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On the peculiar recycling properties of charcoal-supported palladium oxide nanoparticles in Sonogashira reactions

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ABSTRACT

The enhanced recycling properties of 5% PdO NPs/C compared to 5% Pd NPs/C catalyst for the Sonogashira reaction has been unveiled. A simple preparation procedure for 5% Pd NPs/C and 5% PdO NPs/C catalysts is described along with their extensive characterizations. The correlation between the catalyst deactivation and a high content of reduced palladium species for the alkynylation of aryl iodides has been clearly identified with the monitoring of the Pd(0)/Pd(II) ratio over the recycling runs through X-ray photoelectron spectroscopy.

1. Introduction

Activated carbon-supported palladium catalysts have found great interest in organic synthesis. Though Pd/C-catalyzed reductive processes are widely known for decades, the use of Pd/C as homogeneous molecular palladium catalyst surrogates for carbon–carbon bond forming reactions still lacks of recognition [1–5]. Yet, the vast majority of palladium-catalyzed reactions for C—C bond formation including carbonylation [6], C—H activation [7,8], Suzuki [9–11], Heck [12–14], Sonogashira [15–17], Stille [18], Negishi [19], Larock [20,21], Ullmann [22,23], Hiyama [24], Tsuji-Trost [25] and Fukuyama [26] reactions, now considered as classics in organic synthesis, can be carried out with Pd/C as catalyst. This heterogeneous catalyst has many advantages over traditional homogeneous catalysts, especially at an industrial scale [27,28]. Indeed, Pd/C is a relatively inexpensive source of palladium, stable to air and moisture that allows reactions in aqueous media and under ligand-free conditions. Moreover its heterogeneous nature in most aqueous and organic solvents allows an easy recovering through a simple filtration, leaving the solvents and products with low levels of metal contamination. This feature is of special relevance for the synthesis of biologically active compounds or ultra-pure materials where a close monitoring of metal contamination is required. Unfortunately, despite these salient advantages Pd/C still suffers from a poor recyclability especially for demanding processes such as Heck and Sonogashira reactions [16,29–31]. This poor recyclability has been essentially attributed to aggregation phenomena induced by a leaching/re-precipitation mechanism. Indeed, it is now commonly admitted that most Pd/C-catalyzed reactions, entailing a C—C bond formation, follow a quasi-homogeneous mechanism by which active palladium species are leached from the support into the solution and re-precipitated onto charcoal at the end of the catalytic cycle [32–39]. This boomerang effect profoundly modified the size of palladium nanoparticles which inexorably aggregate into large colloids due to the thermodynamic instability of Pd(0) species re-precipitating onto charcoal. In order to avoid aggregation phenomena, we recently reported an unprecedented strategy where a co-metal, inactive for a considered reaction, stabilizes Pd species. The proof-of-concept was described for Pd(0) alloyed with gold atoms and demonstrated its usefulness for the Pd–Au/C-catalyzed arylation of alkynes [40]. This approach is still

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currently under investigation in our laboratory in order to find more recyclable palladium-containing alloys. Apart from the co-metal concept, we worked on alternative strategies that could be synthetically more practical for chemists not well versed in the field of heterogeneous catalysis. We reasoned that in the absence of any stabilizing agents, including ligand, ammonium and co-metal, the high content of Pd(0) species inexorably enhance the aggregation phenomenon driven by the lower surface energy of large colloids. We felt that the unwanted aggregation phenomenon could be dramatically slowed down with a catalyst displaying a high content of stable palladium-oxide nanoparticles (PdO NPs) which could act as a reservoir for active Pd(0) species.

2. Materials and methods

2.1. Preparation of 5% Pd NPs/C

$Pd(OAc)_2$ (110 mg, 0.5 mmol) and charcoal (1 g, 95 wt.%/Pd) were dispersed in MeOH (100 mL). Hydrogen gas was bubbled through the solution for 5 min and the resulting mixture was stirred for 12 h at 25 °C under H_2 (1 atm, balloon). The catalyst was filtered under Millipore membrane (filters nylon 0.45 μm, 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.%.

2.2. Preparation of 5% PdO NPs/C

The 5% Pd NPs/C catalyst previously obtained was calcined in air for 2 days at 200 °C.

2.3. General procedure for the Sonogashira reactions

In a sealed tube, aryl iodide (1 mmol, 1 equiv.), K_3PO_4 (2 mmol, 2 equiv.), catalyst (2 mol% Pd) were suspended in *i*-PrOH (3 mL) and H_2O (3 mL). The acetylene derivative (1.2 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at 80 °C for 20 h. After cooling to room temperature, EtOAc (20 mL) and H_2O (20 mL) were added and the mixture was filtered over a pad of Celite®. The aqueous layer was extracted twice with EtOAc (2 × 20 mL). The collected organics extracts were washed by brine (60 mL), dried on $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography.

2.4. Recycling experiments

After completion of the reaction, the catalyst was separated and recovered by filtration on a Millipore membrane (nylon filters, 0.45 μm), washed with H_2O (10 mL) and EtOAc (2 × 10 mL) and dried under vacuum for 8 h.

3. Results and discussion

With this idea in mind, we prepared charcoal-supported PdO NPs by oxidation of Pd NPs under very simple conditions. Pd NPs were prepared by reduction of $Pd(OAc)_2$ in MeOH under a H_2 atmosphere at room temperature in the presence of activated charcoal acting as support and stabilizer for Pd NPs [41,42]. In the absence of charcoal, only inactive black palladium, precipitating in the solution, is produced. A 5 wt.% loading of palladium onto the support was measured by ICP-MS analysis. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses showed the formation of Pd NPs mainly distributed onto charcoal with a crystallite size in the range of 5–10 nm (Fig. 1a and b).

X-ray photoelectron spectroscopy (XPS) experiments revealed Pd(0) as major species (70%) along with Pd(II) (30%): the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ bands observed at respectively 340.9 and 335.6 eV accounted for Pd(0) species while the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ binding energies of Pd(II) species were recorded at 342.5 and 337.3 eV (Fig. 2b). The absence of diffraction peak on XRD patterns (Fig. 2a) and reticular spacing on HRTEM micrographs (Fig. 1b) accounting for PdO, suggests the formation of a thin oxide layer covering Pd(0) particles due to the oxidation of metallic Pd upon exposure to air (Fig. 2b).

In order to obtain the PdO NPs/C material enhancing the thickness of the native PdO layer, we carried out a further oxidative thermal treatment under air atmosphere at 200 °C. TEM analyses after this treatment evidenced a coalescence phenomenon starting at only 200 °C, far below the Tammann temperature (Fig. 1c). High resolution TEM (HRTEM) analysis of an isolated nanoparticle (Fig. 1d) revealed lattice fringes with a 0.25 nm spacing corresponding to PdO(1 1 1) reticular planes on its tetragonal structure (*P42*/*mmc* space group, JCPDS file number 00-043-1024).

XPS analyses showed that the PdO NPs/C catalyst thus obtained, mainly consisted in Pd(II) species (>80%) along with a low extent of reduced Pd(0) species (<20%) (Fig. 2d). The residual amount of Pd(0) could be explained by a core–shell arrangement of some particles most likely with a thicker oxide shell but still with a metallic core. X-ray diffraction pattern of the PdO NPs/C catalyst (Fig. 2c) confirmed the formation of crystalline palladium oxide in tetragonal phase with the apparition of the diffraction peak at 2θ equal to 34.5° (1 0 1), 41.9° (1 1 0), 54.8° (1 1 2), 61.2° (1 0 3) and 71.3° (2 1 1). Residual signals for metallic palladium in face-centred cubic (fcc) crystalline structure were also identified with peaks at 40.0° (1 1 1), 46.5° (2 0 0) and 67.9° (2 2 0). One can note in Fig. 1d that lattice planes go through the whole particle projected surface with no contrast perturbation around the core region. That probably means that these particles do not exhibit a core–shell nanostructure and is a pure PdO arrangement. We next evaluated both the catalytic activity and the recyclability of 5% PdO NPs/C on a model reaction and compared the results with those obtained with 5% Pd/C catalyst (Table 1). Importantly, we stress that lower and higher Pd loadings onto the support, i.e. 1 wt.% and 10 wt.% respectively, gave lower catalytic activity [40], thereby, our further studies were carried out with 5 wt.% supported Pd catalysts.

The coupling of 4-iodoacetophenone **1** with phenyl acetylene **2** was conducted in aqueous *i*PrOH with K_3PO_4 as a base at 80 °C for 12 h [16]. Fresh 5% PdO/C catalyst displayed a slightly diminished yield compared to the unoxidized 5% Pd/C catalyst (run 1). The first recycle revealed a drop of the reaction yields for the two catalysts, albeit in a higher extent for the 5% Pd/C sample. A more obvious divergent behaviour appeared upon the following reuses. Indeed, the catalytic activity of 5% Pd/C significantly decreased after the third run reaching a stable behaviour at ca. 50% yield. By contrast, upon the third, fourth and fifth reuses, the 5% PdO/C catalyst displayed a constant and significantly higher catalytic activity with yields majored by ca. 20% compared to 5% Pd/C. The rapid decrease of the catalytic activity of the 5% Pd/C catalyst upon ruses cannot be ascribed to Pd leaching since ICP-MS measurements of residual soluble Pd species into the solution after a single filtration gave 0.2, 0.4, 0.2 and 0.2 ppm after respectively the 1st, 2nd, 3rd and 4th runs. These values of leaching correspond to less than 3% of the total amount of Pd introduced. Interestingly, the catalytic activity of the reused 5% Pd/C catalyst could be restored upon a hydrogenation treatment in MeOH prior each reuses.

In order to explain the behaviours of both catalysts, the evolution of the palladium oxidation state over the recycles was monitored by XPS analyses of the palladium 3d region (Table 2). As already stated above, the fresh 5% Pd NPs/C catalyst contains roughly 70% Pd(0) and 30% Pd(II). After the first recycling and over