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A Facile Synthesis of Precious Metal Single Site Catalysts using Organic Solvents

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Abstract

Single site catalysts can present high activity and selectivity in many catalytic reactions. The synthesis of these materials by impregnation from strongly oxidising aqueous solutions or pH-controlled deposition often leads to low metal loadings or a range of metal species. Here, we demonstrate that simple impregnation of the metal precursors onto activated carbon from a low boiling point, low polarity solvent, such as acetone, results in catalysts with an atomic dispersion of cationic metal species. We show the generality of this method by producing single site Au, Pd, Ru and Pt catalysts supported on carbon in a facile manner. With single site Au/C being validated commercially to produce vinyl chloride, we show this facile synthesis method can produce effective catalysts for acetylene hydrochlorination in the absence of highly oxidising acidic solvents.

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Acetylene hydrochlorination using Au/C is an example of a large-scale industrial process that uses single atom catalysts. We show that single atom catalysts can be prepared by impregnation of a metal salt from acetone with comparable activity to catalysts prepared using acidic and oxidising solvents or additional ligands.

The development of heterogeneous catalysts containing stabilised single cationic metal species has resulted in materials that have high metal utilisation, increased selectivity and high efficiency.[1,2] Compared to nanoparticle catalysts in reactions such as alkyne hydrogenation[3,4], C-C coupling[5] and numerous electrochemical processes,[6,7] single site catalysts (SSCs) have promising reactivity. The facile synthesis of these materials is crucial to fully exploit their potential on a larger scale. While many heterogeneous catalysts contain a varied population of metal nanostructures including nanoparticles, clusters and atomic species,[8] the facile targeted synthesis of isolated metal atoms remains a challenge as methods are not currently readily scalable for commercial application.[9-11] .

Many studies have implicated cationic Au as the active species for acetylene hydrochlorination and hence these materials are an important example of SSCs.[15] Currently, 13 Mtpa of VCM are produced by acetylene hydrochlorination using $HgCl_2$ on activated carbon, which poses significant environmental concerns as up to 0.6 kg Hg is lost per tonne of VCM produced.[12] The recently ratified Minamata convention (http://www.mercuryconvention.org/) dictates that all new VCM plants must use mercury free catalysts and in the near future all industrial plants must switch to mercury free alternatives. Recently Au/C has been validated commercially as a replacement for the existing catalyst systems,[12,13] and the active species is an atomically dispersed cationic gold chloride.[14] Au SSCs have been prepared using *aqua regia* as solvent, but lack stability under reaction conditions,[15] but using an aqueous Au-thiosulfate complex leads to a stable potential Au SCC for this process.

In this study, we show that it is possible to prepare highly dispersed metal catalyst materials containing Ru, Pd, Pt and Au using a simple methodology in the absence of highly oxidising acidic solvents, by impregnation from a low boiling point, low polarity solvent such as acetone. We show that gold catalysts prepared in this way have comparable activity for acetylene hydrochlorination to catalysts prepared with acidic and oxidising solvents and that previous correlations of the activities with the standard electrode potential of the cation can be reproduced with this new preparation method.

Results and Discussion

The preparation of SSCs is often carried out in aqueous solutions by deposition or impregnation methods.[16,17,18] This limits the choice of precursor to water soluble metal salts – preventing the use of organometallic metal salts containing organic ligands. In addition, the potential of utilising solvents with lower boiling points than water to reduce the catalyst drying temperature could reduce the likelihood of sintering of the highly dispersed species. To explore this we initially prepared 1wt% Pd, Pt, Ru and Au/C materials through a facile wet impregnation method using Pd, Pt, Ru acetylacetonates, which have limited solubility in aqueous solutions, and chloroauric acid as precursors using acetone as solvent.

Characterisation of the materials by X-ray diffraction, Figure 1a, shows the absence of diffraction patterns consistent with metallic or metal oxide crystallites suggesting high metal dispersions. In addition, XPS analysis (Figure 1b-d) of the Pt ($4f_{7/2}$), Pd ($3d_{5/2}$) and Ru ($3d_{5/2}$) regions of the respective fresh materials suggests that Pt and Pd are present in the +2 oxidation state (with binding energies of 73.0 and 337.9 eV respectively) while Ru is in the +3 oxidation state (with binding energy of 281.9 eV). This confirms the retention of the expected oxidation state of the metal and suggests deposition of the intact acetylacetonates complexes.[19, 20] XRD and XPS analysis of the carbon support are reported in supplementary figures 1 and 2 which show that the carbon surface contains less than 5 at% oxygen, mostly C-O-C/C-OH/C=O functional groups. To probe the Au speciation in the fresh Au/C we conducted Au L_3-edge (11.92 keV) X-ray absorption spectroscopy (XAS). As has been previously reported, cationic Au species can undergo significant photoreduction during XPS analysis, leading to over representation of Au(0) content in this class of catalyst.[21] Due to its lower X-ray absorption cross-sections at high incident photon energy, XAS can be considered a less destructive technique for highly dispered Au-Cl catalysts. Analysis of the normalised white line intensity corresponding to Au $2p_{3/2} \rightarrow 5d$ primary transitions can be used as a direct probe of 5d occupancy of Au species in the catalyst.[14] Comparison of white line intensity with standards for Au(III) (1.1) and Au(I) (0.6), allows quantitative determination of the nature of the cationic Au species present in the catalysts.[22,23]

The FT-EXAFS (Figure 1e) analysis of the Au/C materials prepared by acetone impregnation reveals an intensity consistent with isolated Au chloride species with no evidence of metallic Au-Au interactions, supporting a high dispersion of cationic species. This is confirmed by EXAFS and linear combination fitting (LCF) of the XANES region (supplementary figure 3a). The results suggest that the metal is cationic with a mixture of Au chloride species with 23% Au(III) : 77% Au(I). EXAFS fitting of the fresh Au/C catalyst, using models comprising Au-O, Au-Cl or mixtures of Au-Cl/O were compared, with no satisfying fit for anything other than Au-Cl, with a CN of 2.3(1) (supplementary figure 3b). Therefore, there is no compelling evidence for Au-O containing speciation or anchoring of Au through surface oxygen species. Similar analysis of the Pt L_3-edge, Pd K-edge and Ru K-edge respectively was carried out. The analysis of the XANES region of the 1wt.%$Pd(acac)_2$/C material (supplementary figure 4a) confirms the presence of $Pd(acac)_2$ species with no intensity consistent with Pd-Pd interactions in the FT-EXAFS. (supplementary figure 4b). Similar results have been obtained for 1wt.% $Pt(acac)_2$/C material (supplementary figure 5a and b) and for the 1wt.% $Ru(acac)_3$/C (supplementary figure 6a and b), where the acac complex has also been deposited intact. Fitting of the Pt, Pd and Ru EXAFS data further proves intact metal complex deposition, with metal-O and metal-C CNs and path lengths being comparable to those of metal acac standards (supplementary table 1). Characterisation of the 1wt.% Au/C-Acetone catalyst by high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) revealed the Au speciation to be predominatly atomically dispersed Au species, as well as some occasional dimeric Au species and sub- nanometer

clusters, with no evidence at all of larger Au crystallites. A representative image is shown in Figure 1f, which closely resembles the 1wt.% Au/C-*aqua regia* catalyst extensively studied previously for the acetylene hydrochlorination reaction.[14] Similar high metal dispersions can be observed in the corresponding HAADF-STEM images for the Pd/C, Pt/C and Ru/C catalysts (supplementary figures 7a-f).

We conducted systematic studies into Au/C catalyst synthesis by this facile method for the acetylene hydrochlorination reaction. The preparation of Au/C catalysts via wet impregnation of $HAuCl_4$ from aqueous solution results in Au nanoparticles after the sample has been dried at 140 °C for 16 h under a flow of N_2, which have little activity towards acetylene hydrochlorination.[15] The reduction of $HAuCl_4$ is facilitated partly by the reducing nature of the carbon support material, which can contain oxidisable surface groups, and the reduced stability of $HAuCl_4$ in aqueous solutions according to the Au-Cl-H_2O Pourbaix diagram.[24] As $HAuCl_4$ is highly soluble in many organic solvents, in addition to acetone, we prepared catalysts using a wide range of solvents. Supplementary table 2 lists all the solvents used in this study, together with their boiling points and polarity.[25] Typically, catalysts were dried for 16 h at 5 to 10 °C higher than the boiling point under a flow of N_2. Wherever possible extra dry solvents were used in the preparations (denoted as (dry)).

Steady state acetylene hydrochlorination activity (GHSV = 17,600 h^{-1}) is reported in Figure 2a for catalysts prepared with a series of C_1 – C_4 alcohols. As the alcohol chain length increased, and consequently as the polarity of the solvent decreased, the activity of the catalysts increased, from 3% conversion for catalysts prepared in aqueous solvents to a value of 20% conversion for samples prepared in C_4 alcohols. Ketones such as acetone and 2-butanone, in addition to ethers such as THF, ethyl acetate and diethyl ether, were tested to investigate the effect of decreasing the polarity further, resulting in a slight increase in conversion to 23 %. The well-studied *aqua regia* prepared Au/C catalyst gave a steady state conversion of 18 %, meaning that the catalysts prepared by simple wet impregnation of $HAuCl_4$ from low polarity, easy to handle, solvents such as acetone, 2-butanol and THF performed better than the catalyst prepared in highly acidic oxidising conditions. All catalysts tested displayed a high selectivity to VCM (>99 %).

The plateau of activity at 20-24 % when decreasing the polarity of the impregnation solvents represents a practical limit of dispersion that can be achieved.[14] XRD patterns for samples prepared with varying solvent polarities are displayed in Figure 2b. Wet impregnation from aqueous solutions results in reflections at 2θ angles of 38°, 44°, 64° and 77° which correspond to the face-centred cubic structure of metallic Au with an average crystallite size of *ca.* 20 nm as determined by the Scherrer equation. These features are also present in catalyst samples prepared with high polarity solvents, with reflections indicating average nanoparticle sizes of 18 to 24 nm. The intensity of these reflections systematically decreases as the polarity of the solvent decreases. The samples with the highest activities show very

weak or un-detectable diffraction patterns corresponding to metallic Au, indicating high dispersions and supporting the hypothesis that Au nanoparticles are not the active species for this reaction.

As the solvents used are not strongly acidic or oxidising, the reason for the high activity could arise from: (i) the hydrophilic/hydrophobic nature of the solvents, providing increased wetting of the carbon support materials leading to higher dispersions; (ii) lower drying temperatures preventing Au agglomeration; (iii) the complete absence of water in the catalyst preparation; or (iv) stabilisation of the Au in high oxidation states in the absence of water. We investigated the use of low polarity solvents with high boiling points such as DMF, DMSO and cyclohexanone. Table 1 reports the polarity, boiling points and drying temperatures along with acetylene conversion values. While all the catalysts prepared with high boiling point (>120 °C) solvents performed better than the catalyst prepared in aqueous solution, they were not as active as the samples prepared with low boiling point solvents (<120 °C) suggesting that the drying temperature is also a parameter effecting the performance of the catalysts as well as the reducibility of the solvent at that specific drying temperature. XRD analysis (supplementary figure 8) shows that the catalysts prepared at high drying temperatures contained Au nanoparticles, which is consistent with their lower activity. To probe if drying temperature was the only variable determining high activity and dispersion, catalysts prepared with acetone were dried at 45, 65 and 140 °C for 16 h. As reported in Table 1, these catalysts showed comparable activity to the sample prepared with acetone dried at 45 °C, which demonstrates that effective catalysts can be prepared with low polarity solvents and low drying temperatures. This suggests that it is the increased wettability of the impregnation solution on the carbon support, coupled with mild drying conditions that effectively anchors single highly dispersed Au species, rather than speciation being solely dictated by the drying temperature. Adding increasing amounts of water (5-50 vol.%) to the extra dry acetone decreased the activity of the as-prepared catalyst as shown in Figure 2c, until at 50 vol.% the activity resembled that of samples prepared in aqueous solution. This measured reduction in activity correlated well with the development of reflections from metallic Au in the recorded XRD patterns, (Figure 2d). This confirms the negative impact of the presence of water on the preparation of highly dispersed Au catalysts in the absence of strong oxidising/acidic agents or strongly co-ordinating ligands.

A time-on-line study to compare the activity of the low polarity Au/C-acetone catalyst with the Au/C-*aqua regia* material and high polarity Au/C-H_2O catalyst, supplementary figure 9, shows the high stability of the Au/C-Acetone catalyst under reaction conditions. There is a small (3 %) increase in conversion in the first 100 min, indicating a possible minor change in the Au oxidation state and a minimal induction period, followed by a further 140 min of steady conversion. The Au/C-*aqua regia* catalyst displays a pronounced induction period due to changes in Au oxidation state, which have been previously studied via *in situ* XAS, resulting in a 15 % difference in conversion over the same time. The oxidising *aqua regia* solvent, which has been used historically in the academic literature, resulted in a catalyst with a lower final conversion than that of the more benign acetone-prepared catalyst. This

strongly suggests that the likely different functionality of the carbon supports can play a key role in determining the induction periods of these catalysts, through either stronger Au anchoring or facilitating more facile changes in oxidation state. As noted in previous work,[14] the Au present on Au/C-H_2O is largely unreactive, being predominantly Au(0), hence this catalyst maintains a low (2 %) conversion throughout the test.

We have previously demonstrated that 0.1wt.% Au-S_2O_3/C catalysts, prepared from gold-(I)-thiosulphate on carbon extrudates, have high activity and productivity for acetylene hydrochlorination.[12] Catalysts were therefore also prepared at a 0.1wt.% Au loading using $HAuCl_4$ in acetone to compare the performance of these materials at low gold loadings. Under testing using undiluted gas feeds (HCl: C_2H_2 = 1.2:1, HCl flow = 60 ml min^{-1} , C_2H_2 flow = 50 ml min^{-1}, GHSV = 1737 h^{-1}, bed volume = 3.8 ml), the Au-S_2O_3/C material gave 23% conversion at 130 °C, and a maximum of 56% conversion at 180 °C. A 0.1wt.% Au/C catalyst prepared from $HAuCl_4$ in acetone gave similar activities (27% conversion at 130 °C and 52% at 180 °C) after 24 h of reaction. This is consistent with both materials containing highly dispersed gold cations. At 1wt.% loading the Au/C prepared from Au(I) thiosulphate also gave comparable performance in acetylene hydrochlorination to the acetone prepared material.

The X-ray absorption spectra at the Au L_3-edge of the Au/C-Acetone catalyst before and after reaction for 4 h were recorded, analysed and compared to that for the Au/C-*aqua regia* catalyst. The three Au/C catalysts initially reveal signficantly different post-edge features in comparison to a metallic Au foil, Figure 3a. This supports the XRD and STEM analysis that no extended metallic Au structures are present in the fresh catalysts prepared with acetone or *aqua regia*. In particular, the normalised white line height of the fresh samples prepared with acetone and *aqua regia* suggest that both catalysts are a mixture of Au(I) and Au(III) species, with the acetone catalyst being slightly more Au(I) rich than the comparable samples prepared using *aqua regia*, based on a lower normalised white line height intensity (*ca.* 0.66 for Au/C-Acetone and *ca*. 0.78 for Au/C-*aqua regia,* Figure 1a). Three different Au standards were used to perform a LCF analysis of the Au L_3-edge XANES: Au(III) ($KAuCl_4$/$[AuCl_4]^-$), Au(I) ($[AuCl_2]^-$), and a Au-foil standard spectra, Figure 3b. The LCF confirms the cationic nature of the Au in the acetone derived catalyst, with the Au predominantly existing in the Au(I) oxidation state (77%). This is similar in nature to the catalyst prepared using *aqua regia* albeit with a different distribution of Au(I) – (57%) and Au(III) – (43%). After 5 h of use, a small contribution from Au(0) could be detected in the Au/C-Acetone catalyst, indicating some minor instability of the cationic Au species. It has been postulated that the reduction of Au species is responsible for catalyst deactivation, the stability observed in the acetylene hydrochlorination tests suggests that this agglomeration takes place during the heating ramp to reaction temperatures and not during the reaction itself. Extended X-ray absorption fine structure (EXAFS) data for the fresh Au/C-Acetone and Au/C-*aqua regia* catalysts (Figure 3c and supplementary table 3) had Au-Cl distances and coordination numbers of 2.31(8) Å and 2.58(8) respectively, consistent with the mixed Au(III)/Au(I) determined by XANES. A lack of long-range

order and no characteristic Au-Au distances were also observed in the EXAFS for both catalysts, when compared to the Au foil standard, again in agreement with the XRD and the HAADF-STEM analysis. An increase in intensity of the Fourier transform at distances corresponding to those of the Au foil was observed in the used catalyst, in conjunction with a decrease in Au-Cl bond length to 2.0(1) Å and appearance of a Au-Au CN of 1.6, consistent with the formation of small amounts of Au(0). These Au(0) species have previously been demonstrated to be large (>1 nm) and inactive for acetylene hydrochlorination.[26] LCF analysis of the XANES of the used catalyst (Figure 3b) confirms the presence of 14% Au(0).

To determine the stability of the Au/C-Acetone catalyst, a prolonged reaction was performed. After 4 h of reaction, the catalyst was cooled to room temperature under a flow of Ar, left sealed for 16 h, heated under an Ar flow and then tested under reaction conditions for a further 3 h. The same test was performed with the Au/C-*aqua regia* material for comparison. This test, illustrated in Figure 4, shows the stability of the Au/C-Acetone catalyst, maintaining a conversion between 19-20 % for over 5 h, indicating that after the first 100 min of reaction the Au oxidation states and dispersion remained relatively stable. Supplementary figure 10 shows the XRD pattern of the Au/C-Acetone catalyst after 7 h of reaction, compared with that of the fresh material and the catalyst used for 4 h. The characteristic reflections of Au nanoparticles increased slightly in size after 7 h suggesting the slow sintering of the catalyst at extended reaction times. Furthermore, due to the lack of catalyst deactivation it is likely that this Au(0) forms during the heat-up or initial stages of the reaction before stabilisation.[27] In order to confirm this point, *in situ* XRD of the Au/C-Acetone catalyst (supplementary figure 11a) has been performed while heating the sample under an inert atmosphere up to 250 °C; Au reflections could be observed upon reaching a temperature of 190 °C. A similar analysis was performed on the other supported metal catalysts (Pt/C, Pd/C and Ru/C) (supplementary figure11 b, c and d), which demonstrated their relative thermal stabilities under an inert atmosphere. To further probe the thermal stability of these catalysts, samples prepared with Pd and Ru acetylacetonate in acetone were compared to catalysts prepared from the respective chloride procurers in either acidic or aqueous impregnation solvents. After heating to 450 °C under a N_2 atmosphere XRD (supplementary figure 12) shows that the Pd sample remains highly dispersed in the case of the acac/acetone preparation but undergoes agglomeration from a highly dispersed catalyst in the case of the chloride containing precursor. In both cases Ru was able to be dispersed with high thermal stability in the materials prepared from both $Ru(acac)_3$ and $RuCl_3$.

The correlation in activity of a range of carbon supported metal chlorides with standard electrode potential has previously been reported by Liu *et al* [15] using catalysts prepared with highly oxidising and acidic impregnation solvents at reaction temperatures of 180 ºC. Analysis of the acetone prepared Au catalysts by LCF of XANES spectra (corresponding EXAFS fitting in supplementary table 4 and correlation between CNs determined by XANES and EXAFS in supplementary figure 13 and 14)

at various reaction stages (Figure 5a) shows that the catalyst remains stable upon heating to 180 °C under Ar. On exposure to HCl at this temperature an increase in Au(III)-chloride is observed which is stable on initial exposure to the acetylene hydrochlorination reagents. After 240 mins, the proportion of Au (I) and Au (III) chloride is significantly changed with a minor Au(0) contribution being observed. Analysis of the analogous Pd, Pt and Ru catalysts by ex-situ EXAFS (supplementary figure 13 and tables 5-7) revealed that the metal acetylacetonates were stable to heating to 180 °C under Ar with no indication of metal agglomeration. On introduction of reactants, the acetylacetones were converted to dispersed metal chlorides and remain in that state for the 240 min reaction time. HAADF-STEM (supplementary figure 15) imaging shows that the isolated cation sites remain intact, apart from a few sub-nanometer clusters visible for the Pd/C and the Ru/C samples, and XPS shows that these species remain as oxidised metal centers (supplementary figure 16). As shown in Figure 5b, a linear correlation is observed between the steady state productivity and the standard electrode potential, demonstrating the generality of this new preparation method in being able to produce analogous catalytic trends to the previously reported family of catalysts prepared in highly acidic and oxidising solvents.

Hence we show it is possible to prepare effective Au/C acetylene hydrochlorination catalysts consisting of atomically dispersed cationic Au species by a simple wet impregnation method using low polarity solvents with low boiling points. This method allows the facile preparation of Au SSCs in addition to highly dispersed Ru/C, Pd/C and Pt/C with relatively high metal loadings which allows the potential of these materials to be fully exploited by removing the need to deal with highly acidic waste during catalyst preparation opening the possibility to produce these catalysts without the need for water soluble metal salts.

Methods

Catalyst Preparation

All carbon-supported gold catalysts were prepared via a wet impregnation method previously reported.[3] Activated carbon was initially ground to obtain a powder (150 – 200 mesh). The gold precursor, $HAuCl_4 \cdot 3H_2O$ (Alfa Aesar, 20 mg, assay 49%) was dissolved in the required solvent (2.7 ml). The gold precursor solution was added dropwise, with stirring, to the activated carbon (0.99 g) in order to obtain a catalyst with a final metal loading of 1 wt.%. The resulting powder was dried at 5-10 °C higher than the boiling point of the solvent used, for 16 h under a flow of N_2. The catalysts prepared using different solvents were denoted as Au/C-(solvent) and, wherever possible, extra-dry solvents sealed in nitrogen were used. The Ru/C, Pt/C and Pd/C catalysts were prepared by the same wet impregnation procedure. In this case, Ru(III) acetylacetonate (Aldrich), Pd(II) acetylacetonate (Aldrich) and Pt(II) 2,4-pentanedionate (Alfa Aesar) were used as precursors.

Catalyst Testing

Catalysts were tested for acetylene hydrochlorination in a fixed-bed polyimide (Kapton) microreactor (O.D. 6 mm, length 20 cm) contained within a heating block powered by two heating cartridges inside the block. The temperature was controlled by a Eurotherm controller with a type K thermocouple positioned in the centre of the heater block. C_2H_2/Ar (5.01% balanced in Ar, BOC) and HCl/Ar (5.05% balanced in Ar, BOC) gases were dried, using moisture traps, prior to introduction to the reactor. In all cases, the reactor was purged with Ar (99.99% BIP, Air Products) prior to admitting the hydrochlorination reaction mixture. The reactor was heated to 200 °C at a ramp rate of 5 °C min^{-1} and held at this temperature for 30 min, all under a flow of Ar (50 ml min^{-1}). The reaction gas mixture of C_2H_2/Ar (23.56 ml min^{-1}), HCl/Ar (23.76 ml min^{-1}) and additional Ar (2.70 ml min^{-1}) was introduced into the heated reactor chamber containing catalyst (90 mg) at a total gas hourly space velocity (GHSV) of ~17,600 h^{-1}, keeping the C_2H_2: HCl ratio at a constant value of 1: 1.02. Typical time-on-stream experiments were conducted for 240 min. The gas phase products were analysed on-line using a Varian 450 GC equipped with a flame ionisation detector (FID). Chromatographic separation and identification of the products was carried out using a Porapak N packed column (6 ft × 1/8″ stainless steel). 100 % C_2H_2 conversion gives a VCM productivity of 35.33 mol kg_{cat}^{-1} h^{-1} under the reaction conditions used. The experimental error in acetylene conversion was ±1 % for repeat tests.

Catalyst Characterization

Powder X-ray diffraction (XRD) spectra were acquired using an X'Pert Pro PAN Analytical powder diffractometer employing a Cu K_α radiation source operating at 40 keV and 40 mA. The spectra

were analysed using X'Pert High Score Plus software. The mean crystallite size of the metallic gold nanoparticles, where possible, were determined using the Scherrer equation assuming a spherical particle shape and a K factor of 0.89 at the reflection arising from the set of (111) Au planes, at $2\theta = 38°$. The diffractograms of the catalysts were compared to the following reference files: Pd (00-001-1201), PdO (03-065-5065), Pt (01-080-3828), PtO(01-085-0714) and Au(01-071-4614).

X-ray absorption fine structure (XAFS) spectra for all the Au/C samples were recorded at the Au L_3 absorption edge, in transmission mode, at the B18 beamline of Diamond Light Source, Harwell, UK. The measurements were performed using a QEXAFS set-up with a fast-scanning Si (111) double crystal monochromator. The Demeter software package (Athena and Artemis) was used for XAFS data analysis of the Au/C absorption spectra in comparison to standards and relative to a Au foil.

Materials for examination by scanning transmission electron microscopy (STEM) were dry dispersed onto a holey carbon TEM grid. These supported fragments were examined using BF- and HAADF-STEM imaging modes in an aberration corrected JEOL ARM-200CF scanning transmission electron microscope operating at 200kV. This microscope was also equipped with a Centurio silicon drift detector (SDD) system for X-ray energy dispersive spectroscopy (XEDS) analysis.

XPS was carried out using a Thermo Scientific K-alpha photoelectron spectrometer with monochromatic Al K_α radiation. The resulting spectra were processed in CasaXPS and calibrated against the C(1s) line at 284.7 eV.

Data availability

Data supporting the results presented here, including how to access them, can be found in the Cardiff University data catalogue at http://doi.org/10.17035/d.2020.0098831512

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Author contribution statements

Catalysts were prepared, tested and characterised X.S, S.R.D, T.E.P and G.M under the supervision of S. A. K, S. J. F and G. J. H. Microscopy was carried out by T.E D, Q.H, L.L under the supervision of C.J.K. XPS was carried out by D.J.M & T.E.P. and testing under industrial conditions was carried out by N.C and P. J. The manuscript was written by S.J.F, S.A.K, G. M and G. J. H with input from all authors.

Competing Interests statement

The authors declare no competing financial interests.

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Figure 1 – Characterisation of Ru, Pd, Pt, Au / C catalysts prepared by impregnation of metal precursors from acetone. **a**, X-ray diffraction patterns of the Ru, Pt, Pd and Au catalysts made by wet impregnation with dry acetone. **b-d**, XPS analysis of the Pt $4f_{7/2}$, Pd $3d_{5/2}$ and Ru $3d_{5/2}$ regions of the Pt/C, Pd/C and Ru/C catalysts. **e**, FT-EXAFS and **f**, HAADF-STEM image of the 1wt.% Au/C material made by wet impregnation with dry acetone.

Figure 2 – Characterisation and testing of a series of Au/C catalysts prepared by impregnation of the metal precursor from different solvents. a, Steady state acetylene conversion of 1wt.% Au/C catalysts versus solvent polarity for materials prepared by wet impregnation of $HAuCl_4$ from various alcohol (●), ketone (▲), ether (♦) and aqueous solvents (■); the dotted line indicates the activity of the conventionally prepared *aqua regia* catalyst. The experimental error in the measurements was calculated as a standard deviation determined by repeated tests **b,** X-ray diffraction patterns of fresh 1wt.% Au/C catalysts prepared with these various solvents. **c,** Steady state acetylene conversion of 1wt.% Au/C catalysts prepared by wet impregnation of $HAuCl_4$ from extra dry acetone with the addition of various amounts of water. **d,** X-ray diffraction patterns of fresh 1wt.% Au/C catalysts prepared with various acetone/water mixtures.
Test conditions: 90 mg catalyst, 23.5 mL min^{-1} C_2H_2, 23.7 mL min^{-1} HCl and 2.70 mL min^{-1} Ar, temperature 200 °C.

Figure 3 – Au L_3-edge XAS characterisation of the Au/C-Acetone catalyst. a, Au L_3-edge XANES of 1wt.% Au/C-Acetone catalyst prior to reaction (fresh) and after 5 h of reaction (used), 1wt.% Au/C-*aqua regia* and various Au standards materials (Au foil, Au_2O_3, $KAuCl_4$/$[AuCl_4]^-$ and $[AuCl_2]^-$ from difference spectra calculated in reference 23. **b,** Linear combination fitting of the Au speciation from the Au L_3-edge XANES of the 1wt.% Au/C-*aqua regia* (fresh), 1wt.% Au/C-Acetone (fresh) and 1wt.% Au/C-Acetone (used) catalysts - Au standards used: Au(III)/$[AuCl_4]^-$, Au(I)/$[AuCl_2]^-$ and Au(0)/Au Foil. The error in the Au speciation was calculated by ATHENA during the linear combination fitting process. **c,** Fourier transform of the k^3-weighted χ EXAFS data of 1wt.% Au/C-Acetone (fresh) and 1wt.% Au/C-Acetone (used), 1wt.% Au/C-*aqua regia* (fresh) and references ($KAuCl_4$, Au_2O_3 and Au foil).

Figure 4 – Catalytic performance of the Au/C-Acetone catalyst. Two-day time-on-line acetylene hydrochlorination activity profiles of the Au/C-Acetone (▲) and Au/C-*aqua regia* (■) catalysts.

Test conditions: 90 mg catalyst, 23.5 mL min^{-1} C_2H_2, 23.7 mL min^{-1} HCl and 2.7 mL min^{-1} Ar, Temperature 200 °C.

Figure 5 – Characterisation and Testing of Ru, Pd, Pt, Au / C catalysts prepared by impregnation of metal precursors from acetone. a, Linear combination fitting (LCF) of the Au speciation from the Au L_3-edge XANES of the 1wt.% Au/C-acetone catalyst at different stages of its lifetime, (i.e., fresh, at different times-on-line and under different gas environments). The error in the Au speciation was

calculated by ATHENA during the linear combination fitting process. **b,** Correlation between steady state activities of acetylene hydrochlorination at 100 min of reaction with the standard electrode potential of the constituent catalyst metals. Standard electrode potentials of the metal chloride salts are used as sourced from reference 16. The experimental error in the measurements was calculated as a standard deviation determined by repeated tests

Table 1 – Acetylene conversion values for catalysts prepared with a series of low polarity, high boiling point solvents.

Test conditions: 90 mg catalyst, 23.5 mL min^{-1} C_2H_2, 23.7 mL min^{-1} HCl and 2.7 mL min^{-1} Ar, Temperature 200 °C.

Catalyst	Polarity ($E_T(30)$)[24]	Boiling Point (°C)	Drying Temperature (°C)	Acetylene Conversion (%)
Au/C-DMSO	45.0	189	195	14
Au/C-DMF	43.8	154	160	8
Au/C-Cyclohexanone	40.8	155	160	3
Au/C-Acetone	42.2	56	45	20
			65	20
			140	22