Discovery, Development, and Commercialization of Gold Catalysts for Acetylene Hydrochlorination

Peter Johnston,[†] Nicholas Carthey,[‡] and Graham J. Hutchings*[,§]

[†]Process Technologies, Johnson Matthey plc, Orchard Road, Royston, SG8 5HE, United Kingdom
[‡]Johnson Matthey Technology Centre, Blounts Court, Sonning Common, RG4 9NH, United Kingdom
[§]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, United Kingdom
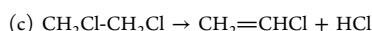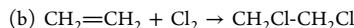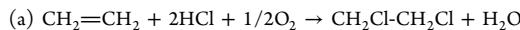
ABSTRACT: Vinyl chloride monomer (VCM) is a major chemical intermediate for the manufacture of polyvinyl chloride (PVC), which is the third most important polymer in use today. Hydrochlorination of acetylene is a major route for the production of vinyl chloride, since production of the monomer is based in regions of the world where coal is abundant. Until now, mercuric chloride supported on carbon is used as the catalyst in the commercial process, and this exhibits severe problems associated with catalyst lifetime and mercury loss. It has been known for over 30 years that gold is a superior catalyst, but it is only now that it is being commercialized. In this Perspective we discuss the use and disadvantages of the mercury catalyst and the advent of the gold catalysts for this important reaction. The nature of the active site and the possible reaction mechanism are discussed. Recent advances in the design and preparation of active gold catalysts containing ultralow levels of gold are described. In the final part, a view to the future of this chemistry will be discussed as well as the possible avenues for the commercial potential of gold catalysis.

■ INTRODUCTION

Vinyl chloride monomer (VCM) is a major commodity chemical with over 40 million tons being produced annually. It is the monomer for the production of polyvinyl chloride (PVC) which is a major nonbiodegradable polymer with numerous uses, particularly in the construction industries, due to its high resistance to photo and chemical degradation. PVC is the third highest selling polymer at this time. VCM has been manufactured on a large scale since the 1950s when the initial process was based on the hydrochlorination of acetylene using mercuric chloride supported on carbon as the catalyst. Acetylene is produced from coal via calcium carbide as an intermediate. The HCl undergoes electrophilic addition across the acetylene triple bond.

$$HC \equiv CH + HCl \rightarrow H_2C = CHCl$$

Subsequently, a newer route, often referred to as the balanced process, was developed in which ethene is converted to ethylene dichloride (EDC) via chlorination and oxychlorination reactions; thereafter the EDC is thermally cracked to VCM.

(a) $CH_2 = CH_2 + 2HCl + 1/2 O_2 \rightarrow CH_2Cl\text{-}CH_2Cl + H_2O$

(b) $CH_2 = CH_2 + Cl_2 \rightarrow CH_2Cl\text{-}CH_2Cl$

(c) $CH_2Cl\text{-}CH_2Cl \rightarrow CH_2 = CHCl + HCl$

Within western world economies in recent decades, the commercial production of VCM has shifted to be almost exclusively from ethene, as this feedstock became widely available from the increased availability of oil.

However, the availability of inexpensive coal in China has led to a resurgence in the acetylene route, and at present over 13 million tons of VCM are manufactured annually in China from acetylene hydrochlorination using the mercury catalyst. This has prompted a lot of interest in this reaction especially in the design of nonmercury catalysts. In this Perspective we discuss the use and major disadvantages of the mercury catalyst and also show that gold is now rapidly becoming the new catalyst of choice for the production of this key commodity polymer.
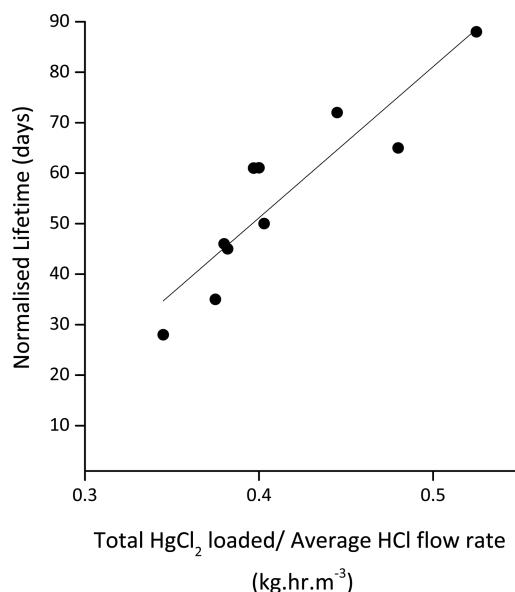
Acetylene Hydrochlorination Using Mercury Catalysts. Mercury was selected as a catalyst at the outset of VCM production from acetylene. The catalysts use a high area activated carbon ($1000-2000$ m^2 g^{-1}) on which mercuric chloride is deposited by adsorption from aqueous solution and typically 10 wt % mercuric chloride is utilized.[1] High surface area activated carbons are effectively the support of choice since they remain stable in the presence of HCl at high temperature, maintaining a high surface area. In addition, activated carbon is very effective in adsorbing HgCl$_2$. Consequently, virtually all studies on acetylene hydrochlorination utilize carbon as the support. While it has been widely used as a catalyst over the last seven decades, it has a number of major disadvantages,[1−3] namely the facile volatility of mercuric chloride at the reaction temperature, which results in a high loss of mercury from the catalyst leading to very short catalyst lifetimes in commercial use, and furthermore, mercury may catalyze the secondary addition of HCl to vinyl chloride leading to an initial loss in selectivity. The latter of these disadvantages may be overcome with use of a downstream ethane dichloride cracking unit to obtain VCM, but obviously this adds to the process complexity. The loss of mercury is, however, the key problem with these catalysts.[2,3]

Studies have shown that at the reaction temperature of 180−220 °C mercuric chloride is volatile. Acetylene hydrochlorination is an exothermic reaction, and as the reaction proceeds it generates a hotspot in the reactor which moves through the fixed bed reactor in the direction of the flow of the reactants. Under these conditions the mercuric chloride sublimes and most, but not all, redeposits on the cooler catalyst downstream. Inevitably mercuric chloride is lost from the catalyst which significantly limits the catalyst lifetime.[2,3] Catalyst lifetime is directly linked to
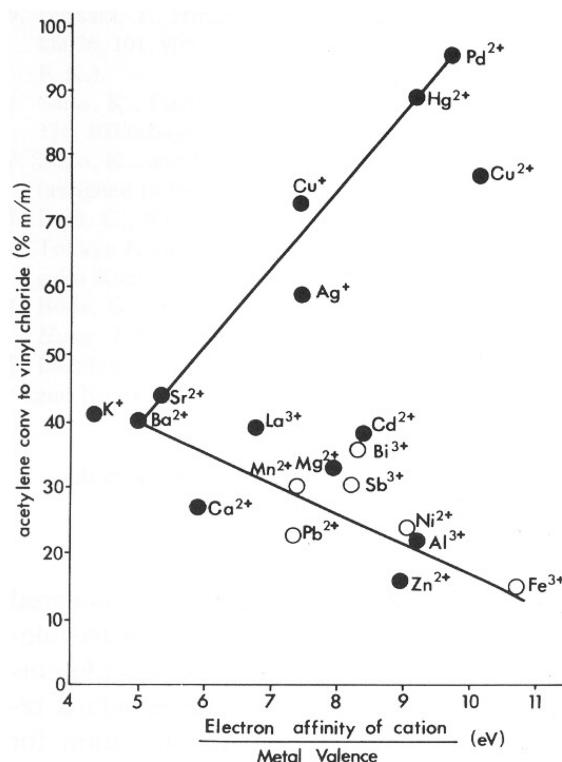
the initial $[HgCl_2]$ and the reactant flow rate as shown in Figure 1. Recent estimates indicate that the loss of mercury from the

Figure 1. Catalyst lifetime of mercuric chloride catalysts showing the relationship with $[HgCl_2]$ and reactant flow rate (data redrawn from ref 2).
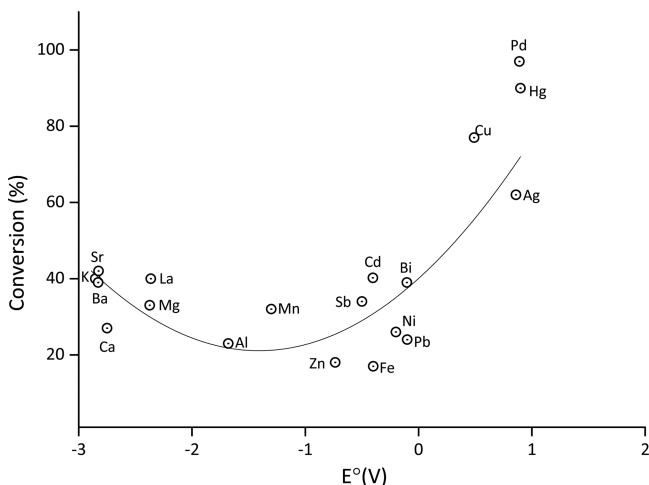
commercial production of VCM in these units is in the region of 600−1000 tonnes Hg per annum.[4] The mercury escapes the production units as it has not proved possible to trap it effectively, which leads to significant environmental problems. The loss of mercury results in short catalyst lifetimes requiring frequent changes of catalyst. At present about 60% of annual mercury production is used to manufacture the catalyst. Clearly this is an unsustainable situation since mercury deposits are being rapidly depleted; but far more importantly are the environmental and health risks associated with the high loss of mercury that occurs from these production units. Where coal is widely available, acetylene hydrochlorination has been increasing in its production capacity. With the clear concerns associated with the severe mercury loss from the commercial units, there is therefore a need to produce a new nonmercury-containing catalyst for this process.

The Advent of Gold Catalysis for Acetylene Hydrochlorination: Early Studies. In 1982 we became interested in the identification of improved catalysts for acetylene hydrochlorination. A key paper by Shinoda[5] proved to be a valuable starting point for research in this area. Shinoda had evaluated over 30 metal chlorides supported on activated carbon for acetylene hydrochlorination and attempted to correlate the catalyst activity with the electron affinity of the metal cation (Figure 2). The data do not statistically correlate with this parameter. Indeed three metal cations, namely Zn^{2+}, Cd^{2+}, and Hg^{2+} span from the least active to the most active yet have similar electron affinities. This means that the data as presented in Figure 2 could not be used in a predictive manner; hence if one wanted to know the activity of a new metal chloride, the experiments would have to be carried out. However, the data in Figure 2 presented a huge opportunity since if a parameter could be identified that did effectively correlate the catalyst activity, then the data could be used to predict improved catalysts. The hydrochlorination of acetylene involves a two-electron addition reaction. The electron affinity is a one electron addition, and so it is not expected that this could have been used as

Figure 2. Correlation of the reactivity for acetylene hydrochlorination with the electron affinity of the cation (data redrawn from ref 5).
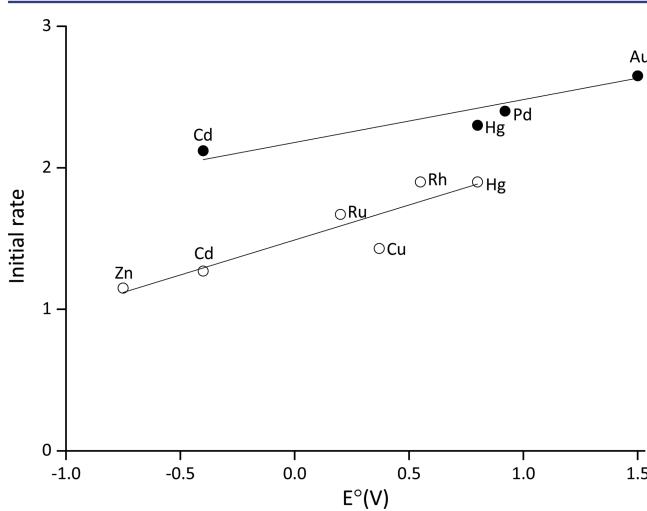
a correlating parameter. As most of the cations studied by Shinoda[5] were divalent, the data in Figure 2 were replotted against the standard electrode potential (Figure 3) which showed a

Figure 3. Correlation between the acetylene conversion to vinyl chloride and the standard electrode potential (data replotted from Figure 2, and redrawn from ref 6).

general correlation that the activity increased with the standard electrode potential.[6] Such a correlation indicates that catalysts with high standard electrode potentials would be the most effective catalysts. Hence the trend observed in Figure 3 can be used predictively, and based on this it was predicted that gold would be a very effective catalyst for this reaction. In addition, the observed correlation of the activity for the acetylene hydrochlorination reaction with the standard electrode indicates that a redox couple is important in the reaction mechanism, and this is

discussed subsequently. Initially, it might be considered that predicting gold to be an effective catalyst is counterintuitive since gold is the most noble of metals. However, it was subsequently shown experimentally that gold is indeed a very effective catalyst for this acetylene hydrochlorination (Figure 4).[7,8] The data

Figure 4. Correlation of the initial activity (mol HCl converted per mol metal per h) with the standard electrode potential for the reaction M^{2+} + $2e^- \rightarrow M$ (M = Zn, Cd, Cu, Ru, Rh, Hg, Pd) and for $Au^{3+} + 2e^- \rightarrow Au^+$. ○ 10^{-4} mol metal, ● 10^{-5} mol metal. Reaction conditions: C_2H_2:HCl = 1:1.1; reactor set point temperature =180 °C. Gas hourly space velocity (GHSV) = 1080 h^{-1}, defined as the total volume of reactant gas passed per volume of catalyst per hour (data redrawn from ref 8).

shown in Figure 4 confirm the correlation with the standard electrode potential. The data shown are based on initial activity (determined as an integrated rate over the catalyst bed) since the catalysts other than those based on gold deactivate rapidly.

A key factor in the discovery of gold as a catalyst for acetylene hydrochlorination is the way in which the catalysts were prepared, since in these early studies the preparation method led to the deposition of small gold nanoparticles onto the carbon support. Contemporaneously, Haruta was showing that small gold nanoparticles supported on oxides were very effective catalysts for low-temperature CO oxidation.[9,10] These two discoveries made in the early 1980s represent the advent of the recent explosion of interest in catalysis by gold.[11−13] Both discoveries relied on the preparation of small gold nanoparticles supported on a suitable matrix to observe the enhanced catalytic activity.

The initial preparation methods used for the gold catalysts for acetylene hydrochlorination were based on the dissolution of metallic gold in aqua regia and the impregnation of this onto the carbon support.[7,8] The reason for this was the need to use very pure sources of gold that would minimize the introduction of impurities that could be problematic for the catalysis; as gold is available in very high purity, this was viewed as the best starting point. In subsequent studies catalysts were prepared by dissolving $HAuCl_4$ in aqua regia. In all cases catalysts prepared using aqua regia were highly active, and catalysts that were prepared using $HAuCl_4$ dissolved in water were ineffective in comparison. This method prepares catalysts comprising small nanoparticles with an average particle size of ca. 4.8 nm in diameter. On reaction both the mercury and the gold catalysts deactivate with time, but the gold catalysts deactivate much more slowly.[14,15] In the case of the mercury catalysts, the loss in activity is due to the rapid loss of mercury. However, gold loss does not occur, and the amount of
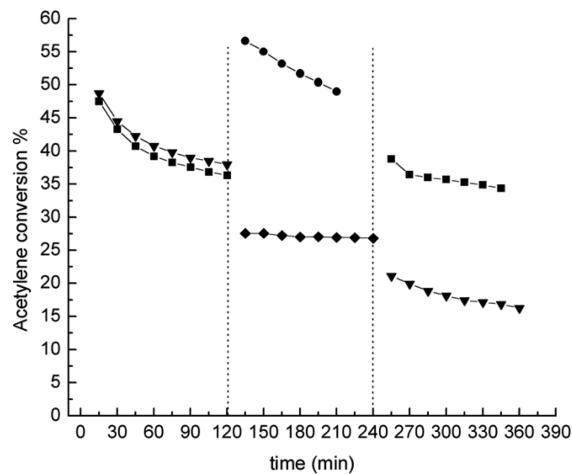
gold on the catalyst does not change during use. The particle size increases slightly to an average particle size of ca. 5.9 nm, and this is not considered to be a major cause of the loss in activity. Detailed X-ray photoelectron and Mössbauer spectroscopy studies have shown that the major effect is on the gold oxidation state, which for fresh catalysts is mainly Au^{3+} and in the deactivated catalysts is mainly Au^0. Reactivation of mercury catalysts has not been found to be feasible, principally because the active component of the catalyst has been lost into the vapor phase. In contrast gold catalysts can be reactivated by treatment with Cl_2, HCl, and NO at reaction temperature.[15] Indeed, we have shown that the Au catalysts can be reactivated by treatment with boiling aqua regia[16] for a short time, which must make it unique in the world of catalysts. In all these reactivation treatments it is the oxidation state of Au that is changed from the inactive form of Au^0 to Au^{3+}. As of yet, no *in situ* studies of the gold catalyst for acetylene hydrochlorination have been carried out, so the detailed changes have yet to be delineated. In part this is due to the highly corrosive nature of the reaction mixture involving roughly a 1:1 mixture of acetylene and HCl at 180−220 °C. As the interest in this reaction is now growing, we anticipate that there will be detailed studies of what in principle appears to be a very simple catalyst and reaction. However, even with gold as the active metal, there is a need to manage and limit the exotherm in the catalyst bed so as to avoid the thermal reduction of Au^{3+} to Au^0 by operating the reactor at controlled temperatures and feed flow rates. Improvements in reactor design and technology are being incorporated in new reactors that enable improved management of the bed exotherm and thereby maximize the catalyst lifetime.

Reaction Mechanism of Acetylene Hydrochlorination. C_2H_2 is a well-known reducing agent, and as catalyst activity declines with use, it is possible that this is due to the reduction of Au^{3+}. Typically the reaction is carried out with a small excess of HCl with no diluent to aim to maintain the gold in a cationic form, as acetylene is a very effective reducing agent for Au^{3+}. To probe this effect, experiments were carried out in which the catalyst is sequentially exposed to individual components of the reactants.[17] To achieve this, an inert gas (He) was added to the reactants to ensure the overall flow could be maintained at a constant rate. Four sets of experiments were conducted, using a 1:1 molar reactant ratio (i.e., flow of 5 mL·min^{-1} for each reactant) at 180 °C, as follows:

- Experiment A: C_2H_2/HCl (2 h) → He/HCl (2 h) → C_2H_2/HCl (2 h)
- Experiment B: He/HCl (2 h) → C_2H_2/HCl (2 h) → He/HCl (2 h)
- Experiment C: C_2H_2/HCl (2 h) → C_2H_2/He (2 h) → C_2H_2/HCl (2 h)
- Experiment D: C_2H_2/He (2 h) → C_2H_2/HCl (2 h) → C_2H_2/He (2 h)

The results of these experiments are shown in Figure 5. The role of HCl is clearly demonstrated in experiments A and B. In experiment A, where the intermediate step is He/HCl, the catalytic activity is maintained when the acetylene is reintroduced in the third phase of the experiment. In experiment B, where the initial treatment is with He/HCl, on introduction of the acetylene, the formation of vinyl chloride is significantly enhanced. In this case, the initial HCl treatment oxidizes some Au^0, and we have noted this previously in catalyst regeneration studies.[17] Conversely, exposure to C_2H_2 leads to catalyst deactivation in the absence of HCl (experiments C and D), and it is clear that, even if no reaction occurred initially (experiment D), the catalyst
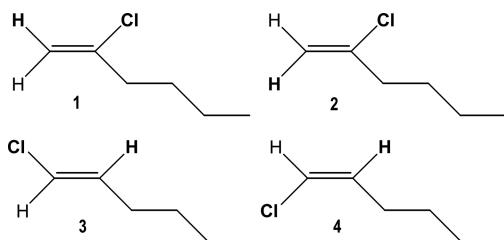
Figure 5. Sequential flow experiments to evaluate the effect of each reactant for the hydrochlorination reaction of acetylene over Au/C catalyst. (Experiment A: ■) C_2H_2/HCl (2 h) → He/HCl (2 h) → C_2H_2/HCl (2 h); (Experiment B: ●) He/HCl (2 h) → C_2H_2/HCl (2 h) → He/HCl (2h); (Experiment C: ▼) C_2H_2/HCl (2 h) → C_2H_2/He (2 h) → C_2H_2/HCl (2 h); and (Experiment D: ◆) C_2H_2/HCl (2 h) → C_2H_2/He (2 h) → C_2H_2/He (2 h). Reaction conditions: reactor set point temperature = 180 °C. GHSV = 870 h^{-1}. Reproduced from ref 17 with permission from Elsevier.

was deactivated by exposure to C_2H_2, and when the reaction was brought online again, the conversion to vinyl chloride was markedly lower when compared to a standard reaction without interruption of the reactants. It is clear that the two reactants can affect the catalyst considerably and play a role in activation/deactivation.

Being a symmetrical molecule, the reaction of acetylene does not provide mechanistic data since only one product is possible. To solve this problem, the mechanism of hydrochlorination of longer chain acetylenes has been investigated.[17] Hex-1-yne was found to be less reactive than acetylene due to steric hindrance. Although there are four possible products (Scheme 1), with the
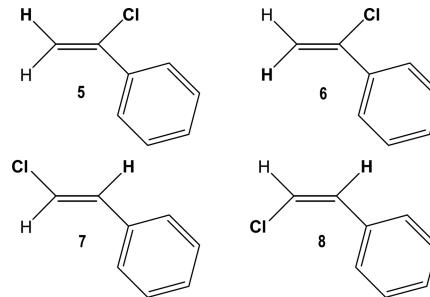
Scheme 1. Possible Regioselectivity and Stereochemistry of the Addition of HCl to hex-1-yne: 1 Markovnikov with *syn* HCl Addition; 2 Markovnikov with *anti* HCl Addition; 3 *anti*-Markovnikov with *syn* HCl Addition; and 4 *anti*-Markovnikov with *anti* HCl Addition

use of ^{1}H NMR spectroscopy we found that there was very high selectivity toward the Markovnikov products **1** and **2**. Only traces of the anti-Markovnikov product **4** were detected (3.7% relative to the Markovnikov product), and product **3** was absent. Hex-2-yne was found to be almost inactive showing the importance of steric hindrance in this reaction.

Phenyl acetylene was found to be slightly less active than hex-1-yne due to the conjugation of the triple bond with the aromatic ring. Of the possible four products (Scheme 2), the major
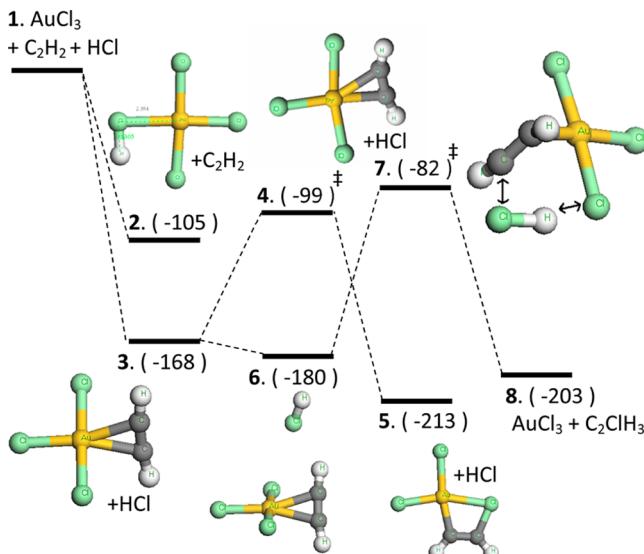
Scheme 2. Possible Regioselectivity and Stereochemistry of the Addition of HCl to Phenyl-Acetylene: 5 Markovnikov with *syn* HCl Addition; 6 Markovnikov with *anti* HCl Addition; 7 *anti*-Markovnikov with *syn* HCl Addition; and 8 *anti*-Markovnikov with *anti* HCl Addition

products were determined to be the Markovnikov products **5** and **6** with traces of the product for the *anti* addition of HCl **8**, while the product for the *syn* addition **7** was absent.
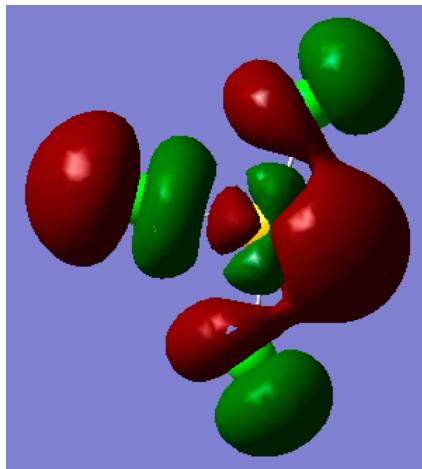
Using ^{1}H NMR spectroscopy the pairs of products **1**, **2** and **5**, **6** are equivalent, and deuterated reagents were used to determine if the Markovnikov products are formed by *syn* or *anti* addition of HCl. For hex-1-yne/DCl only one deuterated Markovnikov product with *anti* stereochemistry was detected, and it was concluded that this product is formed via *anti* addition of DCl to hex-1-yne. Hydrochlorination of phenyl-acetylene using DCl was also investigated, but interestingly no reaction was observed.

DFT calculations have been used to elucidate the overall calculated reaction energy profile (Figure 6).[17] In the complex-

Figure 6. Reaction energy profile for hydrochlorination of acetylene. All energies in kJ mol^{-1}, transition states marked with ‡ (data redrawn from ref 17). Key: Au, yellow; Cl, green; C, gray; H, white.

ation of HCl and acetylene, both have favorable interactions with the Au center in the position expected from the shape of the AuCl$_3$ LUMO (Figure 7). Initial coordination of HCl **2** results in a calculated energy of −105 kJ mol^{-1} with respect to the reference state **1**, whereas placing C_2H_2 into the vacant coordination site of AuCl$_3$ gave structure **3** with a relative energy of −168 kJ mol^{-1}. This indicates that the alkyne is a better ligand than HCl, which is consistent with the requirement to have excess HCl in the reaction mixture. Indeed, the calculations revealed that the

Figure 7. Calculated LUMO state for AuCl$_3$ at the BH and H/6-31(d,p) level. The AuCl$_3$ structure geometry optimization gave a T-shaped complex with a largest Cl−Au−Cl angle of 169°. The lowest unoccupied molecular orbital (LUMO) of this structure has a large lobe in the plane of the complex between the two *trans* Cl ligands. This is consistent with the well-known electrophillic nature of Au(III) and would suggest complexation of a nucleophilic reactant in a square planar geometry (data redrawn from ref 17).

coordination of acetylene in the absence of HCl results in site blocking via the formation of this stable metallocycle structure, and this is consistent with the deactivation observed on exposure to C$_2$H$_2$. The main reaction pathway involves HCl addition to **3**, and this results in Cl addition via the transition state shown as structure **7**. At this point in the reaction the HCl bond is cleaved to add Cl to the alkyne with the H(Cl) atom leaving to one of the Cl ligands on Au. In addition the second carbon atom has a σ-bond to the Au center which is *anti* to the forming Cl−C bond. The final stereochemistry is set by this transition state since transfer of the H atom to replace the Au center is facile and results in a complex with the product.
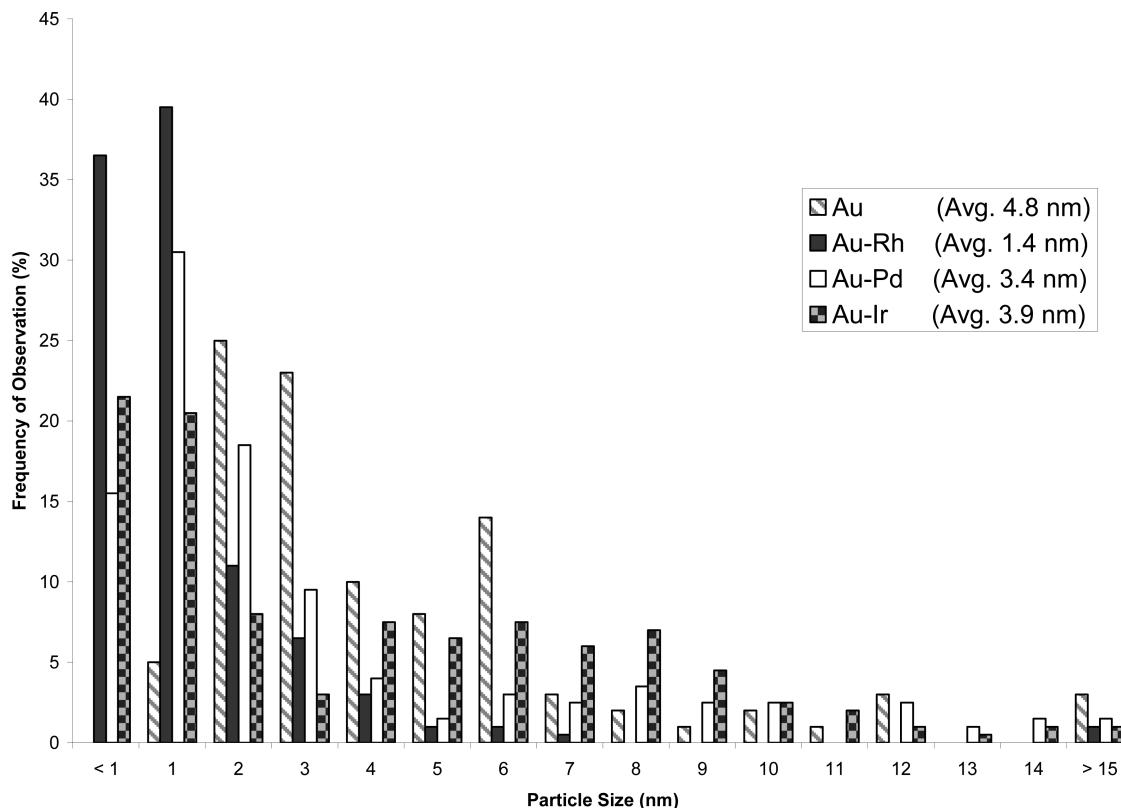
Based on the preceding experimental evidence and discussion, it is possible to comment on the reaction mechanism by which alkyne hydrochlorination occurs using the gold catalyst. The key piece of mechanistic information is that HCl adds in accordance with the Markovnikov rule and in an *anti* configuration to the alkyne. This *anti* addition has also been observed in the hydrochlorination of acetylene using mechanically activated K$_2$PtCl$_6$,[18] where it is proposed that the reaction occurs via a complex formed by adsorption of acetylene at a defect site on the surface of the mechanically activated K$_2$PtCl$_6$ and HCl adsorbed via hydrogen bonding with the surface Cl. It is feasible that a similar mechanism could operate with supported gold catalysts in which a C$_2$H$_2$/Au/HCl complex is formed. We consider that the active center is associated with Au$^+$ and/or Au^{3+} at the surface of a gold nanoparticle which may contain a Au^0 core and the complex switches between Au$^+$ and Au^{3+} as it interacts with C$_2$H$_2$ and HCl, respectively.[19] This is consistent with the initial observation that the catalyst activity correlates with the standard electrode potential,[6,8] indicating that a redox couple is important for the reaction. A number of experimental observations also confirm the involvement of Au$^+$ and Au^{3+} in this reaction mechanism. In detailed Mössbauer spectroscopy, studies show the presence of Au$^+$ and Au^{3+} in fresh catalysts, but only Au^0 is observed in deactivated catalysts.[14] In addition, catalysts prepared comprising essentially Au^0, Au$^+$, and Au^{3+} based on cyanide complexes show a trend in initial activity that Au^{3+} > Au$^+$ > Au^0; catalysts comprising

Au^0 are considered to be activated by HCl at the reaction temperature forming the active higher oxidation states of Au. Hence, the active form of the gold catalyst that is suggested by these mechanistic studies is highly dispersed Au that cycles between the Au$^+$/Au^{3+} redox couple. As noted earlier the initial catalysts can comprise mainly of small gold nanoparticles that on exposure to HCl at high temperatures form the active Au$^+$/Au^{3+} sites. However, it would clearly be better if the gold could be more effectively dispersed since a catalyst that just contained Au$^+$ and Au^{3+} would be a far more effective catalyst, and this is explored in a subsequent section.

Effect of Bimetallic Gold Catalysts for Acetylene Hydrochlorination. In the early years of gold catalysis, studies were concentrated on monometallic Au catalysts. However, a number of studies have shown that alloying Au with Pd or Pt, or even both, can enhance the activity and selectivity for a broad range of redox reactions.[20,21] This prompted us to investigate the use of bimetallic catalysts comprising gold and another metal for acetylene hydrochlorination reaction. The addition of low amounts of Pd, Pt, Rh, and Ir to a 1% Au supported on carbon catalyst was studied.[22] All showed some enhancement in the initial activity. For Pd and Pt addition, this enhancement was accompanied by loss in selectivity, but this was not the case for Rh or Ir. Detailed XPS studies confirmed that deactivation was associated with reduction of Au^{3+}, and the detailed differences in catalyst performance could be explained on the basis of the relative solubilities of the second metal in Au[23−25] and the known interactions of the metallic species with chlorinated hydrocarbons.

Both Au−Pd/carbon and Au−Pt/carbon catalysts showed very similar catalytic effects, i.e., at low levels of Pd and Pt (<5 at%), there was an enhancement in initial activity, but this was associated with loss in selectivity. Au−Pd/carbon and Au−Pt/carbon catalysts exhibited very rapid deactivation as compared with undoped Au/C at all the doping levels investigated. Pd and Pt are both completely soluble in Au across the whole range of compositions.[23−25] Hence these catalysts comprised alloy nanoparticles as confirmed by TPR and STEM-XEDS analysis. However, both Pd and Pt, being very effective dehydrochlorination catalysts, catalyze the reaction of VCM leading to coke deposition on the surface and thereby decreasing the VCM selectivity and catalyst lifetime. Therefore, for these catalysts there is a short-lived enhancement, but this is nonselective leading to coke formation and deactivation. In contrast to Pd and Pt, Ir and Rh are only soluble in Au at very low levels up to 2 at%,[23−25] and so the 1% Ir−Au material can be expected to be a very dilute alloy, and this acts in a similar fashion as the Pd and Pt-doped catalysts. At higher levels of Ir and Rh, there is no effect on selectivity, but there is an enhancement in activity which is due to enhanced dispersion of the Au since the additional Ir and Rh are insoluble in Au at these compositions (Figure 8).

Hence attempts to improve the activity of gold for the hydrochlorination of acetylene by the addition of a second metal have not succeeded. It is clear that the synergistic effect that is observed upon the addition of a second alloyed metal with gold for many reactions[20,21] is not observed for the hydrochlorination reaction. Any enhancement in activity is due to the possible increase in the dispersion of the gold by the second metal; this would enhance the availability of gold cations. The observation that the monometallic gold catalysts could be one of the best catalysts for this reaction is wholly consistent with the correlation previously observed between catalyst activity and the standard electrode potential.[6] Dilution of gold by a second metal when

Figure 8. Particle size distributions of Au/C and Au-M/C bimetallic catalysts for hydrochlorination of acetylene (M = Rh, Pd, and Ir). Pure-Au catalyst analyzed using bright-field TEM imaging with 200 kV JEOL 2000 FX TEM w/LaB$_6$ filament. Bimetallic catalysts analyzed using STEM-HAADF imaging with 300 kV, aberration-corrected FEI Titan 80−300 TEM/STEM (FEG). 200 particles measured for bimetallic samples, 100 for the pure-Au/C catalyst. Reproduced from ref 22 with permission from Elsevier.
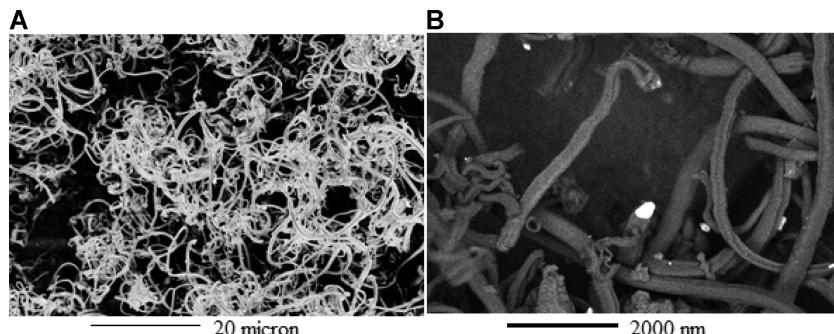
present as a homogeneous alloy, as is the case for Au−Pd, leads to a decrease in the standard electrode potential that is a linear function of the fraction of dopant metal added,[22] and the activity of these Au−Pd catalysts is correlated with the standard electrode potential.[22] Hence it is clear that the addition of a second element in the zerovalent state cannot enhance the activity of the supported Au catalyst since it does not enhance the stabilization of cationic gold species which are essential for the hydrochlorination reaction.

The detailed study of the bimetallic catalysts[22] suggests that improvements in the design of gold-based catalysts for the hydrochlorination of acetylene will need to focus on methods of catalyst preparation. In particular there is a need to decrease the concentration of the gold utilized well below the 1% levels used in the early studies. Methods of preparation clearly need to focus on enhancing the gold dispersion and improved stabilization of its higher oxidation state, as the correlation of activity with the standard electrode potential confirms that the active species for this reaction is cationic gold, as Au$^+$ and Au^{3+}.

Development and Commercialization of Gold Catalysts. In 2007 we started a project within Johnson Matthey to develop catalysts as a replacement of the HgCl$_2$/C catalysts operated in tubular fixed bed reactors in China. Initial studies focused on Au/C catalysts, as this catalyst had been identified as a potential superior replacement.[6] Major targets/requirements in the development of commercially viable catalysts were identified as (a) the need to minimize/eliminate the use of aqua regia in the preparation of these catalysts and (b) to reduce the gold loading significantly from the previously tested 1% Au loadings (or indeed increase the catalyst lifetime and productivity). Preparation of

Au/C catalysts as originally developed using aqua regia would typically require ca. 500 kg aqua regia/tonne of catalyst produced. The handling, recovery, and recycle/disposal of such quantities of aqua regia would represent a significant economic and technical challenge and may indeed have prevented sooner commercialization of these catalysts. We recognized that as a catalyst producer, having a simple and environmentally friendly preparation would significantly benefit the economic and business desirability. For this we set ourselves a minimum catalyst productivity of >2100 kg VCM/kg catalyst, i.e., > twice that of the typical currently operated HgCl$_2$/C catalyst. In addition we set the target at a gold loading <0.25% since loadings higher than this were considered not to be viable, as the capital outlay for the quantity of Au required in a charge of catalyst would be too great to make this attractive for VCM producers.

All attempts to prepare Au catalysts based on HAuCl$_4$ in water or dilute acid gave materials that showed poor activity. Although sufficiently active catalysts could be prepared from HAuCl$_4$ in aqua regia, as had been reported in the earlier work,[7,8] or indeed in nitric acid, these catalysts all showed poor lifetimes under extended duration testing. As discussed earlier in this paper, this loss of activity is not due to loss of Au from the catalyst but by the reduction of the active cationic gold to Au^0. The deactivation route, however, was found to be more significantly a buildup of polymer/carbon on the catalyst, and both of these features had been identified previously.[14,15] Transmission electron microscopy (TEM) analysis of catalyst that had been operated for several months showed significant formation of carbonaceous polymer and carbon-containing nanotubes on the catalyst surface (Figure 9). The composition of the nanotubes indicated that these were
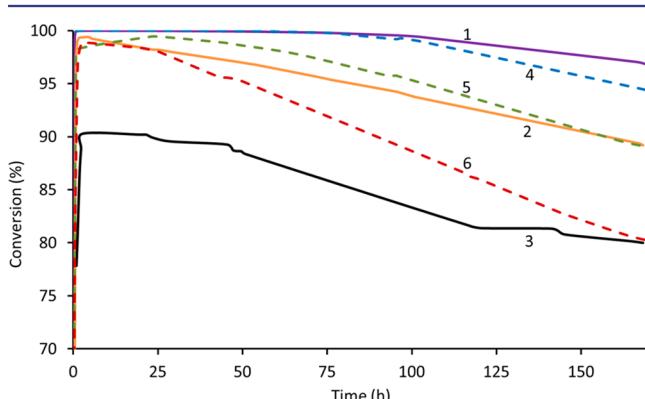
Figure 9. TEM analysis of spent 1% Au/C catalyst prepared using aqua regia after use for 24 days. (A) Low magnification showing the extent of carbon nanofibers formed on the catalyst. (B) Higher magnification showing the gold nanoparticle at the tip of the carbon nanofiber.

acetylene polymers and significantly not VCM polymer. Further studies suggested that nanotube formation resulted from acid-catalyzed polymerization reactions at strong acid sites, introduced from the aqua regia preparation treatment.[19]

Our work thus focused and concentrated on the understanding of the role and need for aqua regia in the preparation. Our studies showed that upon adsorption of the $HAuCl_4$ on the carbon surface, the heat of adsorption released was sufficient to cause significant reduction of the $HAuCl_4$ to Au^0. After a short induction period, the aqua regia reoxidizes the Au^0 species back to Au^{3+}, with consequential formation and evolution of NO_x and HCl from the catalyst.[19]

Evaluation of catalysts at lower metal loadings confirmed that the reaction is first order in Au. The Au loadings of Au/C catalysts prepared from aqua regia could be decreased to a level of ca. 0.5% Au while still maintaining sufficient activity (Figure 10). Decreasing the metal loadings to ca. $\leq$ 0.3% Au resulted in difficulties with activation of this catalyst.

Figure 10. Acetylene hydrochlorination over Au/C catalysts. Key: Line 1 (purple) = 0.6% Au/C, Line 2 (orange) = 0.3%, Line 3 (black) = 0.15% Au/C prepared from $[(NH_4)_3Au(S_2O_3)_2]$, Line 4 (blue) = 1% Au/C, Line 5 (green) = 0.75% Au/C, and Line 6 (red) = 0.5% Au/C prepared from $AuCl_3$/aqua regia. Catalyst = 12 g, reaction conditions: HCl flow = 137 mL/min, C_2H_2 flow = 114 mL/min. Reactor set point temperature = 180 °C. GHSV = 500 h^{-1}.
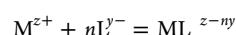
Since deactivation of the catalyst results from decomposition of $AuCl_3$ and consequential reduction of the Au^{3+} to Au^0, we recognized that in order to achieve significant improvements to the catalyst lifetime and productivity, we would need to identify a different gold complex with greater stability under the reaction conditions employed during the catalyst preparation, i.e., the chloride ligands of $AuCl_3$ were too labile and dissociated/disproportionated too readily during the synthesis and use of the

catalyst. Clearly, to prepare and maintain active cationic Au/C catalysts, it is important to disperse and stabilize the Au during preparation and use. The stability constants for a selection of Au^+ and Au^{3+} complexes are given in Table 1 and show the enormous range of stabilities of Au complexes.[26]

Table 1. Stability Constants^a for a Selection of Au Complexes^b

gold(I)		gold(III)	
complex	β_2	complex	β_4
$Au(CN)_2^-$	2×10^{38}	$Au(CN)_4^-$	ca. 10^{56}
$Au(S_2O_3)_2^{3-}$	5×10^{28}	AuI_4^-	5×10^{47}
$Au(CS(NH_2)_2)_2^+$	2×10^{23}	$Au(SCN)_4^-$	10^{42}
AuI_2^-	4×10^{19}	$AuBr_4^-$	10^{32}
$Au(SCN)_2^-$	1.3×10^{17}	$AuCl_4^-$	10^{26}
$AuBr_2^-$	10^{12}		
$AuCl_2^-$	10^9		

^{b}Data taken from ref 27 and references therein. ^{a}The stability constant β_n of a complex, formed from a cation M^{z+} and n ligands L^{y-}, is the equilibrium constant of the reaction for its formation from the free cation and ligands, where [ ] denotes the activity of the species enclosed:

$$M^{z+} + nL^{y-} = ML_n^{z-ny}$$

$$\beta_n = [ML_n^{z-ny}]/[M^{z+}][L^{y-}]^n$$

We reasoned that since complexes with ligands containing soft donor atoms (such as cyanides, thiourea, thiosulfate, thiocyanate) display a greater stability in higher oxidation states (Au^+ and Au^{3+}) over complexes with more electronegative or hard donor ligands (such as halides, nitrogen and oxygen atoms) which tend to disproportionate or be reduced to Au^0, catalysts prepared from complexes containing soft donor ligands may display greater activity and stability for this reaction. We therefore postulated that Au-sulfur complexes might be appropriate for this reaction and that, if dissociated, the presence of the sulfur moiety may serve to immobilize/anchor the Au and also help prevent reduction and sintering of the Au. Hence our goal was to identify a gold complex that could lead to an effective dispersion of gold on the high surface area carbon and to ensure that it remained stable by being effectively anchored, since as we noted earlier a catalyst that comprised fully dispersed Au^+ and Au^{3+} would be the most effective catalyst.

We therefore commenced a series of screening studies in which we supported a wide range of cationic gold complexes onto carbon and evaluated their performance in acetylene hydrochlorination. Selected results are shown in Table 2 and

Table 2. Catalyst Screening of Au/C Catalysts Prepared Using Different Precursor Complexes[a]

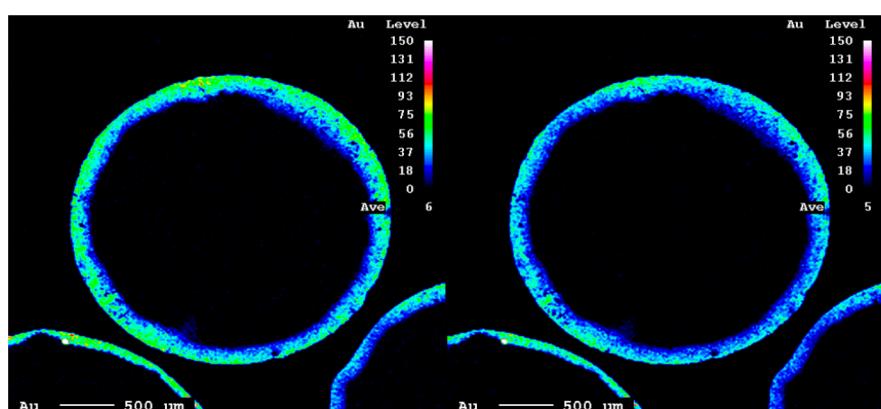| Au precursor complex	Au %	conversion[b] %
$Au(CS(NH_2)_2)_2$	0.1	95
$Na_3Au(S_2O_3)_2$	0.1	86
$KAu(CN)_2$	0.1	85
$(NH_4)_3Au(S_2O_3)_2$	0.1	75
$KAu(SCN)_4$	0.1	74
$Ca_3[Au(S_2O_3)_2]_2$	0.1	74
$KAu(CN)_4$	0.1	69
$Au(NCNH_2)_2$	0.1	55
$HAuCl_4$ + Aqua regia	1.0	52
$HAu(C_3Cl_3N_3O_3)_3Cl$	1.0	52
$[Au(P(NCH_2CH_2OCH_2CH_2)_3)_2]NO_3$	1.0	33
$[(AuCl)_2dppe]$	1.0	14
$[Au(en)_2]Cl_3$	1.0	14
$HAuCl_4$ + H_2O	1.0	11
Blank Carbon extrudate (no Au)	0	7

[a]Test conditions: Catalyst: 5g; HCl flow: 60 mL/min, C_2H_2 flow: 50 mL/min. Reactor set point temperature = 130 °C. Total GHSV = 500 h^{-1}. [b]Conversion measured after 24 h reaction time on line

demonstrated that complexes containing cyanide as well as a wide range of sulfur-containing ligands, in particular, Au-thiosulfate, Au-thiourea, Au-thiocyanate, have significantly greater activity in this reaction than the catalysts derived from $AuCl_3$.[27] These data show that complexes which have high stability constants (Table 1) can be used to form very active catalysts (Table 2); and the use of complexes with soft donor ligands such as sulfur will offer great promise to prepare a new range of active catalysts for reactions other than acetylene hydrochlorination. Furthermore, we found that the catalysts based on these precursors could either be prepared from appropriate preprepared Au complexes or these complexes could be readily formed in situ by the addition of the appropriate sulfur-containing precursor material to a solution of $HAuCl_4$ prior to being deposited onto the carbon support. We have described the novel use of such sulfur-containing ligands for the preparation of highly active supported gold catalysts for acetylene hydrochlorination.[27] To our knowledge this represents the first significant application of sulfur-containing gold complexes in the preparation and use of supported gold catalysts on any scale. Effectively the stability of gold−sulfur bonds is exploited in this methodology to prepare a stable cationic gold catalyst that is highly dispersed. This is a feature that we hope to

investigate using DFT calculations in a future study. The significantly greater hydrochlorination activity of these complexes enabled us to decrease the Au loading from the range of 0.5−1% Au (with the $AuCl_3$ precursor) to the range of 0.15−0.6% Au (with $(NH_4)_2Au(S_2O_3)_3$) or similar S-containing gold complexes) while maintaining comparable hydrochlorination activity, as shown in Figure 10. The greater stability of these complexes enabled the gold complex to be deposited onto the carbon support from aqueous solution, thereby eliminating the need for aqua regia as the impregnation solvent. Initial studies of a 1% Au/carbon catalyst prepared from Au-thiosulfate using X-ray photoelectron spectroscopy shows the material comprises only Au^+ and Au^0, and this is consistent with the formation and deposition of the Au-thiosulfate complex. In contrast the catalyst prepared using aqua regia comprises mainly Au^{3+} together with some Au^+ and Au^0. We consider that some reduction occurs in the XPS beam, but we cannot rule out some reduction upon deposition onto the carbon. As both catalysts show high activity at steady state, this again confirms that active catalysts can be formed starting with either Au^+ or Au^{3+} as previously observed with catalysts formed from gold cyanide complexes.[14]
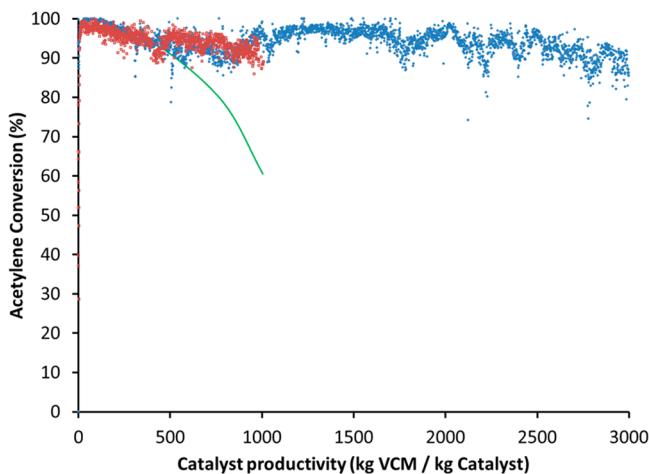
Operation of catalysts prepared with these ultralow levels of Au has the further benefit in that it serves to minimize the reaction exotherm within the reactor bed since the degree of reaction can be more effectively controlled. To facilitate the design of highly active catalysts with ultralow Au loadings, we rationalized that a surface layer of Au deposited on carbon extrudates would be required and the catalyst preparation method was designed so as to achieve this (Figure 11). Even after long duration testing, minimal nanotube and carbon polymer build-up was observed within the reactor using this catalyst. This is consistent with nanotube formation resulting from reaction at strong acid sites on the catalyst that had been introduced during the aqua regia method of preparation.

The successful testing and performance of these catalysts gave us the confidence to construct a pilot plant and operate this at a Chinese PVC producer using their commercial acetylene/HCl feed. The pilot plant contained a full size single tube reactor of the same dimensions as a full scale commercial VCM reactor. The catalyst bed in the reactor tube was 3 m in length and 50 mm diameter and contained ca. 2.0 kg catalyst. The pilot plant trials were operated at a feed rate of 0.6 kg/h. The reactor tube contained a 10 point multipoint thermocouple with temperature measuring points spaced at regular intervals down the catalyst bed. The reactor heating/cooling jacket was maintained at a
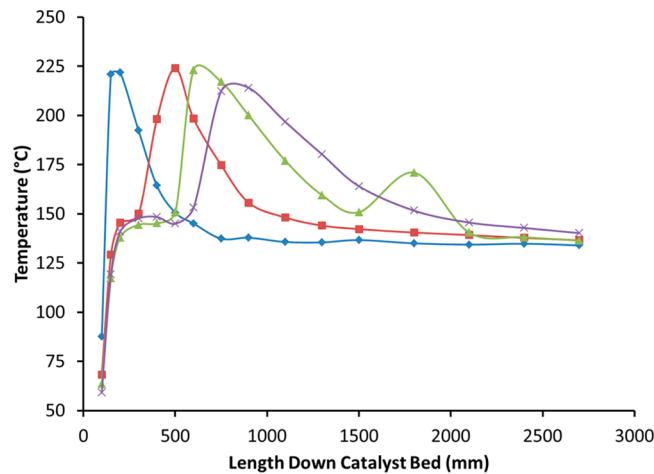

Figure 11. Electron probe micro analysis (EPMA) of a cross section of 0.1% Au/C showing layer of Au at outer surface of the carbon extrudate. Extrudate diameter = 3.0 mm.

temperature in the range of 110−130 °C. As acetylene hydrochlorination is exothermic, the reaction zone can be identified by the exotherm region within the catalyst bed; the temperature in this region was maintained so as not to exceed 250 °C. Exotherms of this type in acetylene hydrochlorination are a feature of commercial large scale reactors where typically the reactor tube is 3 m in length; in small scale laboratory reactors exotherms are not typically observed as the heat of reaction is readily dissipated in small catalyst beds. The exotherm region slowly migrated down the catalyst bed. As this proceeded further down the length of the bed, the exotherm region broadened out, and the rate of migration slowed down. When the catalyst had reached a total productivity of 2000 kg VCM/kg catalyst (i.e., after ca. 12 months time on line), the exotherm was approximately 1.2 m down the length of the catalyst bed. At a productivity of 3000 kg VCM/kg catalyst, the exotherm was approximately 1.8 m down the length of the bed. The rate of migration of the exotherm zone enabled the lifetime of the catalyst in the reactor tube to be estimated at a productivity of >4000 kg VCM/kg catalyst. Throughout the operation of the pilot plant, the catalyst conversion was >85%, and the catalyst selectivity was >99% (Figure 12).

Figure 12. Comparison of catalyst performance in a primary reactor for a 10% HgCl₂/C catalyst (green), pilot plant operation for 0.1% Au/C to a yield of 3000 kg VCM/kg catalyst (blue), full scale commercial reactor for 0.1% Au/C to a yield of 1000 kg VCM/kg catalyst (red). Catalyst = 0.1% Au/C prepared by supporting Na₃Au(S₂O₃)₂ on carbon extrudates. Typical yield for 10% HgCl₂/C catalyst = ca. 1000 kg VCM/kg catalyst.

Following on from this successful pilot plant evaluation of this catalyst, the Chinese PVC producer commissioned a full scale reactor trial with a newly constructed shell and tube reactor containing 790 tubes. The reactor was loaded with ca. 1.6 t of catalyst and was brought on line and operated under equivalent conditions for more than 4500 h time online. At a productivity of 1000 kg VCM/kg catalyst, the performance of the catalyst (and reactor) continued to replicate the pilot plant evaluation. This is greater than the typical yield and productivity that is achieved with the HgCl₂/C catalyst and beyond the point at which this catalyst would be removed from the reactor and replaced (Figure 12). The exotherm in the reactor had migrated approximately 1.2 m down the length of the catalyst tube (Figure 13). The conversion was >90%, and the selectivity was >99%. The full scale demonstration trial data are now being used to provide operational reference data

Figure 13. Temperature profile down catalyst bed of full scale commercial reactor at different VCM yields showing the migration of the exotherm region down the catalyst bed at different catalyst productivities. Catalyst = 0.1% Au/C prepared by supporting Na₃Au(S₂O₃)₂ on carbon extrudates. Blue = ca. 10 kg VCM/kg cat; red = ca. 500 kg VCM/kg cat; green = ca. 600 kg VCM/kg cat; purple = ca. 1000 kg VCM/kg cat.

for the full scale commercial operation of these 0.1% Au/C catalysts in such tubular fixed bed reactors.

Subsequently Johnson Matthey has constructed a world class catalyst manufacturing plant at its Johnson Matthey Shanghai site for the dedicated manufacture and supply of commercial Au/C catalysts for the manufacture of VCM. This heralds a new and exciting era in the development and commercialization of supported gold catalysts and now facilitates a once in a generation change in catalyst technology and formulation away from traditional mercury-based catalysts.

A View to the Future. Gold catalysis has developed rapidly in recent years since the initial discovery that gold nanoparticles are highly effective catalysts for both the low-temperature oxidation of carbon monoxide and acetylene hydrochlorination. This has led to gold catalysts being used for a range of selective oxidation and hydrogenation reactions, e.g., the oxidation of alcohols, hydrocarbons, and the direct synthesis of hydrogen peroxide.[11,13,20,21] Although these reactions are very different, there are some similarities. First, the active catalysts comprise small nanoparticles and small gold nanoclusters. There is considerable debate as the hierarchy of activity associated with these species for CO oxidation.[28] In the case of acetylene hydrochlorination, the most recent advances have involved decreasing the gold concentration and thereby enhancing the dispersion of gold. Initial indications of the importance of enhancing the dispersion of gold were given in the bimetallic catalyst studies where Rh and Ir both enhanced the gold dispersion (Figure 8). Of course, in the reaction environment in acetylene hydrochlorination where acetylene and HCl are present at elevated temperatures, it is possible that the Au nanoparticles are only acting as catalyst precursors. It is known that halogens mobilize and redisperse gold in supported catalysts,[29] and this could be the case during the acetylene hydrochlorination reaction; this would provide one potential reason why gold catalysts for acetylene hydrochlorination are very long-lived.[30] We can now anticipate the commercialization of supported gold catalysts for the production of VCM.[4] The drive toward this is the need to find a more efficient as well as nonmercury-containing catalyst for this process. This will require the production of gold catalysts on a considerable

scale. This would not have been readily feasible for catalysts prepared using aqua regia as the solvent; and hence the development of the new routes based on specifically designed gold complexes, that can be prepared using aqueous preparation routes, is a much preferred pathway for commercialization.

Of course a variety of supported gold and gold alloy catalysts have been commercialized. These catalysts comprise in many cases of metallic gold since this is shown to be the active form for many reactions,[11,20,21] whereas as we have shown in this paper for acetylene hydrochlorination, it is the cationic form of gold that is the active species. For example a Au−Ni alloy catalyst has been commercialized for the manufacture of methyl methacrylate,[31] and silica supported Au−Pd alloy catalysts, where the gold and palladium are both in the metallic state, are extensively used for the manufacture of vinyl acetate monomer in fixed bed reactors.[32−35] In particular, Johnson Matthey developed a fluidized bed Au−Pd catalyst that was operated commercially by BP and Ineos.[32,33] In addition, Johnson Matthey has developed and commercialized supported Au−Pd alloys as diesel oxidation catalysts[36] as well as catalysts for petrol engines,[37,38] where small gold palladium nanoalloys are both very active for CO oxidation but remain stable at the elevated temperatures. It is the alloying of Au with Pd that aids this stability. However, it will be the commercial exploitation of monometallic gold catalysts for VCM production that will herald the true high volume implementation of these highly selective catalysts.

Gold offers a further key advantage as a catalyst and that is selectivity. While supported gold nanoparticles and clusters are very active catalysts, and this is the reason why there were initially discovered and exploited, they are also very selective catalysts for a range of important reactions. In the hydrochlorination of acetylene the only product that is observed is VCM. This is in contrast to supported mercury catalysts where secondary reactions can be prevalent. In redox reactions, gold and gold alloys have been shown to be very effective for the production of various bulk and fine chemicals. It is this unique selectivity that can be achieved with gold that is attracting tremendous interest in gold catalysis. Hence at this point we are poised to see a number of new innovations based on gold catalysis to be feasible. In the past the price of gold would have provided a potential brake on such developments. However, the innovations of the past few years have seen catalysts developed with very low levels of gold. The high activity, enhanced selectivity, long lifetime, and ease of recycling of gold catalysts all bode well for the future.

■ AUTHOR INFORMATION

Corresponding Author
*hutch@cf.ac.uk

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Panfilov, A. A.; Skornyakov, V. P.; Shcheglov, G. G.; Gel'bshtein, A. I. *Soviet Chem. Ind.* **1972**, *10*, 610.

(2) Hutchings, G. J.; Grady, D. T. *Appl. Catal.* **1985**, *16*, 411.

(3) Hutchings, G. J.; Grady, D. T. *Appl. Catal.* **1985**, *17*, 155.

(4) Nat, P. J. *Catalyst Rev.* **2015**, *28*, 8.

(5) Shinoda, K. *Chem. Lett.* **1975**, 219.

(6) Hutchings, G. J. *J. Catal.* **1985**, *96*, 292.

(7) Nkosi, B.; Coville, N. J.; Hutchings, G. J. *J. Chem. Soc., Chem. Commun.* **1988**, 71.

(8) Nkosi, B.; Coville, N. J.; Hutchings, G. J. *Appl. Catal.* **1988**, *43*, 33.

(9) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405.

(10) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301.

(11) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896.

(12) Bond, G. C.; Thompson, D. T. *Catal. Rev.: Sci. Eng.* **1999**, *41*, 319.

(13) Corma, A.; Garcia, H. *Chem. Soc. Rev.* **2008**, *37*, 2096.

(14) Nkosi, B.; Coville, N. J.; Hutchings, G. J.; Adams, M. D.; Friedl, J.; Wagner, F. *J. Catal.* **1991**, *128*, 366.

(15) Nkosi, B.; Adams, M. D.; Coville, N. J.; Hutchings, G. J. *J. Catal.* **1991**, *128*, 378.

(16) Conte, M.; Carley, A. F.; Hutchings, G. J. *Catal. Lett.* **2008**, *124*, 165.

(17) Conte, M.; Carley, A. F.; Heirene, C.; Willock, D. J.; Johnston, P.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. *J. Catal.* **2007**, *250*, 231.

(18) Goldman, A. S.; Goldberg, K. I. *ACS Symp. Ser. 885, Activation and Functionalization of C-H Bonds* **2004**, *885*, 1.

(19) Carthey, N. A.; Johnston, P.; Smidt, M. L. Improvements in Catalytic Processes. WO 2010/055341A3, August 12, 2010.

(20) Hutchings, G. J.; Kiely, C. K. *Acc. Chem. Res.* **2013**, *46*, 1759.

(21) Edwards, J. K.; Freakley, S. J.; Carley, A. F.; Kiely, C. K.; Hutchings, G. J. *Acc. Chem. Res.* **2013**, *47*, 845.

(22) Conte, M.; Carley, A. F.; Attard, G.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. *J. Catal.* **2008**, *257*, 190−198.

(23) Hansen, M. *Constitution of Binary Alloys*, 2nd ed.; McGraw-Hill: New York, 1958.

(24) Elliott, R. P. *Constitution of Binary Alloys, First Supplement*; McGraw-Hill: New York, 1965.

(25) Shunk, F. A. *Constitution of Binary Alloys, Second Supplement*; McGraw-Hill: New York, 1969.

(26) Nicol, M. J.; Fleming, C. A. and Paul, R. L. In *The Extractive Metallurgy of Gold in South Africa*, Stanley, G. G., Ed.; The South African Institute of Mining and Metallurgy: Johannesburg, South Africa, 1987; Chapter 15, 831.

(27) Bishop, P. T.; Carthey, N. A.; Johnston, P. Catalyst Comprising Gold and a Sulphur Containing Ligand on a Support and Method for Its Preparation. WO 2013/008004A3, May 16, 2013.

(28) Haruta, M. *Faraday Discuss.* **2011**, *152*, 11.

(29) Goguet, A.; Hardacre, C.; Harvey, I.; Narasimharao, K.; Saih, Y.; Sa, J. *J. Am. Chem. Soc.* **2009**, *131*, 6973.

(30) Zhou, K.; Jia, J.; Li, C.; Xu, H.; Zhou, J.; Luo, G.; Wei, F. *Green Chem.* **2015**, *17*, 356.

(31) Suzuki, K.; Yamaguchi, T.; Matsushita, K.; Iitsuka, C.; Miura, J.; Akaogi, T.; Ishida, H. *ACS Catal.* **2013**, *3*, 1845.

(32) Baker, M. J.; Couves, J. W.; Griffin, K. G.; Johnston, P.; McNicol, J. C.; Salem, G. F. Catalyst Composition and Process for Making Same. U.S. Patent 2003/0144544, July 31, 2003.

(33) Baker, M. J.; Johnston, P.; Murphy, D. Process for the Preparation of a Microspheroidal Catalyst. WO 2003061829A1, July 31, 2003.

(34) Hanrieder, E. K.; Jentys, A.; Lercher, J. A. *ACS Catal.* **2015**, *5*, 5776.

(35) Chen, M.; Kumar, D.; Yi, C.-W.; Goodman, D. W. *Science* **2005**, *310*, 291.

(36) Bergeal, D.; Chiffey, A. F.; Johnston, P.; Moreau, F.; Phillips, P. R. Alloy-Comprising Catalyst, Method of Preparation and Uses. WO 2012/120292A1, September 13, 2012.

(37) Fujdada, K.; Truex, T.; Cai, J.; Sampara, C. Engine Exhaust Catalysts Containing Palladium-Gold. U.S. Patent 8258070B2, September 4, 2012.

(38) Fisher, J. M.; Goodwin, J. B, Hinde, P. C, Laroze, S. C., Raj, A. S.; Rajaram, R. R.; Schofield, E. R. Exhaust System for Lean-Burn Internal Combustion Engine Comprising Pd-Au-Alloy Catalyst. U.S. Patent 8551411B2, October 8, 2013.