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Acetylene hydrochlorination using Au/carbon: a journey towards single site catalysis

The paper gives a perspective on the development of an Au/C catalyst for the acetylene hydrochlorination reaction as a replacement for the currently used mercuric chloride catalyst. Discussed from discovery to recent advances the paper provides an overview of how this catalyst has become set to contribute to a cleaner environment in the future.

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Acetylene hydrochlorination using Au/carbon: a journey towards single site catalysis

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The replacement of mercuric chloride in the production of vinyl chloride monomer, a precursor to PVC, would greatly reduce the environmental impact of this large scale industrial process. The validation of single Au cations supported on carbon as the best catalyst for this reaction at an industrial scale has resulted from nearly 35 years of research. In this feature article we review the development of this catalyst system and address the limitations of a range of characterisation techniques used previously which may induce damage to the fresh catalyst. Following our latest findings using X-ray absorption spectroscopy, we show that under operating conditions the catalyst is atomically dispersed and can be classed as a single site catalyst, we give a perspective on future directions in single atom catalysis.

Gold sols, fluid suspensions of colloidal particles, have been known since the 17th century but it was Michal Faraday who presented the first scientific paper on the properties and preparation of these vividly coloured nanoscale structures at the Royal Institution in 1847.[1] Over 150 years later, despite the perceived lack of reactivity, these Au nanostructures and

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homogeneous gold complexes have now been shown to be exceptional catalysts for many reactions and are still extensively studied.[2–4] Au catalysis is today moving towards large scale applications, with the validation of Au as a catalyst for the production of vinyl chloride monomer (VCM) *via* acetylene hydrochlorination.[5,6] In this article we give a review of the development and understanding of this class of carbon supported Au catalysts as they move closer to being the benchmark catalyst for this industrial process. The discovery that the active site of the catalyst is a cationic Au complex is discussed. We will also give a perspective on the potential of single site catalysis.

Grazia Malta

Grazia Malta received her master's degree in Industrial Chemistry from the University of Bologna (IT) in 2014. She then benefited from two local scholarships established by the National Interuniversity Consortium of Materials Science and Technology (INSTM) carried out at the University of Bologna. She is currently completing her PhD in heterogeneous catalysis at Cardiff University within the Cardiff Catalysis Institute in collaboration with the MaxNet energy consortium under the supervision of Prof. Graham Hutchings.

Simon J. Freakley

Simon Freakley gained his MChem degree from Durham University (UK) in 2009 including a year-long placement at Johnson Matthey. He completed his PhD in 2012 in heterogeneous catalysis at the Cardiff Catalysis Institute during which he was awarded a JSPS Fellowship to conduct research in Tokyo Metropolitan University. He is currently the senior post-doctoral researcher responsible for the institute's collaborations within the MaxNet energy consortium. He has recently been appointed a Sêr Cymru research fellow by the Welsh government. His research interests include precious metal catalysts, water purification and utilising renewable energy in catalysis.
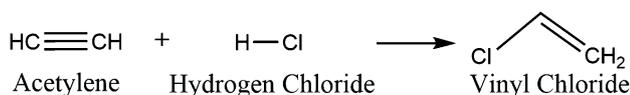
1. Vinyl chloride monomer production

During the first half of twentieth century the demand for rubber substitutes led to the commercial production of poly-vinyl chloride (PVC) as a commodity plastic.[7,8] Today, PVC is one of the most used thermoplastics in healthcare and medical devices,[9] the electronics and automotive industries and also, due to its physical properties and chemical resistance, it is commonly used in building and construction.[10] According to Ceresana, in 2016 over 42 million tonnes of PVC were consumed, around 16% of total plastics demand, making PVC one of the highest volume plastics.[11] PVC is obtained from the polymerization of vinyl chloride monomer (VCM), with ca. 90% of VCM production used to manufacture PVC. VCM production started in the 1930s with the direct hydrochlorination (Scheme 1) of acetylene which had been derived from coal, in a single step process, traditionally catalysed by carbon-supported mercuric chloride.

The growth of PVC demand and the increased availability of oil lead to the development of an alternative industrial process for the production of VCM. This multistep process, known as the balanced process, is comprised of three reaction steps: the direct chlorination and the oxychlorination of ethane to ethylene dichloride (EDC), catalysed by $FeCl_3$ and $CuCl_2$ respectively, and the thermal cracking of EDC to produce VCM.[12]

$$2C_2H_4 + Cl_2 + \tfrac{1}{2}O_2 \rightarrow 2C_2H_3Cl + H_2O \quad \text{(Overall reaction)}$$
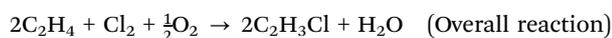
The balanced process is based on low cost oil-derived feed-stocks, ethylene is a by-product of petroleum refining that can also be isolated from natural gas, and is the primary method for the VCM production in the west. The availability of coal makes the acetylene hydrochlorination route the leading process in China. Moreover, Asia still represent the largest sales market for PVC and with a global demand expects to rise by ca. 2.3% per year until the 2024, and VCM production is expected to rise accordingly.[10]

2. Acetylene hydrochlorination catalysts

Mercuric chloride on activated carbon

The industrial catalyst used for this process is traditionally a 5–12 wt% $HgCl_2$ supported on high surface area activated carbon; more than the 60% of the worldwide annual mercury production is used for the catalyst manufacture. In the mid-1980's, several disadvantages associated with the use of mercury based catalysts were investigated:[13–16] at the reaction temperature (180–220 °C) high vapour pressure leads to thermal desorption of the $HgCl_2$ from the support surface. The loss of $HgCl_2$ from the carbon support is also amplified because of the exothermicity of the reaction, with formation of hotspots in the fixed bed reactors. The catalyst life time can be directly correlated to $HgCl_2$ loading in the catalyst as shown in Fig. 1.[5] The result of this, together with the loss in catalytic activity, is the alarming escape of Hg from the production units. In China, over 10 000 tonnes per year of mercury-based catalyst are used for monomer production; in the most optimistic scenario, 3.7% of the total Hg content has been determined to have been released into the environment, ca. 0.6 kg of mercury are lost from the catalyst per ton VCM produced.[17] For this reason, researchers are studying different approaches to improve the thermal stability of the mercury-based catalysts for the hydrochlorination of acetylene; for example using additives in the catalyst preparation in order to decrease the sublimation rates.[18] However, poor thermal stability leading to a very limited catalyst lifetime is still a crucial problem that needs to be overcome. In 2013, the environmental

$HC\equiv CH$ + $H-Cl$ $\longrightarrow$ Cl CH_2
Acetylene   Hydrogen Chloride   Vinyl Chloride

Scheme 1   Hydrochlorination of acetylene to vinyl chloride monomer.

Simon Kondrat received his master's degree from the University of Warwick (UK) in 2007. He then completed his PhD at the Cardiff Catalysis Institute with Prof. Graham Hutchings on the preparation of catalysts using supercritical fluids. Following his PhD he worked as a post-doctoral researcher at Cardiff University and the UK Catalysis Hub. Simon has recently taken a position as lecturer in inorganic chemistry at Loughborough University. His research interests include the preparation and advanced in situ characterisation of heterogeneous catalysts, for application in a range of gas and liquid phase reactions.

Simon A. Kondrat

Graham Hutchings studied chemistry at University College London. His early career was with ICI and AECI Ltd where he became interested in gold catalysis. In 1984 he moved to academia and has held chairs at the Universities of Witwatersrand, Liverpool and Cardiff and currently he is Director of the Cardiff Catalysis Institute and the UK Catalysis Hub. He was elected a Fellow of the Royal Society in 2009 and was awarded the Davy Medal in 2013 and was appointed as Regius Professor of Chemistry at Cardiff University in 2016.
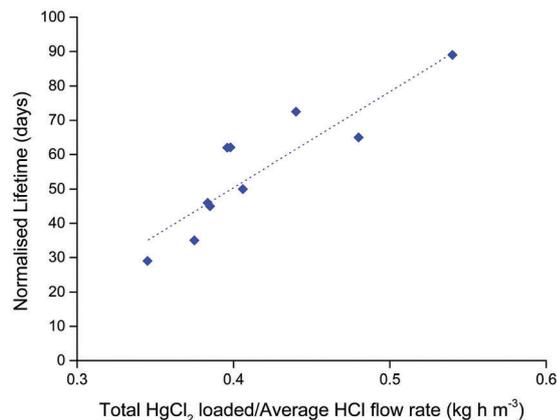
Graham J. Hutchings

Fig. 1 Catalyst lifetime of mercuric chloride catalysts showing the relationship with [HgCl$_2$] and reactant flow rate (replotted from ref. 5).

concerns related to use of Hg for the VCM production were included in the text of the Minamata convention on mercury (10 October 2013, Kumamoto, Japan). Taking its name from Minamata disease, a neurological syndrome caused by mercury poisoning, "The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of mercury" which has been signed by nearly 140 nations and addresses all aspects related to the production, use and storage of mercury with the main objective of protecting the human health and the environment.[19] The convention was ratified on the 18th of May 2017 and so has become legally binding for all its parties. The fifth article in particular, regards the "Manufacturing processes in which mercury or mercury compounds are used" with specific mention to the VCM production. The use of mercury is prohibited in VCM plants constructed after 2017, while the already existing reactors must be mercury-free by 2022, with particular attention to "supporting research and development in respect of mercury-free catalyst and process".

Alternatives to mercury: prediction of Au as a highly active catalyst

As early as 1932 the acetylene hydrochlorination reaction was being studied using a small selection of metal chlorides supported on carbon and silica.[20] This was expanded by Shinoda in 1975[21] who systematically studied a wide variety of metal chlorides and attempted to correlate the activity of the catalysts to the electron affinity of the metal cations divided by the valance as shown in Fig. 2a. While two distinct classes of metal chlorides were identified (I) low activity Friedel–Crafts type catalysts which would bind HCl strongly to form MCl$_x^-$H$^+$ complexes and (II) high activity metal chlorides such as Ag, Cu, Hg, it was clear that electron affinity of the cation was not the appropriate descriptor in determining activity. In fact both the most and least active catalysts had similar values meaning prediction of activity was not possible using this parameter. As the hydrochlorination reaction was proposed to initially involve the oxidative addition of acetylene to metal centres, as evidenced by the reduced bond order of acetylene observed by Smith et al.[22] during ex situ FTIR studies, a correlation with a two electron parameter
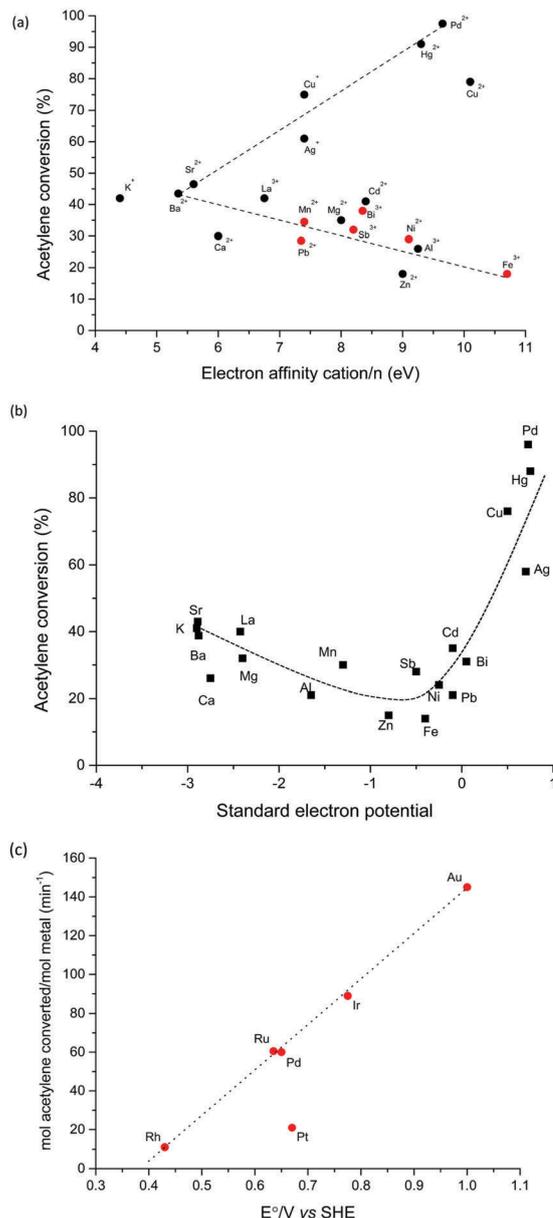

Fig. 2 (a) Correlation of activity for acetylene hydrochlorination with electron affinity/metal valence for a range of carbon supported metal chlorides (replotted from ref. 21). (b) Correlation of activity for acetylene hydrochlorination of carbon supported metal chloride catalysts with the standard electrode potential (replotted from ref. 23). (c) Correlation of initial acetylene hydrochlorination activity of supported metal chloride catalysts with the standard electrode potential of metal chloride salts (replotted from ref. 29).

might be expected. When re-plotting the data for the divalent cations reported by Shinoda[21] against the standard electrode potential a correlation of increasing activity with increasing standard electrode potential was observed, suggesting that the redox properties of the cations were important to the activity of the catalysts and was suggestive of a redox mechanism as shown in Fig. 2b.[23] This led Hutchings to the prediction that Au would be an effective catalyst for this reaction as it had a higher standard electrode potential, a prediction that was subsequently

demonstrated by the preparation of a catalyst from HAuCl$_4$ on activated carbon (Fig. 2c).[24–26]

Other metals and support materials

The performance of monometallic systems other than Au has been further investigated based on the initial separate screenings by Shinoda and Hutchings. Ag,[24] mechanically activated Pt[27] and Pd[28] chloride salts, Pd,[29] Rh,[24] Ir[30] and Cu[31] chlorides have all been studied and found to be active for the acetylene hydrochlorination reaction, but suffer from rapid deactivation, due to loss of active species and the formation of carbonaceous deposits. All monometallic systems show significantly reduced activity and stability compared to Au and in some cases reduced selectivity to VCM due to polymerization reactions.[29] In many catalytic systems the addition of a second metal to form bimetallic catalysts can result in a synergistic effect towards reactivity or stability through electronic or geometric effects in bimetallic nanoparticles.[32–36] In the case of acetylene hydrochlorination many bimetallic combinations containing Au have been investigated including Pd, Pt, Ir, Ru, Rh[29] which in some cases caused an increase in initial activity compared to the monometallic Au catalyst but deactivated quickly in comparison to the monometallic Au catalyst. Additives such as Cu,[37] La,[38] Bi[39] and Cs[40] have been used and shown to aid the stabilization of a high oxidation state of Au, resulting in greater stability. The effects of the addition of a second metal have been extensively reviewed by Dai *et al.*[41]

The choice of a support material for the harsh reaction conditions is crucial, firstly it must be stable to bulk chlorination at high temperature. Support materials are also required to be able to stabilize the high dispersion of metal chloride and prevent agglomeration and reduction of the active phase. The main focus of the literature has been activated carbon as the support of choice for this reaction as it can facilitate high dispersions of Au and is stable to the reaction conditions. Some early studies utilized SiO$_2$ as a support material to aid in spectroscopy studies but noted that the acidic groups caused polymerization of the acetylene[23] also Al$_2$O$_3$ has been utilized as a support for a Au–Cu catalyst but suffered from deactivation caused by carbon deposition.[42]

Metal-free catalysts

An alternative approach to replacing HgCl$_2$ is to exploit the activity of metal-free systems which is a growing research field. The advantages of designing metal-free catalysts are the cost savings associated with the removal of the precious metal and also potential improved stability, compared to metal containing catalysts which can sinter during the reaction. The most common material studied is nitrogen doped carbon, in numerous forms typically generated by heat treating carbons in nitrogen containing atmospheres or direct carbonisation of nitrogen containing precursors, carbon nitrides have also been extensively studied.[43–48] It is postulated that the incorporation of nitrogen can alter the surface properties of carbon by modifying the basicity or generating available lone pairs which can facilitate the reaction. While many studies have been reported, no consensus has been reached on the exact nature of the nitrogen groups required to facilitate the reaction and synthetically it is a challenge to produce materials which only contain one species. In addition, to most activated carbons also having some activity, which could be attributed to impurities, metal free systems can also suffer from carbon deposition and reaction rates are typically 2 orders of magnitude lower than Au/C catalysts. Despite active research continuing into alternatives to Au, the reaction rates, stability and selectivity that are achievable with Au/C catalysts make them commercially viable as an alternative to the currently used Hg based catalyst. This has led to the validation of a Au on carbon catalyst for the reaction, which is the result of catalyst development inspired by the initial prediction that Au would be the best catalyst. The following sections report the current knowledge and understanding we have of this Au/C system and the limitations in the field in characterising these materials.

Au/C catalysts – the effect of the preparation method

The initial studies regarding the preparation of Au/C catalysts for VCM production *via* acetylene hydrochlorination, used an impregnation method with *aqua regia* as a solvent to ensure Au solubility.[24,30,49] Already at this stage, it was understood that deposition of gold in the presence of *aqua regia* led to considerably active catalysts, because of the likely formation of more oxidized gold species in the final material. Conte *et al.* demonstrated that to achieve high dispersion of gold on the support an oxidising/chloride containing impregnation solvent was required.[50]

The study by Conte *et al.* clearly highlights the importance of catalyst preparation conditions on the consequent activity of the catalyst. They investigated the activity of catalysts prepared from HCl and HNO$_3$ containing solutions, along with *aqua regia* solvents with various HCl : HNO$_3$ ratios. *Aqua regia* was found to produce the most efficient acetylene hydrochlorination catalyst, while those prepared by HCl or HNO$_3$ solvents were less active (although still active in their own right). The high activity of the *aqua regia* catalyst was attributed to be due to a combination of the oxidising effect of HNO$_3$ on the carbon support and the nucleating effect of HCl to facilitate high dispersion of Au. These observations were supported by substantial catalyst characterisation, the complex story of which we will discuss in detail in the following section of this perspective article.

More recently, Liu *et al.* investigated the nature of the active species in carbon-supported gold catalysts: in this work the role of the solvent used in catalyst preparation has been considered in more detail.[51] Four catalysts were prepared by a modified wet impregnation method, dissolving the gold precursor, HAuCl$_4$·xH$_2$O, in a water or an acidic solution of HCl, HNO$_3$ or *aqua regia* (Au–H$_2$O/C, Au–HCl/C, Au–HNO$_3$/C and Au–AR/C respectively) which had a strong effect on the catalysts performance (Fig. 3). The use of the different acids for the dissolution of HAuCl$_4$ lead to different functionalization of the carbon support, affecting both the dispersion and the nature of the Au species present on the fresh catalyst; discussed in detail in the following section. The use of *aqua regia* leads to a higher degree of chlorination of the carbon, completely absent in the
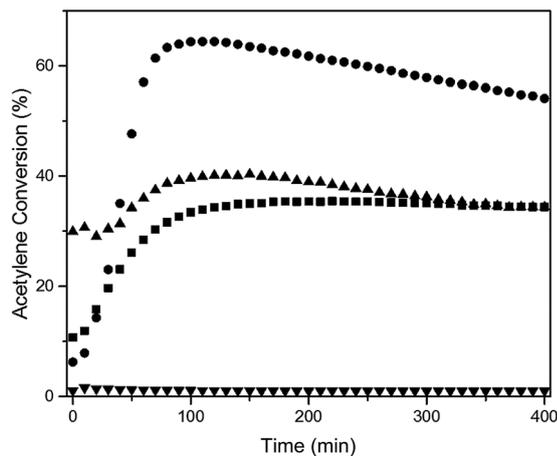
Fig. 3 Catalytic performance of the supported gold catalysts as a function of reaction time, the carbon supported gold catalysts prepared from water, HCl, HNO₃ and *aqua regia*, are labelled as Au/H$_2$O/C (▼), Au–HCl/C (▲), Au–HNO$_3$/C (■) and Au–AR/C (●), respectively (reaction conditions: 150 mg catalyst, 5 mL min^{-1} C$_2$H$_2$, 6 mL min^{-1} HCl and 10 mL min^{-1} N$_2$, 185 °C) (Reproduced from ref. 51 by permission of The Royal Society of Chemistry.).

water preparation. Interestingly, catalysts prepared with water are completely inactive. The most active catalyst was prepared dissolving HAuCl$_4$ in an *aqua regia* solution. This catalyst shown a long induction period, which was hypothesised to be associated with development of the active gold species on the surface of carbon support and the gradual generation of the active sites.

Alternative catalyst preparation methods

Despite the demonstrated high activity of the Au/C catalyst made with *aqua regia*[25] there are several disadvantages which make its industrial application ineffective; first of all, the use of *aqua regia* itself represent a significant concern both from an economic and a technical point of view. The handling of concentrated acid solutions would be highly problematic from an engineering and processing perspective. In addition, this catalyst showed poor stability during extended time on line due to the acid sites on the catalyst and the dynamic nature of the surface Au species.[5,49]

As mentioned previously, attempts at using alternative solvents to *aqua regia* lead to ineffective catalysts.[51] In 2010, Lin *et al.* discovered a new "*organicus liquor regius*" prepared by adding organic compounds to SOCl$_2$, also named Organic *Aqua Regia* (OAR).[52] This simple mixture of thionyl chloride (SOCl$_2$) and some organic solvents/reagents can dissolve noble metals rapidly under mild conditions. Zhao *et al.* employed this alternative solvent for the preparation of active Au/AC catalysts for the hydrochlorination of acetylene.[53] In particular, OAR has been use to activate inactive Au/AC (activated carbon) catalysts prepared from a water solution of the metal precursor (Au(H$_2$O)/AC). The used catalyst can also be reactivated *via* OAR treatment, as already demonstrated to be the case of the normal *aqua regia* preparation.[54] Although, the use of OAR as an alternative solvent is encouraging, at this stage, does not provide a real alternative to more commonly used *aqua regia* preparation methods.

Another important aspect to take in consideration for the practical application of Au/C catalysts is the price of gold, which in the last three years fluctuated around a value of 40 000 USD per kg.[55] For this reason, and also to minimize the reaction exotherm in large fixed bed reactors, a low Au metal loading (<0.25 wt%) is desirable. Johnston *et al.*,[5] showed that it was not possible to decrease the Au loadings of Au/C catalysts prepared from *aqua regia* below *ca.* ≤0.3% without experiencing difficulties with the catalyst activation. For all these reasons, in the last few years, interest has moved towards the identification of a different gold precursor complex to HAuCl$_4$, to produce a catalyst with greater stability under reaction conditions and good activity, even at low metal loading.

Huang *et al.* reported the application of an highly stable Au(III)/Schiff-based catalyst in acetylene hydrochlorination reaction.[56] The stability of this catalysts, was attributed to the presence of the 1,10-phenanthroline ligand that partially inhibited the reduction of the active component of the catalyst. More recently, Wei *et al.* reported an interesting low content Au catalyst for hydrochlorination of acetylene,[57] made by incipient-wetness impregnation of a Au–thiocyanate complex. The enhanced stability of this catalyst was attributed to the enhanced stability of cationic Au species under reaction conditions. This catalyst was also utilised in a pilot experiment which has been running for over 3000 h, maintaining high stability and activity. Unfortunately, the toxicity of the thiocyanate makes its industrial application unsustainable.

A series of sulphur-containing ligands has been employ for the preparation of cationic gold complexes by then immobilized on activated carbon from aqueous solution and utilise as catalysts for acetylene hydrochlorination.[58] The choice of sulphur-containing ligands, *e.g.* Au–thiosulfate, Au–thiourea, Au–thiocyanate, has been made based on the assumption that soft donor atom can better stabilize cationic gold in comparison with electronegative/hard donor ligands, producing catalysts which are more active and stable than the one derived from AuCl$_3$-type precursor. This superior activity allowed Au loading down to ∼0.1% to be utilised while still achieving satisfactory productivity. This catalyst is now marketed as part of the Johnson Matthey's PRICAT catalysts and is utilised in the only mercury-free process (DAVY VCM process) presently accessible for license.[59] We direct the reader to a review article that details this catalysts development from discovery to commercialisation.[5] An interesting point to note is that the development of this commercial catalyst was based on the theory that the active site for the catalyst is cationic Au.

Determination of the active site: past hints of cationic Au

As with many heterogeneous catalysts, there has been significant discussion about the reaction mechanism and the active site of Au catalysts in the acetylene hydrochlorination reaction. The general consensuses found in the literature is that the active site is cationic Au; based on both experimental and theoretical observations. However, until recently the experimental data has not been unambiguous or conclusive beyond doubt, due to the observed presence of metallic Au, in conjunction

with cationic gold from most characterisation techniques. The observed presence of Au(0) has resulted in a range of postulated active species, from Au(0) clusters[60] to cationic Au species at the surface of Au(0) and/or at the Au(0) metal nanoparticle–carbon support interface.[50,61] Further to discussion on the presence and location of cationic Au species, the oxidation state of the cationic Au has been debated, with both Au(I) and Au(III) being postulated as the active species. In addition, the mechanism of the reaction can be explained as a redox process involving Au(I) and Au(III) species or π-coordination of acetylene to Au(III) followed by HCl addition.[50] In the following few paragraphs we will discuss in detail the evidence for cationic Au being the active site and the complications and apparent inconsistencies found from catalyst characterisation.

The importance of cationic Au in the acetylene hydrochlorination reaction is clear from when Au was first predicted by Hutchings to be highly active;[23] from correlation of the standard electrode potential of a range of other metal cations with activity from an earlier study by Shinoda *et al.*[21] The correlation can be rationalised that the cations studied where predominantly divalent and that the reaction with acetylene involves a two-electron process. Indeed the high activity of Au supported on carbon was validated experimentally lending support to the theory that Au(III) species where the active site for the reaction. Later Conte *et al.* correlated the activity of a range of carbon supported metal chloride catalysts with the standard electrode potentials (calculated from the reduction potentials of the metal chlorides to metal). An even stronger correlation was found between activity and standard electrode potential affirming that Au(III) chloride was the active species.[29]

Experimental evidence of the presence of cationic Au in active catalysts, predominantly that of Au(III), has been provided by several characterisation techniques; namely ^{197}Au Mössbauer spectroscopy,[49] X-ray photoelectron spectroscopy (XPS)[62–64] and temperature programmed reduction (TPR).[61,65,66] However, as stated previously most of these techniques either directly show or suggest the coexistence of metallic Au in these samples, which is further corroborated by the frequent observation of metal nanoparticles from several transmission electron microscopy (TEM) studies.[29,51,56] Often the assertion that cationic Au is the active species is that, after catalyst deactivation with prolonged reaction times, the fraction of metallic Au has increased according to XPS and Mössbauer spectroscopy. Complementary with these observations is that several studies have demonstrated catalytic reactivation though oxidative treatments, either by post reaction treatment in *aqua regia* or online by feeding HCl, Cl$_2$, NO and N$_2$O.[30,54,67] XPS and Mössbauer spectroscopy were again used to demonstrate an increase in the fraction of cationic Au in these reactivated catalysts.

Each characterisation technique, while broadly supporting the presence and importance of cationic Au, provides subtlety different information and suffers from difference experimental issues. Comparison of the information that each technique provides and its limitations can allow us to build up a more refined understanding of the role of cationic Au

and apparent presence of metallic Au in the acetylene hydrochlorination catalysts.

Mössbauer spectroscopy, performed by Nkosi *et al.*,[49] of a 2% HAuCl$_4$/C catalyst (prepared using an *aqua regia* solution) before reaction, after deactivation and then after regeneration provides some of the earliest evidence for cationic Au being the catalytically active species in the acetylene hydrochlorination reaction (Fig. 4). The fresh catalyst was found to comprise of both metallic Au, signified by a single line with an isomer shift of -1.23 mm s^{-1}, and a species with a quadrupole doublet
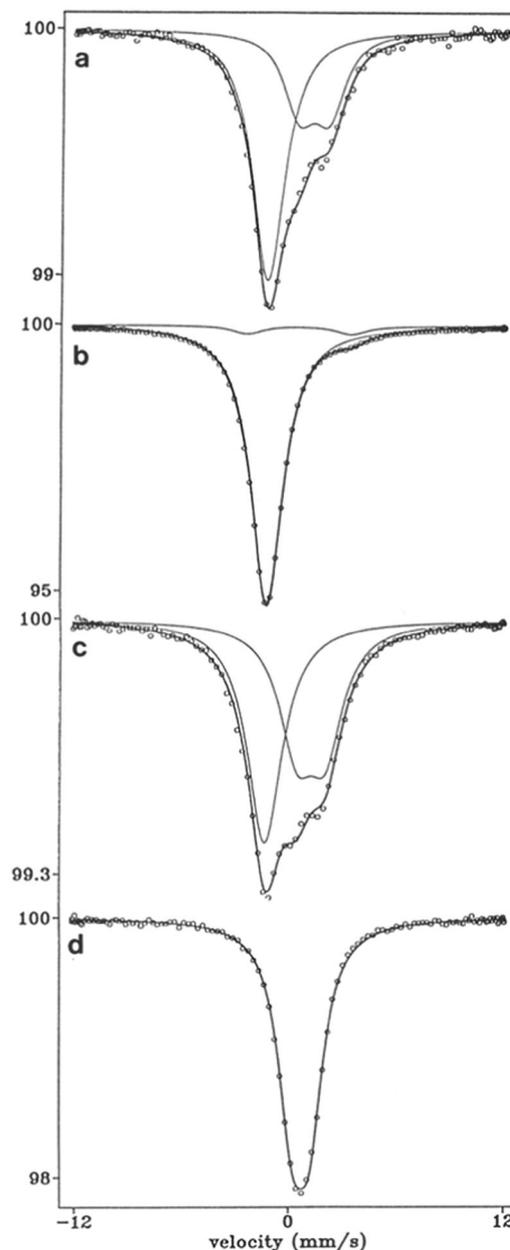

Fig. 4 ^{197}Au Mössbauer spectra of (a) 2% HAuCl$_4$/C absorbed on activated carbon from an *aqua regia* solution, (b) the same catalyst after deactivation at 180 °C for 6 h (GHSV = 1140 h^{-1}, C$_2$H$_2$: HCl = 1 : 1.1), (c) a sample of the same type after reactivation by boiling in *aqua regia*, and (d) HAuCl$_4$·xH$_2$O (Reproduced from ref. 49 by permission of Elsevier.).

with an isomer shift of +1.65. This species was attributed to adsorbed AuCl$_4^-$, due to its closeness to the spectrum of crystalline HAuCl$_4$ with an isomer shift of +0.71. Quantification from Mössbauer spectroscopy can be challenging as the *f*-factor (recoilless fraction) is substantially different for Au metal and cationic Au species. Attempts to determine the mass fraction of the two species, by standardisation using a gold-vanadium alloy, suggested that the signal from Au metal component is significantly enhanced and that the mass of Au metal is approximately only 16 wt%, while its peak area in the Mössbauer spectrum was 63%. The remaining 84% of the gold was attributed to Au(III)Cl$_4^-$ species, although the area under the spectrum was only 37%.

A catalyst collected after the acetylene hydrochlorination reaction, where significant but not complete deactivation was observed, was measured and the Mössbauer spectrum collected was almost completely that of metallic Au, but with an additional weak, but well defined, absorption line at +3.49 mm s^{-1}. Nkosi *et al.* speculated that this could be associated with a Au(I) species but that confident assignment was not possible and therefore quantification was also not possible (due to an unknown *f*-factor). Fascinatingly, if the same *f*-factor as AuCl$_4^-$ is assumed this unknown Au(I) species could account for 30% by mass of the Au. Reactivation of the catalyst in boiling *aqua regia* resulted in a recovery of the Au(III)Cl$_4^-$ species and therefore these where concluded to be associated with the active site. The observation of apparent Au(I) species, recorded by Nkosi *et al.* in 1991, which was acknowledged to be potentially relevant in the catalytic process, was not considered again until 2016, in an in-depth *ex situ* XPS and TEM study by Liu *et al.*[51]

XPS is one of the most commonly used characterisation techniques for supported Au and Au bimetallic catalysts[68] with Au based acetylene hydrochlorination catalysts being no exception. Most recent publications on Au acetylene hydrochlorination catalysts rely on XPS to characterise the Au oxidation state of fresh and used samples.[51] As previously mention most XPS characterisation has shown the presence of two species, Au(0) and Au(III) (Fig. 5a). In common with Mössbauer spectroscopy the predominant signal from XPS, for almost all catalysts, is metallic Au(0); with a small but definable signal attributed to Au(III) being present. However, unlike in analysis of Mössbauer spectroscopy, XPS does not show significantly different extinction coefficients for different species, suggesting that almost in all cases Au(0) is the predominant species. The observation of high Au(0) content in catalysts from XPS is the primary reason for the repeated assertion, that while cationic Au(III) is the active site, it must exist only on the periphery of Au(0) nanoparticles.[50,61] The observation of only Au(0) in some XPS studies has led some researchers to suggest that Au (0) clusters are themselves the active site.[63]

The ratio of Au(0):Au(III) has been found to vary significantly between studies; for novel catalyst preparations but also in different studies of the original HAuCl$_4$/*aqua regia* catalysts. These differences can, in part, be explained by the sensitivity of Au species the preparation method, such as with drying temperature and HCl:HNO$_3$ ratio along with the effect of Au
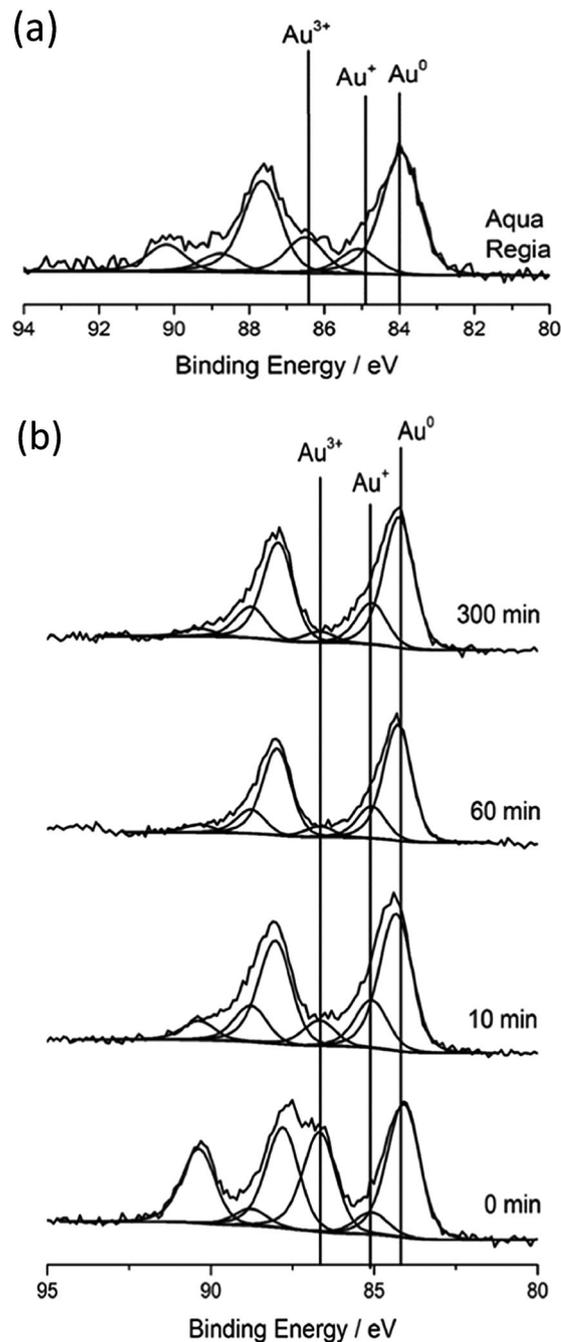

Fig. 5 *Ex situ* recorded X-ray photoelectron Au(4f) spectra for *aqua regia* prepared Au/C catalyst (a) freshly prepared and (b) taken from the reactor at different times on line (reaction conditions: 150 mg catalyst, 5 mL min^{-1} C$_2$H$_2$, 6 mL min^{-1} HCl and 10 mL min^{-1} N$_2$, 185 °C) (Reproduced from ref. 51 by permission of The Royal Society of Chemistry.).

loading. Yet other factors associated with the XPS characterisation method itself, which is frequently not mentioned or discussed in many publications on Au acetylene hydrochlorination catalysts, can influence the apparent Au concentration and oxidation state. Firstly we consider the most obvious limitation of XPS; that it is a surface/near surface technique, due to the limited escape distance of emitted electrons. One publication by Conte *et al.*

noted that the content of Au(III) relative to total Au content in various Au/C catalysts differed substantially between XPS and TPR analysis.[61] The TPR analysis was found to have higher Au(III) content by approximately 20%, relative to XPS values. Given that XPS is a surface technique, they ascribed the discrepancy to subsurface Au(III) not detected by XPS.[61] It should be noted that TPR can demonstrate that Au reducible species are present on the catalyst and represents a relatively simple diagnostic tool for screening catalysts. However, the oxidation state and nature of the cationic Au site can only be speculated from this technique.

The second consideration in regard to XPS analysis, which is often overlooked, is that X-ray radiation at typical XPS incident photon energies (1.25–2.98 keV) can cause significant photo-reduction of cationic metal species. Several reports have shown that $AuCl_4^-$ salts undergo photo-reduction to metallic Au over a short time period, as shown in Fig. 6.[69–72] The extent of photo-reduction will be dependent on a number of parameters, including the incident photon energy, beam flux and irradiation time. While the extent of beam damage is dependent on procedure and the instrument used, we now consider that this photo-reduction effect is strongly responsible for the substantially lower cationic Au(III) content from XPS, relative to other techniques such as Mössbauer spectroscopy (when a suitable f-factor is taken into account) and TPR analysis. Indeed it may be considered that the presence and importance of metallic Au(0)

nanoparticles has been substantially over represented due to photo-reduction in XPS analysis.

While XPS clearly has its limitations, when measured and analysed appropriately it can still provide valuable (if not highly quantitative) information on the active site of the catalyst. Although a minor component in XPS spectra, the correlation of the presence of cationic Au with active catalysts and its absence with deactivated catalysts clearly shows the importance cationic Au in the reaction.[50,54] Further to this, recent studies have shown through carful peak fitting that Au(I) species may well be present in freshly prepared catalysts. Liu et al.[51] also showed that during the induction period of several 1 wt% Au/C catalysts, Au(I) species remain present and that such species may be associated with the reaction. It is important to note that these samples were characterised *ex situ*, in that samples were removed from the reactor at various times during the induction period (Fig. 5b).

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) has, as with many other studies of heterogeneous catalysts, been used in the study of Au acetylene hydrochlorination catalysts. Conventional TEM analysis predominantly showed metal nanoparticles[50,73] however these instruments couldn't provide significantly more information than this, as the postulated surface Au(III) on the metal nanoparticles would be below the possible resolution of many instruments. However, recent advances in both instrument
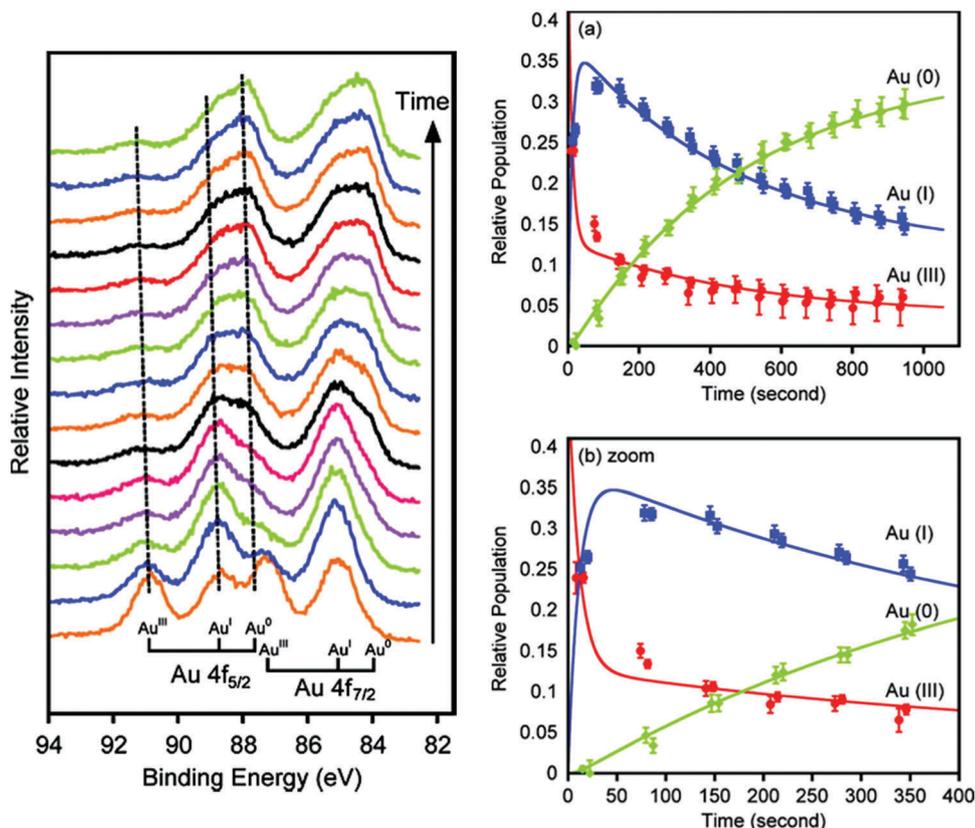

Fig. 6 Photoreduction kinetics of NaAuCl₄. (left) XPS spectra of NaAuCl₄ as a function of time under X-ray exposure. (right) Population of different Au oxidation states as a function of X-ray exposure time (a-full reaction time and b-first 400 s) (Reprinted with permission from ref. 69 Copyright (2011) American Chemical Society.).
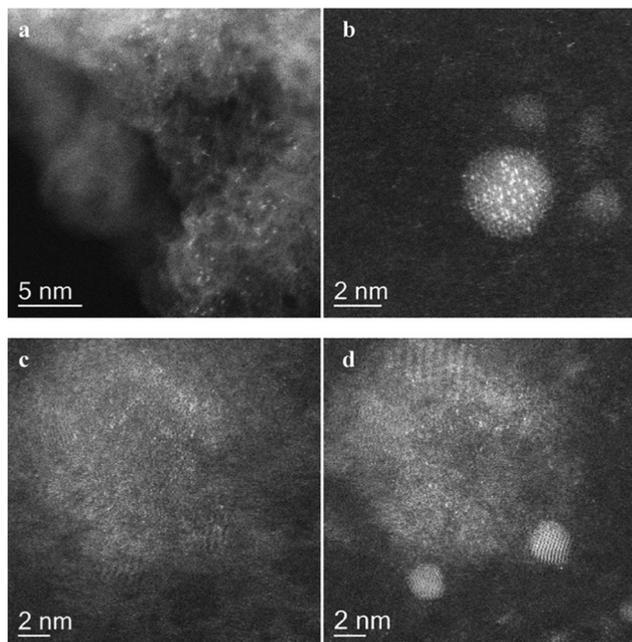
Fig. 7 Representative HAADF–STEM images of an *aqua regia* treated Au/C catalyst. Images show Au speciation below the detection limit of less advanced STEM or TEM equipment. (a) Atomically dispersed Au over carbon support; (b) discreet particles containing Au and Cl; (c) atomically dispersed Au films; (d) atomically dispersed Au films that form nano-particles upon extended electron beam irradiation (Reproduced from ref. 51 by permission of The Royal Society of Chemistry.).

resolution and the control of beam damage has allowed for STEM to provide far more detailed analysis of these Au catalysts (Fig. 7a–d). A key example of this is from the previously mentioned study by Liu *et al.*[51] on the importance of Au(I) species and the evolution of the catalyst during reaction. Firstly, active catalysts prepared using *aqua regia* solvents were found to contain almost no discreet Au nanoparticles, but atomically dispersed Au species. It was concluded, but not exclusively proven, that the cationic Au(III) chloride and Au(I) chloride was not associated with Au(0) nanoparticles, but existed as cationic species directly bound to the carbon support (see Fig. 7c). Secondly, and very importantly, these surface cationic species were not stable to prolonged electron beam exposure (see Fig. 7d). Again we conclude that appropriate care and attention to the effects of damage caused by the characterisation method is essential to observing the relevant cationic Au species responsible for activity.

In summary, a range of characterisation techniques has hinted at the presence and importance of cationic Au(III) or/and Au(I) chloride species in the acetylene hydrochlorination reaction. Sample damage during characterisation or lack of instrument resolution has limited our capability of understanding the detailed nature of these cationic species. Further to this, all techniques discussed so far have been performed *ex situ*, in that the sample has been removed from its reaction environment and studied under often quite different conditions. While the importance of this may not be clear to readers from outside the field, there has been a growing consensuses within the heterogeneous catalysis community that the study of catalysts outside their

reaction environment may lead to us to missing vital information on the catalytically active site. Heterogeneous catalysts have been shown to have structures that are highly dynamic and change considerably under reaction conditions, through a growing research field dedicated to *in situ* or *operando* characterisation of catalysts under such conditions. We direct the reader, interested in the details of such characterisation methods, to a number of excellent reviews on the topic of *in situ*/*operando* characterisation of catalysts.[74–76]

Recent advances in the elucidation of the active site

Past hints of cationic Au and the development and commercial validation of a catalyst based on Au–thiosulfate strongly suggests that cationic Au is the active species in this reaction. To answer questions raised over 30 years of research into these Au/C materials, we recently performed the first *in situ* X-ray absorption Fine Structure (XAFS) spectroscopy under operating conditions, at Diamond Light Source (UK).[77] XAFS has been widely applied to study heterogeneous and homogeneous catalysts,[78] providing information on the electronic and structural properties[79] of catalysts and can be applied while working at realistic reaction conditions through the design of suitable reactor systems. In particular, from the normalized Au L_3-edge XANES, information on Au speciation can be determined from the white line, a sharp intense peak originating from electronic transitions before the adsorption edge that can be indicative of Au oxidation state by comparison with appropriate standards (Fig. 8A and B).[80,81]

Photoreduction, while a serious issue with XPS analysis, is less significant with the XAFS technique. The absence of this photo-reduction phenomena during XAFS analysis can appear to be counter-intuitive, as this technique also subjects the sample to an X-ray beam, but with an incident energy of *ca.* 11.9 keV compared to an Al source XPS incident energy of 1.487 keV. However, the difference in photo-reduction rates can be explained when considering the probability of photon absorption as a function of incident energy (Fig. 9). Taking this into account the probability of the incident X-ray interacting with matter is an order of magnitude greater with XPS than XAFS (at the L_3 Au edge). In addition, the absorption cross section for the C support is considerably more significant at lower incident energies associated with XPS. As emitted electron yield (scattered and Auger) correlates with atomic number,[82] at an XPS incident energy of 1.487 keV the carbon will emit high yields of hot electrons that can cause significant damage to surface Au species.

A series of Au/C materials were prepared with *aqua regia*, HNO_3 or H_2O which were analogous to the previously studied materials. Also a Au/C catalyst prepared using a Au(I)–thiosulfate precursor, analogous to the industrially validated catalyst was analysed. The XAFS study of these catalysts under dilute acetylene hydrochlorination reaction conditions was performed while following the acetylene conversion and VCM production by mass spectrometry. This revealed the highly active catalysts (Au/C-AR, Au/C-HNO_3 and Au/C-S_2O_3) comprise almost entirely of single site cationic Au entities with no evidence of Au nano-particles and lack of Au–Au scattering interactions categorically proving that the active form of these catalysts is cationic Au.
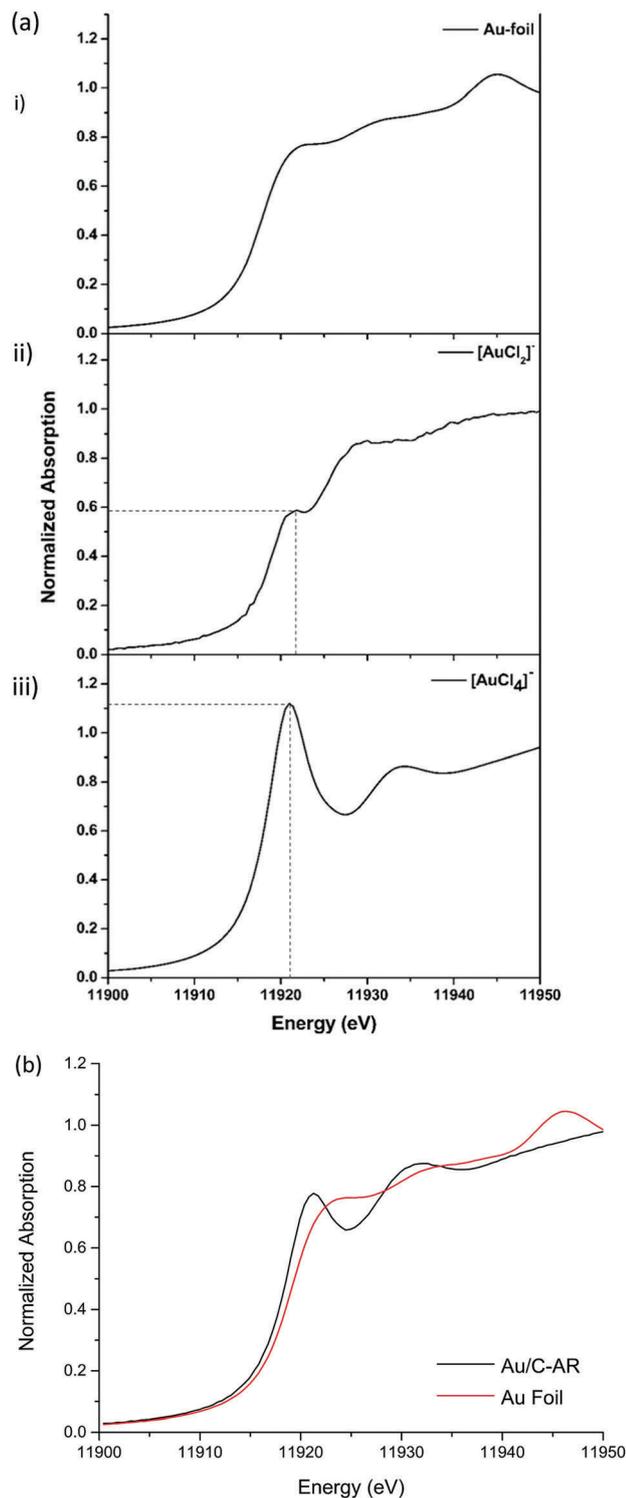
Fig. 8 (a) Au L$_3$-edge XANES region for the Au standards used: (i) Au(0) gold foil, (ii) Au(I) [AuCl$_2$]$^-$ and (iii) Au(III) [AuCl$_4$]$^-$. For the two cationic Au standards, the white line intensity values are ∼1.1 and ∼0.6 respectively. (b) *Ex situ* Au L$_3$ edge-normalized XANES spectra of the Au/C-AR catalyst and a gold-foil reference material (Reproduced from ref. 77 by permission of the American Association for the Advancement of Science.).
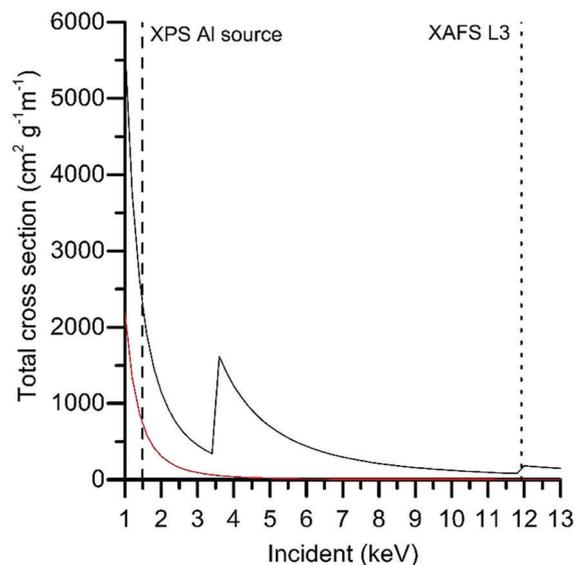

Fig. 9 Photo-reduction of gold chloride species during under X-ray illumination. X-ray absorption cross-section with respect to incident energy for Au (black line) and C (red line) (Reproduced from ref. 77 by permission of the American Association for the Advancement of Science.).

states present supporting the postulated redox mechanism between Au(I)–Au(III). The catalysts composed predominantly of metallic-Au nanoparticles (Au/C-H$_2$O), by both XRD and XAFS analysis, was almost inactive with no improvement with reaction time-on-line.

Analysis of the active catalysts, before introducing the reaction mixture already demonstrates interesting information about the composition of the freshly prepared materials. *Ex situ* scanning transmission electron microscopy – high-angle annular dark-field (STEM-HAADF) analysis and X-ray powder diffraction (XRD) of the Au/C-AR catalyst showed that this material comprises of highly dispersed isolated Au species; in contrast the Au/C-HNO$_3$ sample showed lower Au dispersion, with some evidence of metallic Au particles. However, both catalysts show significant contributions from Au–Cl entities at the extended X-ray absorption fine structure (EXAFS) analysis, and the X-ray absorption near edge structure (XANES) indicate a significantly oxidized Au speciation.

Also the STEM-HAADF imaging studies of the Au/C-S$_2$O$_3$ catalysts showed the presence of atomically dispersed Au on the C support, with only a few dimeric like species, with the EXAFS analysis showing a catalyst comprised predominantly of Au(I). Interestingly, once the reaction temperature was reached the acid media prepared catalysts, are mainly consisting of Au(I) chloride-like species due to the thermal decomposition of Au(III) chloride species. The introduction of the reactant gases caused an instantaneous increase in the white line high, corresponding to the oxidation of the Au(I) chloride-like species to Au(III) chloride, which gradually moved back toward a stable value corresponding to a the Au(I)/Au(III) ratio of ∼1.5, confirming the previous prediction regarding the development of the active sites on the surface and the observed induction periods of some catalyst samples.
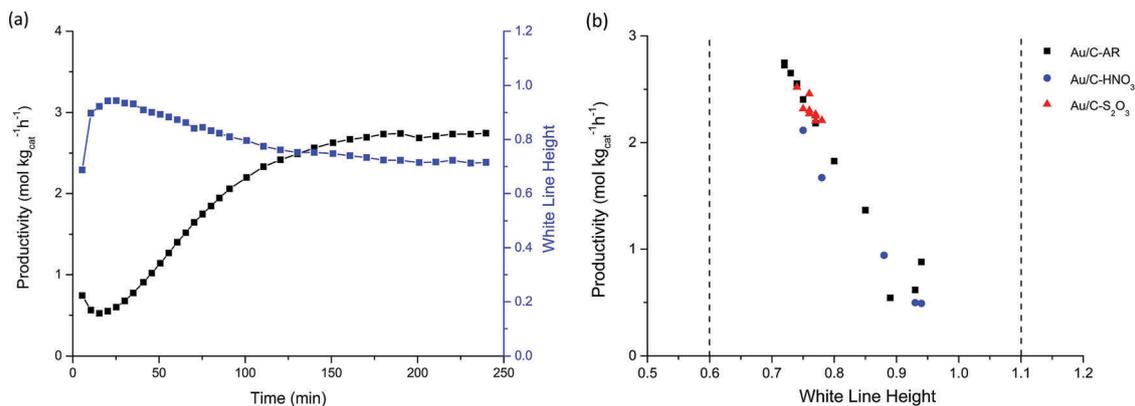
The activity of the best performing catalysts correlates with the ratio of Au(I) : Au(III) present and all catalysts have both oxidation

Fig. 10 VCM productivity and *in situ* characterization the catalysts as a function of time-on-line. (a) Catalytic performance of the 1% Au/C-AR as a function of time-on-line (black) and the change in normalized white-line intensity (blue) as a function of reaction time. (b) Correlation between the variation in the Au L$_3$ white-line intensity and VCM production of the three active catalysts (Au/C-AR, Au/C-HNO$_3$ and Au/C-S$_2$O$_3$) (Reproduced from ref. 77 by permission of the American Association for the Advancement of Science.).

Notably, the white-line intensity correlated strongly with the VCM productivity of the catalyst (Fig. 10a and b).

The change in white line intensity can also be correlated with the EXAFS-derived Au–Cl coordination number (CN) during the time-on-line, showing the changes in the absorption edge intensity observed in the Au L$_3$-edge XANES is directly associated with changes in the Au–Cl speciation. The same correlation between Au L$_3$-edge white-line intensity and catalytic activity found for Au/C-AR materials was observed for both Au/C-HNO$_3$ and Au/C-S$_2$O$_3$. The latter, that was a more stable and active catalyst under reaction conditions than those made with the HAuCl$_4$ precursor, had no induction period. However, at the steady-state both its catalytic activity and the corresponding the white-line intensity was similar to that of the steady-state activity of the Au/C-AR catalyst.

Fig. 10b shows that a correlation can be made between the variation in the Au L$_3$ white-line intensity and VCM production of the three active catalysts (Au/C-AR, Au/C-HNO$_3$ and Au/C-S$_2$O$_3$). This correlation shows the highly dispersed Au(I) species are crucially important for this reaction together with a population of highly dispersed Au(III) like species strongly suggesting that the activity is related to a Au(I)–Au(III) redox couple. Analysis of the spent active catalysts, confirmed the prevalence of atomically dispersed Au species still predominantly composed of cationic AuCl$_x$. This work highlighted the importance of isolated cationic Au chloride species and their ability to catalyse a redox mechanism and clearly demonstrates that the active form of these catalysts can be thought of as analogous to the homogenous single site Au cations.[83] At no stage during the reaction of highly active catalysts were significant populations of Au–Au distances indicative of the formation of metallic Au nanoparticles observed. This combined with the observations that catalysts containing Au nanoparticles were inactive firstly indicates that we should treat *ex situ* characterisation of highly active catalysts with high populations of Au nanoparticles with caution until the issues beam damage during XPS is addressed and secondly that the formation of metallic Au particles is likely to be the predominant deactivation mechanism of these

catalysts as predicted previously when studies were conducting under acetylene rich environments.[49]

Single site catalysts – a perspective

In recent times the re-examination of what is thought of as traditional supported metal heterogeneous catalysts by high resolution HAADF-STEM with sub nm resolution and other spectroscopic techniques has revealed the hidden complexity of many of these materials. In addition to the presence of metallic nanoparticles a whole array of sub nm structures are present which may or may not contribute to the activity of the catalyst.[84,85] The smallest of these structures are single metal atoms anchored to the support materials and a growing research field exists to design and fabricate these so called single atom catalysts (SACs).[86–88] The benefit of carrying out a reaction with single sites is that the dispersion of the active metal is maximised as every atom is taking part in the catalysis. However the challenge is to maintain this dispersion as single atoms have high surface energy and coalesce if they become mobile on the support materials. Despite this; single atoms have been demonstrated to be active for a range of oxidation and reduction reactions,[89–97] in addition to being active in industrially relevant reactions like water gas shift[98] and also in electrochemical systems which have all been extensively reviewed elsewhere.[99]

Single atom catalysts provide intriguing materials to allow reaction mechanisms and metal speciation to be probed spectroscopically with less diversity of potential active sites compared to nanoparticle catalysis. The concept of a uniform heterogeneous catalysis was introduced by Thomas in the 1988 (roughly the time that Au was validated as the best catalyst for acetylene hydrochlorination) while referring to isolated metal sites substituted into a crystalline frameworks such as zeolites as single atoms catalysts.[100] In fact all isomorphous substitution into porous frameworks could be thought of as single site catalysis. The advancements being currently made in the field provides a significant opportunity to probe the identity of the optimum nanostructures needed to carry out target reactions, while it should be considered the target of utilising single sites

might not be the best option for every reaction and these materials could easily evolve into more active structures under reaction conditions. An example of this is the exceptional activity reported in many studies relating to low nuclearity clusters of metal. In fact in some cases it has been shown that while a catalyst consisted of atomically dispersed Au no activity was observed until clusters were formed under reaction conditions and activity was again diminished when nanoparticles began to form again emphasising the importance of characterising these systems as the reaction is happening.[101,102]

Through detailed analysis of previously reported catalysts a whole landscape of potential active species have now been identified including atoms, clusters, monolayers, bilayers and there co-existence is likely to result in a hierarchy of species with each species being active to some extent. Care must be taken to assess the true nature of the most active sites in real catalysts and or indeed when assessing single atom catalysts. The populations of active sites also need to be taken into account as an atomic dispersion of metal will have a significantly higher numerical number of active sites and care should be taken to asses activity in terms activity per available active site when comparisons are made between single atom catalysts and "traditional" heterogeneous catalysts, determination of populations of species in real catalyst is not trivial due to their complexity.

Our recent observation of catalytic turnover with single site Au(I) and Au(III) species for acetylene hydrochlorination demonstrates the importance of these species in this specific case. A clear analogy can be made between this catalyst and homogeneous Au catalysts, which have been highly successful in alkyne chemistry.[103] The chemistry of Au(I) and Au(III) homogeneous catalysts has been studied in depth through theoretical studies[83] and also *in situ* XAFS studies;[104] which can provide a great deal of understanding and aid the rational improvement of Au acetylene hydrochlorination catalysts.

When considering the "single-site" Au acetylene hydrochlorination catalyst, or other atomically dispersed heterogeneous catalysts, as being analogous to homogeneous catalysts, it is clear that not only the metal nuclearity is important but also the metal valency and the nature of associated ligands. In general, the latter two concepts have not been considered sufficiently in the field of atomically dispersed heterogeneous catalysis. An exception to this is the work of Gates and co-workers, which provides an excellent example of an attempt at rational design, including the concepts of ligand effects and support interactions, of which they refer to as supported molecular metal catalysts.[105] The nature of ligand choice in Au acetylene hydrochlorination has been partially investigated, with catalyst preparations using Schiff base Au complexes, thiourea complexes and a range of other Au(III) and Au(I) sulphur containing complexes.[5,57,62,106] However, no significant attempt to characterise these complexes after deposition on the carbon support or their retained presence during reaction has been made to date. Studies monitoring metal–ligand coordination and nature during reaction are not found frequently across the entire field of single-site catalyst and represents to us an important aspect of future research in the field.
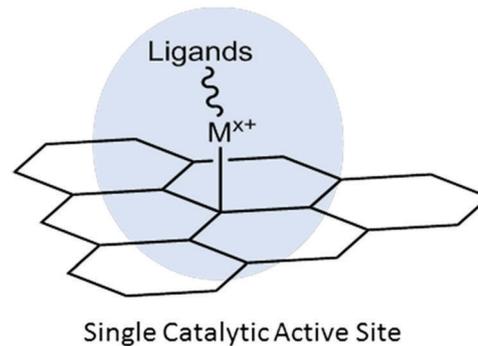

Fig. 11 Schematic of a supported single atom catalyst (SAC) consisting of charged isolated individual atoms coordinated with ligands and strongly anchored on the support.

A field within heterogeneous catalysis that currently receives significant attention and research is the study of metal–support interactions and their impact on catalytic activity, selectivity and stability;[107–109] often this is within the context of metal nanoparticle–support interactions. The importance of the support on the structure and stability of atomically dispersed catalysts should be considered equally, if not more, important. It is fairly evident that without a strong Au–C interaction the acetylene hydrochlorination catalyst would rapidly deactivate through the formation of metal nanoparticles. Gates and co-workers refer to metal–support interactions in atomically dispersed catalysts as effective ligand–metal interactions (with the support acting as a functioning ligand).[108,110] Indeed, we consider that the role of carbon on the active cationic Au centre in the acetylene hydrochlorination reaction as still requiring further understanding. In addition, we consider the role of support structures and interactions with the metal centres and other ligands in the broader field of single site catalysis to be a research area that has to date received insufficient attention particularly in the fields of electro catalysis where the conductivity of the support is key to facilitating redox reactions.

A summary of the importance of the constituent parts of atomically dispersed/molecular heterogeneous catalysts, comprising of metal valency, ligand effects, metal geometry and extended ligand structures (supports) influencing steric effects and charge transfer, leads to inevitable comparison with enzymatic catalysis (Fig. 11). The extent of our control of these components is far less than observed in an enzyme and yet the concept itself is valid. To gain greater control of atomically dispersed/molecular catalyst selectivity and activity we should consider the effect of support and ligand choice, then monitor their evolution under operating conditions. Further development of acetylene hydrochlorination catalysts and other single site catalysts should be thought of in the context of designing of a catalytically active site, rather than simplistically striving to make single isolated atoms.

Conflicts of interest

There are no conflicts to declare.

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