Institution: Cardiff University		
Unit of Assessment: Chemistry (8)		
Title of case study: Novel gold-based catalyst methods for PVC production		
Period when the underpinning research was undertaken: 2007 – 2020		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s): Graham J. Hutchings	**Role(s) (e.g. job title):** Regius Professor	**Period(s) employed by submitting HEI:** 01/08/1997 – 31/12/2020
Period when the claimed impact occurred: 01/08/2013 – 31/12/2020		
Is this case study continued from a case study submitted in 2014? Yes		

1. Summary of the impact (indicative maximum 100 words)

Despite the immediate and environmental dangers of mercury, it remains integral to polyvinyl chloride (PVC) manufacture in China, the world's largest producer. Cardiff researchers developed and optimised a gold-based catalyst system for use in vinyl chloride monomer manufacture, the precursor to PVC, replacing mercury-based catalysts. Global chemicals company, Johnson Matthey, now operates an industrial-scale factory producing this catalyst and are replacing the use of mercury-based catalysts in PVC production facilities across China. This is the first time in over 50 years a complete overhaul in catalyst formulation has been implemented to produce a commodity chemical.

2. Underpinning research (indicative maximum 500 words)

The production of polyvinyl chloride (PVC) requires the precursor material vinyl chloride monomer (VCM). The world's largest PVC producer, China, synthesises VCM from its extensive coal reserves via acetylene hydrochlorination. Until now, this process required the use of mercury-based catalysts, resulting in substantial pollution of mercury in the environment.

Due to dangers from mercury poisoning (including brain damage, kidney failure, and potentially death), the 128 signatories of the Minamata Convention on Mercury (including China in 2016) committed to phasing out its use in products, processes, and industries. Hutchings' catalysis research revealed the high catalytic activity of clusters of gold atoms **[3.1]**, greatly increasing their potential for commercial exploitation by providing a replacement approach to the use of the mercury-based catalyst.

2.1 Determining the catalytic properties of gold

The presence of atomically dispersed gold cations in the proposed catalyst are crucial to the synthesis of VCM from acetylene. Studies of the hydrochlorination of acetylene and higher alkynes **[3.2]** and gold-based bimetallic catalysts revealed that gold is by far the most active and most selective catalyst **[3.3]**. The high cost of gold, however, necessitated a reduction in gold content for the proposed catalyst to be commercially viable.

Following Hutchings' research, and based on its track record in gold-based catalyst formation, Cardiff was approached by Johnson Matthey to address this challenge. In a study sponsored by the company and the World Gold Council **[G3.1]**, the Cardiff team found that dilution of the gold led to untenably low activity in all cases, which was shown to scale with the standard electrode potential of mixed metal compositions. This research also revealed that viable catalysts did not result from alloying with a second metal **[3.3]**.

These fundamental studies showed that gold-only catalysts were superior to other mixed compositions, including mixed metal catalysts, and provided full mechanistic understanding on which to base new catalyst formulations. The research also demonstrated that it is essential to maximise the dispersion of the gold so that the maximum amount of gold can be maintained in the most active state (cationic species) in the working catalyst **[3.4]**.

2.2 Creating the catalyst

Working closely with Johnson Matthey, the Cardiff team devised a catalyst system consisting of a carbon core with a gold 'shell', maximising dispersion of the gold. This catalyst has a very low gold concentration (0.1%) that gives superior performance to the standard mercuric chloride catalyst, extensively used by industry for acetylene hydrochlorination over the last 60 years.

Once the key catalyst features were established, following small-scale tests at Cardiff in 2008, the method of catalyst preparation became the critical means of improving the catalyst. Originally, the carbon-supported gold catalysts were prepared by depositing gold using a strong acid solvent (aqua regia) to produce a 1-2% metal content. For commercial application, a non-aqua regia based route was needed to reproducibly generate catalysts with a controllable, lower gold content.

Research on this problem led to a new water-based route employing small molecule sulphur complexes of gold **[3.5]**. Once this new formulation was established, fundamental studies were undertaken to confirm the nature of the active site of well-dispersed supported gold cations **[3.6]**; an atomic level of understanding that enabled the development of highly active catalysts, readying their commercialisation.

Cardiff research was central in changing the way in which gold catalysts were designed greatly increasing their potential for commercial exploitation by meeting the key innovations required for successful translation to PVC manufacturing.

3. References to the research (indicative maximum of six references)

[3.1] A.A. Herzing, C.J. Kiely, A.F. Carley, P. Landon, **G.J. Hutchings**, 'Identification of active gold nanoclusters on iron oxide supports for CO oxidation', Science, 2008, 321, 1331-1335. http://dx.doi.org/10.1126/science.1159639

[3.2] M. Conte, A.F. Carley, C. Heirene, D.J. Willock, P. Johnston, A.A. Herzing, C.J. Kiely, **G.J. Hutchings**, 'Hydrochlorination of acetylene using a supported gold catalyst. A study of the reaction mechanism', J. Catal., 2007, 250, 231-239. http://dx.doi.org/10.1016/j.jcat.2007.06.018

[3.3] M. Conte, A.F. Carley, G. Attard, A.A. Herzing, C.J. Kiely, **G.J. Hutchings**, 'Hydrochlorination of acetylene using supported bimetallic Au-based catalysts', J. Catal., 2008, 257, 190-198. http://dx.doi.org/10.1016/j.jcat.2008.04.024

[3.4] M. Conte, C.J. Davies, D.J. Morgan, T.E. Davies, D. J. Elias, A.F. Carley, P. Johnston, **G.J. Hutchings**, 'Aqua regia activated Au/C catalysts for the hydrochlorination of acetylene', J. Catal., 2013, 297, 128-136. http://dx.doi.org/10.1016/j.jcat.2012.10.002

[3.5] P. Johnston, N. Carthey, **G.J. Hutchings**, 'Discovery, development and commercialisation of gold catalysts for acetylene hydrochlorination', J. Am. Chem. Soc., 2015, 137, 14548-14557. https://doi.org/10.1021/jacs.5b07752

[3.6] G. Malta, S.A. Kondrat, S.J. Freakley, C.J. Davies, L. Lu, S. Dawson, A. Thetford, E.K. Gibson, D.J. Morgan, W. Jones, P.P. Wells, P. Johnston, C.R.A. Catlow, C.J. Kiely, **G.J. Hutchings**, 'Identification of single-site gold catalysis in acetylene hydrochlorination', Science, 2017, 355, 1399-1403. https://doi.org/10.1126/science.aal3439

Selected grant:

[G3.1] G. J. Hutchings; Replacing mercury-based catalysts for acetylene hydrochlorination using supported gold catalysts; Johnson Matthey Davy Technologies Limited, World Gold Council; 2010-2019, £60,000; ID: 502874

4. Details of the impact (indicative maximum 750 words)

China is the world's largest producer of the ubiquitous material polyvinyl chloride (PVC), and its production is reliant on the precursor material vinyl chloride monomer (VCM). While other countries typically use oil or natural gas to produce VCM, China relies on their coal reserves to produce VCM, necessitating the use of mercury-based catalysts and asserting the country as the biggest global consumer of mercury, chiefly for VCM production (over 800 tonnes a year) **[5.1]**. Cardiff research enabled the development of an alternative gold-based catalyst for VCM production, which is replacing the mercury use in Chinese VCM production and has been recognised through multiple international awards.

4.1 Development of a mercury-free catalyst for VCM production

Since 2007, international chemical company Johnson Matthey PLC collaborated with Cardiff to develop a new series of gold-based catalysts for VCM production. Following over 10 years of research and development costing millions of pounds, the company developed the PRICAT™ MFC (Mercury Free Catalyst) **[5.2]**. Cardiff's role in developing this commercial gold-based catalyst was highlighted by Sebastiaan van Haandel, the New Technologies Licensing Manager at Johnson Matthey as "*critical in optimisation of the catalyst and enabled further improved second generation catalysts to be developed*" **[5.2]**. Johnson Matthey further noted that the new catalyst *"is the first time in over 50 years that a complete overhaul in catalyst formulation has been implemented to produce any commodity chemical*" **[5.2]**.

The intellectual property for PRICAT™MFC was initially shared between Johnson Matthey and Jacobs Engineering Group. After recognising the significant value of the catalyst, as evidenced by research findings, in March 2014, Johnson Matthey made the strategic decision to purchase sole ownership of the catalyst patents for £7.5M **[5.2]**.

4.2 Establishing production and use of the catalysts in China

In 2013, as confirmed by Johnson Matthey, the first full reactor test of the PRICAT™ MFC was commissioned by a major Chinese VCM producer, followed by several further full-scale reactor trials at other major Chinese producers **[5.2]**. These trials demonstrated the acetylene conversion rate and catalyst productivity outperformed the mercury-based catalyst **[5.2]**.

Alongside purchasing the patents for the catalyst in 2014, Johnson Matthey secured the process technology required for building VCM plants, in order to give the company strategic capability to roll out a mercury-free VCM production process across China **[5.2]**. The full product offering became the DAVY™ VCM Process, which utilises PRICAT™ MFC and is the only mercury-free process currently offered for licence **[5.3]**.

In 2015, Johnson Matthey invested in a new manufacturing plant in Shanghai to produce the PRICAT™ MFC catalyst at industrial scale, positioning the catalyst as *"one of the major growth engines for Johnson Matthey over the next 10 years"* **[5.2]**. The plant is designed to meet 20-30% of China's annual VCM demand, and Johnson Matthey anticipates that "*a significant part of the Chinese market will have converted to PRICAT® MFC*" within two years **[5.2]**.

In August 2016, China ratified the Minamata Convention on Mercury, a United Nations Environment Programme treaty committed to the removal of mercury in industrial processes. Particularly, Annex B, Article 5 (v) of the Convention commits members to withdraw mercury-based methods for the production of VCM, and that member states will cease mercury mining by 2032 **[5.4**, p.25**]**. The signing of the Convention by China signalled its intention to adopt new and economically-viable mercury-free processes.

Johnson Matthey noted that the successful testing and implementation of the PRICAT™ MFC catalysts "*is starting to facilitate the widespread transformation of Chinese VCM production*", with the expectation that within a few years a significant amount of VCM production in China will have discontinued use of mercury-based catalysts **[5.2]**.

4.3 Awards and Recognition

The development of the new catalyst, underpinned by Cardiff research, achieved global recognition as a significant step in enabling the reduction of mercury-based PVC manufacturing processes:

- The *Innovative Product of the Year Award* at the 2015 Institution of Chemical Engineers (IChemE) Global Awards **[5.5]**, awarded to Johnson Matthey and Cardiff University **[5.5]**;

- The *GSK Innovation Award* at the 2016 Chemical Industry Awards for the successful commercialisation of the PRICAT™ MFC for mercury-free VCM production **[5.6]**;
- The *Industry-Academia Collaboration Award* at the 2017 Royal Society of Chemistry awards for the development of the mercury-free catalyst for VCM production **[5.7]**;
- In recognition of the beneficial impact of gold catalysts on the environment, in 2017 Hutchings was awarded the Eni Awards' *Advanced Environmental Solutions Prize* for his work creating and optimising the catalyst **[5.8]**.

5. Sources to corroborate the impact (indicative maximum of 10 references)

[5.1] Special Policy Study on Mercury Management in China – presentation by the China Council for International Cooperation on Environment and Development

[5.2] Testimonial: Sebastiaan van Haandel, Licensing Manager New Technologies, Johnson Matthey Plc.

[5.3] Confirmation of process and license, Johnson Matthey website on DAVY Process VCM Technology

[5.4] The Minamata Convention on Mercury, Annex B, p.25

[5.5] Johnson Matthey with Cardiff University, winner of the Innovative Product of the Year, footage of IChemE's Global Awards 2015 from IChemE Youtube channel

[5.6] Johnson Matthey wins GSK Innovation Award at the 2016 Chemical Industry Awards, Johnson Matthey website

[5.7] Professor Graham Hutchings and Dr Peter Johnston, Industry-Academia Collaboration of the Year, Royal Society of Chemistry Prizes and awards 2017, RSC Website

[5.8] Eni Award 2017 for Advanced Environmental Solutions awarded to Professor Graham Hutchings, press release, Eni website