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Rapid ‘Mix-and-Stir’ Preparation of Well-defined Pd/C Catalysts for Efficient Practical Usage

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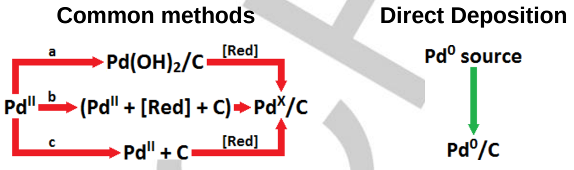
Abstract: A facile direct deposition approach for the preparation of recyclable Pd/C catalysts simply by stirring a solution of Pd_2dba_3 with a suitable carbon material was evaluated. An extraordinary rapid catalyst preparation procedure (< 5 min) under mild conditions and its excellent performance in cross-coupling and hydrogenation reactions were demonstrated. The key point for catalyst design was to directly deposit Pd(0) centers onto highly accessible surface area and to avoid ill-defined Pd(II)/Pd(0) states.



limitations:	advantages:
- multi-step process	- fast one-step approach
- special equipment	- only routine equipment
- harsh reaction conditions	- mild reaction conditions
- incomplete reduction	- Pd(0) precursor
- Pd(II)/Pd(0) ratio difficult to control	- visual process control

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

Supported Pd/C catalysts have been extensively developed and ubiquitously applied 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 preparation of Pd/C systems include deposition-reduction, deposition-precipitation and impregnation (Figure 1).[1-3] The deposition-reduction method involves treatment of suspension of a carbon material and a Pd(II) salt with reductants (additional chemicals), which may lead to contamination of carbon surface due to adsorption of the additives. In the deposition-precipitation method, Pd(II) salts serve as a source of $Pd(OH)_2$ in the presence of bases. The impregnation method involves wetting of a support material by a solution of Pd(II) salt and subsequent solvent removal. In the latter two methods, treatment under H_2 atmosphere is usually carried out for reduction of Pd(II) species. This requires special equipment for treatment with the hydrogen gas at elevated pressure (up to 10 bar) and temperature (200-500°C).[2a-c,3]

In overall, preparation of Pd/C catalysts is technically rather difficult, and it is very rarely done in regular organic synthesis laboratories. Moreover, incomplete reduction to Pd(0) may occur when Pd(II) precursors are used as a source of palladium.[5] Even in the presence of an excess of reducing agent, the amount of unreacted Pd(II) may exceed 25%.[1a-c,2d,4f-g] Thus, such catalysts may contain a combination of Pd(II)/Pd(0) centers, where the ratio is difficult to control. Preparation of Pd/C catalysts starting with zero-valent metal complexes was previously studied; however, it required a lengthy procedure or special equipment.[6a-d] Usage of microwave heating during catalyst preparation may initiate modification of carbon surface depending on the conditions and particles morphology.[6e] Application of commercially available catalysts is accompanied with a series of well-known problems: large batch-to-batch differences, ill-defined active centers with varying Pd(II)/Pd(0) ratio and variations in composition and properties. Even within the same research group, sometimes it is difficult to reproduce own previous results when a new batch of commercial catalyst arrives. Such critical parameters as catalyst selectivity and efficiency are especially sensitive.

In the present study, we report a fast and efficient approach for preparation of Pd/C catalysts based on direct deposition (Figure 1). A very simple protocol was developed involving only standard laboratory glassware and a magnetic stirrer. The whole procedure of catalyst preparation can take < 5 min. The Pd(0) 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 substrates in two most representative synthetic transformations – cross-coupling and hydrogenation.

We utilized commercially available Pd_2dba_3 as a metal precursor for deposition of Pd nanoparticles. Easy generation of reactive Pd(0) species and convenient determination of purity by ^1H NMR are important advantages of Pd_2dba_3.[7] Several different carbon materials were used to prepare Pd/C catalysts: graphite, multiwall carbon nanotubes (MWCNT), Vulcan XC72 (Vulcan) and nanoglobular carbon (NGC). In the designed procedure (Figure 1), the catalyst preparation was performed as a single-stage process in a fairly simple procedure: mixing of carbon material with the solution of Pd_2dba_3, heating of the obtained mixture, and filtration and washing of the Pd/C catalyst. The overall procedure including preparation and isolation could take less than 5 min and the deposition itself could take 2 min (video is available in the Supporting Information) and could be performed using routine laboratory equipment.

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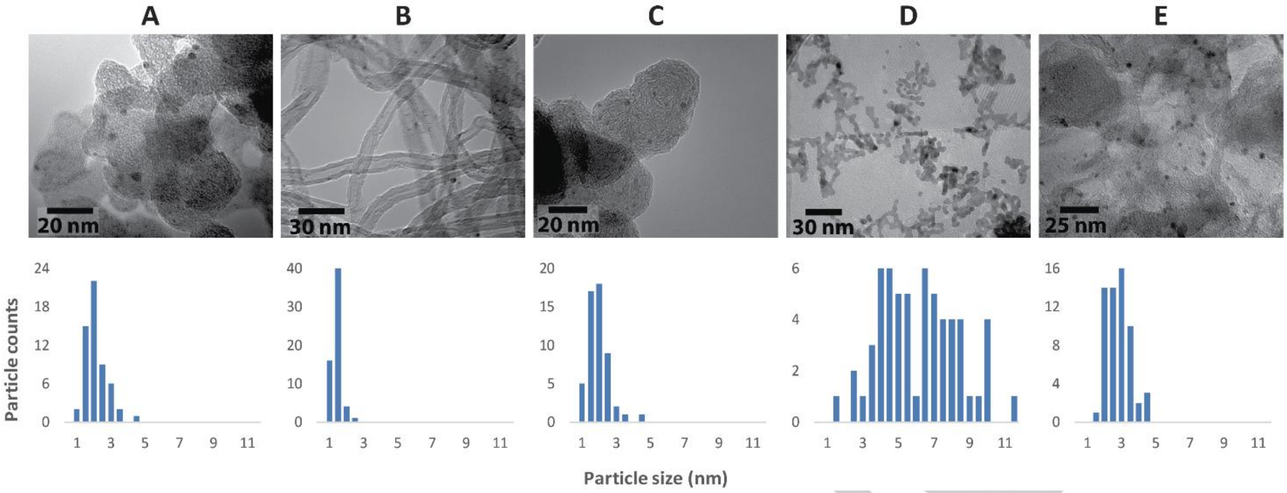
Supporting information for this article is given via a link at the end of the document.



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Carbon support	Surface area, $m^2 \cdot g^{-1}$	Vmicro, $cc \cdot g^{-1}$	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

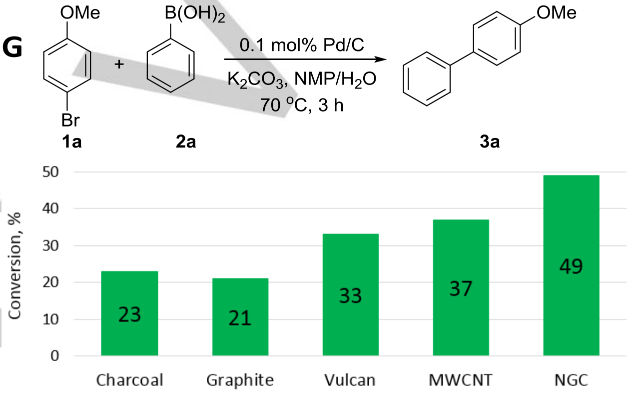


Figure 2. TEM images and particle size distribution histograms of prepared catalysts: Pd/NGC (A), Pd/MWCNT (B), Pd/Vulcan (C), Pd/graphite (D), and commercially available Pd/charcoal catalyst (E); structural data of these Pd/C catalysts (F) and comparison of catalytic activity (G) in the Suzuki-Miyaura reaction (evaluated as an average value from three independent experiments).

At the beginning of the procedure, the solution of the Pd_2dba_3 complex was dark red, and complete discoloration occurred at the end of the deposition process. Thus, the process of Pd/C formation can be visually controlled. As a result, all the palladium species were attached to the carbon surface quantitatively as confirmed by ICP-AES and elemental analysis to form catalysts with a content of the metal of 1wt.%.

The prepared supported Pd/C catalysts were characterized by transmission and scanning electron microscopy (Figure 2A-E, 3 and Supporting Information). Results of BET analysis of the carbon materials are shown in Figure 2F. The microscopy study showed the formation of spherical metal nanoparticles dispersed across the surface of the carbon material. Excellent morphologies of Pd/C consisting of small nanoparticles with narrow particle size distribution were found for nanoglobular carbon, MWCNT and Vulcan (Figure 2A-C). Averaged nanoparticle diameters of 2.1±0.6nm, 1.4±0.3nm and 1.9 ±0.6nm were found for these carbon materials, respectively (Figure 2F). Larger average particle size and wider size distribution of 6.2±2.2nm were observed in the case of graphite. A relatively low surface area of graphite led to high arrangement density, and the metal particles became relatively larger with a pronounced tendency to agglomerate. Agglomeration was not observed in the case of the other studied carbon materials with larger surface area. For comparative purpose, we also 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 carried out in the presence of 0.1mol% of a catalyst. The process was stopped after 3h for a reliable comparison of catalytic activity (at longer time or higher temperature, the complete conversion is achieved, but comparison of 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 in case of Pd/graphite. Much better performance was observed for Pd/Vulcan and Pd/MWCNT (33% and 37%, respectively); the highest catalytic performance was found for the nanoglobular carbon-derived catalyst (Figure 2G). The Pd/graphite catalyst exhibited low activity owing to the larger size of Pd nanoparticles and to its agglomeration. Although small metal nanoparticles were present in the Pd/charcoal catalyst, some of them might be confined into micropores (V_{micro}

= 0.42cc g^{-1}; Figure 2F), where mass-transfer is hindered. The presence of diffusion-limited micropores in the carbon material can significantly decrease the number of accessible active sites in the Pd/charcoal catalyst. The highly accessible surface of Vulcan and MWCNT (V_{micro} = 0.06 and 0.01cc g^{-1}, respectively) gave these Pd/C catalysts with better activity. The Pd/C catalyst with an outstanding morphology was prepared using nanoglobular carbon as a support (Figure 3).

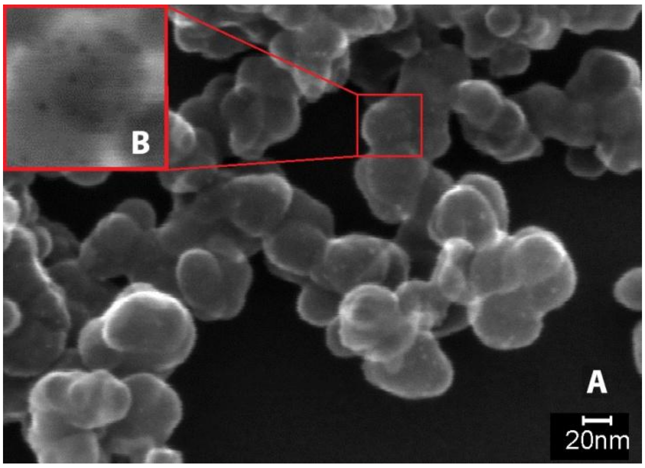
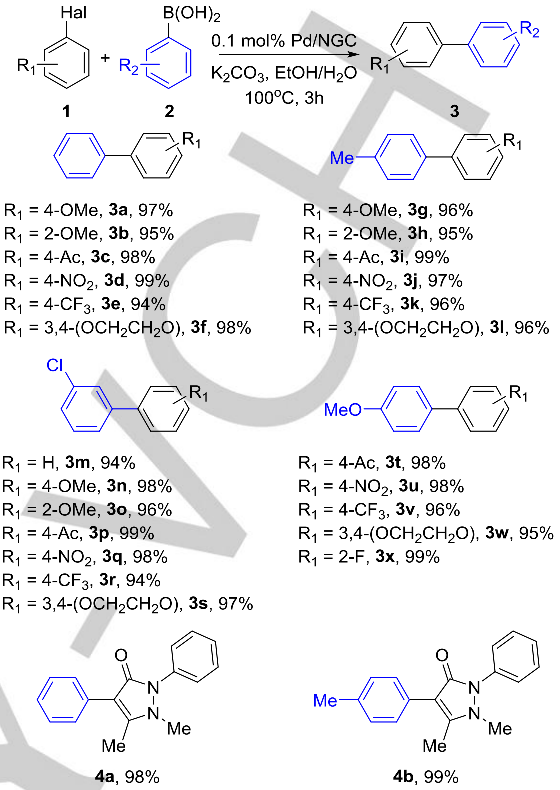


Figure 3. SEM image of Pd/C catalyst prepared on nanoglobular carbon support (A) and STEM image of the selected region showing Pd NPs (B).

All the metal nanoparticles 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 non-uniform surface defects (Figure 3).

After optimization of the reaction conditions (Table S1 in the Supporting Information), we studied the performance of the Pd/C catalyst with the nanoglobular carbon support for a large scope 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 electronic properties and steric hindrance, 26 different cross-coupling products were synthesized in > 94% isolated yields. The cross-coupling reaction was also successfully carried out with the iodantipirin drug as a substrate (**4a** and **4b**).



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

To further evaluate the performance of the prepared catalysts, we examined their activity in the hydrogenation reaction. Hydrogenation is the process of paramount importance in modern organic synthesis, and about 75% of these transformations are carried out 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 nanoglobular carbon support showed the best activity. It is notable that similar relative activities were observed for different carbon supports, as compared to the cross-coupling reaction (cf. Figure 2G and Figure 4A). Under optimized conditions, alkenes **5a-g** were fully hydrogenated into corresponding products **6a-g** (Figure 4B).

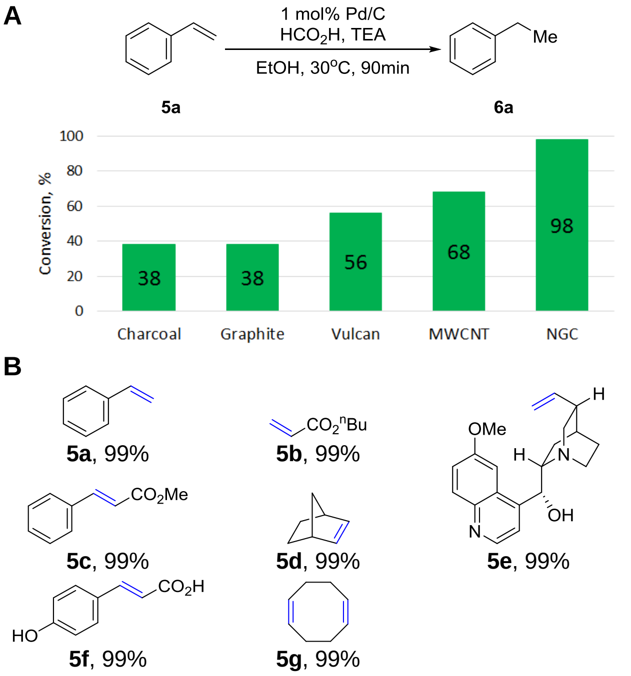


Figure 4. Comparison of activity of catalysts in styrene hydrogenation (A) and scope of hydrogenation reaction (B). Unsaturated C-C bonds, which are reduced during the reaction, are shown in blue.

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

Entry	Conditions	Pd/NGC	Pd/MWCNT	Pd/Graphite
		Cross-coupling[a]		
1	NMP/H_2O, 3h, 70°C	> 98%	69-92%	68-74%
2	EtOH/H_2O, 3h, 100°C	> 99%	> 99%	> 99%
		Hydrogenation[b]		
3	EtOH, 2h, 50°C	> 99%	35-85%	10-20%
4	EtOH, 4h, 70°C	> 99%	> 99%	> 99%

[a] Cross-coupling of phenylboronic acid with **1c**, **1d**, and **1i** [b] Hydrogenation of **5a** – **5c**. See Supporting Information.

The catalyst derived from nanoglobular carbon showed the highest activity and could be suggested as the catalyst of choice. However, for regular synthetic transformations Pd nanoparticles supported on MWCNT or even on graphite could also be used. Applying 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.

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

To summarize, direct deposition of Pd(0) from the solution of Pd_2dba_3 represents a convenient approach for preparation of recyclable Pd/C catalysts. Demanding Pd/C catalysts can be made in regular organic synthesis laboratories without usage 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. Specific morphology of nanoglobular carbon made it an excellent choice for preparation of Pd/C catalysts with maximized accessibility of catalytic 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 correct determination of the amount of Pd(0) centers available for deposition onto a carbon support. For commercially obtained samples, purity of Pd_2dba_3 should be evaluated by ^1H NMR.[7b] Fresh Pd_2dba_3 can also be synthesized as described previously.[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 into an oil bath at 80 °C under stirring. After dissolution of Pd_2dba_3 a dark red solution was formed, and stirring was carried out until the red color of the solution disappeared. The Pd/C catalyst was separated from the solution by filtration or centrifugation and was washed with sufficient amount of acetone (30 mL) to remove free dba, followed by drying under reduced pressure (10-2 mbar, 100 °C). Detailed step-by-step procedure is provided in the dedicated video movie (video is available in the Supporting Information).

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

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Keywords: Pd/C, catalyst preparation, cross-coupling, hydrogenation, catalyst recycling

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