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Activity of palladium on charcoal catalysts in cross-coupling reactions

Anna Komáromi, Fruzsina Szabó, Zoltán Novák *

Eötvös Loránd University, Institute of Chemistry, Pázmány Péter Stny. 1/a, Budapest, Hungary

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ABSTRACT

Comparison of the activity of several commercially available Pd/C catalysts in C–C, C–N, and C–S bond forming cross-coupling reactions has demonstrated the importance of the choice of the catalyst source. Investigations showed marked difference in activity between the catalysts. Moreover, the catalytic activity of each catalyst varies with respect to the coupling. The first Pd/C catalyzed Hiyama coupling is reported.

Palladium on charcoal,[1] is a widely used solid-supported catalyst for various cross-coupling reactions,[2] which is frequently used in synthetic chemistry. The charcoal as metal carrier is easily accessible from commercial sources, is inexpensive, and ensures a resistant, stable support with relatively high surface area. Filtration of this support from reaction mixtures is a simple and rapid process which is beneficial for industrial applications. Additionally, the transition metals deposited onto the surface of the charcoal can be easily recovered and recycled.

Although there are several examples of the use of Pd/C catalysts in Heck,[3] Suzuki[4] and Sonogashira[5] reactions, application of this catalyst in carbon-heteroatom bond forming reactions is scarce.[6] Moreover, there is no procedure for coupling silanes with aromatic halides.

In the case of solid-supported catalysis, the type, commercial source, and origin of the Pd/C catalyst is very important for a successful coupling. This issue, in most cases, is not examined, or mentioned in research reports. Obviously, besides the palladium content of the catalysts, the size of the palladium particles and their distribution on the surface also determine the catalytic activity of the transition metal. The type and the surface area of the charcoal support, and the conditions for the preparation of the catalyst could also be important issues. For a synthetic chemist, who generally follows a synthetic procedure for cross-coupling, the only given information is the wt % palladium content of the Pd/C catalyst.

In this context, we aimed to compare the catalytic activity of some commercially available 10 wt % Pd/C catalysts in four different types of cross-coupling reactions.

Additionally, to demonstrate the effect of the support we prepared two different Pd/C catalysts under the same conditions[7] using Norit A, and multi-walled carbon nanotubes (MWCNT) as the carbon support. Transition electron microscopy (TEM) images

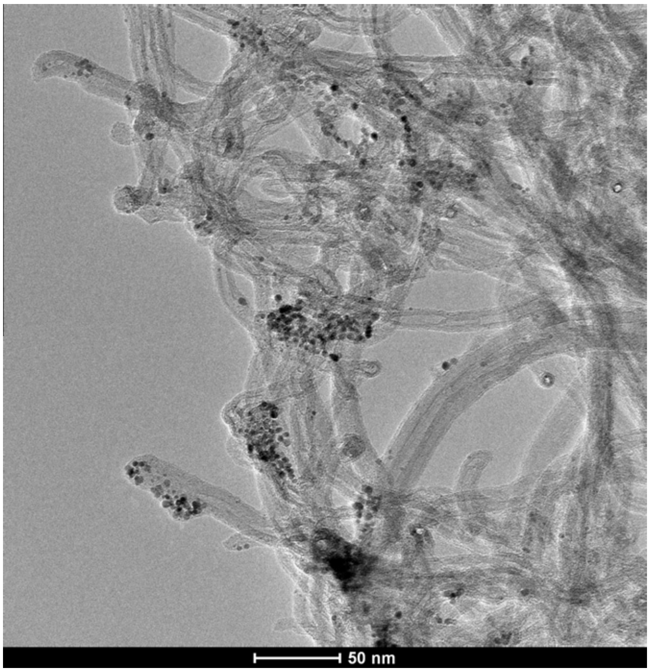

Figure 1. TEM image of Pd/MWCNT catalyst.

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* Corresponding author. Tel.: +36 1 372 2500x1610; fax: +36 1 372 2909.
E-mail address: novakz@elte.hu (Z. Novák).

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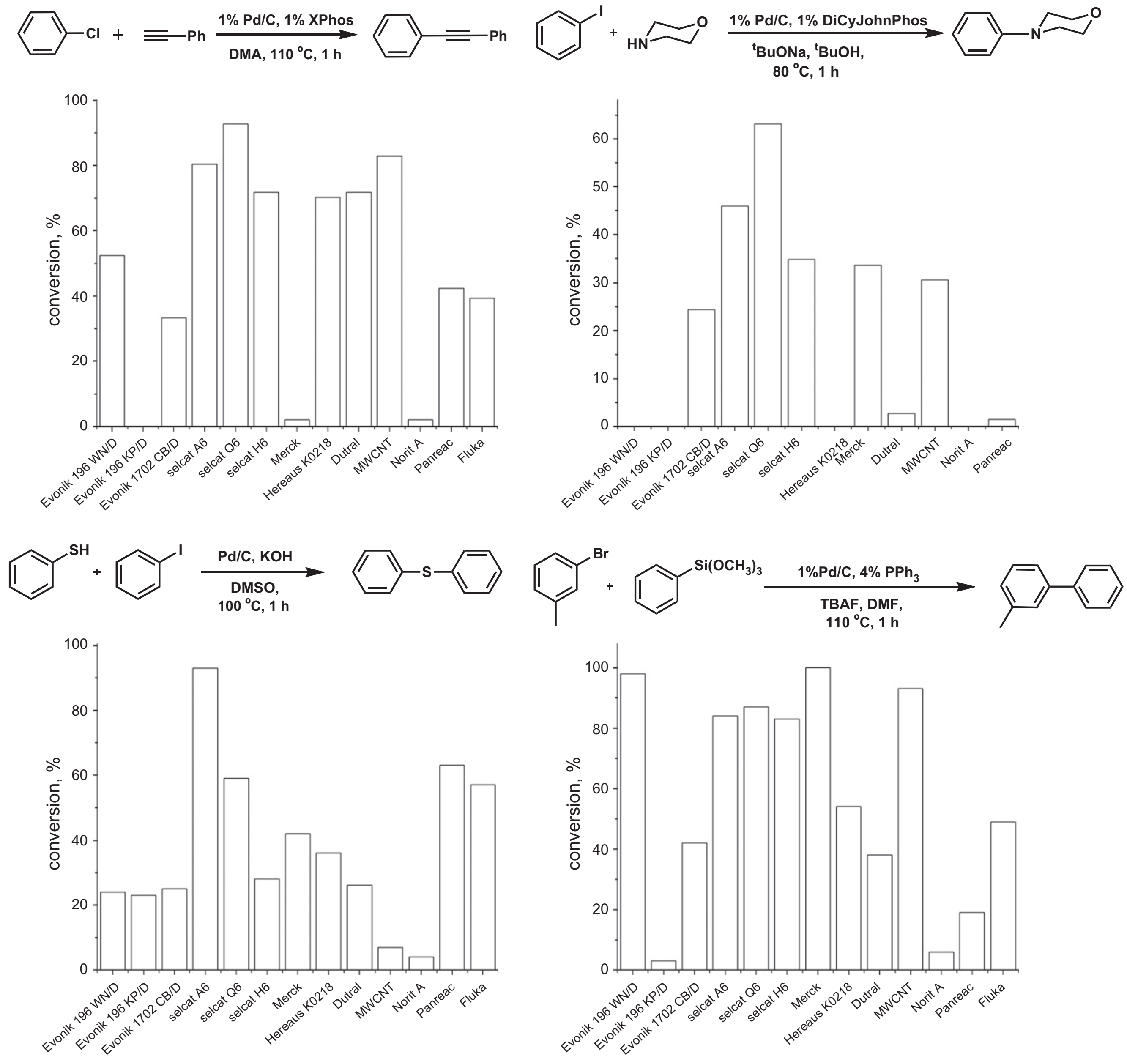


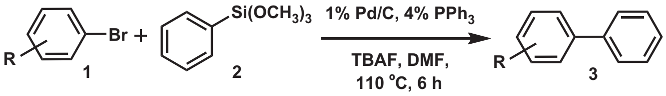
Figure 2. Graph A (top left): chlorobenzene (0.5 mmol), phenylacetylene (0.75 mmol), K_2CO_3 (0.75 mmol), DMA (0.25 mL), Pd/C (10 wt %, 1 mol %), and XPhos (1 mol %), at 110 °C under an Ar atmosphere. Graph B (top right): iodobenzene (0.5 mmol), morpholine (0.75 mmol), ^{t}BuONa (0.7 mmol), Pd/C (10 wt %, 1 mol %),and L = DiCyJohnPhos (1 mol %) in ^{t}BuOH (0.5 mL) at 80 °C under an Ar atmosphere. Samples were taken after 1 h. Graph C (bottom left): iodobenzene (0.5 mmol), thiophenol (0.55 mmol), KOH (0.75 mmol), Pd/C (10 wt %, 0.01 mmol, 2 mol %),and DMSO (0.5 mL) at 110 °C under an Ar atmosphere. Samples were taken after 1 h. Conversions were determined by GC from the average of four runs. Graph D (bottom right): 3-bromotoluene (0.5 mmol), phenyltrimethoxysilane (0.75 mmol), TBAF (0.75 mmol), Pd/C (10 wt %, 0.005 mmol, 1 mol %), PPh_3 (0.02 mmol, 4 mol %mol %), DMF (0.75 mL),and DMSO at 110 °C under an Ar atmosphere. Samples were taken after 1 h. Conversions were determined by GC from the average of four runs.

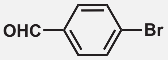
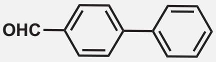
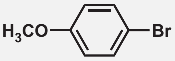
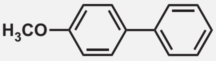
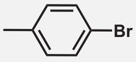
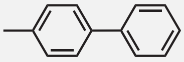
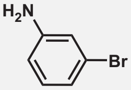
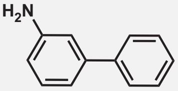
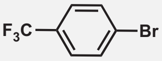
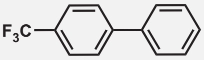
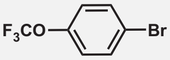
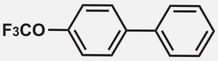
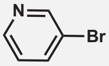
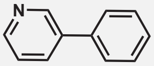
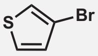
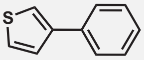
of the latter catalyst showed that the palladium catalyst deposited onto the carbon nanotubes consisted of 4–10 nm metal particles (Fig. 1).

In our earlier reports on the Pd/C-catalyzed Sonogashira coupling of aryl chlorides[8] and the Buchwald–Hartwig amination,[9] we found that the choice of the solid-supported catalyst was very important to achieve coupling efficiently. Comparison of these results showed that some catalysts had completely different activity in Sonogashira, and amination reactions (Fig. 2, graphs A and B). The Evonik 196 WN/D, Dutral and Panreac Pd/C catalysts showed no or low catalytic activity in the Buchwald–Hartwig coupling of iodobenzene and morpholine, but for the Sonogashira coupling of chlorobenzene with phenylacetylene these catalysts showed average catalytic activity compared to other palladium sources. Additionally to previous studies, we compared the catalytic activity of the Pd/MWCNT catalyst with Pd/C (Norit A) in Sonogashira and Buchwald–Hartwig reactions. We found marked differences in the activity of the catalysts in both coupling reactions. Palladium deposited onto the nanotube support gave almost full conversions, but Norit A did not show significant catalytic activity. This finding demonstrates the importance of the choice of carbon carrier.

For further investigations we chose the palladium-catalyzed thiolation[10] and the Hiyama coupling[2b] of aryl halides as additional examples. The C–S bond-forming reaction catalyzed by palladium on charcoal was demonstrated for the first time by Lin and co-workers,[6b] but there was no precedent for the solid-supported

Table 1
Hiyama coupling of aryl bromides in the presence of Pd/C Selcat Q6 catalyst.[a]



Entry	Aryl bromide	Product	Yield[b] (%)
1			68
2			64
3			76
4			72
5			59
6			48
7			76
8			45

[a] Aryl bromide (1 mmol), phenyltrimethoxysilane (1.5 mmol), TBAF (1.5 mmol), Pd/C Selcat Q6 (10 wt %) (0.01 mmol, 1 mol %), PPh_3 (0.04 mmol, 4 mol %), DMF (1.5 mL), 110 °C, 6 h.

[b] Isolated yield.

palladium-catalyzed coupling of silyl reagents and aryl halides. In our preliminary investigations, we have found that coupling iodobenzene and thiophenol in the presence of 2% Pd/C took place in 30 min at 110 °C under similar conditions to those applied by Lin and co-workers. As Lin's procedure required 9 h for completion of the reaction, we envisaged that the type of supported catalyst would be very important in this kind of cross-coupling. Next, we compared the catalytic activity of several Pd/C catalysts in the coupling of iodobenzene and thiophenol. The reactions were conducted in DMSO in the presence of 1.5 equiv KOH at 100 °C, and we used 2 mol % of palladium in each reaction. The results of these studies, summarized in Figure 2, graph C, show that there were significant differences in the catalytic activity of the solid-supported catalysts. After 60 min reaction time the conversions were in the range of 7–90%. The catalyst sold by Panreac proved to be the second most efficient catalyst after Selcat A6. However, this catalyst gave moderate activity in the Sonogashira coupling previously, and it was not significantly active in the amination. The Pd/C catalyst supplied by Merck (sold as the oxidized form of Pd) was also ineffective in the amination, but the thiolation took place with good efficiency in the presence of this catalyst.

To the best of our knowledge, among the cross-coupling reactions, the Hiyama coupling of silanes, and aryl halides has not yet been achieved with palladium on charcoal catalysts. Therefore, we developed conditions for this synthetic transformation. We found that in the presence of 1% Pd/C and 4% PPh_3 as a ligand, iodobenzene could be arylated with phenyltrimethoxysilane in DMF at 100 °C with the addition of tetrabutylammonium fluoride (TBAF) as an activator. The choice of DMF and TBAF was crucial for the reaction; other solvents and fluoride sources proved to be unsuitable for this coupling. The developed conditions were also applicable for the coupling of aryl bromides. However, coupling of aryl chlorides was unsuccessful, even with bulky phosphane ligands.[11]

Once we had appropriate reaction conditions for the coupling in hand we next examined the activity of different palladium on charcoal catalysts in the reaction of bromotoluene, and phenyltrimethoxysilane. Comparative studies showed that the Merck catalyst had superior activity in this reaction. In contrast, this catalyst was average in the thiolation and was completely ineffective in the Buchwald–Hartwig amination and Sonogashira couplings. This phenomenon was also observed in the case of Evonik 196WN/D. In the Hiyama reaction Pd on Norit A catalyst also showed poor reactivity, but Pd/MWCNT had excellent activity.[12]

Following these optimization and comparative studies, we synthesized several substituted biaryls using solid-supported palladium via the Hiyama reaction (Table 1). Aromatic bromides with electron-withdrawing and electron-releasing groups and hetaryl bromides were applicable for the Hiyama coupling under the developed conditions, and we were able to prepare the products in moderate to good yields (45–76%).

In conclusion, we have shown that the source and type of palladium on charcoal catalyst strongly determine the efficiency of cross-coupling reactions. Moreover, the catalytic activity of the various Pd/C catalysts was found to be different in cross-coupling reactions. These comparative studies provide important information for synthetic chemists for applications of solid-supported palladium catalysts in different cross-coupling reactions. On the basis of our studies the Selcat catalyst family proved to be the most reliable source of palladium for cross-coupling reactions. We have also demonstrated that the choice of the carbon support determines the activity of the catalyst. Our palladium on MWCNT catalyst showed enhanced activity in all the coupling reactions with the exception of the C–S bond forming reaction. Additionally, for the first time, we have developed conditions for the Pd/C-catalyzed Hiyama coupling of aryl halides and aryl silanes.

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Supplementary data

Supplementary data (procedures, optimization studies and characterization of the materials) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.170.

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