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Stabilisation of Carbon-Supported Palladium Nanoparticles through the Formation of an Alloy with Gold: Application to the Sonogashira Reaction

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Catalysis plays a pivotal role in chemical sciences, especially in the challenge of sustainability.^[1] The impact of catalysis using transition metals in promoting faster and cleaner processes is now well established. However, being extracted from depletive resources, transition metals should be recycled, particularly those from periods 5 and 6 of the periodic table. Moreover, contamination of the products by metallic residues remains an acute problem when a close monitoring of the metal level is required, for instance in the pharmaceutical industry. The heterogenisation of transition metals on a solid support as molecular complexes or nanoparticles has been thus widely studied in the last 20 years to solve these issues.^[2] Among the myriad of supports reported in the literature, carbon-based materials, including charcoal and graphite, have been extensively used due to their good stability, high surface area, good mechanical properties, insolubility in most organic solvents and commercial availability at a low cost.^[3]

We have reported our own contribution to this approach in the chemistry of palladium by developing various methodologies involving the use of a Pd/C catalyst for the creation of C-C bonds.^[4,5] Unfortunately, we and others have observed that the catalytic activity of the recycled Pd/C rapidly decreased, especially with demanding transformations, such as the Heck and the Sonogashira reactions.^[4e,6] This unwanted behaviour has been mostly attributed to the significant morphological modifications of palladium nanoparticles at the surface of charcoal. Indeed, it is commonly admitted that most of the cross-coupling reactions follow a mechanism by which the palladium is leached from the support

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during the oxidative addition step and later reprecipitated onto the charcoal after the reductive elimination,^[7,8] although a fully heterogeneous mechanism has also been claimed in water.^[9] Actually, the very low concentration of solubilised active palladium species often renders a definitive conclusion very difficult. However, it is usually admitted that this mechanistically complex boomerang effect progressively leads, at least in part, to the aggregation of small nanoparticles into larger crystallites having a lower active surface area. This quasi-homogeneous mechanism is, however, essential for attaining a high catalyst efficiency under rather mild conditions. We felt that the search for a strategy by which palladium would not be leached in the solvent and, thereby, soluble palladium species would not be responsible for the catalytic activity, should not give successful results. As a consequence, an inventive strategy that would maintain the nanoparticle shape constant over the reuse cycles and that would allow the catalyst to be recycled while keeping a good catalytic activity, remains to be discovered, since very high temperatures (160°C)^[10] or phosphine ligands^[11] are required for an efficient recycling. Here, we describe a conceptually novel strategy based on the use of a bimetallic Pd-Au/C catalyst and its application to the Sonogashira reaction under ligand- and additive-free conditions.

The aggregation of palladium nanoparticles is a thermodynamic phenomenon that could be easily explained by the low stability of Pd⁰ species in the absence of any stabilising agent, such as ligands and ammonium salts, although the charcoal helps nanoparticle stabilisation through different types of anchoring sites. This phenomenon is the result of many factors including, the nature of the solvent, temperature, reactants as well as the reaction mechanism.^[12] We reasoned that palladium nanoparticles, deposited on charcoal, could be stabilised by another metal, also called co-metal, through the formation of a stable alloy. The proof-of-concept of this uncovered strategy requires, however, a number of factors to be controlled. The first one is that the co-metal must be fully inert toward the studied reaction. In other words, it must not promote a synergistic effect, but at the same time, it must not inhibit the catalytic activity of the palladium catalyst either. Moreover, the co-metal must easily form a stable alloy with palladium that would not evolve or degrade when exposed to air, moisture and solvents. Last but not least, the co-metal should not inhibit the

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leaching-reprecipitation process required for an efficient catalysis, but at the same time it must preserve the crystalline form of the alloy to limit the aggregation phenomenon. With these requirements in mind, we reasoned, that gold could be, if not ideal, a good candidate for the validation of the proof-of-concept of our strategy since it is well known that gold forms stable alloy with palladium.^[13] Pd and Au atoms are miscible over a wide range of composition. The equilibrium phase diagram predicts that a face-centred cubic (fcc) solid solution of Au and Pd would be formed over the entire compositional range, with no specific ordering (except for Au₃Pd and AuPd₃).^[14]

With this concept in mind, we first worked on the development of a direct way to prepare the bimetallic Pd–Au/C catalyst, as well as the monometallic Pd/C and Au/C catalysts for comparative evaluations. We recently reported that palladium nanoparticles could be efficiently deposited on charcoal from a methanolic solution of Pd(OAc)₂ under an atmosphere of H₂ (1 atm).^[15] We set up for an extension of this strategy for the preparation of bimetallic Pd–Au/C catalysts. To our great pleasure, we discovered that the reduction of a methanolic mixture of Pd(OAc)₂, KAuCl₄ and charcoal under H₂ at 25 °C led to a charcoal-supported Pd–Au alloy (Scheme 1). Importantly, the mild and easily reproducible



Scheme 1. Preparation of Pd-Au/C catalysts.

conditions allowed the quantitative deposition of the metal onto the charcoal leaving the solvent almost free of metal residues after a single filtration through a nylon membrane (0.45 μ M), as determined by ICP-MS analysis. This feature, frequently overlooked by chemists preparing heterogeneous catalysts, remains essential for developing sustainable chemistry since metallic wastes are not produced with our process. Three different Pd–Au/C catalysts were prepared, according to the metal loading on the support (i.e., 2.5, 5 and 10 wt.% per metal). We selected charcoal as support for its robustness toward a variety of conditions and for its low cost.

With the bimetallic catalyst in hand we extensively analysed its chemical composition through a full set of standard characterisations. Transmission electron microscopy (TEM) investigations evidenced the formation of nanoparticles mainly distributed onto the support. A bimodal distribution, containing small particles in the range of 10–15 nm along with very rare aggregated particles of about 100 nm (standard deviation ~10%) was observed (Figure S4 in Supporting Information). The X-ray diffraction (XRD) pattern of the bimetallic solid sample exhibits the expected reflexion peaks of an fcc phase. The average cell parameter of 4.005 Å confirms a bimetallic structure considering the value of the monometallic phase (a_{Au} =4.05 Å and a_{Pd} =3.96 Å; Fig-



ure 1 d). Their broad line-width could be explained by the presence of small particles (~5 nm) as well as the local chemical composition heterogeneity of the Pd_xAu_{1-x} nanoparticles. We underline that the presence of PdO was not observed on the diffractogram. Chemical mapping of the asprepared samples were acquired thanks to the scanning TEM technique coupled with energy dispersive X-ray spectroscopy analysis (STEM-EDX; Figure 1 e and f). It shows homogeneous Pd–Au nanostructures and no development of Pd-rich or Au-rich nanoparticles, excluding the common and unwanted segregation phenomenon. The mean chemical composition of the whole zone represented on Figure 1 could be measured; Au: 55 at. % and Pd: 45 at. %.

Although X-ray photoelectron spectroscopy (XPS) analysis identified Au⁰ and Pd⁰ as the major species present in the as-prepared material, some ionic palladium (19 at.%) was also detected (Figure S3 in the Supporting Information). The absence of signal accounting for PdO in the XRD pattern presented on Figure 1, suggests that Pd_xAu_{1-x} particles are likely covered by a thin oxide layer. The layer is too thin to be detected by XRD as well as HRTEM. All these analyses definitively confirmed the formation of the expected Pd-Au alloy. Similarly, 2.5, 5 and 10% (wt.%) Pd/C and 5% Au/C catalysts were also prepared following the same experimental procedure for their catalytic evaluation (see the Supporting Information). The common features in both monometallic systems were: 1) the existence of homogeneously distributed nanosized particles onto the carbon support, and 2) their well-defined crystalline fcc structure. However, the particle size of the Pd/C samples ranges from 2 to 30 nm (Figure 1a) causing broader XRD peaks than those observed for the Au/C samples (Figure 1b). Contrary to Au_n samples, XPS analysis also revealed that about 1:3 of the total Pd species were under their +II oxidation state. This result suggests the formation of Pd-O bonds at the nanoparticle surface since palladium oxidises more readily than gold (Figure 2). The extent of oxidation is higher in the monometallic sample with respect to the bimetallic catalyst.

The freshly prepared 5 % Pd/C and 5 % Pd-Au/C catalysts were also analysed by electrochemistry to evaluate their catalytic efficiency. For this purpose, catalysts were deposited on a glassy carbon surface in a Nafion diffusion layer (see the Supporting Information). In a first step, electrodes were examined in acidic aqueous medium ($H_2SO_4 0.1 \text{ mol } L^{-1}$) by using cyclic voltammetry. The electrodes containing 5% Pd/ C and 5% Pd-Au/C catalysts were then compared with an electrode only covered with pure carbon. Cyclic voltammograms for each electrodes (Figure S5 in the Supporting Information) showed a classical metallic behaviour with redox peaks associated to the oxidation/reduction of palladium as well as the reduction of water beyond -0.3 V (vs. SCE) and the H_2 oxidation around -0.25 V. Interestingly, the hydrogen adsorption/desorption give two redox systems, exhibiting two different peaks, likely attributed to two different H₂ binding sites. More importantly, the over-potential of water reduction and H₂ oxidation on Pd is not affected by the presence of Au, but the charge required for the anodic oxi-





Figure 1. a, b, c) TEM micrographs of Pd/C, Au/C and Pd–Au/C catalysts, respectively; scale bars: 20, 20 and 100 nm, respectively; d) HR-TEM micrographs of Pd–Au/C catalysts; scale bar: 5 nm; e) X-ray diffraction patterns of the Pd–Au/C, Au/C and Pd/C catalysts. Diffraction lines marked with asterisks are due to the C support; f, i) STEM micrograph and RG-2 colours chemical maps of a Pd–Au/C catalyst; scale bars: 100 nm; g,h) STEM-EDX elemental maps of Au and Pd, respectively; scale bars: 100 nm.

dation of H_2 after subtracting capacitive current was found to be almost two-times higher for 5% Pd–Au/C compared to 5% Pd/C. The charge required for the anodic oxidation of H_2 being directly correlated to the number of Pd active sites, this result suggest that the bimetallic catalyst displays a higher active surface area compared to the monometallic one. This interesting feature could be advantageously exploited for cross-coupling reactions (vide infra).

Having a well-defined set of catalysts in hands (Pd/C, Au/C and Pd–Au/C), we initiated the evaluation of their catalytic performance on a cross-coupling reaction. We selected the Sonogashira reaction for its high synthetic usefulness in many aspects of organic synthesis including medicinal chemistry and materials science.^[16,17] Moreover, it is a rather demanding reaction that would better discriminate our catalytic systems.

Therefore, we studied the coupling of 4-iodoacetophenone (1) with phenylacetylene (2) in aqueous *i*PrOH at 80 °C and in the presence of K_3PO_4 as a base, following the experimental conditions reported

by the group of Sajiki, under copper-free conditions (Table 1).^[6b] We initially focused on the influence of the metal concentration for the coupling of 1 with 2. Two differ-

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ent metal concentrations should be considered: the metal loading on the support, and the metal loading in the reaction. These two parameters are frequently used in the literature with some confusion. For instance, the abbreviation "5% Pd/C (1 mol%)" denotes that the catalyst is composed of 5 wt.% of palladium metal and 95 wt.% of charcoal, and that 0.01 equivalent of Pd metal is used for the considered reaction. For the bimetallic Pd-Au/ C catalysts, we only indicate the loading per metal in the Table 1 for clarity, considering an approximately 1:1 Pd/Au ratio in weight for the bimetallic catalysts. We initially studied the monometallic Pd/C catalysts. We observed that the metal loading on the support has a rather weak influence of the reaction efficiency (entries 1-4). We, however, determined that a metal/support ratio of 5:95 was the best compromise (entry 7). The evaluation of the bimetallic catalysts showed a similar trend for the metal loading on the support and confirmed that gold nanoparticles did not

induce any synergistic or inhibiting effects on the reaction outcome when associated to palladium. This result suggests the absence of electron transfer from the active surface of palladium to the gold atoms.^[18] The inactivity of gold was secured with the evaluation of the monometallic 5% Au/C catalyst in the model reaction (entry 9). With these encouraging results in hands, we then worked on the recycling

Table 1. Optimisation studies.

MeO

| | $/= \setminus$ | Catalyst | | /= |
|---|----------------|---|----|----|
| | \mathbb{Z} | K ₃ PO ₄ , <i>i</i> PrOH/H ₂ O | | |
| 1 | 2 | 80 °C, 12 h | 3a | |

| Entry | Catalyst | Loading per metal [wt. per wt.%] | Loading Pd/Au [mol %] | Yield [%] ^[a] |
|-------|----------|-------------------------------------|--------------------------|-----------------------------|
| 1 | Pd/C | 2.5 | 1:0 | 80 |
| 2 | Pd/C | 5 | 0.5:0 | 83 |
| 3 | Pd/C | 5 | 1:0 | 86 |
| 4 | Pd/C | 10 | 1:0 | 77 |
| 5 | Pd-Au/C | 2.5 | 1:0.5 | 68 |
| 6 | Pd-Au/C | 5 | 0.5:0.25 | 80 |
| 7 | Pd-Au/C | 5 | 1:0.5 | 85 |
| 8 | Pd-Au/C | 10 | 1:0.5 | 86 |
| 9 | Au/ | 5 | 0:1 | 0 |

[a] Isolated yields.

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Figure 2. TEM images of: a, b) Pd/C, and c, d) Pd–Au/C catalysts before (left) and after the different catalytic cycles (right; after 2 (b) and 4 cycles (b)). Scale bars: 20 (a), 100 (b), 100 (c) and 100 nm (d).

| Table 2. | Recycling | studies. |
|----------|-----------|-----------|
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| MeOC | | Catalyst [1 mol%] K ₃ PO ₄ , /PrOH/H ₂ O 80 °C, 12 h | c-<>><>>3a |
|-------|-------|--|---------------------------|
| Entry | Cycle | Yield [%], ^[a] | Yield [%], ^[a] |
| | | 5% Pd/C | 5% Pd–Au/C |
| 1 | 1 | 86 | 85 |
| 2 | 2 | 68 | 74 |
| 3 | 3 | 46 | 71 |
| 4 | 4 | 50 | 68 |
| 5 | 5 | 49 | 65 |

[a] Isolated yields.

studies for the validation of our hypothesis (Table 2). Gratefully, we determined over the recycling runs that the bimetallic 5% Pd–Au/C (1 mol % Pd) catalyst displayed a significant enhanced catalytic activity in comparison to the monometallic 5% Pd/C (1 mol %). In order to gain a deeper understanding of this uncovered and interesting behaviour, we finely analysed the catalysts after each recycling run. As previously reported on related catalytic systems,^[8] the Pd/C catalyst showed a strong tendency to form large nanoparticles after the first recycling and this phenomenon was amplified after the second recycling as evidenced by HRTEM (Figure 2). The growth of palladium nanoparticles seems to attain a limit after the third recycling. This observation correlates well with the reaction yield, which stabilises after three cycles (~50%).

On the other hand, the bimetallic catalyst shows a much slower deactivation over the recycling runs and gives consistently higher yields compared to the Pd/C. TEM imaging of the reused catalyst also shows much less aggregation with the Pd–Au/C catalyst compared to the monometallic Pd/C (Figure 2). In order to understand these divergent profiles,

additional analyses were carried out. The oxidation state of palladium at the surface of the nanoparticles was determined by X-ray photoelectron spectroscopy (XPS) after each run. On the fresh Pd/C catalyst the nanoparticles contain 67 % Pd^0 and 33 % Pd^{II} at their surface whereas the Pd-Au/C catalyst is in a more reduced state with 81 % Pd⁰ and 19% Pd^{II}. Interestingly, after the first recycling step and over those that followed, a constant oxidation state, roughly determined as 95% Pd⁰ and 5% Pd^{II}, was observed for both catalysts (Table S1 in the Supporting Information). This particularly informative result suggests that the higher catalytic activity of Pd-Au/C compared to Pd/C cannot be directly correlated to the content of Pd⁰. The high content of Pd nanoparticles having a low oxidation state after the first recycling step and over those that followed, explains the rapid aggregation observed with the Pd/C catalyst. Indeed, in the absence of any stabilising agent (ligand or ammonium salt) the low stability of Pd⁰ species thermodynamically favours the aggregation phenomenon. This trend is reinforced by the leaching mechanism likely occurring during the reaction.^[8] On the other hand, with the Pd–Au/C catalyst the aggregation of unstable Pd⁰ nanoparticles can be considerably slowed down over the recycles (Figure 2c vs. d). This result strongly suggests that gold acts as a stabilising agent for Pd⁰ species, allowing the conservation of the nanoparticle morphology. As observed in Figure 2d, only a few aggregates can be detected. This phenomenon suggests that only a marginal segregation of Pd⁰ nanoparticles occurs through the recycling experiments, likely due to the leaching mechanism. A very small fraction of leached Pd atoms does not reprecipitate onto the support into the alloy structure and aggregates in isolated sites. We measured the content of soluble residual Pd and Au species in solution after the first run by ICP-MS analysis. With the bimetallic catalyst, a very low content of Pd (<45 ppb) and Au (<60 ppb) was detected in solution whereas a four-times higher content of Pd (~ 160 ppb) was measured with Pd/C. This result confirms the stronger durability of the bimetallic catalyst over the monometallic one.

A variety of examples reported in Table 3 attests the good catalytic efficiency of the heterogeneous Pd–Au/C catalyst. Electron-poor as well as electron-rich aryl iodides were successfully coupled to phenylacetylenes and aliphatic acetylenes. It is worth mentioning that unprotected amines and alcohols were compatible with this catalytic system (compounds 3g,h). Aryl iodides bearing a bromine or chlorine atom gave reduced yields of the corresponding coupling product, likely due to a non-chemoselective process (compounds 3n, o).

In summary, we have devised a novel strategy to increase the recyclability of palladium on carbon-based catalysts for the Sonogashira reaction. The origin of the reusability enhancement can be found in the stabilisation of Pd nanoparticles through the formation of an alloy with gold atoms, without altering its initial shape. Detailed HR-TEM analyses established that the aggregation phenomenon can be considerably slowed down thanks to the stabilising, but catalytically

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inactive, gold atoms. Although we are still working on the improvement of this approach by exploring less expensive metals and more recyclable alloys, we have validated the challenging proof-of-concept stage. We believe that such a strategy could be appealing for a variety of Pd-catalysed coupling reactions. Further developments in this area are actively pursued in our laboratory and will be reported in due course.

Experimental Section

Catalyst preparation: The 5% Pd/C catalyst was prepared by the following procedure. Pd(OAc)₂ (110 mg, 0.5 mmol) and charcoal (1 g, 95% wt./ Pd) were dispersed in MeOH (100 mL). Then, hydrogen gas was bubbled through the solution for 5 min to remove the oxygen. The resulting mixture was stirred for 12 h at 25 °C under H₂ (1 atm, balloon). The catalyst was filtered under Millipore membrane (filters nylon 0.45 μ m, 47 mm), washed with MeOH and dried under vacuum. ICP analyses were performed on the filtrate to verify the final Pd metal loading on carbon to be 5% wt.

General procedure for cross-coupling reactions: In a sealed tube, aryl iodide (0.5 mmol, 1 equiv), K_3PO_4 (1 mmol, 2 equiv) and the catalyst (2 mol % Pd) were suspended in *i*PrOH (1.5 mL) and H₂O (1.5 mL). The acetylene derivative (0.6 mmol, 1.2 equiv) was added and the resulting mixture was stirred 20 h at 80 °C. After being cooled to room temperature, CH₂Cl₂ (10 mL) and H₂O (10 mL) were added and the mixture was filtered over a pad of Celite. The aqueous layer was extracted twice with CH₂Cl₂ (2×10 mL). The collected

organic extracts were washed with brine (20 mL), dried on MgSO₄, fil-

tered and concentrated under reduced pressure. The crude product was purified by flash chromatography.

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Keywords: electrochemistry • heterogeneous catalysis • palladium nanoparticles • Pd–Au alloys • Sonogashira reaction

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Oh my Gold! Gold atoms stabilise catalytically active palladium nanoparticles when engaged in an alloy heterogenised on carbon. The increased durability makes the Pd–Au/C catalyst more recyclable than the gold-free Pd/ C catalyst for the Sonogashira reaction.



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Heterogeneous Catalysis

C. Rossy, J. Majimel, E. Fouquet, C. Delacôte, M. Boujtita, C. Labrugère, M. Tréguer-Delapierre,* F.-X. Felpin*.....

Stabilisation of Carbon-Supported Palladium Nanoparticles through the Formation of an Alloy with Gold: Application to the Sonogashira Reaction

