

Institution: Cardiff University
Unit of Assessment: Chemistry 8
Title of case study: Gold Catalysts for Vinyl Chloride Manufacture
<p>1. Summary of the impact</p> <p>Vinyl chloride is a major monomer used in the production of the non-biodegradable plastic PVC. Research undertaken in the Cardiff Catalysis Institute, within the School of Chemistry, has resulted in a pioneering new catalyst for the manufacture of vinyl chloride from acetylene hydrochlorination. The research has demonstrated for the first time that supported gold nanoparticles are the best catalysts for this reaction. Importantly this can be applied to replace the current commercial catalyst, mercuric chloride supported on carbon. The new process has been endorsed by Johnson Matthey, a leading speciality chemicals company (serving the automotive, environmental, medical and oil and gas industries), and Jacobs (formerly Aker) which, operate on a global basis, in approximately 30 countries. These major corporations have invested significantly to date for commercial validation, including full pilot plant trials in China. Moreover, the results have been used in policy reports regarding the environmental threat associated with the use of mercury. Therefore the impacts claimed are impact on practitioners and professional services, economic impact, and impact on public policy and services.</p>
<p>2. Underpinning research</p> <p>Catalysis by gold has been pioneered by Professor Graham Hutchings (Professor of Physical Chemistry at Cardiff University since 1st August 1997) and seminal studies have been carried out since 1997 in the Cardiff Catalysis Institute in the School of Chemistry. This research has led to a number of scientific innovations. In particular, it has shown that very small clusters of atoms of gold can be associated with high catalytic activity [3.1]. This discovery changed the way in which gold catalysts are designed and has greatly increased their potential for commercial exploitation, particularly for the hydrochlorination of acetylene. The use of small gold nanoparticles has been shown to be crucial for the synthesis of vinyl chloride monomer from acetylene. Indeed, gold is the best (i.e. most active and most selective) catalyst; there is none better [3.2, 3.3]. Professor Hutchings demonstrated this by detailed studies which showed that gold-only catalysts were superior to other compositions, and gained the full mechanistic understanding on which to base new catalyst formulations [3.2, 3.3, 3.4, 3.5]. The research focused on the examination of mixed metal catalysts, and in all cases dilution of the gold led to lower activity. The activity was shown to scale with the standard electrode potential of the mixed metal compositions. This was an important finding, made as part of a study sponsored by Johnson Matthey and the World Gold Council, because the Cardiff work has also shown that improved catalysts have not resulted from alloying with a second metal. Once this was established, the method of catalyst preparation became the key means of improving the catalyst. In this case the research at Cardiff showed that it is essential to maximise the dispersion of the gold to ensure the maximum amount of gold can be maintained in the cationic state in the working catalyst.</p>
<p>3. References to the research</p> <p>[3.1] Identification of active gold nanoclusters on iron oxide supports for CO oxidation. A.A. Herzing, C.J. Kiely, A.F. Carley, P. Landon and G.J. Hutchings, <i>Science</i>, 321 (2008) 1331-1335, http://dx.doi.org/10.1126/science.1159639</p> <p>[3.2] Hydrochlorination of acetylene using a supported gold catalyst: A study of the reaction mechanism. M. Conte, A.F. Carley, C. Heirene, D.J. Willock, P. Johnston, A.A. Herzing, C.J. Kiely, G.J. Hutchings,</p>

J. Catal., **250** (2007) 231-239, <http://dx.doi.org/10.1016/j.jcat.2007.06.018>

[3.3] Hydrochlorination of acetylene using supported bimetallic Au-based catalysts.

M. Conte, A.F. Carley, G. Attard, A.A. Herzing, C.J. Kiely and G.J. Hutchings,
J. Catal., **257** (2008) 190-198, <http://dx.doi.org/10.1016/j.jcat.2008.04.024>.

[3.4] Aqua regia activated Au/C catalysts for the hydrochlorination of acetylene. **M. Conte, C.J. Davies, D.J. Morgan, T.E. Davies, D. J. Elias, A.F. Carley, P. Johnston and G.J. Hutchings**,
J. Catal., **297** (2013) 128-136, <http://dx.doi.org/10.1016/j.jcat.2012.10.002>

[3.5] Modifications of the metal and support during the deactivation and regeneration of Au/C catalysts for the hydrochlorination of acetylene. **M. Conte, C.J. Davies, D.J. Morgan, T.E. Davies, A.F. Carley, P. Johnston and G.J. Hutchings**,
Catal. Sci. Tech., **3** (2013) 128-134, <http://dx.doi.org/10.1039/C2CY20478A>

4. Details of the impact

Impact on Public Policy and Services

Over 20 million tonnes per annum of vinyl chloride monomer (VCM) are manufactured every year. This is used for the manufacture of polyvinyl chloride (PVC) a non-biodegradable plastic. Acetylene hydrochlorination is used in 60% of this manufacture, which is predominantly based in China. Presently the catalyst used in this process is mercuric chloride supported on carbon. Current use (installed capacity) of the mercuric chloride catalyst by the major PVC producers in China is greater than 4000 tonnes per annum. However, the widespread use of mercury for this purpose (China accounts for 50% of the World's mercury releases) is contentious for several reasons [5.1]. Firstly, the supply of mercury is becoming limited. Secondly, it is globally recognised that the use of mercury is seriously harmful to human health and is environmentally damaging. The World Health Organisation (WHO) has documented the dangers of exposure that can affect the human brain, heart, kidneys, lungs and immune system. In animals, this can lead to death and reproductive problems. The United Nations Environment Programme has been working to address these issues since 2003 and is currently leading negotiations on a global treaty on restricting mercury usage [5.2].

Cardiff University's research has been used to inform policy debate on this issue. Gold has been identified as a suitable alternative catalyst for VCM production. Key advantages of the gold catalyst are its long lifetime even at very low metal loading and its high specificity to the desired product. The results of the pilot plant trials in China that were commissioned by Johnson Matthey and Jacobs, as a direct consequence of the research, have been used in a policy study of mercury management in China. This was conducted by CCICED (China Council for International Cooperation on Environment and Development). The report states that Johnson Matthey and Jacobs (Aker) reported "promising results from a pilot scale test of a catalyst that may be affordable. If this catalyst proves to be effective and affordable under commercial operating conditions, optimistic estimates are that the technology could be available for initial commercial use as early as 2013" [5.1].

Economic Impact and Impact on Practitioners and Professional Services

Johnson Matthey and Jacobs have sanctioned the research and have been working on the commercialisation of a supported gold catalyst for the last six years. Each of these companies has made a considerable financial investment based on Cardiff University's pioneering findings. Peter Johnston who is leading the work for Johnson Matthey states that

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“Johnson Matthey have invested significantly in terms of manpower, equipment and analytical methods” [5.3]. In 2010, following extensive laboratory tests, in which the performance of the gold catalyst reached the required benchmark performance target, the decision was made to proceed to pilot plant trials. Jacobs have commissioned a pilot plant at a commercial VCM manufacturer in western China. This is a single tube (3 m x 1 inch diameter with 2 kg catalyst charge) and replicates exactly a single tube from a commercial reactor. This has operated continuously for 2 years and 6 catalysts have been successfully tested to fine-tune the catalyst formulation. The last test has shown successful operation over a 9 month period.

On the basis of the successful pilot plant trials, a full reactor test has been commissioned and is now in operation in China. This involves a commercial reactor with 1000 reactor tubes and 2 tonnes of the gold catalyst, which has been made by Johnson Matthey and shipped to China. The catalyst was made in 2012, the cost of its gold component is significant at the current gold market price. Peter Johnston from Johnson Matthey stated that “this is the first time in about 50 years where a complete change in catalyst formulation is being evaluated for the production of this bulk chemical, the pilot plant trials have confirmed that the gold catalyst is highly active and selective and we are now commissioning a full commercial reactor trial” [5.3].

In summary, Cardiff University’s research has led to a new process to produce VCM that absolves the necessity for mercury. This has been supported by two leading organisations, which have made substantial investments in developing the new catalyst. The findings have been incorporated in policy debate regarding the global concern attached to the use of Mercury and its risks to human health and the environment.

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

[5.1] <http://www.cciced.net/enciced/policyresearch/report/201205/P020120529368288424164.pdf>
A report that provides evidence of China’s contentious use of Mercury. Page 414 shows that China accounts for 50% of the world’s mercury emissions and that PVC production accounts for 60% of China’s emissions. Page 424 corroborates the inclusion of the research and trials in a policy report for CCICED (China Council for International Cooperation on Environment and Development) and also gives details of the plant trials with the non-mercury catalyst and provides further references.

[5.2] <http://www.unep.org/hazardoussubstances/mercury/tabid/434/default.aspx>
Evidence that the UN are seeking to reduce the use of Mercury

[5.3] Scientific Consultant, Chemical Catalysis Business Unit, Johnson Matthey plc.
Corroborates the use of the research by Johnson Matthey and the resulting impact (letter on file at UoA).