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Nanoparticle Catalysts

Palladium Nanoparticles Supported on Polyaniline Nanofibers as a Semi-Heterogeneous Catalyst in Water**

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Interest in catalysis by metal nanoparticles is increasing dramatically due to the advantages offered by these "semi-heterogeneous catalysts".[1] These advantages combine the characteristics of heterogeneous catalysis (recovery and recyclability) with those of homogeneous catalysis (relatively low catalyst loadings and good selectivity). In addition, because of their large surface area,[1] metal nanoparticles usually show enhanced reactivity under mild conditions. Metal nanoparticles are prepared generally from a metal salt, a reducing agent, and a stabilizer and can be supported on an oxide, charcoal, or a zeolite.[1] When polyaniline (PANI) is used as support, it also functions as reducing agent and stabilizer. These advantages translate into easy and reproducible syntheses that make metal nanoparticles supported by PANI[2,3] promising candidates for organic catalysis.

Palladium nanoparticles supported on polyaniline have been the subject of interest of several groups.[2,3] In general, these nanoparticles are prepared by adding a palladium(II) salt to an aqueous dispersion of PANI.[2] When interfacial polymerization is used for the synthesis of PANI, nanofibers are formed.[4] The high surface area and porosity of the PANI nanofibers serve as an ideal environment to make metal/polyaniline nanocomposites.[5,6] To take advantage of these characteristics, we used PANI nanofibers as a support for palladium nanoparticles. Our synthesis involved simply mixing palladium nitrate with PANI nanofibers. This method eliminated the need for a separate reduction step[3,7] or gamma irradiation,[8] while maintaining a nanofibrillar morphology.[9] Scanning and transmission electron microscopy (SEM and TEM) images showed that the palladium nanoparticles on nanofibrillar PANI had a roughly bimodal size distribution with non-single-crystal particles in the 50–100-nm regime and additional particles roughly 2 nm in diameter (Figure 1 B, C).

With the PANI nanofiber-supported palladium nanoparticles in hand we became interested in evaluating the activity of these nanoparticles as catalysts and concentrated our first attempts on Suzuki coupling. The Suzuki reaction is one of the most versatile methods for the formation of C−C bonds.[10–12] In general, methods for cross-coupling of aryl halides with hydrophilic functional groups are not well developed in organic solvents as a result of their insolubility. One solution is the use of polar solvents, such as water, for the reactions of aryl halides with hydrophilic substituents. Because the polyaniline nanofibers stabilize the palladium nanoparticles in water, it was our goal to determine their activity in this reaction medium. In addition, water is an attractive "green" solvent and very inexpensive.[13–16]

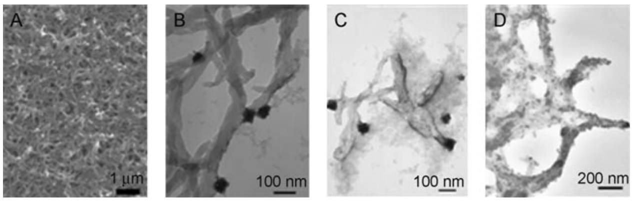

Figure 1. A) SEM image of PANI nanofibers prior to palladium growth. B) TEM image of catalyst after palladium growth. C) TEM image of reaction mixture halfway through reaction. D) TEM image of catalyst after two cycles.

Another limitation of Suzuki coupling is that more economical aryl chlorides are less reactive than aryl bromides and iodides, and protocols for such reactions conducted in water are few.[17–23] Furthermore, Suzuki coupling catalyzed by other palladium nanoparticles[24,25] generally does not work with aryl chlorides.[26] Consequently, we first tested the Suzuki coupling between *p*-chlorobenzoic acid and phenylboronic acid in water. The reaction proceeded in less than 4 h at 80 °C in air (Table 1, entry 1). Additionally, the products were separated by simple organic extraction and purified by crystallization. This is significant because we eliminated the need to employ an organic solvent as reaction medium and therefore could develop environmentally friendly processes.

We obtained high yields with aryl chlorides bearing a variety of substituents (Table 1). As expected,[26,27] carboxylic acids or phenols were high yielding (Table 1, entries 1 and 2), but so were substrates without hydrophilic substituents (Table 1, entries 3–6). These facile coupling reactions of substrates with hydrophobic groups stand in contrast to other Suzuki couplings in water. Since reactions conducted in any of the usual organic solvents did not give the expected products, we speculate that a combination of the hydrophobic effect of water[27,28] and an interaction with the polyaniline support is responsible for this favorable behavior.

Notably, we were able to use activated (Table 1, entries 1, 7, 8) and deactivated aryl chlorides (Table 1, entries 3, 4). This is significant, since deactivated aryl chlorides are known to be sluggish coupling partners.[29] The catalyst was insensitive to

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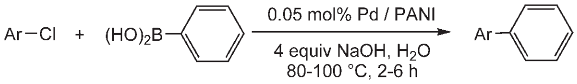
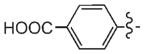
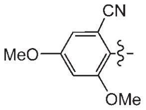
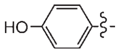
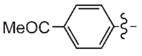
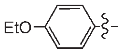
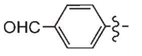
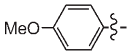
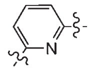
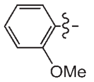
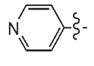
Table 1: Suzuki coupling of aryl chlorides and $PhB(OH)_2$.

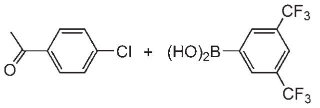
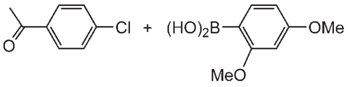
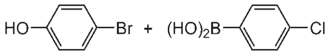
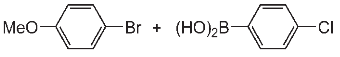
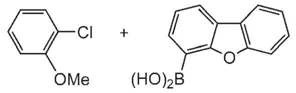


Entry	Substrate, Ar	Yield [%]	Entry	Substrate, Ar	Yield [%]
1		97	6		–[a]
2		88	7		91
3		92	8		99
4		92	9		96
5		92	10		89

[a] Mixture of products formed.

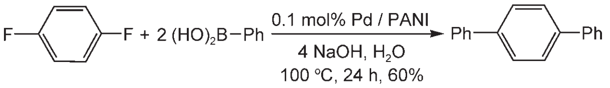
the presence of one *ortho* substituent (Table 1, entry 5), but it gave a mixture of products if both *ortho* positions were substituted (Table 1, entry 6). Since the coupling of 2-pyridyl halides is not as straightforward as coupling of most aryl halides,[30] we also looked at 2,6-dichloropyridine and found that a high conversion was obtained under similar conditions (Table 1, entry 9). Reactions with boronic acids other than $PhB(OH)_2$ also gave high yields (Table 2).

Table 2: Suzuki coupling of aryl chlorides and $ArB(OH)_2$.

Entry	Reaction[a]	Yield [%]
1		92
2		70
3		80
4		82
5		71[b]

[a] 1 mol% Pd/PANI, 4 equiv NaOH, H_2O, 100 °C, 6–8 h. [b] Before recrystallization, not optimized.

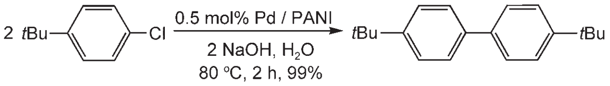
All these results point to an exceptionally active palladium catalyst, and we found that even 1,4-difluorobenzene [Eq. (1)] and 2-fluorobenzoic acid (see Supporting Information) could be used as well. In these cases, the reaction was considerably slower, requiring 24 h at 100 °C. Catalytic C–C cross-coupling reactions of fluoro derivatives are rare[31] because of the strong C–F bond. Such reactions usually employ elaborate ligands to increase the reactivity of the catalytic center.



(1)

We verified that the Pd/PANI nanocomposites are recyclable and can be used in low catalyst loadings, since these are two pronounced advantages of nanoparticle catalysts.[1] We obtained a yield of 89% after ten cycles (see Supporting Information), and a loading of 10^{-5} mol% Pd (see Supporting Information) can be used in the reaction between 4-acetylphenyl chloride and phenylboronic acid. More importantly, from a mechanistic point of view, it has been shown that in many couplings between aryl bromides or iodides and aryl boronic acids, concentrations as low as parts per billion of palladium suffice for product formation,[32] but this is not true for aryl chlorides. Analysis of the filtrate from two consecutive reactions shows that the amount of palladium lost in solution is on the order of parts per million. Although the filtrate led to product formation in about 40% yield, it could not be reused, and this points to the importance of PANI nanofibers in stabilizing the Pd nanoparticles. Even after heating at 80 °C for two cycles (4 h each), no large palladium agglomerates are seen (Figure 1 D). We did notice a decline in the quality of the nanofiber support along with a change in the distribution of nanoparticle sizes that might be responsible for the decrease in yield over extended recycling. We are currently investigating this phenomenon.

With respect to the reducing nature of the polymer support, we determined that the present Pd/PANI system effected the homocoupling of deactivated aryl chlorides [Eq. (2)]. Palladium-catalyzed homocoupling reactions offer a mild alternative to the classical Ullman coupling, usually conducted with copper catalysts under rather harsh conditions.[33] Although homocoupling reactions of deactivated aryl chlorides catalyzed by heterogeneous palladium have been reported to take place even in water with moderate yields,[34] the novelty of our system is that the polyaniline nanofibers also act as the reductant, a role usually played by an external reducing agent such as formate salts,[35] hydrogen gas,[36] or zinc.[37]

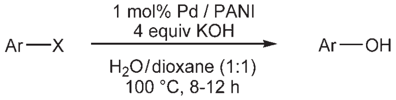


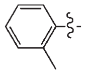
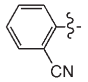
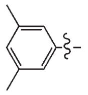
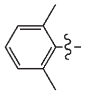
(2)

We tested the Pd/PANI system as catalyst for other reactions. Inspired by a recent report of Buchwald et al.,[38] we looked into phenol formation from aryl halides (Table 3) in water/dioxane. Aryl bromides (Table 3, entries 2–4) provided the corresponding phenols in high yields, and so did aryl chlorides (Table 3, entry 1).

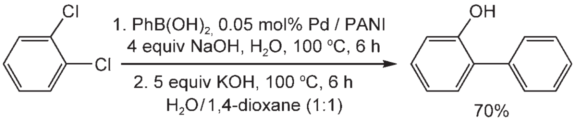
The similarity in conditions between Suzuki coupling and phenol formation suggested that the Pd/PANI system could be used as a tandem catalyst,[39] and this was indeed the case [Eq. (3)]. The synthesis of 2-phenylphenol was achieved by starting with the cross-coupling reaction between one of the

Table 3: Phenol formation from aryl halides.



Entry	X	Substrate, Ar	Yield [%]
1	Cl		81
2	Br		80
3	Br		90
4	Br		89

C—Cl bonds of 1,2-dichlorobenzene, followed by phenol formation on increasing the temperature and reaction time.



(3)

In conclusion, we have shown that palladium nanoparticles supported on polyaniline nanofibers are active catalysts for Suzuki coupling between aryl chlorides and phenylboronic acid and for phenol formation from aryl halides and potassium hydroxide in water and air. Applications of this catalyst system, with an emphasis on the scope of tandem reactions, are in development.

Experimental Section

All manipulations were carried out in air unless otherwise stated.

Synthesis of Pd nanoparticles supported by polyaniline nanofibers: Polyaniline/Pd composite was prepared by first synthesizing polyaniline nanofibers in a rapidly mixed reaction.[40] An aqueous solution of camphorsulfonic acid was used as reaction medium and ammonium peroxodisulfate as oxidant. Aniline was distilled immediately before use. The crude fibers were purified by centrifugation and washing with deionized water, NaOH, and then three more times with water. Palladium nanoparticles were grown by combining a 2 $\mathrm{g\,L^{-1}}$ aqueous nanofiber dispersion with a 10 mM solution of palladium(II) nitrate (4:1) and incubation for one day. The resulting solution was then dialyzed to remove any remaining palladium salt in fresh deionized water every 4 h for 2 d. ICP analysis of the filtrates after dialysis showed no palladium. Elemental analysis (wt%) found for dried samples of Pd/PANI: C 65.70, H 4.39, N 12.72, Pd 10.9; calcd: C 65.15, H 3.79, N 12.66, Pd 10.3. Most Pd/PANI suspensions have 2 mM Pd.

General protocol for Suzuki coupling: Aryl halide (1 equiv), phenylboronic acid (1.5 equiv), and base (4 equiv) were added to 20 mL of deionized water. The solution was stirred at 80–100 °C. Pd/PANI (0.05 mol%) was added to the stirred solution, and the reaction mixture stirred for 2–4 h or for the time indicated. After the reaction mixture had cooled to room temperature, the organic product was extracted with diethyl ether (3 × 75 mL). The organic fractions were washed with deionized water and then dried with $MgSO_4$. After filtration, volatile substances were removed under reduced pressure to yield the final product.

General procedure for synthesis of phenols from aryl halides:[38] A mixture of PANI/Pd (1 mol% Pd), KOH (5.0 equiv), and aryl halide (1.0 equiv) was stirred at 100 °C for the indicated time. The reaction mixture was cooled to room temperature, carefully acidified with dilute aqueous HCl until the pH reached ca. 1, and extracted with diethyl ether. The separated organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by crystallization. Yields depended on scale and the precision of workup.

Experimental details, NMR spectra of products, and details of catalyst-loading results and recycling experiments are available as Supporting Information.

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Keywords: C—C coupling · nanostructures · palladium · polymers · supported catalysts

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