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Rapid "Mix-and-Stir" Preparation of Well-Defined Palladium on Carbon Catalysts for Efficient Practical Use

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A facile direct deposition approach for the preparation of recyclable Pd/C catalysts simply by stirring a solution of tris(dibenzylideneacetone)dipalladium(0) with a suitable carbon material was evaluated. An extraordinarily rapid catalyst preparation procedure (< 5 min) under mild conditions and its excellent performance in cross-coupling and hydrogenation reactions were demonstrated. The key point for catalyst design is the direct deposition of Pd⁰ centers onto the highly accessible surface area and the avoidance of ill-defined Pdᴵᴵ/Pd⁰ states.

Supported Pd/C catalysts have been developed extensively and applied ubiquitously in numerous reactions in organic synthesis.[1–4] Indeed, in the current research practice, Pd/C catalysts have become an indispensable synthetic tool. The most common techniques for the preparation of Pd/C systems include deposition–reduction, deposition–precipitation, and impregnation (Figure 1).[1–3] The deposition–reduction method in-

Figure 1. Preparation of Pd/C catalysts: a) deposition–precipitation, b) deposition–reduction, c) impregnation ([Red] = reducing agent).

volves the treatment of a suspension of a carbon material and a Pdᴵᴵ salt with reductants (additional chemicals), which may lead to the contamination of carbon surface because of the ad-

sorption of the additives. In the deposition–precipitation method, Pdᴵᴵ salts serve as a source of Pd(OH)₂ in the presence of bases. The impregnation method involves the wetting of a support material by a solution of a Pdᴵᴵ salt and subsequent solvent removal. In the latter two methods, treatment under H₂ atmosphere is usually performed to reduce the Pdᴵᴵ species. This requires special equipment for treatment with H₂ at elevated pressures (up to 10 bar) and temperatures (200–500 °C).[2a–c, 3]

Overall, the preparation of Pd/C catalysts is technically rather difficult and it is very rarely done in regular organic synthesis laboratories. Moreover, incomplete reduction to Pd⁰ may occur if Pdᴵᴵ precursors are used as a source of Pd.[5] Even in the presence of an excess of reducing agent, the amount of unreacted Pdᴵᴵ may exceed 25 %.[1a–c, 2d, 4f–g] Thus, such catalysts may contain a combination of Pdᴵᴵ/Pd⁰ centers, the ratio of which is difficult to control. The preparation of Pd/C catalysts from zero-valent metal complexes has been studied previously; however, it required a lengthy procedure or special equipment.[6a–d] The use of microwave heating during catalyst preparation may initiate the modification of the carbon surface, which depends on the conditions and particle morphology.[6e]

The application of commercially available catalysts is accompanied by a series of well-known problems: large batch-to-batch differences, ill-defined active centers with various Pdᴵᴵ/Pd⁰ ratios, and variations in composition and properties. Even within the same research group, it is sometimes difficult to reproduce previous results if a new batch of commercial catalyst arrives. Critical parameters such as catalyst selectivity and efficiency are especially sensitive.

In the present study, we report a fast and efficient approach for the preparation of Pd/C catalysts based on direct deposition (Figure 1). A very simple protocol was developed that involves only standard laboratory glassware and a magnetic stirrer. The whole catalyst preparation procedure can take < 5 min. A Pd⁰ complex is used for the catalyst preparation; thus, the reduction of metal species is not required. The scope of the developed approach was investigated for various carbon materials, and its efficiency was tested for a variety of
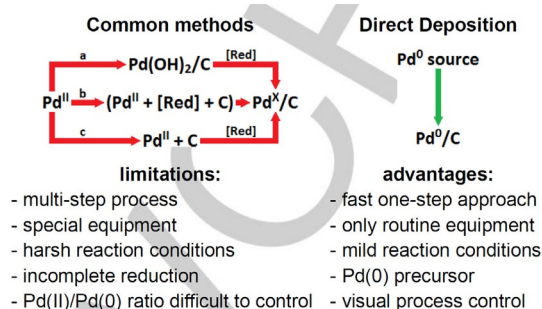
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substrates in two representative synthetic transformations: cross-coupling and hydrogenation.

We utilized commercially available tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$dba$_3$) as a metal precursor for the deposition of Pd nanoparticles (NPs). The easy generation of reactive Pd^0 species and the convenient determination of purity by ^{1}H NMR spectroscopy are important advantages of Pd$_2$dba$_3$.[7] Several different carbon materials were used to prepare Pd/C catalysts: graphite, multiwalled carbon nanotubes (MWCNT), Vulcan XC72 (Vulcan), and nanoglobular carbon (NGC). In the designed procedure (Figure 1), the catalyst preparation was performed as a one-step process in a fairly simple procedure: the mixing of the carbon material with a solution of Pd$_2$dba$_3$, the heating of the obtained mixture, and the filtration and washing of the Pd/C catalyst. The overall procedure, which includes preparation and isolation, could take less than 5 min, and the deposition itself could take 2 min (a video is available in the Supporting Information) and could be performed using routine laboratory equipment.

At the beginning of the procedure, the solution of Pd$_2$dba$_3$ was dark red, and complete discoloration occurred at the end of the deposition process. Thus, the process of Pd/C formation can be controlled visually. As a result, all the Pd species were attached to the carbon surface quantitatively, which was confirmed by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and elemental analysis, to form catalysts with a metal content of 1 wt%.
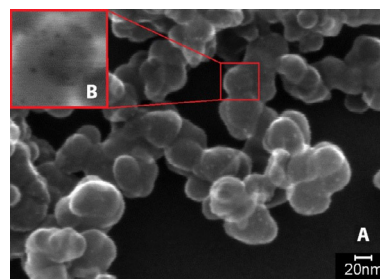

Figure 3. A) SEM image of Pd/NGC and B) scanning transmission electron micrograph of the selected region that shows Pd NPs.

The prepared supported Pd/C catalysts were characterized by TEM and SEM (Figures 2 A–E and 3 and Supporting Information). The results of the BET analysis of the carbon materials are shown in Figure 2 F. The microscopy study showed the formation of spherical metal NPs dispersed across the surface of the carbon material. Excellent morphologies of Pd/C that consist of small NPs with a narrow particle size distribution were found for NGC, MWCNT, and Vulcan (Figure 2 A–C). Average NP diameters of (2.1 ± 0.6), (1.4 ± 0.3), and (1.9 ± 0.6) nm were found for NGC, MWCNT, and Vulcan, respectively (Figure 2 F). A larger average particle size and wider size distribution of (6.2 ± 2.2) nm were observed in the case of graphite. The relatively low surface area of graphite led to a high arrangement density, and the metal particles became relatively larger with a pro-
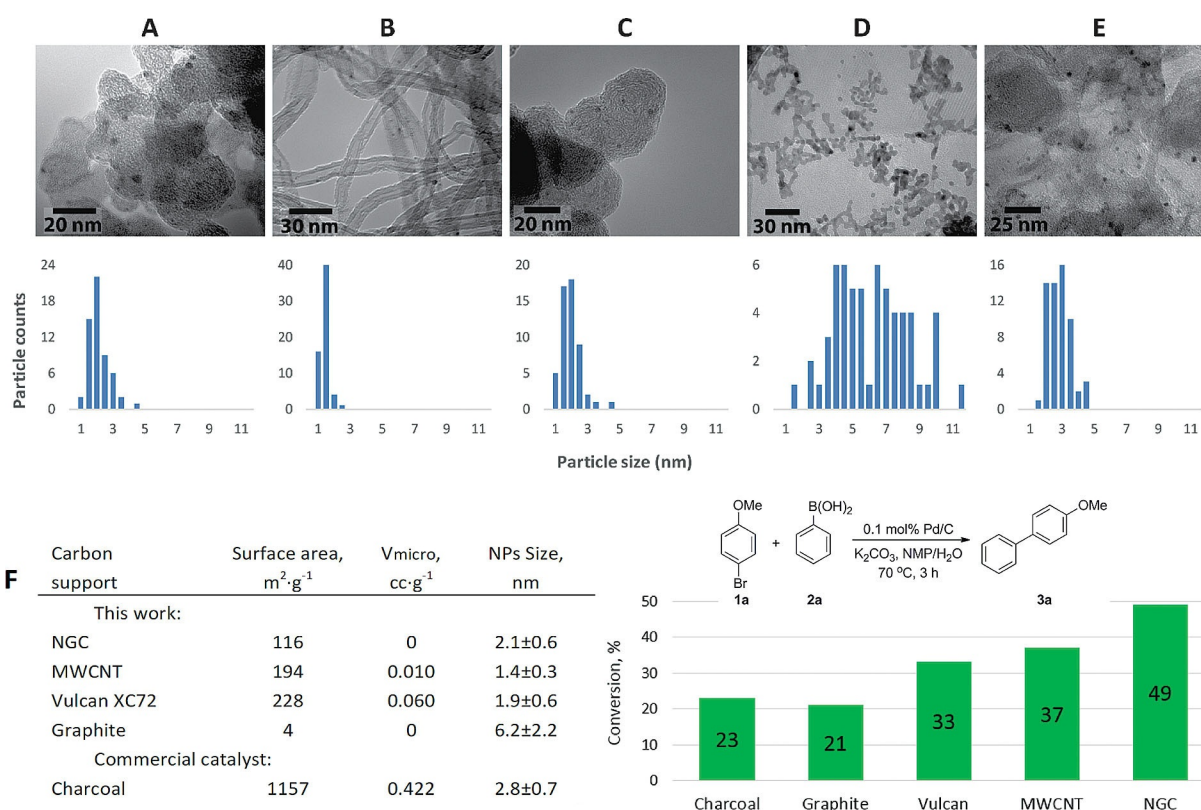

Carbon support	Surface area, m^2·g^{-1}	Vmicro, cc·g^{-1}	NPs Size, nm
This work:			
NGC	116	0	2.1±0.6
MWCNT	194	0.010	1.4±0.3
Vulcan XC72	228	0.060	1.9±0.6
Graphite	4	0	6.2±2.2
Commercial catalyst:			
Charcoal	1157	0.422	2.8±0.7

Figure 2. TEM images and particle size distribution histograms of A) Pd/NGC, B) Pd/MWCNT, C) Pd/Vulcan, D) Pd/graphite, and E) commercially available Pd/charcoal; F) structural data of these Pd/C catalysts and G) comparison of their catalytic activity in the Suzuki–Miyaura reaction (evaluated as an average value from three independent experiments).
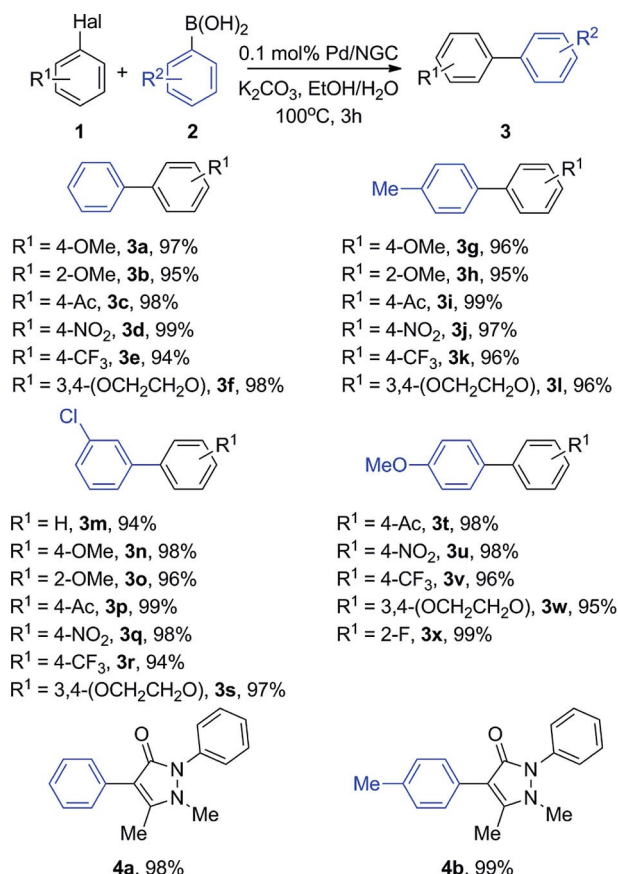
nounced tendency to agglomerate. Agglomeration was not observed for the other studied carbon materials with larger surface areas. For comparison, we included a commercial Pd/C catalyst made of charcoal as a carbon support (Figure 2E).

Next, we evaluated the performance of the Pd/C catalysts in the Suzuki–Miyaura cross-coupling as a model reaction. The reaction between 4-bromoanisole (**1a**) and phenylboronic acid (**2a**) was performed in the presence of 0.1 mol% of a catalyst. The process was stopped after 3 h for a reliable comparison of the catalytic activity (at longer times or higher temperatures, a complete conversion is achieved and a comparison of the relative activity is not possible). The commercial Pd/C catalyst showed yield of the product of 23%, and a close value of 21% was obtained for Pd/graphite. A much better performance was observed for Pd/Vulcan and Pd/MWCNT (33 and 37%, respectively); the highest catalytic performance was found for the NGC-derived catalyst (Figure 2G). The Pd/graphite catalyst exhibited a low activity because of the larger size of the Pd NPs and their agglomeration. Although small metal NPs were present in the Pd/charcoal catalyst, some of them might be confined in micropores ($V_{micro} = 0.422$ cc g^{-1}; Figure 2F), in which mass transfer is hindered. The presence of diffusion-limited micropores in the carbon material can decrease the number of accessible active sites in the Pd/charcoal catalyst significantly. The highly accessible surface of Vulcan and MWCNT ($V_{micro} = 0.060$ and 0.010 cc g^{-1}, respectively) gave Pd/C catalysts with a better activity.

A Pd/C catalyst with an outstanding morphology was prepared using NGC as a support (Figure 3). All the metal NPs were located on the surface of the carbon material and were easily accessible for catalysis. The spherical morphology of the carbon units ensured a large surface area and the absence of nonuniform surface defects (Figure 3).

After the optimization of the reaction conditions (Table S1), we studied the performance of the Pd/C catalyst with the NGC support for a wide range of substrates. A variety of aryl iodides as well as electron-rich and electron-poor aryl bromides reacted smoothly to provide biaryl products in excellent yields (Scheme 1). Irrespective of the electronic properties and steric hindrance, 26 different cross-coupling products were synthesized in >94% isolated yields. The cross-coupling reaction was also performed successfully with the iodantipirin drug as a substrate (**4a** and **4b**).

To further evaluate the performance of the prepared catalysts, we examined their activity in the hydrogenation reaction. Hydrogenation is a process of paramount importance in modern organic synthesis and approximately 75% of these transformations are performed using Pd/C catalysts.[8] A well-known and convenient technique of transfer hydrogenation using formic acid was chosen as a model reaction (Figure 4). Again, the Pd/C catalyst with the NGC support showed the best activity. Notably, similar sequence of relative activities in the case of different carbon supports was observed, as compared to Suzuki-Miyaura reaction (cf. Figures 2G and 4A). Under the optimized conditions, alkenes **5a–g** were hydrogenated fully into the corresponding products **6a–g** (Figure 4B).

The catalyst derived from NGC showed the highest activity and could be suggested as the catalyst of choice. However, for regular synthetic transformations, Pd NPs supported on MWCNT or even on graphite could also be used. The application of a higher temperature and longer reaction time resulted in excellent yields in the studied representative cross-coupling (cf. entries 1 and 2, Table 1) and hydrogenation (cf. entries 3 and 4, Table 1) reactions. Thus, by using the developed catalyst preparation approach efficient Pd/C catalysts can be prepared from a variety of carbon supports.

Scheme 1. Pd/C-catalyzed Suzuki–Miyaura reaction. Isolated yields are shown. For **3a–3w** Hal = Br; for **3x**, **4a,b** Hal = I. Part of the biaryl structure, derived from boronic acid, is shown in blue. Pyrazolone derivatives **4a,b** were obtained according to the same procedure.

Table 1. Performance of the prepared Pd/C catalysts under different conditions.

Entry	Conditions	Pd/NGC	Pd/MWCNT	Pd/Graphite
Cross-coupling[a]				
1	N-Methyl-2-pyrrolidone/H₂O, 3 h, 70 °C	>98%	69–92%	68–74%
2	EtOH/H₂O, 3 h, 100 °C	>99%	>99%	>99%
Hydrogenation[b]				
3	EtOH, 2 h, 50 °C	>99%	35–85%	10–20%
4	EtOH, 4 h, 70 °C	>99%	>99%	>99%

[a] Cross-coupling of phenylboronic acid with **1c**, **1d**, and **1i**; [b] Hydrogenation of **5a–5c**. See Supporting Information.
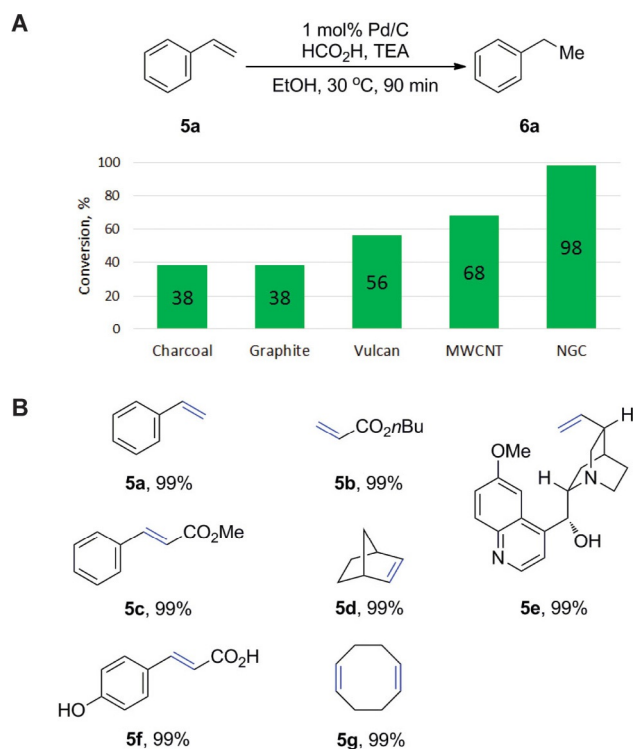
Figure 4. A) Comparison of the activity of catalysts in styrene hydrogenation and B) scope of the hydrogenation reaction. Unsaturated C—C bonds, which are reduced during the reaction, are shown in blue.

Stability and recycling are important properties of heterogeneous catalysts. The recycling of the Pd/MWCNT and Pd/NGC catalysts, prepared in the present study, was evaluated in successive reaction runs. Both catalysts were recycled successfully five times simply by separation from the reaction mixture after the reaction. An excellent conversion of 100 % was observed in all runs (Supporting Information). After the fifth cycle, the catalysts were studied by electron microscopy. Remarkably, the size of the Pd NPs remained very small (2.1 ± 0.4 and 2.0 ± 0.5 nm for MWCNT and NGC, respectively); and, to our great delight, NP sintering did not take place and no Pd agglomerates were observed. Thus, the activity of the catalysts was retained after five successive runs without an indication of significant catalyst degradation.

To summarize, the direct deposition of Pd^0 from a solution of Pd_2dba_3 represents a convenient approach for the preparation of recyclable Pd/C catalysts. Demanding Pd/C catalysts can be made in regular organic synthesis laboratories without the use of dedicated equipment and harsh reaction conditions. The scope of the developed approach was studied for various carbon supports, and the utility of the prepared catalysts was confirmed for a wide range of substrates in cross-coupling and hydrogenation reactions. The specific morphology of NGC made it an excellent choice for the preparation of Pd/C catalysts with a maximized accessibility to the catalytically active centers on the carbon surface.

Experimental Section

Preparation of Pd_2dba_3 as source of Pd^0 species

The quality of Pd_2dba_3 is important for the correct determination of the amount of Pd^0 centers available for deposition onto a carbon support. For commercially obtained samples, the purity of Pd_2dba_3 should be evaluated by using ^1H NMR spectroscopy.[7b] Pd_2dba_3 can also be synthesized as described elsewhere.[7b]

Experimental procedure for the preparation of Pd/C catalysts

$Pd_2dba_3 \cdot CHCl_3$ (25.0 mg), carbon material (500 mg), $CHCl_3$ (25 mL), and a magnetic stirrer were loaded into a screw-capped reaction vessel and placed in an oil bath at 80 °C under stirring. After the dissolution of Pd_2dba_3, a dark red solution was formed, and stirring was performed until the red color of the solution disappeared. The Pd/C catalyst was separated from the solution by filtration or centrifugation, washed with acetone (30 mL) to remove free dba, and dried under reduced pressure (0.01 bar, 100 °C). A detailed step-by-step procedure is provided in the dedicated video (Supporting Information).

More information on the experimental procedure, NMR spectroscopy monitoring of the deposition process, catalyst characterization, analytical data, catalyst recycling, cross-coupling, and hydrogenation reactions is provided in the Supporting Information.

Conflict of interest

The authors declare no conflict of interest.

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