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UC Pd: A New Form of Pd/C for Sonogashira Couplings

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Abstract: Screening of different sources of Pd/C shows reagents of highly variable nanoparticle sizes and oxidation states of the metal. Typically, catalysts with higher surface area are viewed as likely to be the more reactive. In this paper a new form of Pd/C, “UC Pd” is described that is shown to contain larger nanoparticles yet it is the most reactive catalyst of those sold commercially for Sonogashira coupling reactions. UC Pd functions efficiently in the absence of a copper co-catalyst, under very mild and “green” conditions using inexpensive 95 % EtOH at 50 °C. It is also the only form of Pd/C that can be recycled. In side-by-side reactions with several commercially available forms of Pd/C, none compete successfully with UC Pd under standardized conditions. Physical data obtained from extensive surface analysis using TEM, XRD, XPS, and CO-TPD measurements lead to an explanation behind the unique reactivity of this new recyclable form of Pd/C.

Keywords: cross-coupling · green chemistry · heterogeneous catalysis · palladium · Sonogashira couplings

Introduction

One approach to enhancing the appeal of green chemistry[1] is to improve the range of transition metal-catalyzed cross-coupling reactions conducted under heterogeneous conditions.[2] Palladium-on-charcoal is a well-established reagent[3] that has found increasing popularity in several of the more common C–C bond-forming name reactions (e.g., Suzuki–Miyaura,[4] Heck[5] and Sonogashira[6–8]). However, there are issues associated with its use (e.g., levels of leaching) and, perhaps more difficult to address, consistency among suppliers of Pd/C. Indeed, as a catalyst for hydrogenation, the level of success can be quite variable and several different sources of Pd/C are often required for evaluation.[9] Hence, variation might be expected as well among non-hydrogenative processes, such as Pd-catalyzed cross-coupling reactions. The reasons for such variation among Pd/C catalysts could lie in the source of carbon (e.g., wood, coconut, peat moss), the temperature of treatment, and the levels of exposure to oxygen, among other oxidants.[10] Given the multiple parameters associated with Pd/C formation, in addition to other reaction conditions to be optimized (e.g., ligand, solvent), perhaps it would not be surprising if the many commercial forms of Pd/C were found not to be equally effective. Arriving at a reliable, reproducible Pd/C catalyst capable of mediating selected heterogeneous cross-couplings seems not only potentially important to synthesis and green chemistry, but long overdue. In this report we describe the preparation of a new, active form of palladium-on-charcoal (“UC Pd”) that is unlike any of the existing commercial materials. Such differences are not only manifested by comparisons of measurable physical data (e.g., TEM, XRD, XPS, and CO-TPD), but also by direct side-by-side experiments in catalyzed Sonogashira couplings. It has been shown that UC Pd uniquely serves as the first effective and recyclable catalyst for copper-free Sonogashira couplings with aryl bromides as substrates. Moreover, given the reactivity of newly fashioned UC Pd, the conditions under which these reactions occur are very mild and take into consideration environmental concerns, safety issues, and economic factors.

Results and Discussion

Preparation and reactivity of UC Pd: As previously described for both Ni/C[11] and Cu/C,[12] UC Pd is prepared by simply dissolving $Pd(NO_3)_2$ in water to which is added commercially available activated charcoal (Aldrich catalog #278092; Scheme 1). Ultrasonication for 20 h is then followed by distillation of the water, subsequent washing with

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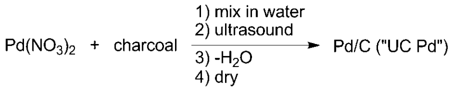
toluene and diethyl ether, and drying overnight at 80 °C under high vacuum. While metal reduction usually involves flammable hydrogen or sodium borohydride, in this procedure it is accomplished in situ by the charcoal support throughout the course of the distillation of water. Ultrasonication presumably helps greatly in distributing the metal particles throughout the charcoal matrix, as seen previously for both Ni[11] and Cu.[12]

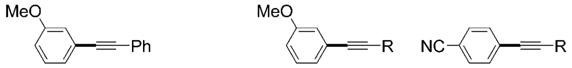


Scheme 1. Preparation of UC Pd.

The catalytic activity of UC Pd versus that of commercial sources was tested in Sonogashira coupling reactions. Pd/C, in general, is known to promote couplings between terminal acetylenes and either aryl iodides[7a–e] or aryl chlorides[7f] in the absence of copper salts. Inexplicably, related couplings with readily available aryl bromides have never been described. Notably, existing procedures whether involving aryl iodides or chlorides, while copper-free, are not truly heterogeneous in nature; that is, each describes Pd/C as providing a catalytic amount of metal that mediates homogeneous catalysis. On the other hand, UC Pd catalyzes heterogeneous sp–sp^2 cross-couplings with aryl bromides, and applies to a broad range of substrates. UC Pd samples containing loadings of 6, 8, and 10 % (by weight) were screened for activity toward *m*-bromoanisole with a terminal alkyne (phenylacetylene; Table 1). Most effective was 10 % metal (2 mol % vs substrate); lower percentages gave dramatically reduced levels of conversion after five hours at 50 °C. Triphenylphosphine (10 mol %) serves well as ligand for this coupling, but only when assisted by microwave irradiation at higher temperature (entry 1). However, use of reduced levels of both UC Pd (2 mol %) and ligand (2 mol %) are effective by replacing Ph_3P with XPhos. Inexpensive K_2CO_3 serves as the base, and 95 % ethanol is the solvent of choice in all cases studied (0.3 M).

Comparison with commercial sources of Pd/C: Remarkably, each of the commercially available sources of Pd/C tested displayed considerably lower activity compared with UC Pd under otherwise identical conditions (Table 2). UC Pd displayed a similar trend in activity in each of these substrate combinations. By contrast, a fresh sample of 10 % Pd/C from Aldrich[13] led to moderate conversion of *m*-bromoanisole or *p*-bromobenzonitrile under optimized conditions. Likewise, Pd^{II}/C Degussa E101[14] was found to be even less prone to mediate these couplings. Pd/C from Alfa Aesar,[15] as well as the Pd/C catalyst Selcat Q6,[16] were far more active toward catalysis, but neither was competitive with UC Pd.

Table 2. Comparisons between Pd/C reagents for three cross-couplings.[a]



1 (3 h) **2** (R = *n*-C_6H_{13}; 3 h) **3** (R = *n*-C_6H_{13}; 2 h)

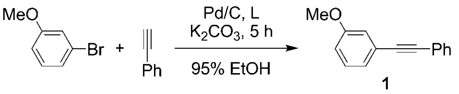
	Conversion [%]	Conversion [%]	Conversion [%]
UC Pd	100	100	100
Alfa Aesar	60	45	65
Selcat Q6	55	53	70
Aldrich	45	38	54
Degussa E101	25	5	22

[a] Pd/C, XPhos (2 mol %), K_2CO_3 (2 equiv), 95% EtOH, 50 °C; same Pd loading: 10 % by weight.

Effect of copper(I): Liebscher[6k] and Novák[7f] have both found that rates of Sonogashira couplings slow significantly with Pd/C in the presence of a copper salt as co-catalyst. Results from our study also show this tendency. With only 5 mol % of CuI present, UC Pd loses half of its activity under microwave assistance (conditions A), and essentially all activity is gone at 50 °C (conditions B; Table 3, entry 1). A similar trend was observed with others sources of Pd^0/C (e.g., entry 2). Surprisingly, added CuI to Pd^{II}/C Degussa E101 enhanced the isolated yield of product alkyne (Table 3, entry 3). These results, while not readily explained, clearly establish how the source and oxidation state of such a fundamental reagent can play dramatic roles in catalysis by "Pd/C".

Reclaimed catalyst upon filtration retains most of its reactivity, which was determined using successive reactions on the aryl bromide, *m*-bromoanisole (Table 4). Good isolated yields were observed through four cycles, results that could only be achieved with UC Pd notwithstanding the extended time frame (12 h vs 3 h; see Table 2). All vendor-supplied catalysts, however, gave low yields after initial use. Such losses of reactivity associated with commercially available sources of Pd/C have also been noted previously in Heck,[5g,j,k]

Table 1. Optimization of conditions for Sonogashira couplings catalyzed by UC Pd.

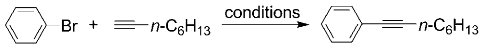


1

Entry	Pd/C loading [%][a]	Pd [mol %]	L	Ratio Pd/L	*T* [°C]	Conversion [%][b]
1	6	5	PPh_3	1:3	130[c]	95
2	6	5	PPh_3	1:3	50	< 5
3	6	2	XPhos	1:1	50	20
4	8	2	XPhos	1:1	50	45
5	10	2	XPhos	1:1	50	100 (95[d])

[a] Measured by ICP. [b] Decane was used as internal standard. [c] The reaction was performed in a microwave (130 °C, 30 min). [d] Isolated yield on 2 mmol scale.

Table 3. Influence of copper iodide as co-catalyst.[a]



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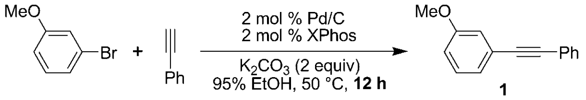
Entry	Catalyst	Conditions A[b] no CuI	 5 mol% CuI	Conditions B[c] no CuI	 5 mol% CuI
1	UC Pd	95%	55%	90%	traces
2	Aldrich	90%	40%	–	–
3	Degussa E101	45%	95%	26%	68%

[a] Isolated yield on 2 mmol scale. [b] 5 mol% Pd/C, 10 mol% PPh_3, 95% ethanol, 120°C (microwaves), 15 min. [c] 2 mol% Pd/C, 2 mol% XPhos, 95% ethanol, 50°C, 5 h.

Suzuki–Miyaura[17] couplings, as well as in Sonogashira reactions.[7e]

Table 4. Recycling of catalysts (isolated yields).



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Run	UC Pd [%]	Alfa Aesar [%]	Degussa E101 [%]	Aldrich [%]	Selcat Q6 [%]
1st	95	94	75	84	90
2nd	92	45	21	49	54
3rd	89	10	–	15	20
4th	87	–	–	–	–

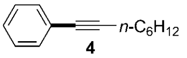
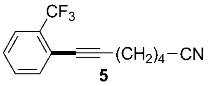
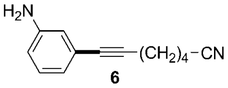
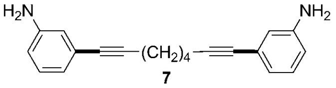
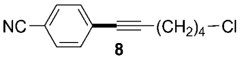
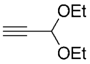
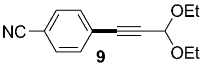
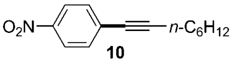
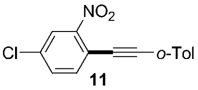
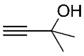
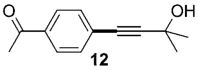
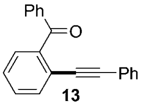
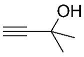
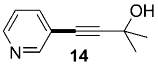
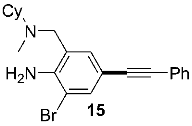
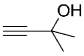
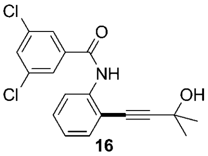
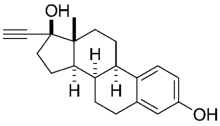
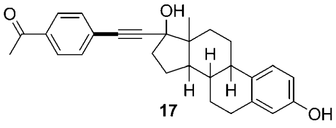
Several examples that lead to products **4**–**17** and attest to the generality of this mild, heterogeneous cross-coupling are illustrated in Table 5. Aryl bromides bearing either activating or deactivating substituents gave the corresponding disubstituted acetylenes in high isolated yields. Successful cross-couplings involving an assortment of terminal acetylenes containing a variety of functional groups, such as nitrile, chloride, acetal, and alcohol groups, lend further credence to the attractiveness of this protocol. Featured cases include aryl bromides bearing *o*-CF_3 (entry 2), *m*-amino (entries 3, 4), *p*-cyano (entries 5, 6), *p*-nitro (entry 8), keto (entries 9, 10), and 3-pyridyl groups (entry 11), and more highly functionalized substrates (entries 12 and 13). Acetylenes containing an ω-cyano (entries 2, 3), α-quaternary carbon (entries 9, 11, 13), and a cholesteryl residue (entry 14) all reacted smoothly. Double arylation of a diyne (entry 4) is also worth mentioning. Tests were conducted on UC Pd to assess the extent to which it provides mainly heterogeneous catalysis. Analysis of a reaction mixture (as in Table 4) prematurely stopped (at 60% conversion) and filtered hot to remove Pd/C showed no further consumption of educts upon further treatment at 50°C. ICP-AES analysis on the filtrate further confirmed that only traces of Pd are detected in solution (2–4 ppm).

Analyses of Pd/C: Bright field transmission electron microscopy (TEM) imaging of UC Pd shows palladium nanoparticles with a fairly broad size distribution, in the 10–300 nm range, both before and after catalysis (Figure 1). This contrasts with related samples of Pd/C, which, likewise using TEM analyses, tend to form much larger, less reactive, and non-recyclable aggregates during the reaction.[5l,17] These observations correlate well with the X-ray diffraction (XRD) pattern that indicates Pd^0 crystallites of 60 nm average diameter (Figure 2). By contrast, all commercially available catalysts examined by XRD consist of smaller nanoparticles (6–15 nm on average).

Carbon monoxide temperature programmed desorption (CO-TPD) was used to quantify the Pd surface sites due to the specificity of the Pd-CO bonding ratio of 1:1. It is observed (Figure 3) that the relative accessible palladium surface areas (as integrated area under each desorption curve) are dependent on the source. Additionally, there are small differences in the effective binding/desorption energies (peak positions) suggesting slightly different chemical environments for Pd in each catalyst. Both samples of Pd/C either sold by Alfa Aesar, or prepared as UC Pd, show the greatest surface area of Pd (Table S1, entries 5, 6), even though the size of the nanoparticles for UC Pd is larger than that of all other commercial samples (Figure 2).

Since the data as to particle size alone cannot be used to explain both the greater reactivity and unique recyclability of UC Pd compared to other sources of Pd/C, additional surface analyses were conducted. X-ray photoelectron spectroscopy (XPS) was employed to determine the oxidation state of palladium at the surface. Given that the "escape depth" for photoelectrons generated within any given substance is quite shallow, XPS measures a signal from only the top 2–4 nm of a material. This surface specificity is particularly informative, in contrast to the "bulk" signal observed in XRD. All Pd/C catalysts examined by this technique contain roughly 30% Pd^0 at their surface, with the exception of Degussa E101 that shows 15% (Table S2). The amounts of Pd^{II} and Pd^{IV} present vary widely between samples, and hence, no trend with respect to particle size or activity is observed. However, after use, UC Pd retains its distribution of oxidation states (ca. 30% Pd^0; Figure 4), while the Degussa E101 and Alfa Aesar catalysts drop from 15 to 5%, and from 27 to 9% Pd^0, respectively. The substantially better stability of UC Pd may derive from its higher levels of reduced metal at the surface relative to other catalysts due to its larger metal nanoparticles. These are less likely to stabilize oxides on their surface relative to smaller nanoparticles.[18] The implication is that there exists an optimum particle size which balances surface area with surface stability. Thus, while to some extent counterintuitive, using smaller size particles does not translate into greater reactivity. This balance impacts both catalyst activity and recyclability; only UC Pd emerges with minimal modification to its surface following participation in Sonogashira cross-couplings.

Table 5. UC Pd-catalyzed cross-couplings to form functionalized alkynes.

Entry	Alkyne	Product	Yield [%][a,b]
1	$\equiv$–n-C$_6$H$_{12}$	 **4**	90
2	$\equiv$–(CH$_2$)$_4$–CN	 **5**	95
3	$\equiv$–(CH$_2$)$_4$–CN	 **6**	96[c]
4	$\equiv$–(CH$_2$)$_6$–$\equiv$	 **7**	82[c,e]
5	$\equiv$–(CH$_2$)$_4$–Cl	 **8**	91
6		 **9**	85
7	$\equiv$–n-C$_6$H$_{12}$	 **10**	88
8	$\equiv$–o-Tol	 **11**	80[d]
9		 **12**	87
10	$\equiv$–Ph	 **13**	80[c]
11		 **14**	92
12	$\equiv$–Ph	 **15**	55[d,f]
13		 **16**	81[d]
14		 **17**	90[c,g]

[a] Conditions: aryl bromide (2 mmol), alkyne (4 mmol), K_2CO_3 (4 mmol), 2 mol% UC Pd, 2 mol% XPhos, 95% ethanol (6 mL), 50°C, 5 h. [b] Isolated yield. [c] Run over 10 h. [d] Run over 15 h. [e] Alkyne (2 mmol), aryl bromide (8 mmol), K_2CO_3 (4 mmol). [f] 5 mol% of Pd/C, 5 mol% XPhos, K_2CO_3 (6 mmol). [g] Alkyne (1 mmol), aryl bromide (2 mmol), K_2CO_3 (2 mmol).

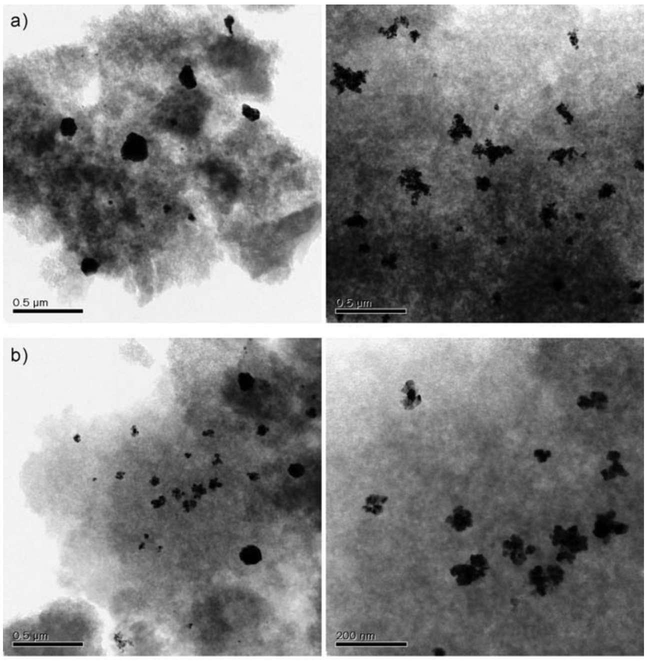


Figure 1. TEM analysis a) initial reagent, UC Pd; b) UC Pd after catalysis.

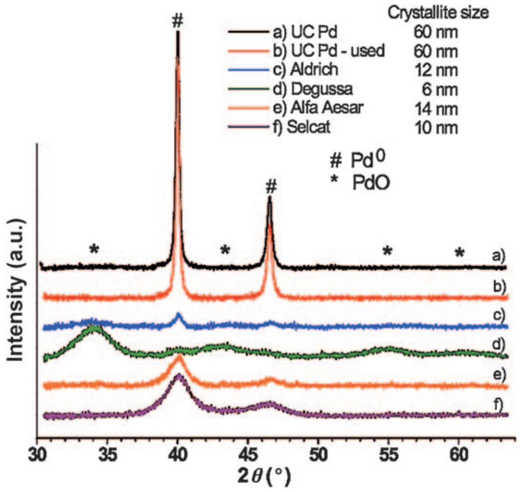


Figure 2. XRD profiles of Pd/C catalysts.

Conclusion

A novel form of palladium-on-charcoal (UC Pd), easily prepared from $Pd(NO_3)_2$ in water, has been developed. Several commercially available sources of Pd/C were compared directly with UC Pd in terms of reactivity profile, recyclability, and nature with respect to particle size and metal oxidation state(s): all were found to vary widely; none is as reactive, nor can any be recycled effectively. Representative cross-couplings, as illustrated with the Sonogashira coupling reaction, support these differences and highlight the counterintuitive notion in catalysis that smaller particle size is typically correlated with greater reactivity, which is not the case with UC Pd.

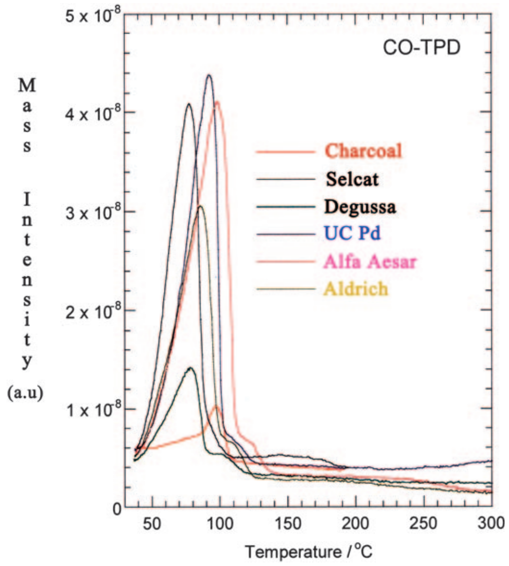


Figure 3. CO-TPD profiles of Pd/C catalysts.

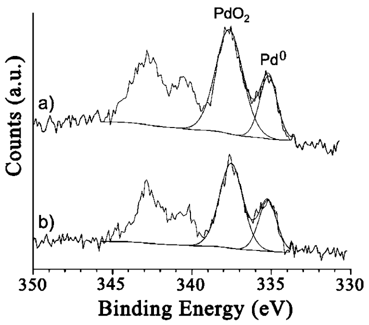


Figure 4. Distribution of oxidation states as measured by XPS for a) initial reagent, UC Pd; b) UC Pd after catalysis.

Experimental Section

Preparation of 10 % UC Pd: Darco KB activated carbon (Aldrich, catalog #278092, 100 mesh, ≈25 % H_2O) was dried overnight under vaccum at 150 °C. The dry activated carbon (3.6 g) was added to a 100 mL round-bottom flask containing a stir bar. A solution of $Pd(NO_3)_2{\cdot}H_2O$ (Strem Chemicals, catalog #93-4608, Pd ≈40 %, 1 g, 3.75 mmol) in deionized H_2O (50 mL) was added to the activated carbon, and additional deionized H_2O (30 mL) was added to wash down the sides of the flask. The flask was stirred vigourously at RT for 1 h and then submerged in a ultrasonic bath for 20 h. It was then attached to a distillation setup and placed in a pre-heated (175–180 °C) sand bath while stirring. As the distillation ended, the sand temperature began to rise and was held below 200 °C. After cooling the charcoal to RT, it was washed with toluene (50 mL) and then ether (50 mL), and the resulting solid filtered in vacuo in a fritted funnel. The fritted funnel was turned upside down under vaccum overnight until the Pd/C fell from the frit into the collection flask placed in a preheated 80 °C sand bath. The impregnated charcoal (ca. 3.94 g) was transferred to, and stored in, separate vials. Thus, 10.2 wt. % Pd/C (calculated by ICP analysis), or 0.93 mmol Pd/g catalyst was obtained.

General procedure for Pd/C-catalyzed cross-coupling reaction between aryl bromides and terminal alkynes: In a 10 mL round-bottom flask under argon containing Pd/C (42 mg, 0.93 mmol g^{-1} ca. 0.04 mmol), XPhos (18 mg, 0.04 mmol) and potassium carbonate (552 mg, 4 mmol) was added 95 % ethanol (6 mL) followed by the aryl bromide (2 mmol) and then the terminal alkyne (4 mmol). The flask was submerged in a pre-heated 50 °C water bath and stirred vigorously for the indicated time. The mixture was then poured into a flask containing silica (3–4 g) and the sides of the reaction flask were washed with diethyl ether. Solvents were removed under vaccum and the resulting dry, crude silica was introduced on top of a silica gel chromatography column to purify the product.

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