

Article

Pd/DNA as Highly Active and Recyclable Catalyst of Suzuki–Miyaura Coupling

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Abstract: Pd/DNA catalysts were prepared in a mixed H₂O/EtOH solvent using palladium precursors, Pd(OAc)₂ and PdCl₂, in different dosages and salmon fish sperm DNA. As prepared, the Pd/DNA contained Pd(II) and Pd(0) nanoparticles of various sizes and morphologies, depending on the preparation method. Pd/DNA efficiently catalyzed the Suzuki–Miyaura cross-coupling of various aryl bromides with phenylboronic acids. The catalyst was recovered by simple phase separation and then reused in seven consecutive cycles with a high activity.

Keywords: palladium; nanoparticles; DNA; Suzuki–Miyaura; carbonylative coupling

1. Introduction

Many aryl compounds, such as acids, amides, ketones, or biaryls are products of palladium-catalyzed coupling reactions which offer efficient and simple procedures for their production [1–7]. Biaryls are used in the production of various pharmaceuticals, polymers, liquid crystals, and ligands. One of the most effective routes to biaryls is the Suzuki–Miyaura cross-coupling of arylboronic acids and aryl halides [8,9]. Ketones are common structural motifs of many natural products, e.g., pharmaceuticals and agrochemicals [10].

The importance of palladium based heterogeneous catalytic systems is growing because of their easy separation from the reaction mixture and their recycling potential. Until now, carbon, magnetic materials, silica, hydroxyapatite, zeolites, nanoparticles, metal organic frameworks (MOFs), organic polymer, clay minerals and bio-supports have been used for this purpose [11]. Among heterogeneous catalytic systems palladium nanoparticles (Pd NPs) have a special place. Pd NPs are used as catalysts in many kinds of reactions, for instance hydrogenation and cross-coupling [12–27].

Recently the peculiar structure of DNA as well as its non-toxicity have attracted the interest of researchers of catalysis and it has been used as a support for immobilization of Pd NPs [28–30]. But until now only one article has been published on testing DNA supported Pd NPs in Suzuki–Miyaura reaction. In this study low efficiency has been achieved with bromobenzene derivatives [31].

Our studies aimed at the synthesis of DNA-supported Pd NPs using different precursors and reaction conditions. We expected to receive active and recyclable catalysts for the Suzuki–Miyaura coupling and to find correlation between the catalyst structure and its activity.

2. Results and Discussion

2.1. Structure of Pd/DNA

Four Pd/DNA samples were prepared under different conditions. As a source of palladium, Pd(OAc)₂ (C1–C3) or PdCl₂ (C4) were used. The Pd/DNA samples, C1–C4, were characterized structurally using Fourier-transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Transmission electron microscopy (TEM).

Comparison of the Fourier-transform infrared spectroscopy (FT-IR) spectra of pure DNA with C2 Pd/DNA indicated some differences. Thus, symmetric and antisymmetric stretching peaks of PO₄³⁻ observed in pure DNA at 1064 and 1237 cm⁻¹ were weakened for Pd/DNA and shifted to 1055 and 1211 cm⁻¹. In addition, changes were observed in the 1605–1693 cm⁻¹ region, assigned to ν(C=C), ν(C=N), and ν(C=O), as well as the weakening of the ν(C=N) band at 1484 cm⁻¹. These FT-IR data indicated that Pd NPs interacted with the PO₂⁻ group of DNA and the nitrogen atom that belongs to the base pairs of DNA (see Figure S1).

It was expected that Pd/DNA contained Pd(II) bonded to functional groups of DNA and the XPS method was used in order to confirm oxidation state of palladium. However, the XPS analysis of Pd/DNA (C1,C2) showed Pd 3d spectra (Figure 1) characterized by the typical two spin-orbit components Pd (3d_{5/2}) and Pd (3d_{3/2}) separated by approximately 5.4 eV. Figure 1b,c shows a Pd 3d line deconvoluted into two doublets attributed to two different chemical species, Pd(0) and Pd(II). The first peak centered at 335.5 ± 0.1 eV (3d_{5/2}) corresponded to Pd(0) [12]. The second peak centered at 338.2 eV (3d_{5/2}) corresponded to Pd(II) with binding energy exactly the same as in the primary form of palladium in Pd(OAc)₂ (Figure 1a). The calculated content of Pd(0) present in the catalysts prepared at RT (C1) and at 80 °C (C2) was 20% and 45%, respectively.

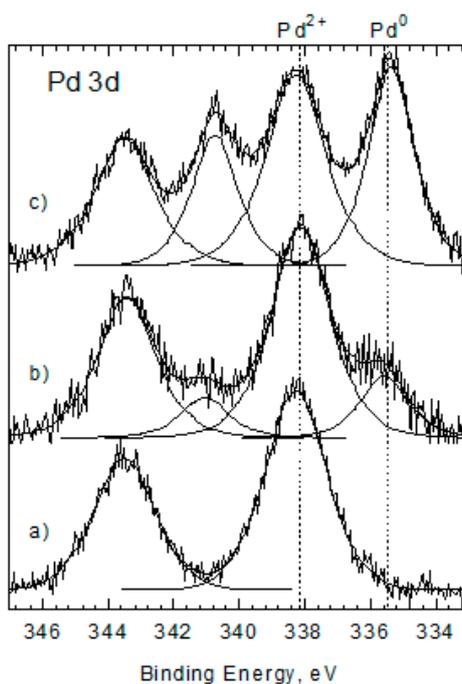


Figure 1. Pd 3d core level spectra for Pd(OAc)₂ as reference (a), Pd/DNA (C1) prepared at RT (b), and Pd/DNA (C2) prepared at 80 °C (c).

Figures 2 and 3 present N 1s and P 2p spectra of C1 and C2. The binding energies, BE 132.89 eV and BE 133.74 eV, were attributed to P 2p_{3/2} and P 2p_{1/2}, respectively. These values are characteristic of PO₄³⁻ of DNA. Similarly, the N 1s peak at 399.32 eV was assigned to N-C bond in DNA. In both cases, the N 1s and P 2p signals, small chemical changes of BE values relative to pure DNA were

observed after the introduction of Pd (Figures 2 and 3). The chemical shift of peaks increased with the increase in the Pd(0) content indicating the interaction of Pd NPs with the DNA surface. The observed shifts of Pd/DNA peaks to higher binding energy values were estimated for C1 and C2 and amounted to 0.3 and 0.5 eV for N 1s and to 0.2 and 0.4 eV for P 2p.

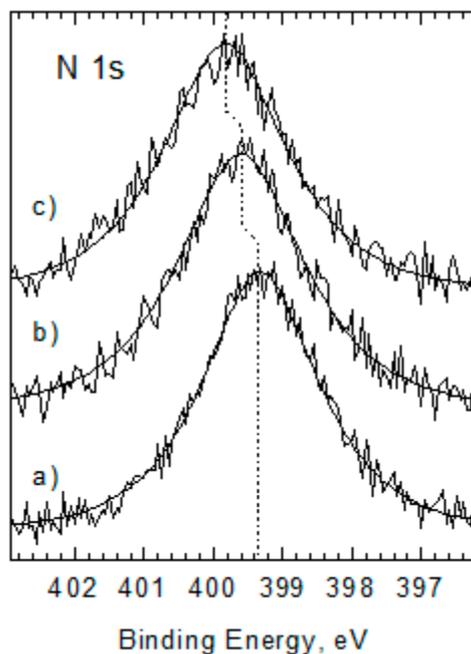


Figure 2. N 1s core level spectra for DNA surface (as reference) (a), Pd/DNA (C1) prepared at RT (b), and Pd/DNA (C2) prepared at 80 °C (c).

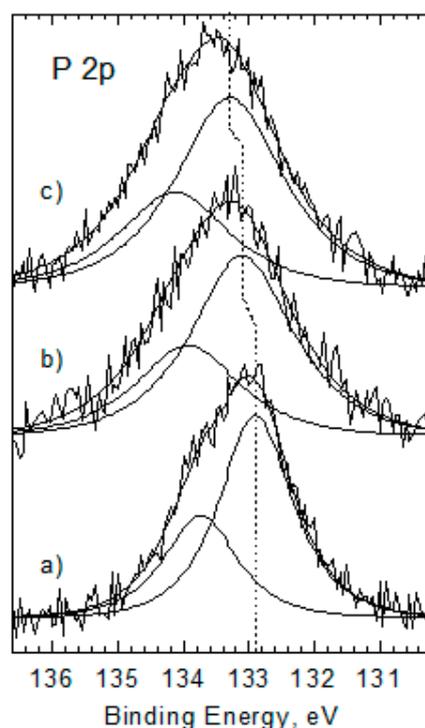


Figure 3. P 2p core level spectra for DNA surface (as reference) (a), Pd/DNA (C1) prepared at RT (b), and Pd/DNA (C2) prepared at 80 °C (c).

Figure 4 shows the Pd 3d spectra of C2 catalyst surface after Suzuki–Miyaura reaction. The optimal fit was obtained by assuming the presence of two palladium forms. The dominant component

with binding energy of 335.0 eV for Pd ($3d_{5/2}$) was assigned to Pd(0). The amount of Pd(0) was estimated as 76.6% (Figure 4). The remaining part of the Pd 3d spectrum was assigned to Pd(II) with peak at binding energy 337.8 eV. With deconvolution the Pd(0) peak asymmetry was taken into account [32]. The chemical shifts between Pd(0) and Pd(II) of 2.5–2.6 eV were very similar to those shown in Figure 1 between the reduced Pd(0) in C2 and Pd(II) in Pd(OAc)₂, what allows to formulate analogous conclusions. Slightly lower binding energies, 0.3–0.5 eV can be explained by the inaccuracy in estimating the reference energy C 1s, due to the possible different proportions of CC bonds in the straight and ring chains or larger Pd dispersion after the reaction.

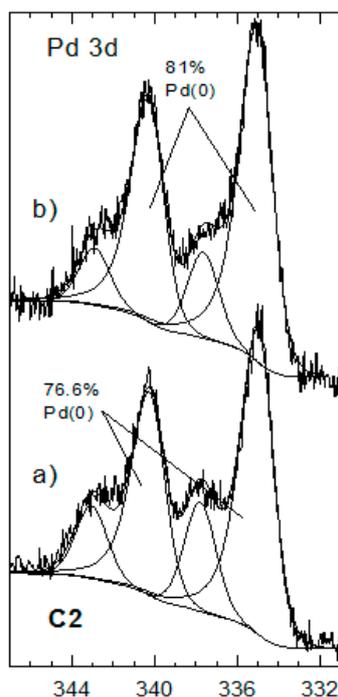


Figure 4. Pd 3d core level spectra for Pd/DNA (C2) recovered after the Suzuki–Miyaura reaction ‘as received’ form (a) and after smooth Ar⁺ sputtering (500 eV, 1 min, 0.2 $\mu\text{A}/\text{cm}^2$ + 1 keV, 1 min, 1.3 $\mu\text{A}/\text{cm}^2$) (b).

The procedure used for recovering the ‘powder’ catalyst for analytical purposes of XPS required long-term contact with air at elevated temperature, hence on the surface of the metallic palladium also PdO could be present in addition to carbon contaminations and its oxidized forms (CO, C=O). To solve this problem, the grain surfaces of the catalyst samples were cleaned with Ar + beam. To completely avoid the possible Pd(II) photoreduction, the second series Ar + sputtering was performed, with very mild etching: I—500 eV, 1 min, 0.2 $\mu\text{A}/\text{cm}^2$ and II—1 keV, 1 min, 1.3 $\mu\text{A}/\text{cm}^2$. It turned out that as a result, contribution of Pd(0) increased to 81%.

The performed X-ray photoelectron spectroscopy (XPS) studies evidenced increase of Pd(0) amount in catalyst C2 from ca. 45% at the beginning to ca. 81% in the end of catalytic reaction. Thus, Pd(II) was reduced in situ forming catalytically active Pd(0) as Pd(0) nanoparticles. Identification of Pd(0) nanoparticles was based on XRD and TEM analyses.

Typical XRD diffractogram of C2 reveal several well-defined peaks. These peaks are attributed to Pd(0) crystallizing in the Fm3m space group (JCPDS card number 5–681). Broadening of the diffraction lines indicated small size of Pd NPs (Figure 5). The XRD picture obtained for C2 catalyst recovered after the Suzuki–Miyaura reaction was very similar and indicated that the size of Pd NPs did not change (Figure 5).

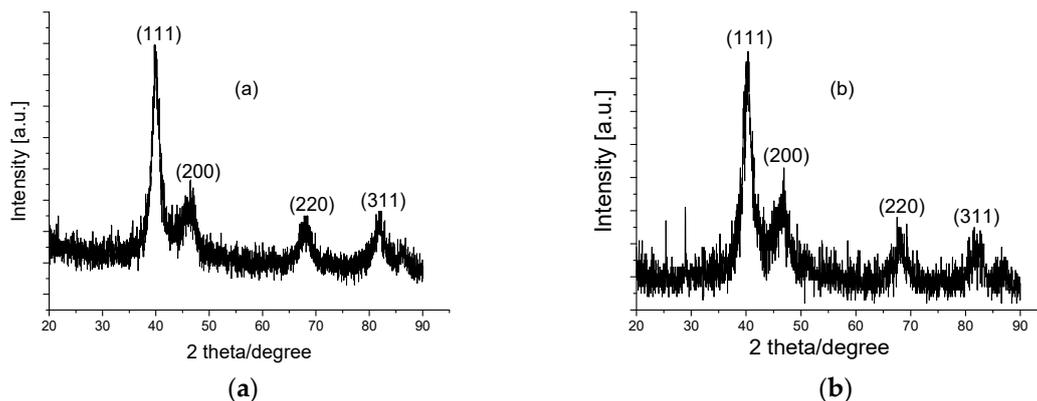


Figure 5. XRD patterns of C2 (a), and C2 recovered after the Suzuki–Miyaura reaction (b).

TEM studies were carried out to get deeper insight into characteristics of the Pd/DNA samples. First, the catalyst C1 obtained at room temperature was analyzed. A wide range of nanoparticle sizes (3–25 nm) was observed with a maximum of ca. 13–15 nm, together with some aggregates (Figure 6).

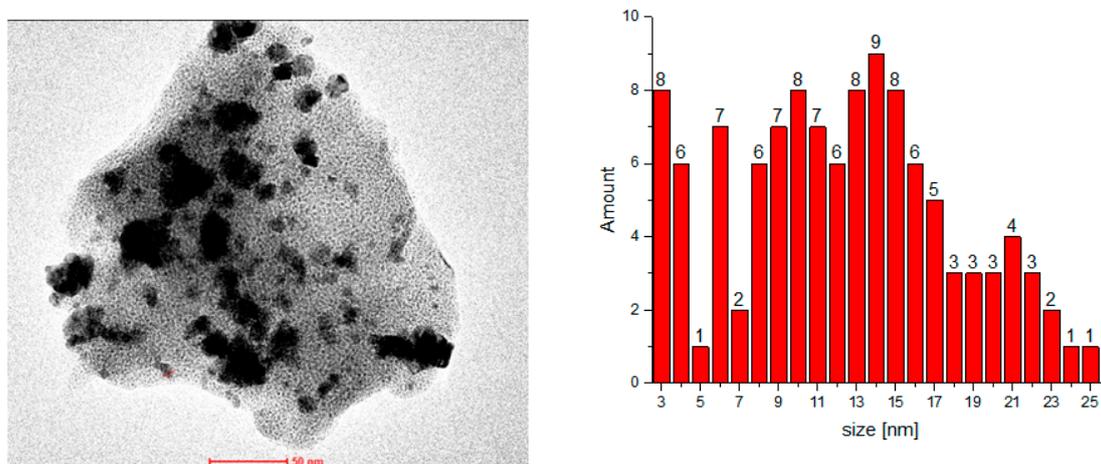


Figure 6. Morphology and size distribution of C1 Pd/DNA [33].

The second sample, C2, was prepared from DNA and Pd(OAc)₂ stirred within the H₂O/EtOH mixed solvent system for 2 h at 80 °C. As the temperature rose from room temperature to 80 °C, smaller nanoparticles were formed. In addition, some nanoparticles took a cylinder shape (Figure 7).

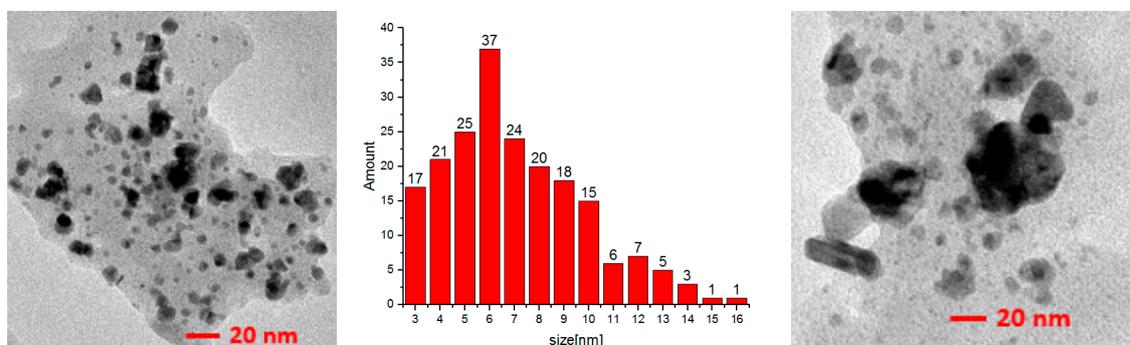


Figure 7. Morphology and size distribution of C2 Pd/DNA.

The next synthetic method was different from the previous one in only one respect. The amount of Pd(OAc)₂ used for the preparation of C3 Pd/DNA was reduced by half (to 56 mg). Interestingly,

this resulted in a decrease in the Pd NP size to 4–7 nm, and the size distribution became narrower (Figure 8).

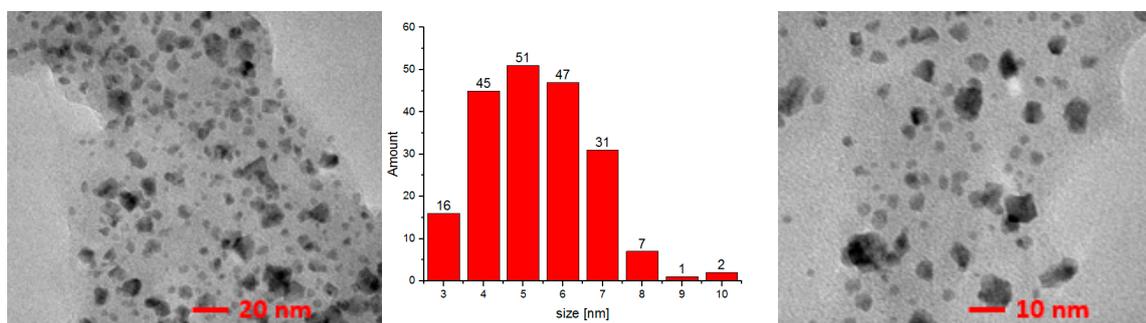


Figure 8. Morphology and size distribution of C3 Pd/DNA.

When PdCl₂ was used instead of Pd(OAc)₂ for the preparation of C4 Pd/DNA, nanoparticles of well-defined shapes were obtained. In Figure 9, nanoparticles prepared in this manner appear in triangular, cubic, and unidentified shapes. The size of most of the nanoparticles ranged between 9 and 12 nm (Figure 9).

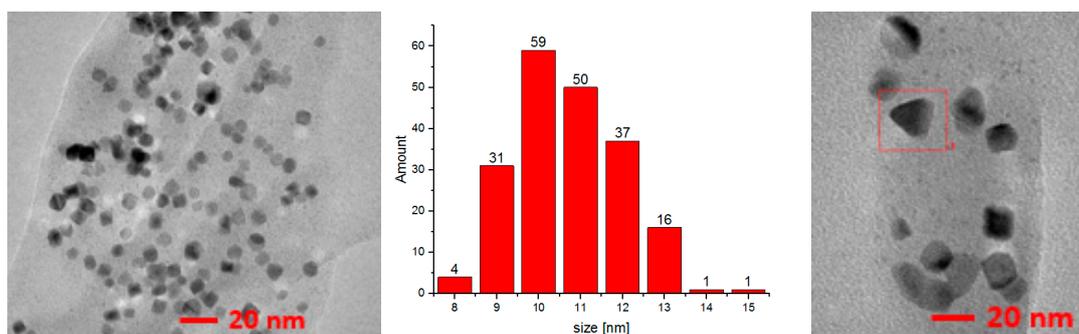


Figure 9. Morphology and size distribution of C4 Pd/DNA.

A TEM micrograph of C4 recovered after the Suzuki–Miyaura reaction showed some aggregates, but there were still plenty of well-dispersed nanoparticles. Interestingly, their shapes were identical to those before the reaction, for instance triangular (Figure 10).

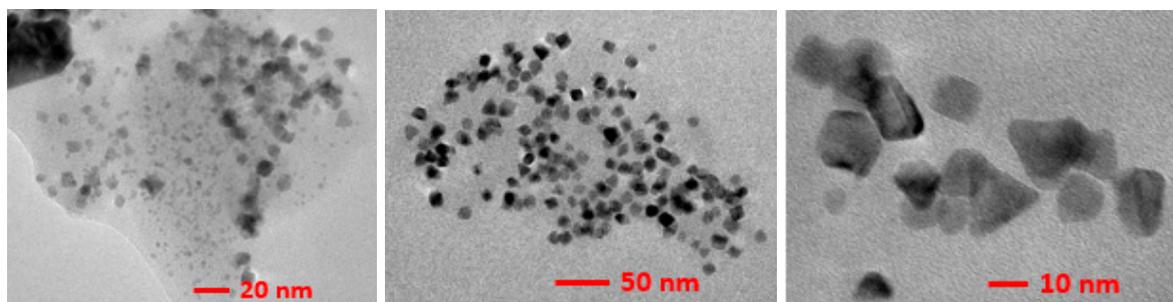
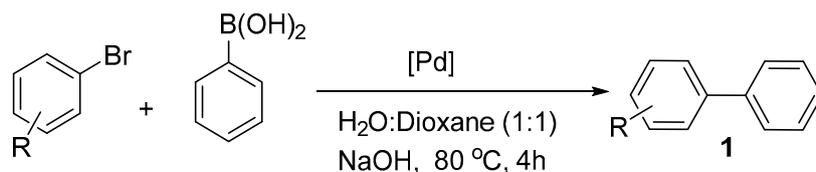


Figure 10. Morphology of C4 Pd/DNA recovered after the Suzuki–Miyaura reaction.

2.2. Suzuki–Miyaura Cross-Coupling Reaction

Under optimized conditions (Table S1), Pd/DNA catalysts C1–C4, were tested in the Suzuki–Miyaura reaction of three different aryl bromides with phenylboronic acid (Scheme 1, Table 1).



Scheme 1. Suzuki-Miyaura coupling of aryl bromides catalyzed by C1-C4.

Table 1. The Suzuki–Miyaura coupling of various aryl bromides and phenylboronic acid catalyzed by the catalysts C1–C4 ^a.

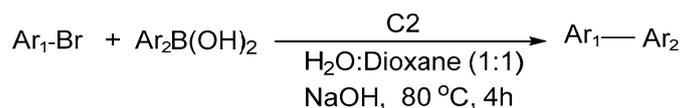
Entry	[Pd]	R	Yield 1 ^b (%)
1	Pd/DNA (C1)	2-OCH ₃	83
2	Pd/DNA (C2)	2-OCH ₃	77
3	Pd/DNA (C3)	2-OCH ₃	74
4	Pd/DNA (C4)	2-OCH ₃	64
5	Pd/DNA (C1)	2-Me	73
6 ^c	Pd/DNA (C1)	2-Me	58
7	Pd/DNA (C2)	2-Me	75
8	Pd/DNA (C3)	2-Me	64
9	Pd/DNA (C4)	2-Me	59
10	Pd/DNA (C1)	4-Me	85
11	Pd/DNA (C2)	4-Me	75
12	Pd/DNA (C3)	4-Me	70
13	Pd/DNA (C4)	4-Me	54

^a [Pd] (1 mol%), NaOH (1.2 mmol), dioxane/water (1:1) (5 mL), aryl halide (1 mmol), phenylboronic acid (1.2 mmol), 80 °C, 4 h. ^b Yields were determined by (GC) using dodecane as an internal standard. ^c 50 °C, 12 h.

Surprisingly, the catalyst C1, containing only 20% of Pd(0) as relatively big nanoparticles, gave the best conversion of 2-bromoanisole and 4-bromotoluene (Table 1, entries 1 and 10). In reaction of 2-bromotoluene, C1 and C2 gave similar results, 73 and 75%, respectively (Table 1, entries 5 and 7). Catalysts C2 and C3 which have similar morphologies, differ in activity and C3 gave lower conversion in all cases. However, the catalyst C4, which contained slightly bigger nanoparticles than C2 and C3, provided a conversion of 54–64% only (Table 1). Thus, catalytic activity cannot be directly correlated with nanoparticle size.

It can, therefore, be assumed that the most active catalyst was formed in situ from Pd(II) under catalytic reaction conditions. In our previous studies, we observed a similar phenomenon for Pd/Al₂O₃ [34] or Pd supported on glycidyl methacrylate polymer (GMA-CHDA) [35], which formed active Pd(0) from Pd(II) during the Suzuki reaction. The activity of these in situ formed Pd NPs was higher than that of pre-made ones [34,35]. The similar activity of C1 and C2 catalysts, containing different amounts of Pd(0) nanoparticles, indicated on the relatively fast reduction of Pd(II) to Pd(0) under catalytic conditions.

The substrate scope was next surveyed applying catalyst C2 (Scheme 2, Table 2).



Scheme 2. Substrate scope in the Suzuki-Miyaura coupling.

Table 2. Substrate scope in the Suzuki–Miyaura coupling catalyzed by C2 ^a.

Entry	Ar ₁	Ar ₂	Yield 1 ^b (%)
1	2-Cl-C ₆ H ₄	Ph	81
2	3-Cl-C ₆ H ₄	Ph	95
3	4-Cl-C ₆ H ₄	Ph	92 (91) ^c
4	4-NO ₂ -C ₆ H ₄	Ph	93
5	4-CHO-C ₆ H ₄	Ph	95 (90) ^c
6	2-CH ₃ O-C ₆ H ₄	Ph	77
7	4-CH ₃ O-C ₆ H ₄	Ph	64
8	2-CH ₃ -C ₆ H ₄	Ph	79
9	4-CH ₃ -C ₆ H ₄	Ph	73
10	2-CN-C ₆ H ₄	Ph	85 (70) ^c
11	4-CN-C ₆ H ₄	Ph	84
12	4-COCH ₃ -C ₆ H ₄	Ph	95
13	Ph	Ph	94 (89) ^c
14	2-CH ₃ -C ₆ H ₄	4-CH ₃ -1-naph	64 (52) ^c
15	2-CH ₃ -C ₆ H ₄	1-naph	72
16	Ph	3-BnO-C ₆ H ₄	80
17	Ph	3-CF ₃ -C ₆ H ₄	83
18	Ph	4-COCH ₃ -C ₆ H ₄	87 (80) ^c
19	Ph	1-naph	87
20	Ph	4-CH ₃ -1-naph	84
21	Ph	(CH ₃) ₃ C-C ₆ H ₄	89
22	1,3-dimethyl-C ₆ H ₃	Ph	33 (15) ^d
23	Ph	1,3-dimethyl-C ₆ H ₃	trace (trace) ^d (14) ^e
24	Ph	1,3-dimethoxy-C ₆ H ₃	0
25	3-Py	Ph	42
26	pyrimidine	Ph	62

^a [Pd] (1 mol%), NaOH (1.2 mmol), dioxane/water (1:1) (5 mL), aryl halide (1 mmol), arylboronic acid (1.2 mmol), 80 °C, 4 h. ^b Yields were determined by (GC) using dodecane as an internal standard. ^c Isolated yield. ^d C1 was used instead of C2. ^e 100 °C, 4 h.

For this purpose, reactions were first carried out between phenylboronic acid and bromobenzene derivatives. Meta-, para-, and ortho-chloro-bromobenzenes were tested as substrates (Table 2, entries 1, 2 and 3). As for the activities depending on the position of substituents the highest yield was obtained with *m*-chloro-bromobenzene (Table 2, entry 2). While good yield was obtained with *p*-chloro-bromobenzene the yield was lower with *o*-chloro-bromobenzene (Table 2, entries 1 and 3). Under these conditions only the C–Br bond was activated, while C–Cl remained unchanged. The high yield was noted when an electron-withdrawing substituent was present at the *para* position of bromobenzene (Table 2, entries 4, 5, 11 and 12). Other substituents promoted lower yield, up to 79%. Among the reactions conducted with phenylboronic acid derivatives, the best conversion was obtained with phenylboronic acid (Table 2, entry 13). When electron-withdrawing and electron-donating groups were present at the *para* position of phenylboronic acid, yields were close to one another (Table 2, entries 18 and 21) and increased to 80–89%. As expected, in reactions conducted with bulky bromobenzene and aryl boronic acid derivatives, lower yields of products were obtained (Table 2, entries 22, 23 and 24). While in reaction conducted with 3-bromopyridine low yield of product was obtained, the yield was modest with 5-bromopyrimidine (Table 2, entries 25 and 26).

2.3. Catalyst Recycling in Suzuki–Miyaura Reaction

Recyclability is one of the desired properties of supported catalysts [36]. The recycling potential of Pd/DNA was therefore investigated. For this purpose, a reaction was implemented between 4-bromobenzaldehyde and phenylboronic acid with 1 mol% and 0.5 mol% of Pd. At the end of the catalytic reaction, the organic products were separated by extraction, and the catalyst was recovered for the next run by simple phase separation. After the first run, the palladium content in the reaction

solution was determined as 0.152 ppm. Such a low amount of palladium evidenced its negligible leaching from the DNA support. In our study, Pd/DNA was recycled for seven consecutive runs with 1 mol% of Pd (Figure 11) and five consecutive runs with 0.5 mol% of Pd (Figure 11). Although some conversion decrease was observed during recycling, the stability of Pd/DNA, at least in five runs, was quite satisfactory.

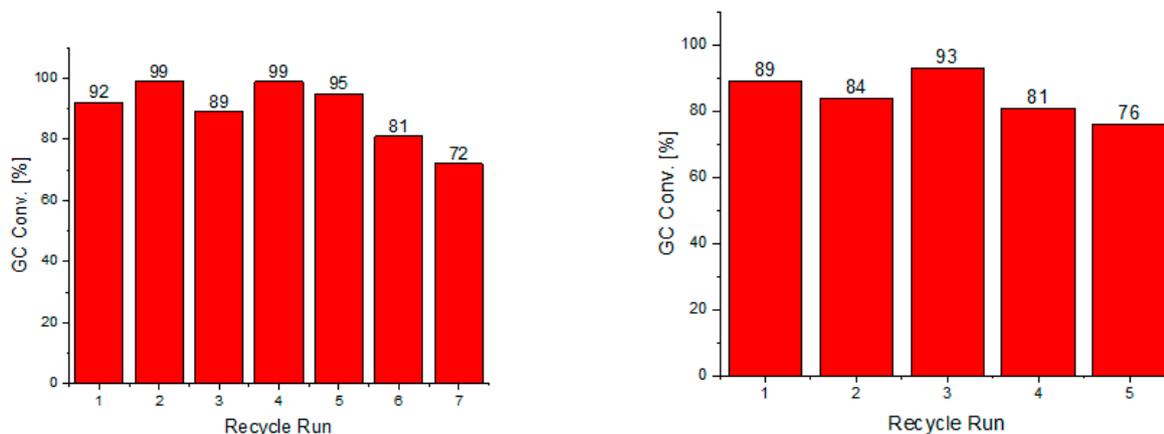


Figure 11. Recycling of C2; (left) 1 mol% of Pd, (right) 0.5 mol% of Pd.

The TEM analysis of the catalyst C2 recovered at the end of the recycling experiment showed some increase in the average diameter of Pd NPs, with the maximum at ca. 9–10 nm, but without significant agglomeration (Figure 12).

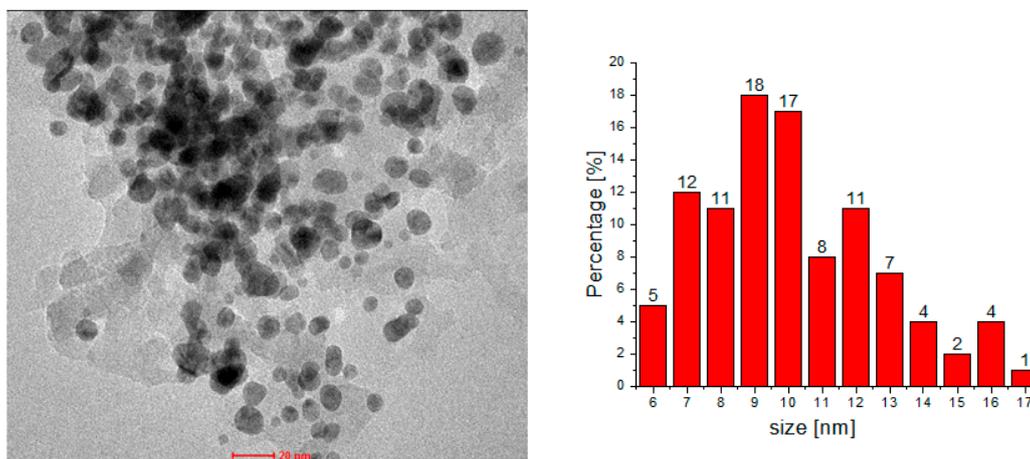


Figure 12. TEM images of C2 after seven catalytic runs and particle size distribution [33].

The activity of the solution remaining after the separation of Pd/DNA from the reaction mixture was also studied. Thus, the Suzuki–Miyaura reaction of 2-bromotoluene with phenylboronic acid catalyzed by Pd/DNA was stopped after 30 min, and the reaction solution was subjected to hot filtration through Celite. The as-obtained filtrate was next re-heated for 3.5 h at 80 °C. After that time the GC analysis showed 40% conversion of 2-bromotoluene, which was comparable to that obtained after 30 min of the standard reaction (32%, Figure 13) and significantly lower than that noted after 4 h (75%, Figure 13). This result indicated a heterogeneous reaction pathway, in agreement with the good recyclability of Pd/DNA and the insignificant level of palladium leaching.

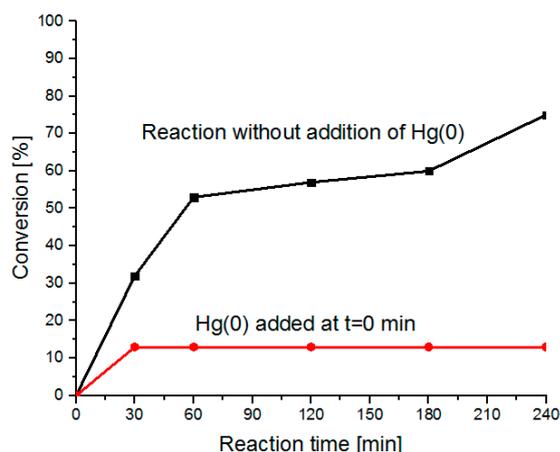


Figure 13. Suzuki–Miyaura reaction of 2-bromotoluene in the presence of Hg(0).

2.4. Treatment of C2 with Hg(0)

The above-reported results made it possible to propose a heterogeneous reaction pathway with the performance of the catalytic reaction on the surface of Pd NPs supported on DNA. In order to confirm this assumption, the catalytic reaction was performed in the presence of an Hg(0) inhibitor which can amalgamate Pd NPs, blocking their activity [37–39]. When Hg(0) was added to the catalytic system together with the substrates, the conversion of 2-bromotoluene was 13% (Table 3, entry 2). When Hg(0) was added 30 min later, the conversion was 53% (Table 3, entry 3). Thus, the presence of Hg(0) resulted in decrease of the reaction yield.

Table 3. Suzuki–Miyaura reaction of 2-bromotoluene with phenylboronic acid catalyzed by Pd/DNA (C2) in the presence of Hg(0) ^a.

Entry	Poison Additive	GC Conv. [%]
1	None	75
2	Hg added at the beginning of the reaction	13
3	Hg added after 30 min	53

^a [Pd] (1 mol%), NaOH (1.2 mmol), dioxane/water (1:1) (5 mL), 2-bromotoluene (1 mmol), phenylboronic acid (1.2 mmol), 80 °C, 4 h, [Hg]/[Pd] = 500.

The SEM image of the catalyst C2 treated with Hg(0) is presented in Figure 14 together with EDX analyses performed at four points to estimate the Pd/Hg ratios. Importantly, both elements were found in the same places and the Hg/Pd ratios calculated from the weight % varied from 1.14 to 0.44. At three points, the amount of Hg was found higher than the amount of Pd (Figure 14). Presumably, a Pd–Hg amalgam (alloy) was formed during the catalytic reaction on the surface of DNA. That is why the catalytic activity of the catalyst decreased remarkably when Hg(0) was present. The similar effect was also observed for the catalyst Pd/Al₂O₃ [40].

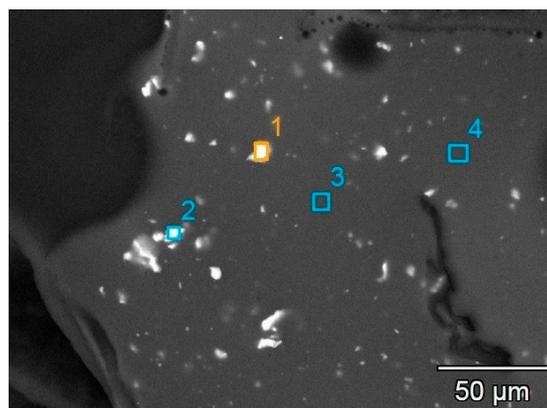
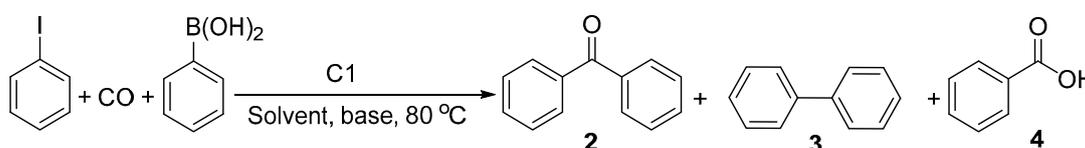


Figure 14. SEM image of C2 Pd/DNA after the Suzuki–Miyaura reaction with Hg(0). Pd/Hg: 1—1.14; 2—0.91; 3—0.87; 4—0.44.

2.5. Carbonylative Couplings

Interesting results with Pd/DNA obtained in the Suzuki–Miyaura reaction encouraged us to test its catalytic activity for the first time in carbonylative coupling.

The carbonylative Suzuki coupling was studied using the catalyst C1. For this purpose, the coupling of iodobenzene (PhI) and phenylboronic acid (PhB(OH)₂) carried out under CO atmosphere was selected as a model reaction (Scheme 3, Table 4). Regardless of all attempts to optimize the conditions, only a limited amount of benzophenone, max. 35%, could be produced in this system (also see Table S3).



Scheme 3. Carbonylative Suzuki coupling.

Table 4. Carbonylative Suzuki coupling catalyzed by C1: solvent, base and CO pressure testing ^a.

Entry	Solvent	Base	Conv. ^b (%)	Yield 2 ^b	Yield 3 ^b	Yield 4 ^b
1	H ₂ O	NEt ₃	88	25	41	22
2	IPA/H ₂ O (1/1)	NaHCO ₃	100	34	38	28
3	Dioxane/H ₂ O (1/1)	NaHCO ₃	100	26	55	19
4 ^c	Dioxane/H ₂ O (1/1)	NaHCO ₃	24	0	0	24
5	Dioxane/H ₂ O (4/1)	K ₃ PO ₄	80	29	20	31
6	Anisole	K ₂ CO ₃	0	0	0	0
7 ^d	Anisole	K ₂ CO ₃	0	0	0	0
8 ^d	Anisole/H ₂ O (9/1)	K ₂ CO ₃	66	35	31	0

^a [Pd] (1 mol%), base (1.2 mmol), solvent (5 mL), iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), 80 °C, CO (balloon pressure), 4 h. ^b Conversion and yield were determined by (GC) using mesitylene as an internal standard.

^c 5 bar, 80 °C, 4 h. ^d 100 °C, K₂CO₃ (3 mmol), phenylboronic acid (2 mmol).

However, another carbonylation product, benzoic acid (4), was formed under these conditions in amount up to 31%. Interestingly, isopropyl benzoate was not obtained in reaction performed in IPA/H₂O (Table 4, entry 2). It was different than in the previously studied system which produced preferably ester but not acid under CO atmosphere [41]. Moreover, an increase of CO pressure even increased selectivity to benzoic acid, most probably due to the additional influence of the DNA. Also, the choice of solvent greatly affected the yield of carbonylative Suzuki coupling. In reactions carried out in pure organic solvents no conversion was obtained (Table 4, entries 6 and 7, also see Table S3). This can be explained by poor solubility of Pd/DNA in organic solvents. In Suzuki carbonylation

conducted with bromobenzene no conversion was obtained. In reactions carried out without phenyl boronic acid, with iodobenzene benzoic acid was obtained but bromobenzene was not converted [33].

3. Experimental

All chemicals were purchased commercially and used without further purification. Fish sperm DNA (CAS:438545-06-3) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

3.1. Preparation of Pd/DNA (C1, C2, C3, C4)

In order to prepare Pd/DNA, four different methods were applied. While in methods 1–3 Pd(OAc)₂ was used as the source of palladium, in method 4 PdCl₂ was used. Ambient temperature was used in method 1 and 80 °C in methods 2–4.

Method 1 (C1) [33]: 50 mg of fish sperm DNA was dissolved in 5 mL of water. Then, 112 mg of Pd(OAc)₂ and 5 mL of ethanol were added in turn. The combined solution was stirred for 24 h at room temperature. During the reaction, the mixture changed in color from brown to black. Then with the aid of centrifugation at 7000 r/min, Pd/DNA was precipitated. The clear solution was poured out, and Pd/DNA was washed with acetone and dried in vacuo. Pd/DNA (C1) was obtained as a dark powder. (Pd target loading: 3.56 mmol/g).

Method 2 (C2): 50 mg of fish sperm DNA was dissolved in 5 mL of water. Then, 112 mg of Pd(OAc)₂ and 5 mL of ethanol were added in turn. The combined solution was stirred for 2 h at 80 °C. During heating, the mixture changed in color from brown to black. Finally, after cooling down to ambient temperature, Pd/DNA was precipitated. Then, by direct decantation, the clear solution was poured out, and Pd/DNA was washed with acetone and dried in vacuo. Pd/DNA (C2) was obtained as a dark powder. (Pd target loading: 3.61 mmol/g).

Method 3 (C3): 50 mg of fish sperm DNA was dissolved in 5 mL of water. Then, 56 mg of Pd(OAc)₂ and 5 mL of ethanol were added in turn. The combined solution was stirred for 2 h at 80 °C. During heating, the mixture changed in color from brown to black. Finally, after cooling down to ambient temperature, Pd/DNA was precipitated. Then, by direct decantation, the clear solution was poured out, and Pd/DNA was washed with acetone and dried in vacuo. Pd/DNA (C3) was obtained as a dark powder. (Pd target loading: 2.98 mmol/g).

Method 4 (C4): 50 mg of fish sperm DNA was dissolved in 5 mL of water. Then, 88 mg of PdCl₂ and 5 mL of ethanol were added in turn. The combined solution was stirred for 2 h at 80 °C. During heating, the mixture changed in color from dark red to black. Finally, after cooling down to ambient temperature, Pd/DNA was precipitated. Then, by direct decantation, the clear solution was poured out, and Pd/DNA was washed with acetone and dried in vacuo. Pd/DNA (C4) was obtained as a dark powder. (Pd target loading: 3.52 mmol/g).

3.2. General Procedure for the Suzuki–Miyaura Reaction

In a typical reaction, a 50 mL Schlenk flask was charged with aryl halide (1 mmol), aryl boronic acid (1.2 mmol), base (1.2 mmol), and the Pd/DNA catalyst (containing 0.01 mmol of Pd). Then, 5 mL of the solvent was added. The resulting mixture was stirred for 2–4 h at 80 °C. After that time, the Schlenk flask was cooled down, and the organic products were extracted with 3 × 7 mL of diethyl ether. The extracts were GC-FID analyzed with dodecane (0.076 mL) as an internal standard. The products of the reaction were determined by Gas chromatography-mass spectrometry (GC-MS).

3.3. General Procedure for the Carbonylative Suzuki Coupling Reaction

In a typical reaction, a 50 mL Schlenk flask was charged with iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), base (1.2 mmol), and the Pd/DNA catalyst (containing 0.01 mmol of Pd). Then, 5 mL of the solvent was added. Under the balloon pressure of CO, the resulting mixture was stirred for 4 h at 80 °C. After that time, the Schlenk flask was cooled down, and the organic products were extracted with 3 × 7 mL of diethyl ether. The extracts were Gas chromatography-flame ionization

detector (GC-FID) analyzed with mesitylene (0.076 mL) as an internal standard. The products of the reaction were determined by GC-MS.

3.4. General Procedure for Pd/DNA Recycling

After the first run, the Schlenk flask was cooled down and the organic products were extracted with 3×7 mL of diethyl ether. Then by the aid of centrifugation at 7000 r/min the catalyst was precipitated. The clear solution was then poured out by direct decantation, and the catalyst was washed with acetone and dried in vacuo. The dried catalyst was used for the next run in order to test its recyclability. Pd/DNA could also be recovered for recycling by simple decantation while filtration was not successful for this catalyst.

4. Conclusions

DNA-supported palladium catalysts were prepared using cheap natural DNA at mild conditions in an EtOH/H₂O solution. Pd/DNA catalysts contained Pd(II) and up to 45% of Pd(0) nanoparticles. EtOH was considered as the main reducing agent in the syntheses of Pd/DNA, in particular at 80 °C. However some contribution of DNA in reduction of Pd(II) to Pd(0) can not be excluded at ambient temperature. This effect will be further studied.

An effect of the palladium precursor and its dosage on the morphology of Pd/DNA was observed. For instance, the catalyst C4, prepared from PdCl₂, contained the biggest nanoparticles and showed the lowest activity in the Suzuki–Miyaura reaction. The Pd/DNA catalysts prepared from Pd(OAc)₂ exhibited various activities; however, the best result was noted for Pd/DNA containing mainly Pd(II) and therefore it can be proposed that the most catalytically active Pd(0) was formed under the catalytic reaction conditions.

The Pd/DNA catalyst showed good stability. It was recycled seven times in the Suzuki–Miyaura reaction with satisfactory results.

Pd/DNA showed ability to activate CO with the tendency to form benzoic acid under carbonylative Suzuki conditions. It is a characteristic feature of Pd/DNA, most probably influenced by the DNA biopolymer. As a consequence, only a limited amount of benzophenone, up to 35%, could be produced in this system.

Our research revealed that DNA interacts with palladium complexes and small molecules [42,43] and Pd/DNA is a promising catalyst for coupling reactions.

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