

Research Article

# Influence of Surface Functionalities on Au/C Catalysts for Oxidative Homocoupling of Phenylboronic Acid

Published as part of ACS Sustainable Chemistry & Engineering special issue "Single-Atom Catalysts: Synthesis and Sustainable Applications".

Tanja E. Parmentier, Anna Lazaridou, Joseph Cartwright, Ben Davies, Simon Dawson, Grazia Malta, Simon Freakley, Thomas E. Davies, David J. Morgan, Simon Kondrat, Christopher J. Kiely, Samuel Pattisson, Nicholas F. Dummer,\* and Graham J. Hutchings\*



develop nanoparticulate Au species early in the reaction; however, only the *aqua regia* prepared catalyst is active. We ascribe the activity of the *aqua regia* prepared Au catalyst to excess Cl and the presence of C–Cl surface species in combination with Au. Carbon treated with *aqua regia* was inactive; however, when used as a support for Au deposited with acetone or via a sol immobilization method, activity was comparable to the *aqua regia* prepared catalyst. The role of C–Cl and Au nanoparticles is discussed with respect to their correlation to the biphenyl yield, which is shown to be significant only when the C–Cl species are present on the catalyst.

KEYWORDS: gold, homocoupling, single site catalyst, phenylboronic acid, surface chloride

# 1. INTRODUCTION

The formation of new C-C bonds through coupling reactions is of interest to many sectors, including pharmaceutical, agrochemical, and fine chemical industries.<sup>1-</sup> <sup>o</sup> Homogeneous Pd-based catalysts are typically employed in Suzuki coupling reactions to form C-C bonds from organoboron compounds such as phenylboronic acid.<sup>3,7-9</sup> As an example, the catalytic cycle using Pd-based catalysts in basic conditions initially requires the oxidative addition of the aryl halide to a Pd<sup>0</sup> center. Transmetalation of an aryl substituent is required from a boronate species to form a di(aryl)  $Pd^{II}$  species, followed by reductive elimination of the di(aryl) species to regenerate the Pd<sup>0</sup> center.<sup>10</sup> Homogeneous catalysts are subject to issues of separation, and reports have emerged whereby immobilizing such Pd complexes on metal oxide, carbon, or zeolitic supports can overcome this.<sup>11</sup>

The use of heterogeneous catalysts is well-known for homocoupling reactions, with examples including nanoparticulate Pd<sup>7</sup> and, more recently Au<sup>12-16</sup> and AuPd.<sup>17,18</sup> Corma et al. demonstrated that Au<sup>III</sup> could be used as an active center for homocoupling as it is isoelectronic with Pd<sup>II</sup>.<sup>12</sup> The coupling reaction of boronic acids, such as phenylboronic acid, proceeds in a manner similar to that over the Pd catalysts described above. That is, two nucleophilic aryl boron compounds (Ar-M') can undergo transmetalation with the aid of a higher valent metal ( $M^{n+2}$ ). This is followed by reductive elimination to release the biaryl product for the low-valent metal species ( $M^n$ ). Reoxidation of the low-valent metal species is necessary to restart the catalytic cycle.<sup>19</sup> Recent progress in this field has revealed the challenges associated with identifying the definitive active center as three active Au states (0, +1, +3) that commonly coexist on a catalyst, and Au nanoparticles may possess a slight surface charge usually expressed as Au<sup> $\delta$ +15,20,21</sup>

Received:	March 20, 2025
Revised:	June 5, 2025
Accepted:	June 6, 2025

Α

Deconvolution of the competing Au species, by Corma and co-workers, demonstrated that the concentration of cationic Au present at the nanoparticle/support interfaces or as highly dispersed species on the support is strongly related to activity.<sup>22</sup> To support this inference, cationic Au salts (AuCl, NaAuCl<sub>4</sub>)<sup>23</sup> and Au<sup>III</sup> complexes<sup>24,25</sup> have been reported to be active for the homocoupling of phenylboronic acid. On the basis of these studies, the concentration of Au<sup>III</sup> may be considered to be related to catalytic activity. However, as unsupported Au nanoparticles stabilized by PVP<sup>16</sup> and basefree reactions over metallic Au supported on Al-Mg oxides<sup>26</sup> exemplify, elucidation of the active site is not conclusive. Recently, Sakurai et al. demonstrated that modifying the surface of a hydroxyapatite support for Au nanoparticles could stabilize the reusability of this catalyst.<sup>27</sup> In their work, Au nanoclusters stabilized by PVP were deposited on hydroxvapatite or fluoride-modified hydroxyapatite. The phosphate group present was reported to enhance the stability of the Au nanoparticles, and furthermore, the presence of surface fluoride ions facilitated C-B bond activation.

We have previously reported that carbon-supported Au single metal site heterogeneous catalysts (SMSHCs) are active for the oxidative homocoupling of phenylboronic acid to biphenyl (BP).<sup>13</sup> However, under reaction conditions, the dispersed Au species, which were comprised of a near 1:1 mixture of Au<sup>1</sup> and Au<sup>III</sup>, rapidly agglomerated into Au nanoparticles within the first 5 min of the reaction, and the catalyst was found to be almost completely reduced, with only a minor concentration of Au<sup>III</sup> remaining. Consequently, the activity of the used 1% Au/C catalyst was found to be comparable to that of the as-prepared catalyst over 2 h of time online. We postulated at the time that the stability of supported Au–Cl<sub>x</sub> was low and that stabilizing this species may prove to be advantageous.

Here we report the activity of Au/C SMSHCs for the oxidative homocoupling reaction of phenylboronic acid through investigating the evolution of the catalyst following use. The two Au/C SMSHC catalysts were prepared using different solvents, namely *aqua regia* and dry acetone, and consequently possess significantly different Cl concentrations. The different carbon surface functionalities in both catalysts were studied by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FT-IR) spectroscopy, and Cl edge X-ray absorption spectroscopy (XAS), and their influence on the catalyst performance was investigated.

#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** Activated carbon (100–140 mesh, Norit ROX 0.8), chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O, Alfa Aesar, 99.9%), hydrochloric acid (HCl, Thermo Scientific Chemicals 6M), nitric acid (HNO<sub>3</sub>, Thermo Scientific Chemicals, 70%,), extra-dry acetone (Thermo Scientific Chemicals, 99.8%, AcroSeal), NaBH<sub>4</sub> (Merck,  $\geq$ 99.99%), methanol (Thermo Scientific Chemicals,  $\geq$ 99.6% reagent grade), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, Merck ACS reagent,  $\geq$ 99.9%), phenylboronic acid (Merck,  $\geq$ 97.0% HPLC grade), and o-xylene (Merck,  $\geq$ 98.0%) were used as received.

**2.2. Catalyst Preparation.** 2.2.1. Wet Impregnation with Extra Dry Acetone. A wet impregnation method with extra dry acetone for the preparation of Au/C SMSHCs was followed.<sup>28</sup> The catalysts were prepared by dissolving the chloroauric acid in 5.4 mL of extra-dry acetone. Here, the use of extra dry acetone minimizes the effect of additional water during preparation, the presence of which has previously been found to increase nanoparticle formation.<sup>28</sup> The metal precursor solution was added dropwise to the activated carbon support and left to stir for 1 h at room temperature in a covered

vessel. Subsequently, the catalyst was dried in a furnace at 45 °C for 16 h under a N<sub>2</sub> flow. The catalyst made by this method is referred to as **Au/C-acetone** and has a theoretical weight loading of 1 wt % Au unless otherwise noted.

2.2.2. Wet Impregnation with Aqua Regia. Activated Carbon supported SMSHCs Au catalyst was prepared by a wet impregnation with aqua regia, as established previously for the hydrochlorination of acetylene.<sup>29</sup> Chloroauric acid was dissolved in 5.4 mL of aqua regia (HCl/HNO<sub>3</sub> vol/vol = 3) and added dropwise to the activated carbon while being stirred continuously. The mixture was left to stir for 1 h at room temperature until the NO<sub>x</sub> formation subsided. It was then transferred to a furnace to dry at 140 °C. for 16h under a N<sub>2</sub> flow. The catalyst prepared by this method is referred to as Au/C-AR and has a theoretical weight loading of 1 wt % Au unless otherwise noted.

2.2.3. Sol Immobilization. Sol-immobilization methodology was used to prepare carbon-supported gold nanoparticle catalysts without a stabilizer.<sup>30</sup> For the synthesis of 1 g of catalyst with a theoretical weight loading of 1 wt %, an aqueous solution of chloroauric acid  $(12.25 \text{ mg L}^{-1})$  was prepared. The chloroauric acid solution (0.815) mL) was added to a beaker containing 400 mL of deionized water, and the obtained yellow solution was stirred. A fresh solution of the reducing agent, 0.1 M sodium borohydride NaBH<sub>4</sub>, was added to the required amount (mol. NaBH4:mol. Au = 5:1) to form a red sol and stirred for 30 min to allow the sol to generate. The formed sol was then immobilized by adding the activated carbon support (0.99 g)and 8 drops of H<sub>2</sub>SO<sub>4</sub> until a pH of 1 was reached. A low pH ensures an optimum interaction of the sol and the support. After 1 h of stirring, the mixture was filtered, washed thoroughly with 2 L of distilled water to remove any traces of H<sub>2</sub>SO<sub>4</sub>, and left to dry for 16 h at 110 °C. The catalyst obtained following this procedure is labeled Au/C-sol.

2.2.4. Aqua-Regia-Treated Carbons. Activated carbon was treated with 5.4 mL of aqua regia (HCl/HNO<sub>3</sub> vol/vol 3) added dropwise while being stirred continuously. The mixture was left to stir for 1 h at room temperature until the NO<sub>x</sub> formation subsided. It was then transferred to a furnace to dry at 140 °C for 16h under a N<sub>2</sub> flow and referred to as C-AR. This material was used as a support for Au/(C-AR)-acetone and Au/(C-AR)-sol following the respective methods detailed above, substituting the untreated support for C-AR.

**2.3. Catalyst Testing.** In a typical catalytic test, methanol (5 mL) was added to a flask (50 mL) containing phenylboronic acid (0.3 mmol), potassium carbonate (0.4 mmol), and catalyst (100 mg of 1 wt % Au/C). Catalytic testing was performed by using a Radleys carousel magnetic stirrer at 45 °C and 800 rpm, open to air at atmospheric pressure. o-Xylene was used as an internal standard. The catalytic activity of Au(III) chloride was tested by using a solution of HAuCl<sub>4</sub>·3H<sub>2</sub>O. The reaction mixture was analyzed by using an Agilent Technologies 1200 series HPLC equipped with two reverse-phase columns (Agilent Poroshell 120, SB-C18, 4.6 × 150 mm, 2.7  $\mu$ m) connected in series and a DAD detector (G1315D-1260 DAD VL). Acetonitrile (50%, Fischer, HPLC gradient grade) and water (50%, Fischer, HPLC gradient grade) and water (50%, Fischer, HPLC gradient grade) were used as the mobile phase (0.5 mL min<sup>-1</sup>).

**2.4. Characterization.** Powder X-ray diffraction (XRD) spectra were acquired between  $\theta$  = 5 and 80° using an X'Pert Pro PANalytical powder diffractometer employing a CuKa radiation source operating at 40 keV and 40 mA. Analysis of the spectra obtained was performed by using X'Pert High Score Plus software.

Materials for examination by scanning transmission electron microscopy (STEM) were dry-dispersed onto a 300-mesh copper holey-carbon grid. These supported fragments were examined using the HAADF–STEM imaging mode in aberration-corrected (AC) imaging mode ThermoFisher Scientific Spectra 200 scanning STEM operating at 200 kV. Probe currents were 50-150 pA, and a convergence angle of 30 mrad was used.

For the analysis of O functionalities of the activated carbons, the samples were heated at a constant rate under a  $N_2$  flow. The adsorbed CO and CO<sub>2</sub> caused by the decomposition of the surface oxygenated species on the carbon were monitored by FT-IR. The activated



Figure 1. Au  $L_3$  edge-normalized XANES spectra of (a) the Au/C-acetone catalyst (blue, squares) and metallic Au foil (black, spheres) and (b) the Au/C-AR catalyst (red, triangle) and metallic Au foil (black, spheres). Fourier transform of the k<sup>3</sup>-weighted Au  $L_3$  EXAFS of (c) the Au/C-acetone catalyst (blue, squares) and metallic Au foil (black, spheres), (d) the Au/C-AR catalyst (red, triangle), and metallic Au foil (black spheres). Representative high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of (e) are the Au/C-acetone catalyst and (f) are the Au/C-AR catalyst.

carbons were heated in a fixed-bed flow reactor. The sample (150 mg) was fixed in a quartz tube (7 mm i.d.) between two pieces of quartz wool. The sample was heated from 25 to 600 °C in 5 °C steps under a constant N<sub>2</sub> flow (100 mL min<sup>-1</sup>). Analysis of the effluent gases was carried out by a Gasmet FT-IR with a 0.4 L sample cell. For analysis of O functional groups on carbons, samples should be heated up to 1100 °C; however, due to equipment limitations, heating was only feasible to a maximum of 600 °C.

X-ray absorption fine structure (XAFS) data on Au L3-edge and Cl K-edge were collected at the B18 beamline at the Diamond Light Source in Harwell, UK. The measurements were performed using a QEXAFS setup with a fast-scanning Si (111) double crystal monochromator and a 36-element Ge fluorescence detector. Data were processed by using Athena software.

XPS was performed using a Thermo Scientific K-alpha<sup>+</sup> photoelectron spectrometer with micro-focused monochromatic  $Al_{K\alpha}$ radiation operating at 72 W (6 mA × 12 kV). The resulting spectra were processed in CasaXPS<sup>31</sup> and calibrated against the C(1s) line at 284.5 eV, typical for graphitic carbons. Spectra are quantified after removal of a Shirley background using Scofield sensitivity factors and an electron energy dependence according to the TPP-2 M formulation. Curve fitting, where applicable, was achieved using line shapes derived from bulk standards, such as metallic Au, acquired under identical analysis conditions. Where bulk materials were not available, peaks are fitted using a pseudo-Voigt function defined by the LA(50) line shape in CasaXPS.

## 3. RESULTS AND DISCUSSION

3.1. Characterization of Au on the As-Prepared Au/C SMSHCs. The preparation of 1 wt % Au/C SMSHCs was achieved via two preparative techniques, whereby chloroauric acid was dissolved in either aqua regia or extra dry acetone. Both materials have been reported previously and extensively characterized in respective publications.<sup>28,29</sup> Initially, the two 1 wt % Au catalysts, denoted Au/C-AR and Au/C-acetone, were analyzed using powder XRD and compared to the activated carbon support (Figure S1). The diffraction patterns are characteristic of carbon with the presence of graphitic domains with broad reflections at 24° and 44°. Sharp reflections present in the diffractogram of the Au/C-acetone sample correspond to NaCl, which exists as an impurity. The treatment with acetone during the preparation and drying step facilitates crystallization and deposition of NaCl from the carbon. No reflections corresponding to Au are observed in either sample, confirming that Au nanoparticles >3 nm in size are not present.

To confirm that Au was dispersed as single atoms on the carbon support in both samples, we used XAS and AC-STEM. Analysis of the normalized Au L3-edge X-ray absorption near edge structure (XANES) region demonstrates that neither catalyst is comparable to the Au foil standard (Figure 1a,b). A linear combination fitting (LCF) of the XANES region allowed determination of Au speciation and confirmed that both catalysts are exclusively composed of cationic Au species, with the Au/C-acetone sample containing an increased concentration of Au (III), with an Au(I):Au(III) ratio of (1.33:1) compared to (3.35:1) in the Au/C-AR sample (Figure S2). No metallic Au species were observed in either sample. Similarly, the Fourier transform of the EXAFS region of both samples was comparable, with the presence of a clear peak associated with the Au-Cl distance of ca. 1.85 Å and the absence of any peak relating to Au-Au distances (Figure 1c,d). This indicates that, in both catalysts, the cationic Au species present on the support are stabilized by Cl ligands. Furthermore, AC-STEM imaging shows that in both cases, the Au is well dispersed, and the species were present mostly as single atomic species (Figure 1e,f). Inspection at low magnification electron micrographs over multiple areas also showed the absence of large Au particles or agglomerations consistent with the XANES data. (Figure S3)

**3.2. Surface Functionalities Introduced by the Impregnation Solvent.** Factors such as the surface functionality of the support can affect the performance of a catalyst. O-containing groups can, for example, affect the stability of the catalysts, metal dispersion, and absorption of reaction species.<sup>32–34</sup> Figueiredo et al. illustrated the different types of O-containing functional groups that can be present on the surface of carbon.<sup>35</sup>

Both acetone and aqua regia prepared samples contain exclusively atomically dispersed cationic Au based on XAS measurements, although metallic Au is noted in XPS and has been attributed to reduction caused by photon absorption cross sections.<sup>29</sup> However, the interest herein is the modification of the surface during the impregnation step to determine if they contribute to the differences observed in the Au speciation.

The XPS-derived wt % concentrations are given in Table 1, with the full deconvoluted regions given in Figure S4. It is evident that the acetone preparation yields surface concentrations similar to those of the virgin carbon, whereas the aqua-

# Table 1. XPS Derived wt % of the Fresh and Treated Carbons

	total XPS derived elemental wt %						
carbon	C 1s	O 1s	Cl 2p	S 2p	Si 2p	Na 1s	Au 4f
virgin	91.3	6.1	0.3	0.5	1.1	0.4	0.0
Au/C-acetone	90.0	5.6	0.9	0.5	0.9	0.6	1.1
Au/C-AR	83.8	9.0	5.7	0.5	0.9	0.3	0.9

regia preparation has a change in both Cl and O concentrations, from 0.3 to 5.7 wt % and 5.6 to 9.0 wt % respectively.

Analysis of the C 1s spectrum can be complex due to asymmetric peak shapes, which can change with carbon morphology,<sup>36</sup> so instead, we focus here on the O 1s spectra. The O 1s region itself is generally free form spectral overlap, although with Al radiation, the Na KLL Auger-Meitner peak does interfere, this is ca. 20% of the Na 1s intensity and given the low concentrations of Na found in the carbons, this will have a negligible influence on the O 1s concentrations, and consequently we do not account for this in our calculations.

Analysis of the O 1s region reveals a series of oxygen signals with binding energies ( $\pm 0.2 \text{ eV}$ ) of 531.1, 532.2, 533.4, 535.4, 537.3, and 539.3 eV. Signals above 534 eV have previously been attributed to occluded water,<sup>37</sup> but Pi–Pi\* transitions of the oxygen in carbonyl species or conjugated ring-bound oxygen functions also yield satellite structure here and are readily observable in polymeric materials such as PEEK and PET due to electron delocalization.<sup>38</sup> These higher energy signals are, therefore, diagnostic of such functionalities. The signals at ca. 531, 532, and 533 eV have been identified, through previous chemical derivatization studies, as ketone carbonyl, carboxylic carbonyls, and C–O–C/OH groups.<sup>36</sup>

The Cl 2p signal changed dramatically with treatment. The trace chlorine is found on the virgin carbon can fitted to two states with Cl  $2p_{3/2}$  energies of 197.8 and 200 eV, which we attribute to chloride (presumably from NaCl) and C–Cl bonds, respectively. Acetone-based preparation reveals a change in the Cl 2p speciation. The chloride signal at 196.7 eV is seen to increase and is linked to the presence of Au–Cl species; the C–Cl functionality also increases, likely through reaction of chloride ions with the carbon surface. Intensity is also noted above ca. 202 eV, which can be fitted to spin–orbit split peaks with binding energies of 201.6 and 203.0 eV and assigned as C–O–Cl and  $-ClO_2^-$  moieties.<sup>37</sup>

However, aqua-regia preparation has a significant effect on the oxygen and chlorine content. First, the preparation has a marked change in the Cl 2p region. Although similar binding energies are noted for the fitted species as those observed for the acetone preparation, their concentration is significantly higher. Moreover, significant intensity is noted above 204 eV and suggests direct chlorination of the phenyl rings of the graphitic carbon, as noted for chlorinated carbon black<sup>39</sup> and chlorinated benzene polymers such as polychlorostyrenes.<sup>38</sup>

Table 2 shows the relative percentages of the oxygen functionalities revealed by the curve fitting. Despite the known increase in O 1s wt % for the aqua-regia treatment, the relative percentages of oxygen functionalities do not vary drastically, although the acetone preparation does have a higher percentage of species at ~533 eV of 45.1 compared to 32.9 for the virgin carbon and 37.0 for the Au/C-AR catalyst.

Thermal analysis with FT-IR was used to analyze the untreated carbon support (Figure 2a), as well as the Au/C-

D

pubs.acs.org/journal/ascecg



#### Table 2. Ratios of Oxygen Species for Virgin Carbon and the Preparations

Figure 2. Temperature ranges of decomposition of various types of O functional groups resulting in evolution of CO (black squares) and  $CO_2$  (blue circles) from (a) the untreated carbon support, (b) Au/C-acetone, and (c) Au/C-AR.

acetone and Au/C-AR samples (Figure 2b,c), and corroborate the XPS analysis with respect to surface functionality. Gas evolution when the sample was heated to 600 °C can be related to the following functional groups: carboxylic acids (CO<sub>2</sub> evolution in a range of 95-460 °C), anhydrides (CO evolution from 380  $^\circ C$  and CO\_2 evolution from 380  $^\circ C)$  and phenols (CO evolution from 480 °C).<sup>35,40,41</sup> The samples were heated from 30 to 600  $^\circ C$  under  $N_{2_{\rm c}}$  and the concentration of CO<sub>2</sub> and CO was monitored with FT-IR, resulting in a corresponding concentration, given in ppm. Impregnation with aqua regia has a very distinct oxidizing effect on the carbon surface, resulting in a higher concentration of O-containing groups, present as carbonyl and ether groups (Figure 2c), which is in agreement with the XPS results. A significantly higher concentration of CO2 evolved from the Au/C-AR material between temperatures of ca. 250 and 500 °C, which can be ascribed to the decomposition of carboxylic acids. A higher concentration of desorbed CO was also found between temperatures of ca. 200 and 550 °C, which is ascribed to anhydrides and phenolic species. Conversely, impregnation with acetone does not introduce sufficiently higher Ocontaining groups on the surface compared to untreated carbon (that can be detected using this FT-IR technique),

despite a higher concentration of ether being observed via XPS.

**3.3. Catalyst Testing.** The performance of the SMSHCs was tested in the oxidative homocoupling of phenylboronic acid in the presence of a base ( $K_2CO_3$ ). Blank tests led to no BP product formation with either no catalyst or untreated carbon, or base-free reaction over Au/C-AR. For comparison, a homogeneous catalyst, HAuCl<sub>4</sub>, was tested. The catalysts were tested for five individual reactions over different time periods, namely, 30, 60, 120, 180, and 240 min. The BP yields of each of these tests were averaged to form one point in the time-online (TOL) plot of the catalyst as presented in Figure 3. The selectivity to BP was ca. 60% across the TOL range as reported previously.<sup>13</sup>

In the case of the homogeneous catalyst (HAuCl<sub>4</sub>), reduction of the Au species was observed during the reaction. Figure 3 illustrates that the homogeneous catalyst (black circle) achieved lower BP yields than Au/C-AR (red triangle) across the reaction time, and the reduction of HAuCl<sub>4</sub> can explain this lower activity. The Au/C-AR material demonstrated good activity in the coupling reaction, with the yield of BP increasing linearly over time following an induction period of ca. 30 min. In contrast, the Au/C-acetone sample (blue square) was completely inactive.



**Figure 3.** Biphenyl yield as a function of reaction time over the SMSHCs, Au/C-AR (red triangle) and Au/C-acetone (blue square), in the homocoupling reaction of phenylboronic acid, compared to HAuCl<sub>4</sub> (black circle), a homogeneous catalyst. *Reaction conditions:* 100 mg of catalyst (or equivalent Au concentration), 0.3 mmol of phenylboronic acid, 0.4 mmol of K<sub>2</sub>CO<sub>3</sub>, 45 °C, 800 rpm, open to atmosphere.

The difference between the Au/C-acetone and Au/C-AR catalyst was studied in more detail by monitoring the concentration of leached Au species, the pH of the reaction mixture, and particle size at certain stages of the reaction. These results can be seen in Table S1 for the Au/C-AR and

Au/C-acetone catalysts. There is a clear difference in the concentration of leached Au in the reaction mixtures of each catalyst; 17 ppb of Au was leached from the Au/C-AR catalyst at the start of the reaction (2 min), and during the reaction, no further Au was detected in the liquid phase. This confirms that the Au/C-AR catalyst remains mostly as a heterogeneous catalyst, unlike many heterogeneous Pd-based Suzuki crosscoupling catalysts, where the leached Pd species are often the actual active species in the reaction.<sup>42</sup> On the other hand, the Au/C-acetone catalyst was found to be more prone to leaching than the Au/C-AR catalyst; with 571 ppb Au being leached at 2 min and a further 960 ppb by 240 min of reaction. This could be related to the lower concentration of functional groups on the carbon support and the presence of the base. The inactivity of the leached Au from the Au/C-acetone catalyst in comparison to the HAuCl<sub>4</sub> salt (Figure 3) suggests that homogeneous Au is not active, but rather that an Au-Cl species is required to complete the formation of BP.

The outcome of Suzuki-type coupling reactions can be highly dependent on the pH of the reaction mixture.<sup>43</sup> Therefore, the pH of the reaction over the Au/C-AR and Au/ C-acetone catalysts was measured at several stages of the reaction (Table S1). One can see that the pH of the reaction mixture of the Au/C-AR catalyst is lower than that of the Au/ C-acetone catalyst. To investigate if the higher pH of the reaction solution of the Au/C-acetone catalyst is responsible for the inactivity, the pH was lowered to a similar pH value to that observed in the reaction with the *aqua regia* catalyst by the addition of a small amount of HNO<sub>3</sub>. The results presented in



Figure 4. Representative HAADF-STEM images of the (a) Au/C-acetone and (b) Au/C-AR catalysts after 240 min of reaction. (c) EXAFS spectra and (d) LCF of the XANES region of the spent Au/C-AR catalyst which was used for 360 min of reaction. (e) Cl K-edge XANES spectrum of the fresh (red) and spent Au/C-AR catalyst after 240 min of reaction (black). The prepeak is marked with an  $\blacklozenge$ , and the main absorption peak is marked with an  $\blacklozenge$ .

	oxygen			chlorine			
sample	531 eV	532 eV	533 eV	535–539 eV	M-Cl	C-Cl	ClOx
untreated carbon	1.45	1.8	2.14	1.12	0.16	0.06	0
Au/C-acetone	0.79	1.32	2.54	0.99	0.42	0.43	0.11
Au/C-AR	2.25	1.76	3.3	1.6	0.48	4.24	1.15
Au/(Cox0.5)-acetone	5.52	2.65	8.41	2.57	0.22	0.15	0
Au/(Cox10)-acetone	5.59	10.83	14.45	3.45	0.15	0.15	0

Table 3. Distribution of O and Cl Groups (as wt %) of the Catalysts as Determined by XPS of the O 1s and Cl 2p Regions, Compared to Untreated Carbon

Table S2 demonstrate that when the reaction is performed at a pH of 10, the Au/C-acetone catalysts show no activity. Therefore, we conclude that the different pH values of the reaction mixtures did not influence the homocoupling reaction.

The state of the catalysts prior to the reaction was shown to be comparable, apart from the presence of increased surface O and C–Cl concentrations on the Au/C-AR catalyst. Therefore, the inactivity of the Au/C-acetone catalyst was somewhat surprising. Spent catalysts were studied with AC-STEM and XAS to understand the state of the Au species present on the catalysts after the reaction and to corroborate the Au particle diameters calculated from XRD data (Table S1). HAADF-STEM images revealed that the dispersed cationic Au initially present in both catalysts had agglomerated to form large Au particles within 30 min of reaction, some as large as 0.5  $\mu$ m in diameter (Figure 4a,b). However, the activity of the Au/C-AR catalyst was not perturbed by this agglomeration effect and continued to be active across the entire 240 min timespan of the reaction (Figure 3).

Figure 4c illustrates the Fourier transform of the EXAFS region of a spent Au/C-AR catalyst (red triangles) compared to that of a Au(0) reference foil (black squares). One can see that both these spectra are comparable, and the Au-Cl contribution that was observed in the as-prepared catalysts, at around 1.85 Å, is absent in the spent catalyst. The LCF of the XANES region, shown in Figure 4d, reveals that Au in the spent catalyst is now predominantly metallic Au. Additionally, the Cl K-edge spectra of the fresh and spent Au/C-AR catalyst are compared in Figure 4e. A pre-edge peak, visible in the Cl K-edge XANES of the fresh Au/C-AR catalyst (red line), arises from a transition from the Cl 1s orbital to a partially filled antibonding wave function  $(\psi^*)$  formed by covalent bonding of the Cl 3p and the d-orbital of the Au. In the spent catalyst (black line), this peak is absent, which indicates that no Cl-Au bonds are present and suggests that only Au nanoparticles are present. However, HAADF-STEM showed that some single atoms are still present in both catalysts post-reaction, albeit at a far lower concentration (Figure S5) when compared to the fresh catalyst (Figure 1e,f). The induction period noted in Figure 3 suggests that Au nanoparticle formation restricts efficient homocoupling in the first 30 min of reaction. As previously reported, nanoparticle formation was noted after 5 min of reaction.<sup>13</sup>

**3.4. Influence of O Groups on the Support.** To investigate how the observed differences in the O functionality on the catalyst support may influence the activity of Au/C-AR and Au/C-acetone, three additional catalysts were prepared with a high concentration of surface O-containing groups. The first catalyst, denoted as Au/C-HNO<sub>3</sub>, was prepared by a wet impregnation using solely concentrated nitric acid. This method has been reported previously<sup>29</sup> to prepare active catalysts for the acetylene hydrochlorination reaction and has

been characterized here using XAS (Figure S6). The EXAFS region of this catalyst (Figure S6a) is comparable to that of the Au/C-AR catalyst (Figure 1d) had a clear contribution of Au-Cl around 1.5 Å. From the LCF of the XANES region (Figure S6b) it is clear that this catalyst is comprised mainly of cationic Au, but also contains a small amount of Au(0) in the form of nanoparticles smaller than the detection limit of XRD (Figure S7). The two other catalysts with a higher surface O content were prepared using a carbon support that was oxidized using the Hummers oxidation method according to a previously reported procedure.<sup>33</sup> In this case, either 0.5 g or 10 g of potassium permanganate per 5 g of carbon support was utilized to achieve drastically different O contents. Au was deposited on these supports as before by using dry acetone solvent preparations. The synthesized catalysts are referred to as Au/ (Cox0.5)-acetone and Au/(Cox10)-acetone hereafter. There were no reflections generated by nanoparticulate Au in the XRD diffractograms acquired from these catalysts (Figure S7). In the case of the Au/(Cox0.5)-acetone catalyst, some NaCl reflections were visible.

The surface O and Cl content of these specially prepared additional catalysts was determined by XPS (Table 3). Oxidative pretreatment of the carbon support via the Hummers method (Au/(Cox0.5)-acetone and Au/(Cox10)-acetone) results in a highly oxidized surface, demonstrated by the high O 1s wt %. Notable is the decrease in the satellite structure in the Au/(Cox10)-acetone O 1s spectrum, suggesting significant disruption of the conjugated graphitic network and supported by the broadening of the sp2 peak at 284.5 eV, due to either increased sp3-like defects or sp3-carbon.

Significantly, these materials have only a small chlorine content with Au–Cl and C–Cl species as previously noted. Moreover, the gold speciation is markedly different from the acetone or aqua-regia preparations. For the Au/(Cox0.5)-acetone catalyst, only a small fraction of the total Au content is cationic (ca. 15%), whereas the total Au detectable by XPS for the Au/(Cox10)-acetone catalyst is low but does have an approximate 4:2:1 ratio between metallic, Au<sup>1+</sup> and Au<sup>3+</sup> species (Figure S8).

The total O content of all three catalysts was higher than that of the Au/C-AR catalyst, which is primarily due to an increase in the concentration of carbonyl and ether groups on the carbon surface (Table 4). However, no significant product formation was observed over any of these oxidized carbon catalysts (Table 4). These findings suggest that O groups do not play a role in the activity of the catalyst. From comparison of the O 1s and Cl 2p (Table 3), it is clear that a high Cl content, specifically C–Cl, is very distinctive for the Au/C-AR catalysts.

**3.5. Influence of Impregnation with Aqua Regia.** Thus far, only Au/C-AR was active for the homocoupling reaction.

Table 4. O Content of the Additionally Prepared Catalysts and Biphenyl Yield after 240 min of the Homocoupling Reaction<sup>a</sup>

catalyst	O content (wt %)	BP yield (%)			
untreated carbon	4	0			
Au/C-AR	9	44			
Au/C-acetone	5	0			
Au/C-HNO <sub>3</sub>	13	0.5			
Au/(Cox0.5)-acetone	17	0.3			
Au/(Cox10)-acetone	29	1			
<sup>a</sup> The O content was determined by XPS.					

To study whether the formation of C-Cl surface species via impregnation with aqua regia is essential in creating an active catalyst for this reaction, we treated the carbon support with aqua regia and subsequently used this material to synthesize various catalysts. For the treatment with aqua regia, the same procedure was followed as for the synthesis of the Au/C-AR catalysts, with the exception of the introduction of HAuCl<sub>4</sub>. Two different catalysts were prepared using this aqua regiatreated support, one by impregnation with dry acetone (Au/ (C-AR)-acetone) and one by sol-immobilization in the absence of a stabilizer (Au/(C-AR)-sol). We previously reported the low activity of the Au/C-sol catalyst, prepared with PVA stabilizer,<sup>13</sup> which was ascribed to the blocking of active sites by the stabilizer. Here, we used a stabilizer-free preparation to compare the catalysts such that, if nanoparticulate Au is the active species, then the reaction should proceed unhindered.<sup>30</sup>

It is evident that the impregnation with *aqua regia* plays an essential role in the homocoupling reaction, as catalysts prepared using the *aqua regia*-treated support are all active, which is in stark contrast to the analogous materials made on the untreated support, which were all inactive (Figure 5). At 240 min of reaction, the BP yields over the Au/C-AR, Au/(C-AR)-acetone, and Au/(C-AR)-sol were significantly different at 45, 36, and 28%, respectively. Interestingly, the initial BP



**Figure 5.** Yield of BP over catalysts prepared on an *aqua regia* treated support (C-AR) and nontreated analogues; Au/C-AR (red triangle), Au/(C-AR)-acetone (violet circle), Au/(C-AR)-sol (yellow diamond), Au/C-acetone (blue square), Au/C-sol (black downward triangle). Reaction conditions: 100 mg of catalyst (or equivalent Au concentration), 0.3 mmol of phenylboronic acid, 0.4 mmol of K<sub>2</sub>CO<sub>3</sub>, 45 °C, 800 rpm, open to atmosphere.

formation rate was in the reverse trend order of the final BP yield value.

**3.6. Influence of Cl on the Support.** There is a large difference in the concentration and type of Cl surface functionalities between the Au/C-AR and the Au/C-acetone catalysts, despite their role acting as a stabilizing ligand for the Au species in both catalysts. To study if there is a difference in the ligand-metal interaction between the two catalysts, the catalysts were studied using Cl K-edge XAS. Furthermore, the catalysts were tested for their ability to catalyze a Suzuki-type cross-coupling reaction. Hypothetically, this reaction could proceed through the in situ halodeboronation of phenylboronic acid to form chlorobenzene, followed by a cross-coupling between phenylboronic acid and chlorobenzene to form biphenyl.<sup>44</sup>

3.6.1. Cl Ligand K-Edge XAS. Cl functions as a stabilizing ligand for the Au species in both of the as-prepared SMSHCs. Ligand K-edge XAS can provide complementary information to the Au  $L_3$ -edge data, such as information on the electronic structure of the transition metal complexes.<sup>45–48</sup> Illustrated in Figure 6 are the Cl K-edge XANES spectra of the Au/C-AR



**Figure 6.** Cl K-edge XANES spectra of Au/C-AR (red line) and Au/C-acetone (blue line). The pre-edge peak ( $\blacklozenge$ ) arises from a Cl 1s  $\rightarrow$  Au d8 ( $\psi^*_{\text{HOMO}}$ ) transition. The main absorption peak ( $\blacklozenge$ ), appears at a slightly different energy for each catalyst. The postedge peak (\*) indicates the presence of NaCl and NaClO<sub>x</sub> species.

(red line) and the Au/C-acetone (blue line) catalysts. The preedge peak, which is marked by  $\blacklozenge$ , can be seen in both spectra at the same position for the Au/C-AR and the Au/C-acetone catalysts. The presence of the pre-edge peak confirms that Au is in a cationic state in both catalysts, as a pre-edge is only present when the d-orbital of the transition metal is partially filled, which is only the case for cationic Au, and not metallic Au. The position of the rising edge is the same for both catalysts; however, the peak of maximum absorption is different. In the case of the Au/C-AR catalyst, it is positioned at  $\sim 2825$  eV, which corresponds to a Cl atom that is bonded to carbon.<sup>49,50</sup> This is in agreement with the XPS results, which also showed that a large amount of Cl bonded to the carbon surface is present. The main absorption peak of the Au/Cacetone catalyst is slightly offset to higher energy than the Au/ C-AR catalysts, as marked with a  $\blacklozenge$  symbol. It is the position and that of the post edge peak, which is marked by a \* symbol, indicates the presence of NaCl and NaClO<sub>x</sub> species.<sup>46</sup> The



Figure 7. BP yield as a function of (a) the surface Cl content and (b) the surface C-Cl content in a series of Au/C catalysts prepared using different ratios of aqua regia (violet square). Cl content was determined by Cl 2p XPS analysis.

presence of NaCl species in the Au/C-acetone catalyst was previously also confirmed by XRD.

These results indicate that different Cl species are present on the surface of the supports of both catalysts. In the case of the Au/C-AR catalyst, Cl is present as C–Cl, whereas the Cl in the Au/C-acetone catalyst seems to be more strongly associated with sodium. The prepeak is located at the same position in both catalysts, which suggests that the ligands around the Au are of a similar nature for both catalysts.

3.6.2. Cross-Coupling between Phenylboronic Acid and Chlorobenzene. Homogeneous and heterogeneous Au catalysts that are active in Suzuki cross-coupling reactions have been reported.<sup>51-53</sup> In general, homogeneous Au organometallic catalysts have demonstrated that the activity for a Suzuki cross-coupling reaction comes from small traces of Pd in the Au source or other reaction components. Only a few ppb of palladium in the reaction mixture can result in activity.<sup>53,54</sup> The HAuCl<sub>4</sub> used to prepare the Au catalysts in this study is not known to contain any Pd. Au supported on metal oxides such as MgO and CaO have been tested for the Suzuki cross-coupling between phenylboronic acids and several aryl halides.<sup>52</sup> The activity was found to be strongly influenced by the nature of the support and aryl halide. Au nanoparticles attached to graphene also showed good activity in a Suzuki cross-coupling reaction between 4-bromoanisol and phenylboronic acid in water with 93% yield.<sup>51</sup> Other Au catalysts active for the Suzuki cross-coupling reaction include starch stabilized colloids and thiol stabilized colloids.55,56 To the best of our knowledge, there have been few reports of heterogeneous Au catalysts that are capable of catalyzing Suzuki-type cross-coupling reactions.

The presence of the O groups on the surface of Au/C SMSHCs did not influence their performance in the homocoupling reaction. Consequently, the main difference between the Au/C-acetone and Au/C-AR catalysts was the greater concentration of C-Cl present in the latter. This catalyst (Au/C-AR), with a high Cl content, is active in the homocoupling reaction, which suggests that an alternative reaction pathway is taking place. Chlorobenzene could be formed by an in situ halodeboronation reaction of the phenylboronic acid.<sup>44</sup> This reaction is known to be catalyzed by Cl<sub>2</sub>, Cl<sup>+</sup>, and CuCl<sub>2</sub>, and possibly the Cl on the Au/C-AR catalyst could catalyze this step.<sup>44</sup> Subsequently, a Suzuki-type cross-coupling reaction could then take place between the in situ formed chlorobenzene and phenylboronic acid. To test if such an alternative reaction could take place, Au/C-acetone, Au/C-AR, and Au/C-sol catalysts have been tested in a crosscoupling reaction between (i) phenylboronic acid and chlorobenzene and (ii) between phenylboronic acid and iodobenzene. The catalysts were tested in two different cross-coupling reactions because a cross-coupling reaction with iodobenzene is more likely to proceed compared to a reaction with chlorobenzene, as the bond dissociation energy of iodobenzene is much lower than for chlorobenzene.<sup>54,57</sup> However, it was found that the three Au/C catalysts were not active in a cross-coupling reaction of phenylboronic acid with either chlorobenzene or iodobenzene.

Two additional homocoupling reaction tests were carried out with the two inactive, low Cl content catalysts, Au/Cacetone and Au/C-sol, in the presence of CuCl<sub>2</sub>. CuX<sub>2</sub> is known to catalyze the halodeboronation reaction of phenylboronic acid and be able to form chlorobenzene in situ.<sup>44</sup> However, no BP was measured in these reactions. Chlorobenzene was detected in the reaction mixture, which confirms that CuCl<sub>2</sub> can catalyze the halodeboronation step; however, a cross-coupling reaction between the in situ formed chlorobenzene and phenylboronic acid did not take place. Other sources of Cl, namely NaCl and HCl, were added to the reaction mixture with the Au/C-acetone catalyst present; however, this did not lead to any conversion either.

Another Au/C catalyst with a high Cl content was prepared by using solely concentrated HCl as the impregnation solvent. This catalyst, named Au/C-HCl, was comprised of large Au nanoparticles with an average size of ca. 25 nm as determined by XRD (Figure S9). XPS was used to determine the concentration of surface functionalities on the surface of the catalyst; Figure S10 shows the distribution of surface functional groups on the Au/C-HCl catalyst and how they compare to the Au/C-AR and Au/C-acetone catalysts. It is clear that impregnation, solely with HCl, leads to much less C-Cl formation than with aqua regia. The total Cl content of the Au/C-HCl catalyst is only 1.8 wt % compared to 6.6 wt % for the Au/C-AR catalyst. These results suggest that the highest Cl incorporation is achieved by using a mixture of HNO3 and HCl as the impregnation solvent. Despite the presence of an elevated concentration of C-Cl, no BP was observed over the Au/C-HCl catalyst when tested for the homocoupling reaction.

**3.7.** Influence of the Cl Concentration on the Support. The Au/C-HCl catalyst that was discussed in the previous section contains only 1.8 wt % Cl, which is significantly less than the Au/C-AR catalyst (6.6 wt %). Therefore, the combination of HNO<sub>3</sub> and HCl that is used for the impregnation with *aqua regia* results in high concentrations

of Cl. To further study the effect of Cl on the performance of the catalysts, a range of catalysts were prepared using different ratios of HCl: HNO<sub>3</sub> as the impregnation solvent (Table S3). XPS was used to determine the Cl and O content in these catalysts, and they were tested for 240 min in the homocoupling reaction. However, the Cl content of the catalysts does not increase linearly with the vol % of HCl used in the impregnation solvent. The highest Cl weight percentage was achieved at an optimum of 75 vol % HCl, which corresponds to the amount of HCl present in the 'standard' *aqua regia* ratio.<sup>58</sup>

The BP yield after 240 min of homocoupling reaction was plotted as a function of the Cl content of the catalysts (Figure 7a). A trend with an increase in biphenyl yield with increasing Cl content is clearly visible. This correlation is also present when looking at the amount of C–Cl present specifically (Figure 7b), with the more active catalysts having a higher C–Cl content. These results can explain why the Au/C-acetone catalyst and the catalysts prepared on oxidized carbon have no activity in the homocoupling reaction (Table 4), as they contain virtually no C–Cl groups. Similarly, the Au/C-HCl catalyst possesses a low concentration of incorporated C–Cl and is therefore not active in the homocoupling reaction.

3.8. Discussion on the Role of Cl on the Au/C Catalysts. Bouleghlimat et al. reported an enhanced catalytic activity for a Pd-catalyzed Suzuki-type homocoupling reaction when the reaction was performed in the presence of halides.<sup>5</sup> The Pd catalyst, a polypyrrole-palladium nanocomposite immobilized on polystyrene microspheres,<sup>60</sup> functioned as a recoverable and recyclable catalyst for the homocoupling of aryl boronic acids. When halides, in the form of NaCl or NaBr, are added to the aqueous reaction mixture, the catalytic activity doubles. However, this increase in activity came at the cost of a significant decrease in the recovery of the catalytic activity in further cycles. Three possible explanations for these observations were discussed. First, if the reaction occurs on the surface of the Pd nanoparticles, then the halide could have an activating effect on the Pd surface. Second, Pd nanoparticles could leach from the composite material due to a weakened interaction between the nanoparticles and the polypyrrole in the presence of salt. And last, halide ions could help leach Pd atoms or ions into the reaction solution, where they could homogeneously catalyze the reaction. The significant increase in catalytic activity, accompanied by poor recovery of catalytic activity, is more in line with the third explanation. Furthermore, the reaction mechanism could be significantly affected by reaction conditions such as the choice of solvent and additives, such as halides, in the reaction mixture.

In our materials, the leaching of the active metal species is not likely, as a low concentration of leached Au is present at the start of the reaction (first 30 min), and after this, no leached Au was detected (Table S1). Several other hypotheses could explain the correlation between the yield of the reaction and the Cl coverage of the carbon support. For example, Cl on the carbon could stabilize the Au active site, or Cl itself could take some part in the reaction. Particle growth is observed in all spent Au/C-AR catalysts, and therefore, it is possible that the true active site forms in situ and is different from the morphology of the as-prepared catalyst. Cl on the carbon support could play a role in stabilizing these active sites formed in situ. Potentially, Au atoms locate to step and/or corner sites of the in situ formed nanoparticles. Such sites can be active as homocoupling catalysts, as reported by Willis and Guzman<sup>61</sup> Alternatively, the active site is not part of the Au nanoparticles. In general, nanoparticle formation can proceed via two different mechanisms. Ostwald ripening can occur where metal species from small metal particles migrate toward bigger particles, which will grow at the expense of smaller ones. Conversely, nanoparticles can form via particle migration and coalescence, which can take place when there is poor interaction between the metal particle and the support.<sup>62</sup> The smaller metal species that migrate during Ostwald ripening are often cationic and are stabilized by a ligand.<sup>63</sup> Ostwald ripening has been reported to occur through the transport of cationic Au–Cl species on Au/SiO<sub>2</sub> catalysts when Cl ions are present in the reaction solution.<sup>63</sup>

The latter hypothesis, that Cl takes part in the reaction mechanism, is supported by reusability tests of the Au/C-AR catalyst and further study of the used catalysts. The Cl content of an as-prepared and used catalyst is compared in Table 5.

Table 5. Cl Content of the as Prepared and Used Au/C-AR Catalysts Prepared as Determined by XPS

catalyst	total Cl content (wt %)	C-Cl content (wt %)	M-Cl content (wt %)
as-prepared	6	4.7	0.7
used	2.5	1.9	0.6

The as-prepared catalyst was tested for 240 min in the homocoupling reaction, after which it was washed twice with methanol and then dried at room temperature before reuse (Figure S11). The C–Cl content of the catalyst has reduced significantly after the reaction. When the used catalyst was retested in a homocoupling reaction, the conversion was significantly lower than as-prepared catalyst. This measured activity loss is most likely related to the loss of the C–Cl moiety during the reaction.

To investigate whether Cl is used in the reaction, the Cl content of the series of used Au/C-AR catalysts made with different ratios of HCl: HNO<sub>3</sub> in the impregnation solvent was studied by using XPS. Figure 8a illustrates the correlation between the fraction of C-Cl lost after 240 min of reaction versus the yield of BP. A trend can be observed of an increase in BP yield with an increasing fraction of C-Cl lost during the reaction. The carbon support treated with standard aqua regia (C-AR, black circle), which is inactive, contains approximately 3 wt % C-Cl and only loses around 20% of this value during reaction. All the other catalysts lose a much higher percentage of their total C-Cl content after reaction, and the biphenyl yield increases sharply with the increasing fraction of C-Cl lost. This suggests that C-Cl could be taking an active part in the reaction; however, it may control how mobile, or easily deactivated, certain sites are. To investigate if Cl is used stoichiometrically in the reaction, the C-Cl (in mmol) lost after the reaction was plotted against the amount of biphenyl formed (in mmol), as illustrated in Figure 8b. The exponential increase in BP yield as a function of Cl lost during the reaction is indicative that Cl plays a role in the reaction; however, this is unlikely to be due to cross-coupling as discussed above. These results indicate that the C-Cl moieties are being consumed during the reaction, perhaps through reaction with the base. However, the exact role of Cl during the reaction remains unclear and requires further study.



**Figure 8.** (a) Correlation between the fraction of Cl from the C–Cl content lost after reaction with the yield of BP. (b) Amount of Cl from C–Cl (in mmol) lost after reaction versus the amount of BP formed (in mmol); analysis from the reaction mixture at 240 min from (violet square) Au/C-AR made by different ratios of HCl:HNO3 and (black circle) C-AR support treated with *aqua regia* without Au.

#### 4. CONCLUSIONS

Two Au/C SMSHCs were synthesized employing either dry acetone or aqua regia as the impregnation solvent. The asprepared catalysts were confirmed to comprise solely atomically dispersed cationic Au via AC-STEM and XAS analysis. However, the surface of the carbon support was found to be modified during the impregnation step, depending on the nature of the impregnation solvent. Specifically, the impregnation step with aqua regia results in an enhanced concentration of O-containing groups and C-Cl moieties. Of the two Au/C catalysts studied initially, only the one prepared with aqua regia, Au/C-AR, was active in the Suzukitype homocoupling reaction of phenylboronic acid. The rapid in situ formation of Au nanoparticles and the presence of some atomically dispersed Au remaining even after 240 min of reaction, observed for both Au/C-AR and Au/C-acetone catalysts, suggests that excess Cl is the differentiator. Thus, the distinct performance of these catalysts was attributed to the presence of C-Cl groups in the Au/C-AR catalyst, with O content having no influence on the reaction. When using aqua regia-treated carbon as the support, both acetone- and solimmobilized prepared Au/C catalysts were found to be active, when previously inactive.

The reusability of the Au/C-AR catalyst is low, however, which is suggested to be due to the loss of C–Cl moieties during the reaction. The fraction of C–Cl lost during the reaction was shown to be strongly correlated to the amount of product formed, which indicates that C–Cl is consumed during the reaction. The exact nature of the C–Cl and its involvement in the homocoupling reaction requires further study, but our results suggest that care must be taken with assigning reactivity solely to cationic Au or Au nanoparticles.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.5c02262.

Detailed characterization of Au leaching and solution pH during reactions, detailed elemental composition under varied preparative conditions, additional characterization of catalysts with pXRD, XAS, STEM-HAADF, XPS, and reuse catalytic testing, with BP yield according to TOL (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Authors**

- Nicholas F. Dummer Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.; orcid.org/0000-0002-0946-6304; Email: dummernf@cardiff.ac.uk
- Graham J. Hutchings Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.; orcid.org/0000-0001-8885-1560; Email: hutch@cardiff.ac.uk

# Authors

- Tanja E. Parmentier Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.
- Anna Lazaridou Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.
- Joseph Cartwright Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.
- Ben Davies Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.
- Simon Dawson Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.
- Grazia Malta Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.
- Simon Freakley Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.; Department of Chemistry, University of Bath, Bath BA2 7AY, U.K.
- **Thomas E. Davies** Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff

Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.

- David J. Morgan Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.; orcid.org/0000-0002-6571-5731
- Simon Kondrat Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.; Department of Chemistry, Loughborough University, Leicestershire LE113TU, U.K.; @ orcid.org/0000-0003-4972-693X
- Christopher J. Kiely Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, United States
- Samuel Pattisson Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.5c02262

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We would like to thank MaxNet Energy for financial support, and we thank the Max Planck Society and Cardiff University for financial support to create the FUNCAT Centre. We would also like to thank the Cardiff University TEM facility for the electron microscopy. We used beamline B18 at the Diamond Lightsource for the XAS measurements (proposal number: SP15151-7).

#### REFERENCES

(1) Farhang, M.; Akbarzadeh, A. R.; Rabbani, M.; Ghadiri, A. M. A Retrospective-Prospective Review of Suzuki–Miyaura Reaction: From Cross-Coupling Reaction to Pharmaceutical Industry Applications. *Polyhedron* **2022**, 227, No. 116124.

(2) Wu, X.-F.; Anbarasan, P.; Neumann, H.; Beller, M. From Noble Metal to Nobel Prize: Palladium-Catalyzed Coupling Reactions as Key Methods in Organic Synthesis. *Angew. Chem., Int. Ed.* **2010**, 49 (48), 9047–9050.

(3) Budarin, V. L.; Shuttleworth, P. S.; Clark, J. H.; Luque, R. Industrial Applications of C-C Coupling Reactions. *Curr. Org. Synth.* **2010**, 7 (6), 614–627.

(4) Wu, X.-F.; Neumann, H.; Beller, M. Palladium-Catalyzed Coupling Reactions: Carbonylative Heck Reactions To Give Chalcones. *Angew. Chem., Int. Ed.* **2010**, *49* (31), 5284–5288.

(5) Torborg, C.; Beller, M. Recent Applications of Palladium-Catalyzed Coupling Reactions in the Pharmaceutical, Agrochemical, and Fine Chemical Industries. *Adv. Synth. Catal.* **2009**, *351* (18), 3027–3043.

(6) Colacot, B. T. J. The 2010 Nobel Prize in Chemistry: Palladium-Catalysed Cross-Coupling: The Importance of Carbon–Carbon Coupling for Real World Applications. *Platin. Metal Rev.* 2011, 55 (2), 84–90.

(7) Yin; Liebscher, J. Carbon-Carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. *Chem. Rev.* 2007, 107 (1), 133–173.

(8) Zapf, A.; Beller, M. Fine Chemical Synthesis with Homogeneous Palladium Catalysts: Examples, Status and Trends. *Top. Catal.* **2002**, *19* (1), 101–109.

(9) Suzuki, A. Recent Advances in the Cross-Coupling Reactions of Organoboron Derivatives with Organic Electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576* (1), 147–168.

(10) Smith, G. B.; Dezeny, G. C.; Hughes, D. L.; King, A. O.; Verhoeven, T. R. Mechanistic Studies of the Suzuki Cross-Coupling Reaction. J. Org. Chem. **1994**, 59 (26), 8151–8156.

(11) Mora, M.; Jiménez-Sanchidrián, C.; Ruiz, J. R. Heterogeneous Suzuki Cross-Coupling Reactions over Palladium/Hydrotalcite Catalysts. J. Colloid Interface Sci. **2006**, 302 (2), 568–575.

(12) Carrettin, S.; Guzman, J.; Corma, A. Supported Gold Catalyzes the Homocoupling of Phenylboronic Acid with High Conversion and Selectivity. *Angew. Chem., Int. Ed.* **2005**, *44* (15), 2242–2245.

(13) Parmentier, T. E.; Dawson, S. R.; Malta, G.; Lu, L.; Davies, T. E.; Kondrat, S. A.; Freakley, S. J.; Kiely, C. J.; Hutchings, G. J. Homocoupling of Phenylboronic Acid Using Atomically Dispersed Gold on Carbon Catalysts: Catalyst Evolution Before Reaction. *ChemCatChem.* **2018**, *10* (8), 1853–1859.

(14) Paul Reddy, K.; Murugadoss, A. Microcrystalline Cellulose-Supported Gold Nanoparticle Catalysts for Homocoupling of Phenylboronic Acids. *Langmuir* **2022**, *38* (7), 2205–2212.

(15) Li, G.; Jin, R. Catalysis by Gold Nanoparticles: Carbon-Carbon Coupling Reactions. *Nanotechnol. Rev.* **2013**, *2* (5), 529–545.

(16) Tsunoyama, H.; Sakurai, H.; Ichikuni, N.; Negishi, Y.; Tsukuda, T. Colloidal Gold Nanoparticles as Catalyst for Carbon–Carbon Bond Formation: Application to Aerobic Homocoupling of Phenylboronic Acid in Water. *Langmuir* **2004**, *20* (26), 11293–11296.

(17) Ehara, M.; Priyakumar, U. D. Gold-Palladium Nanocluster Catalysts for Homocoupling: Electronic Structure and Interface Dynamics. *Chem. Rec.* **2019**, *19* (5), 947–959.

(18) Chen, Z.; Shen, R.; Chen, C.; Li, J.; Li, Y. Synergistic Effect of Bimetallic PdAu Nanocrystals on Oxidative Alkyne Homocoupling. *Chem. Commun.* **2018**, *54* (93), 13155–13158.

(19) Dhital, R. N.; Sakurai, H. Oxidative Coupling of Organoboron Compounds. *Asian J. Org. Chem.* **2014**, 3 (6), 668–684.

(20) Stratakis, M.; Garcia, H. Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes. *Chem. Rev.* **2012**, *112* (8), 4469–4506.

(21) Takei, T.; Akita, T.; Nakamura, I.; Fujitani, T.; Okumura, M.; Okazaki, K.; Huang, J.; Ishida, T.; Haruta, M. Chapter One -Heterogeneous Catalysis by Gold. In *Adv. Catal.*; Gates, B. C.; Jentoft, F. C., Eds.; Academic Press: 2012; Vol. 55, pp 1–126.

(22) Carrettin, S.; Corma, A.; Iglesias, M.; Sánchez, F. Stabilization of Au(III) on Heterogeneous Catalysts and Their Catalytic Similarities with Homogeneous Au(III) Metal Organic Complexes. *Appl. Catal., A: General* **2005**, *291* (1), 247–252.

(23) Matsuda, T.; Asai, T.; Shiose, S.; Kato, K. Homocoupling of Arylboronic Acids Catalyzed by Simple Gold Salts. *Tetrahedron Lett.* **2011**, 52 (37), 4779–4781.

(24) Hashmi, A. S. K.; Ramamurthi, T. D.; Rominger, F. Synthesis, Structure and Reactivity of Organogold Compounds of Relevance to Homogeneous Gold Catalysis. *J. Organomet. Chem.* **2009**, *694* (4), 592–597.

(25) Hashmi, A. S. K.; Ramamurthi, T. D.; Todd, M. H.; Tsang, A. S.-K.; Graf, K. Gold-Catalysis: Reactions of Organogold Compounds with Electrophiles. *Aust. J. Chem.* **2010**, *6*3 (12), 1619–1626.

(26) Wang, L.; Zhang, W.; Su, D. S.; Meng, X.; Xiao, F.-S. Supported Au Nanoparticles as Efficient Catalysts for Aerobic Homocoupling of Phenylboronic Acid. *Chem. Commun.* **2012**, *48* (44), 5476–5478.

(27) Haesuwannakij, S.; Yakiyama, Y.; Sakurai, H. Partially Fluoride-Substituted Hydroxyapatite as a Suitable Support for the Gold-Catalyzed Homocoupling of Phenylboronic Acid: An Example of Interface Modification. *ACS Catal.* **2017**, 7 (4), 2998–3003.

(28) Sun, X.; Dawson, S. R.; Parmentier, T. E.; Malta, G.; Davies, T. E.; He, Q.; Lu, L.; Morgan, D. J.; Carthey, N.; Johnston, P.; Kondrat, S. A.; Freakley, S. J.; Kiely, C. J.; Hutchings, G. J. Facile Synthesis of Precious-Metal Single-Site Catalysts Using Organic Solvents. *Nat. Chem.* **2020**, *12* (6), 560–567.

(29) Malta, G.; Kondrat, S. A.; Freakley, S. J.; Davies, C. J.; Lu, L.; Dawson, S.; Thetford, A.; Gibson, E. K.; Morgan, D. J.; Jones, W.; Wells, P. P.; Johnston, P.; Catlow, C. R. A.; Kiely, C. J.; Hutchings, G. J. Identification of Single-Site Gold Catalysis in Acetylene Hydrochlorination. *Science* **2017**, *355* (6332), 1399–1403.

(30) Abis, L.; Freakley, S. J.; Dodekatos, G.; Morgan, D. J.; Sankar, M.; Dimitratos, N.; He, Q.; Kiely, C. J.; Hutchings, G. J. Highly Active Gold and Gold–Palladium Catalysts Prepared by Colloidal Methods in the Absence of Polymer Stabilizers. *ChemCatChem.* **2017**, *9* (15), 2914–2918.

(31) Fairley, N.; Fernandez, V.; Richard-Plouet, M.; Guillot-Deudon, C.; Walton, J.; Smith, E.; Flahaut, D.; Greiner, M.; Biesinger, M.; Tougaard, S.; Morgan, D.; Baltrusaitis, J. Systematic and Collaborative Approach to Problem Solving Using X-Ray Photoelectron Spectroscopy. *Appl. Surf. Sci. Adv.* **2021**, *5*, No. 100112.

(32) Lin, B.; Guo, Y.; Cao, C.; Ni, J.; Lin, J.; Jiang, L. Carbon Support Surface Effects in the Catalytic Performance of Ba-Promoted Ru Catalyst for Ammonia Synthesis. *Catal. Today* **2018**, *316*, 230– 236.

(33) Pattisson, S.; Dawson, S. R.; Malta, G.; Dummer, N. F.; Smith, L. R.; Lazaridou, A.; Morgan, D. J.; Freakley, S. J.; Kondrat, S. A.; Smit, J. J.; Johnston, P.; Hutchings, G. J. Lowering the Operating Temperature of Gold Acetylene Hydrochlorination Catalysts Using Oxidized Carbon Supports. ACS Catal. **2022**, *12* (22), 14086–14095. (34) Kaiser, S. K.; Surin, I.; Amorós-Pérez, A.; Büchele, S.; Krumeich, F.; Clark, A. H.; Román-Martínez, M. C.; Lillo-Ródenas, M. A.; Pérez-Ramírez, J. Design of Carbon Supports for Metal-Catalyzed Acetylene Hydrochlorination. *Nat. Commun.* **2021**, *12* (1), 4016.

(35) Figueiredo, J. L.; Pereira, M. F. R. The Role of Surface Chemistry in Catalysis with Carbons. *Catal. Today* **2010**, *150* (1), 2–7.

(36) Burgess, R.; Buono, C.; Davies, P. R.; Davies, R. J.; Legge, T.; Lai, A.; Lewis, R.; Morgan, D. J.; Robinson, N.; Willock, D. J. The Functionalisation of Graphite Surfaces with Nitric Acid: Identification of Functional Groups and Their Effects on Gold Deposition. *J. Catal.* **2015**, 323, 10–18.

(37) NIST X-ray Photoelectron Spectroscopy Database. https://srdata. nist.gov/xps/ (accessed Mar 10, 2025).

(38) High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database (Beamson, G.; Briggs, D.). J. Chem. Educ. 1993, 70 (1), A25. .

(39) Papirer, E.; Lacroix, R.; Donnet, J.-B.; Nansé, G.; Fioux, P. XPS Study of the Halogenation of Carbon Black—Part 2. Chlorination. *Carbon* **1995**, 33 (1), 63–72.

(40) Dandekar, A.; Baker, R. T. K.; Vannice, M. A. Characterization of Activated Carbon, Graphitized Carbon Fibers and Synthetic Diamond Powder Using TPD and DRIFTS. *Carbon* **1998**, *36* (12), 1821–1831.

(41) Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Órfão, J. J. M. Modification of the Surface Chemistry of Activated Carbons. *Carbon* **1999**, 37 (9), 1379–1389.

(42) Mpungose, P. P.; Vundla, Z. P.; Maguire, G. E. M.; Friedrich, H. B. The Current Status of Heterogeneous Palladium Catalysed Heck and Suzuki Cross-Coupling Reactions. *Molecules* **2018**, *23* (7), 1676.

(43) Senter, C.; Rumple, A.; Medina-Ramos, W.; Houle, D.; Cheng, Z.; Gelbaum, C.; Fisk, J.; Holden, B.; Pollet, P.; Eckert, C. A.; Liotta, C. L. The Effects of  $CO_2$  Pressure and pH on the Suzuki Coupling of Basic Nitrogen Containing Substrates. *Org. Biomol. Chem.* **2014**, *12* (38), 7598–7602.

(44) Molloy, J. J.; O'Rourke, K. M.; Frias, C. P.; Sloan, N. L.; West, M. J.; Pimlott, S. L.; Sutherland, A.; Watson, A. J. B. Mechanism of Cu-Catalyzed Aryl Boronic Acid Halodeboronation Using Electrophilic Halogen: Development of a Base-Catalyzed Iododeboronation for Radiolabeling Applications. Org. Lett. **2019**, *21* (7), 2488–2492.

(45) Rompel, A.; Andrews, J. C.; Cinco, R. M.; Wemple, M. W.; Christou, G.; Law, N. A.; Pecoraro, V. L.; Sauer, K.; Yachandra, V. K.; Klein, M. P. Chlorine K-Edge X-Ray Absorption Spectroscopy as a Probe of Chlorine–Manganese Bonding: Model Systems with Relevance to the Oxygen Evolving Complex in Photosystem II. J. Am. Chem. Soc. 1997, 119 (19), 4465-4470.

(46) Glaser, T.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. Ligand K-Edge X-Ray Absorption Spectroscopy: A Direct Probe of Ligand-Metal Covalency. *Acc. Chem. Res.* **2000**, 33 (12), 859–868.

(47) Shadle, S. E.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. Ligand K-Edge X-Ray Absorption Spectroscopy as a Probe of Ligand-Metal Bonding: Charge Donation and Covalency in Copper-Chloride Systems. *Inorg. Chem.* **1994**, 33 (19), 4235–4244.

(48) Shadle, S. E.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. Ligand K-Edge x-Ray Absorption Spectroscopic Studies: Metal-Ligand Covalency in a Series of Transition Metal Tetrachlorides. *J. Am. Chem. Soc.* **1995**, *117* (8), 2259–2272.

(49) Newton, M. A.; Nicholls, R.; Brazier, J. B.; Nguyen, B. N.; Mulligan, C. J.; Hellgardt, K.; Barreiro, E. M.; Emerich, H.; Hii (Mimi), K. K.; Snigireva, I.; Thompson, P. B. J. Effect of Retained Chlorine in ENCAT<sup>TM</sup> 30 Catalysts on the Development of Encapsulated Pd: Insights from in Situ Pd K, L3 and Cl K-Edge XAS. *Catal. Struct. React.* **2017**, 3 (4), 149–156.

(50) Lee, K.; Blake, A. V.; Donahue, C. M.; Spielvogel, K. D.; Bellott, B. J.; Daly, S. R. Quantifying the Interdependence of Metal-Ligand Covalency and Bond Distance Using Ligand K-Edge XAS. *Angew. Chem., Int. Ed.* **2019**, 58 (36), 12451–12455.

(51) Mondal, P.; Salam, N.; Mondal, A.; Ghosh, K.; Tuhina, K.; Islam, S. M. A Highly Active Recyclable Gold–Graphene Nanocomposite Material for Oxidative Esterification and Suzuki Cross-Coupling Reactions in Green Pathway. *J. Colloid Interface Sci.* **2015**, 459, 97–106.

(52) Dumbre, D. K.; Yadav, P. N.; Bhargava, S. K.; Choudhary, V. R. Suzuki–Miyaura Cross-Coupling Reaction between Aryl Halides and Phenylboronic Acids over Gold Nano-Particles Supported on MgO (or CaO) and Other Metal Oxides. *J. Catal.* **2013**, *301*, 134–140.

(53) Thomé, I.; Nijs, A.; Bolm, C. Trace Metal Impurities in Catalysis. *Chem. Soc. Rev.* **2012**, 41 (3), 979–987.

(54) Livendahl, M.; Espinet, P.; Echavarren, A. M. Final Analysis: Is Gold a Catalyst in Cross-Coupling Reactions in the Absence of Palladium? *Platin. Metal Rev.* **2011**, *55* (3), 212–214.

(55) Han, J.; Liu, Y.; Guo, R. Facile Synthesis of Highly Stable Gold Nanoparticles and Their Unexpected Excellent Catalytic Activity for Suzuki–Miyaura Cross-Coupling Reaction in Water. *J. Am. Chem. Soc.* **2009**, *131* (6), 2060–2061.

(56) Selvam, T. S.; Chi, K.-M. Synthesis of Hydrophobic Gold Nanoclusters: Growth Mechanism Study, Luminescence Property and Catalytic Application. *J. Nanopart. Res.* **2011**, *13* (4), 1769–1780.

(57) Khan, M.; Albalawi, G. H.; Shaik, M. R.; Khan, M.; Adil, S. F.; Kuniyil, M.; Alkhathlan, H. Z.; Al-Warthan, A.; Siddiqui, M. R. H. *Miswak* Mediated Green Synthesized Palladium Nanoparticles as Effective Catalysts for the Suzuki Coupling Reactions in Aqueous Media. J. Saudi Chem. Soc. **2017**, 21 (4), 450–457.

(58) Renner, H.; Schlamp, G.; Hollmann, D.; Lüschow, H. M.; Tews, P.; Rothaut, J.; Dermann, K.; Knödler, A.; Hecht, C.; Schlott, M.; Drieselmann, R.; Peter, C.; Schiele, R. Gold, Gold Alloys, and Gold Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd: 2000.

(59) Bouleghlimat, A.; Othman, M. A.; Lagrave, L. V.; Matsuzawa, S.; Nakamura, Y.; Fujii, S.; Buurma, N. J. Halide-Enhanced Catalytic Activity of Palladium Nanoparticles Comes at the Expense of Catalyst Recovery. *Catalysts* **2017**, *7* (9), 280.

(60) Fujii, S.; Matsuzawa, S.; Hamasaki, H.; Nakamura, Y.; Bouleghlimat, A.; Buurma, N. J. Polypyrrole–Palladium Nanocomposite Coating of Micrometer-Sized Polymer Particles Toward a Recyclable Catalyst. *Langmuir* **2012**, *28* (5), 2436–2447.

(61) Willis, N. G.; Guzman, J. Influence of the Support during Homocoupling of Phenylboronic Acid Catalyzed by Supported Gold. *Appl. Catal., A: General* **2008**, 339 (1), 68–75.

(62) Campbell, C. T.; Parker, S. C.; Starr, D. E. The Effect of Size-Dependent Nanoparticle Energetics on Catalyst Sintering. *Science* **2002**, 298 (5594), 811–814. (63) Lou, X. W.; Yuan, C.; Rhoades, E.; Zhang, Q.; Archer, L. A. Encapsulation and Ostwald Ripening of Au and Au–Cl Complex Nanostructures in Silica Shells. *Adv. Funct. Mater.* **2006**, *16* (13), 1679–1684.