalloyed

metallic Pd reappeared but at a lower intensity, which may be explained by a partial decoration of the Pd by patches of ZnO.

The theme of this paper was continued in a subsequent presentation from the same group, given by Christian Weilach, who extended the range of spectroscopic methods to expose more detail of the surface transformations associated with alloy formation and the change in the selectivity pattern observed during MSR (Figure 4).

Characterisation

Gary Attard (Cardiff Catalysis Institute, UK) gave a thought-provoking lecture on electrochemical perspectives on catalysis. This addressed the challenges of specifically identifying those surface topographies and two-dimensional morphologies that are associated with selective catalytic transformations. The presentation concentrated upon the application of cyclic voltammetry (CV) as a means of characterising surface states – including the existence of defects. Typical CV data collected from a series of palladium-gold alloys supported on graphite (0.4%–3% total metal loading) spanning the whole range of alloy composition were presented. Referring to one set of voltammograms, it was shown that the number of Pd surface sites is signified by the area of the CV peaks between 0 and 0.3 V associated with hydrogen electroadsorption. The oxide stripping peaks also provide a measure of the available Pd and Au surface area (for example, the Au oxide stripping peak area

at 1.1 V). More interestingly, the extent to which the surface is alloyed is given by a systematic shift in the potential of the Pd oxide peak to more positive potentials as surface Au composition increases. Similar studies using single crystal electrodes allow for direct comparison between supported metal catalysts and shape-controlled nanoparticle behaviour in catalytic and electrocatalytic reactions, since it can be demonstrated that the electroadsorption charge between 0 and 0.3 V acts as a ‘finger-print’ analytical technique for the presence of particular step, terrace and kink sites (Figure 5).

Concluding Remarks

The study and use of pgms continues to be an essential component of catalyst research, both to extend fundamental understanding and to allow industrial exploitation. The three application areas reviewed in this article: Fischer-Tropsch, biomass conversion and methanol reforming, are linked by the challenge of meeting the world’s future energy demands and requirements. The pgms find use in a wide range of chemical reactions as demonstrated by this conference, and their use is also essential in several exciting new areas of research not reviewed here (for example, NO_x storage and reduction for lean-burn gasoline and diesel vehicles and the direct synthesis of hydrogen peroxide from H₂ and O₂). The versatility of the pgms and the reaction selectivity they impart will make them an integral part of many future catalytic processes.

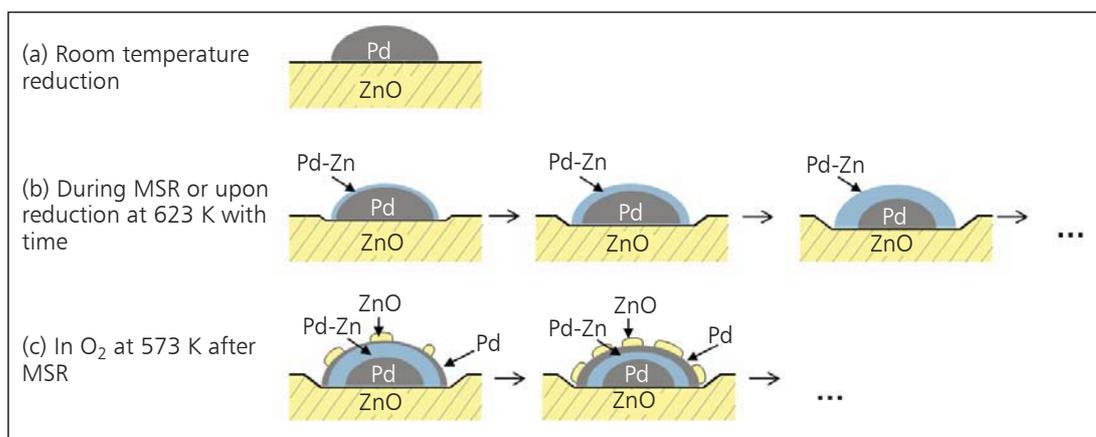


Fig. 4. Illustration of the suggested structural changes of Pd/ZnO in various environments (Reprinted with permission from (4) © 2011 American Chemical Society)

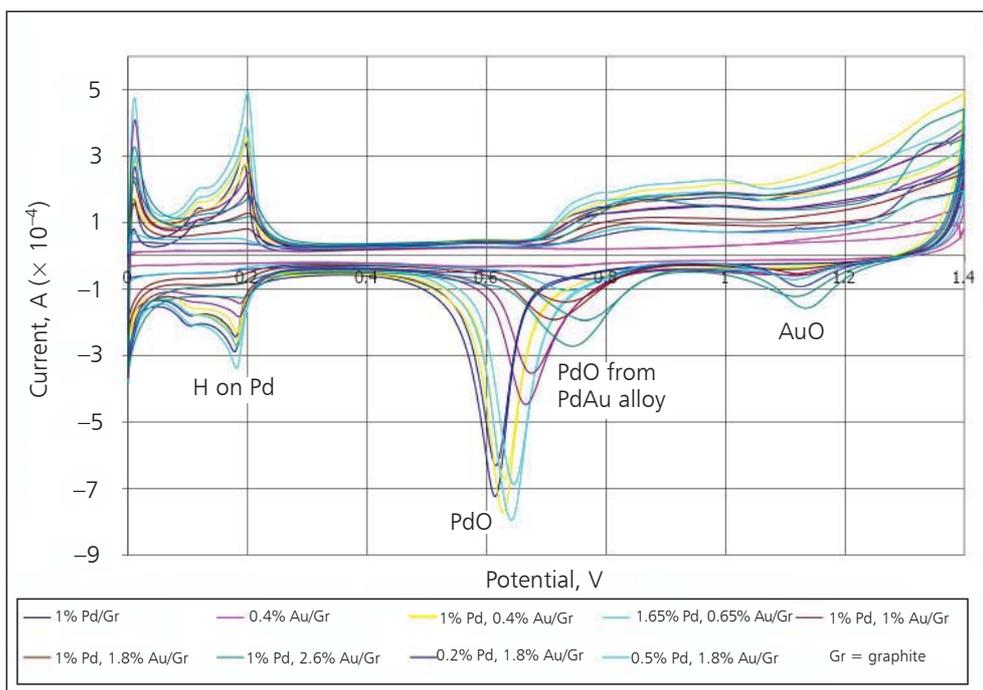


Fig. 5. Systematic changes in the CV response for a series of PdAu catalysts supported on graphite. Sweep rate = 50 mV s^{-1} in 0.5 M aqueous sulfuric acid. The reference electrode was a saturated Pd/H electrode in contact with the electrolyte (Courtesy of Gary Attard, Cardiff Catalysis Institute, UK)

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The Reviewers



Gordon Kelly joined Johnson Matthey in 1994 following a Chemistry degree and PhD in Catalysis at Glasgow University, UK. He has worked in various research roles in areas such as solid base catalysis, hydrogenation, methanol synthesis, low-temperature shift and Fischer-Tropsch catalysis. He has over 40 catalysis publications including eight patents. Currently he is the Johnson Matthey Fischer-Tropsch Development Manager.



Steve Bailey has a PhD and over 20 years' experience working in the fields of catalyst development and characterisation. He began his catalysis career at ICI where his principal roles were to apply surface characterisation methods to assist the understanding of catalyst performance across a broad range of industrial processes. He then moved into the roles of catalyst development and project management, focusing upon selective hydrogenation and gas purification, and more recently, has led the growth of catalyst characterisation capabilities within Johnson Matthey's Process Technologies R&D centre.