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PALLADIUM-POLYMER NANOCOMPOSITE: AN EFFICIENT CATALYST FOR GREEN SUZUKI-MIYAURA CROSS-COUPLING AND MOTT-SCHOTTKY NITROBENZENE REDUCTION PROCESSES

Abstract. A new catalyst for green Suzuki–Miyaura cross-coupling and Mott-Schottky nitrobenzene reduction processes was prepared by thermolysis of palladium (II) poly-5-vinyltetrazolate. Heterogeneous catalyst includes Pd-nanoparticles supported on polymeric matrix. It presents recoverable and recyclable catalyst and the catalyzed reactions proceed in aqueous media at room temperature in aerobic conditions.

Keywords: palladium(II) poly-5-vinyltetrazolate; palladium nanoparticles; Suzuki–Miyaura cross-coupling; Mott-Schottky nitroarene reduction; 1,1'-biphenyl

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ПАЛЛАДИЙ-ПОЛИМЕРНЫЙ НАНОКОМПОЗИТ: ЭФФЕКТИВНЫЙ КАТАЛИЗАТОР ЗЕЛЕННЫХ ПРОЦЕССОВ КРОСС-СОЧЕТАНИЯ ПО СУЗУКИ-МИЯУРЕ И ВОССТАНОВЛЕНИЯ НИТРОБЕНЗОЛА ПО МОТТ-ШОТКИ

Аннотация. Посредством термолиза поли-5-винилтетразолата палладия(II) был получен новый катализатор для зеленых процессов кросс-сочетания Сузуки–Мияуры и восстановления нитробензола по Мотт–Шотки. Гетерогенный катализатор содержит наночастицы Pd, стабилизированные полимерной матрицей. Данный катализатор является легко восстанавливаемым и пригодным для повторного использования, а также катализирует реакции, проводимые в водной среде при комнатной температуре в аэробных условиях.

Ключевые слова: поли-5-винилтетразолат палладия(II), наночастицы палладия, кросс-сочетание Сузуки–Мияуры, восстановление нитробензола по Мотт–Шотки, 1,1'-бифенил

Для цитирования. Палладий-полимерный наноккомпозит: эффективный катализатор зеленых процессов кросс-сочетания по Сузуки–Мияуре и восстановления нитробензола по Мотт–Шотки / А. В. Зураев [и др.] // Вес. Нац. акад. навук Беларусі. Сер. хім. навук. – 2019. – Т. 55, № 2. – С. 196–204. <https://doi.org/10.29235/1561-8331-2019-55-2-196-204>

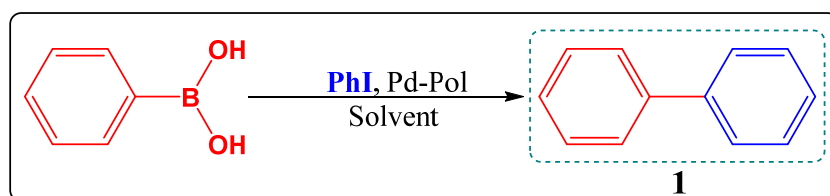
Introduction. Nanostructured materials have been burgeoning in recent years due to their application in such areas as sensory systems, electronics, catalysis, environmental and biological applications [1–4]. Among such materials, palladium nanoparticles have been attracting huge attention owing to their unique catalytic properties. It is a well-known fact that palladium nanoparticles are excellent catalysts in various reactions, in particular in Suzuki–Miyaura C–C coupling, and nitroarene to aminoarene Mott-Schottky reduction [5–8].

Usually, nanoparticles can be prepared through various chemical and physical techniques. When nanoparticles are synthesized in solutions, they aggregate together due to Van der Waals forces. Therefore, in such cases, it is necessary to introduce suitable stabilizers to prevent the agglomeration of nanoparticles. Nowadays, the immobilization of palladium nanoparticles onto supports to produce heterogeneous and reusable catalysts has attracted much attention [9]. Different inorganic, organic, and hybrid porous

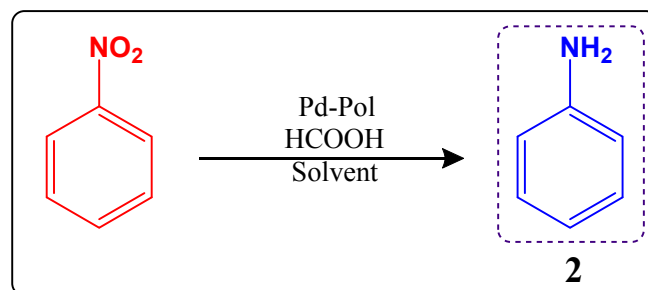
systems such as polymers [10], zeolites [11], and metalloorganic frameworks (MOFs) [12] have been applied for supported palladium catalysts. Such heterogeneous catalysts are highly efficient, but sometimes the reagents for synthesis of nanoparticles and supported materials are expensive, and the synthesis of the catalysts can be quite time-consuming. Therefore, the search for alternative catalysts, being less expensive and more conveniently produced, remains relevant for many catalyzed systems.

In the present work, we propose an efficient heterogeneous catalyst for Suzuki–Miyaura C–C cross-coupling and Mott-Schottky nitrobenzene reduction processes. Although many heterogeneous catalytic systems have been proposed for these processes to date [5–8], the synthesis of most of them is quite difficult and expensive. Taking into account these circumstances, we have synthesized nanopalladium-based heterogeneous catalyst and studied its catalytic activity in relation to a) catalytic synthesis of 1,1'-biphenyl by Suzuki–Miyaura reaction; b) the catalytic Mott-Schottky nitrobenzene reduction.

Results and Discussion. 1,1'-Biphenyl (**1**) was obtained by the catalyzed reaction between phenylboronic acid and benzene iodine (Scheme 1), and the catalytic Mott-Schottky reduction of nitrobenzene to aniline (**2**) was carried out in water media with formic acid as hydrogen source (Scheme 2). The product of thermolysis of palladium(II) poly-5-vinyltetrazolate (hereinafter referred to as Pd–Pol) was used as a catalyst for these reactions.



Scheme 1. Synthesis of 1,1'-biphenyl

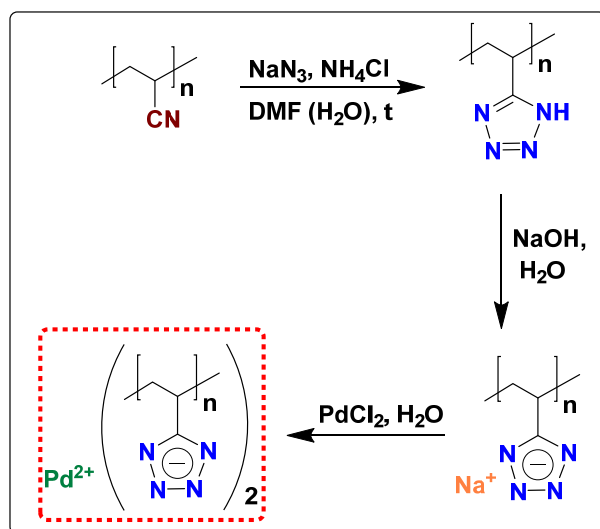


Scheme 2. Synthesis of aniline

The palladium(II) poly-5-vinyltetrazolate was obtained from poly-5-vinyltetrazole, synthesized by polymer-analogous reaction from polyacrylonitrile [13] and palladium(II) chloride (Scheme 3) by the method described in our previous works [14–15] for the synthesis of copper (II) poly-5-vinyltetrazolate.

Characterization of the prepared poly-5-vinyltetrazole by IR spectroscopy, thermogravimetric (TG) and differential scanning calorimetry (DSC) showed that all the obtained data corresponded to those presented for this polymer in the literature [16]. For synthesis of palladium(II) poly-5-vinyltetrazolate, poly-5-vinyltetrazole was dissolved in aqueous solution of sodium hydroxide to give sodium poly-5-vinyltetrazolate, which then resulted in palladium(II) poly-5-vinyltetrazolate in the reaction with palladium (II) chloride. The metal content of palladium(II) poly-5-vinyltetrazolate was found to correspond to the molar ratio $\text{Pd}^{2+} : (\text{CH}_2\text{-CH-CN}_4)\text{-} \approx 1 : 2$. The palladium content in palladium(II) poly-5-vinyltetrazolate was found equals to 31 wt-%.

As a result of the thermolysis of palladium(II) poly-5-vinyltetrazolate, a black powder product was obtained. The obtained powder was investigated by X-ray diffraction (XRD). As can be seen from Fig. 1, XRD pattern of the powder revealed Bragg's reflections 111, 200, 220 and 311 of metallic palladium (PDF #5–681) in 2θ range of 5–84°. As follows from the analysis of reflections broadening,



Scheme 3. Synthesis of palladium(II) poly-5-vinyltetrazolate

the palladium particles show an average size of about 20 nm, indicating the formation of palladium nanocrystals (hereinafter referred to as Pd NCs). Besides nanosized metallic palladium, practically no other crystalline phases are found on XRD pattern. However amorphous component is clearly seen if to pay attention to the scattering in the first half of the registered pattern.

SEM investigation, focused on a separate powder particle of the thermolysis product, was carried out to characterize the components of particles. It is seen from SEM image (Fig. 2) that the above-mentioned amorphous component is a polymeric matrix, and palladium particles are deposited onto its surface. According to SEM, the average size of palladium particles is about 350 nm, so that they are nanoparticles (NPs). However, this value is higher in comparison with that obtained from XRD data (about 20 nm). This difference cannot be attributed to particles agglomeration, because the particles seen in SEM image are rather uniform. We believe that Pd NPs are polycrystalline particles composed of Pd NCs. The obtained data showed that thermolysis of palladium(II) poly-5-vinyltetrazolate resulted in Pd–polymer (Pd–Pol) nanocomposite. Palladium content of nanocomposite was found to be 37 wt.%.

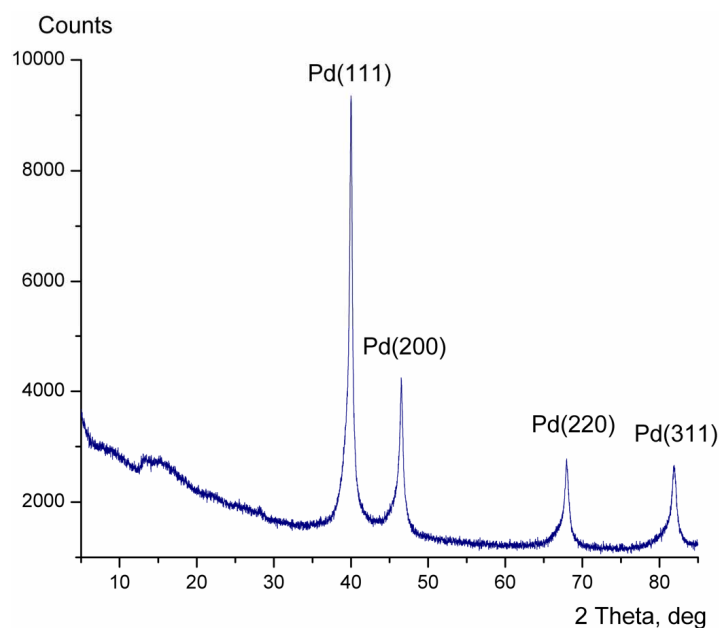


Fig. 1. XRD pattern of a powder obtained by thermolysis of palladium(II) poly-5-vinyltetrazolate (Cu-K α radiation, $\lambda = 1.5405 \text{ \AA}$)

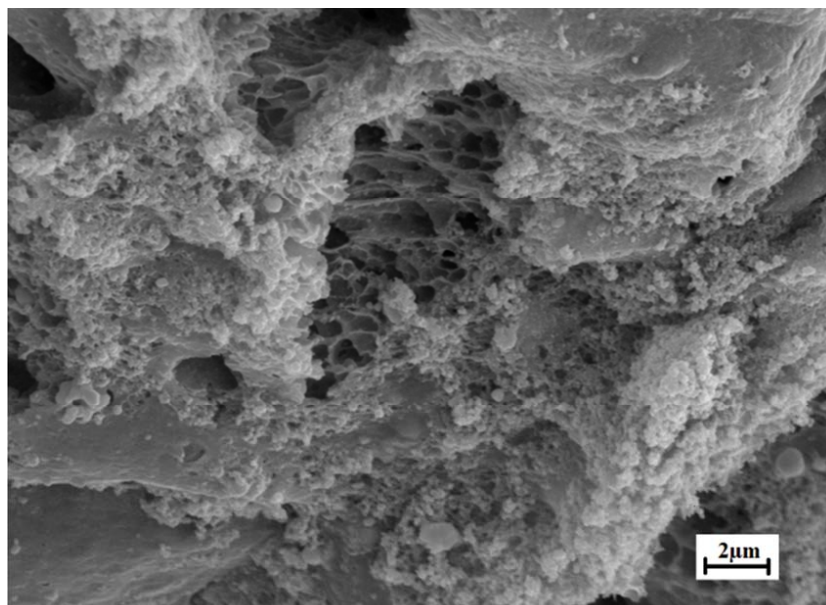


Fig. 2. SEM image of a powder obtained by thermolysis of palladium(II) poly-5-vinyltetrazolate

IR spectrum of Pd–Pol nanocomposite was registered to characterize polymeric matrix. The IR spectrum reveals continuous absorption region $3000\text{--}3600\text{ cm}^{-1}$, corresponding to stretching N–H vibrations (the bands of high-frequency part of the region are probably caused by $=\text{N}\text{--H}$ vibrations). There are also weak bands at $2800\text{--}3000\text{ cm}^{-1}$, which can be due to C–H stretching vibrations. Registered continuous absorption in the region $1000\text{--}1600\text{ cm}^{-1}$ includes the bands of C–H ($1376, 1409\text{ cm}^{-1}$) and N–H (1534 cm^{-1}) bending vibrations. There are also weak bands at $2031, 2134, \text{ and } 2180\text{ cm}^{-1}$, which can be assigned to nitrile $\text{C}\equiv\text{N}$ or to conjugated imine $\text{C}=\text{N}$ groups. These data are consistent with the expectation that amorphous polymeric matrix belongs to a nitrogen-containing polymer.

Noteworthy, that palladium nanoparticles, supported on polymer matrix, are resistant to oxidation on air and to solvents action including water. Hence, polymer matrix increases stability of the particles despite their inherent sensitivity to oxygen and solvents.

By investigating the catalytic activity of the obtained Pd–Pol nanocomposite in the synthesis of **1** (Scheme 1), different solvents were scanned to find their effect on the activity of the catalyst. As can be seen from Table 1, compound **1** was obtained in good yields in all protonic solvents (Entries 4–6), the best result being obtained for water. This result is important, because water is a green solvent. It should be noted that other heterogeneous catalysts for Suzuki–Miyaura C–C coupling also showed the best results in water as a solvent. Thus, Pd–Pol nanocomposite is highly effective catalyst for Suzuki–Miyaura C–C cross-coupling reaction, proceeding in water at room temperature.

Table 1. Effects of solvents on the catalytic activity of Pd–Pol in Suzuki–Miyaura cross-coupling reaction^{1, 2}

No	Solvent	Time/h	Isolated yield of 1 /wt-%
1	THF	12	42
2	1,4-Dioxane	48	37
3	Toluene	14	65
4	MeOH	6.5	83
5	EtOH	7	81
6	H ₂ O	5	92

¹ All reactions were performed with benzene boronic acid (1.0 mmol), benzene iodide (1.0 mmol), Pd–Pol nanocomposite (5.7 mg, 5 mol-%) and 3.0 mL of solvent under air at room temperature.

² The structure of **1** was confirmed by mass-spectrometry and ¹³C NMR spectroscopy.

It should be noted, that high catalytic activity of Pd–Pol nanocomposite can be explained by its high dispersity in water and interaction of organic reactants with the surface of Pd NPs attached to polymeric matrix. During the reaction, the hydrophobic nature of the polymeric matrix surface allows the phenylboronic acid and benzene iodine to interact on the surface of polymeric matrix thereby increasing the yields of **1**.

The influence of Pd–Pol catalyst loading on the reaction time and yield of **1** is demonstrated in Table 2. As can be seen, the catalyst loading of 5–15 mol-% (Entries 1–4) provides good reaction characteristics, namely reaction time of 5h and the yield of **1** 91–93 wt-%.

Table 2. Different amounts of Pd–Pol nanocomposite catalyst in synthesis of **1**¹

No	Catalyst loading/mol-%	Synthesis duration/h	Isolated yield of 1 /wt-%
1	15	5	91
2	12	5	93
3	9	5	90
4	5	5	92
5	1	7	89
6	0.8	14	87
7	0.5	19	89
8	0.1	48	87

¹ All reactions were performed with benzene boronic acid (1.0 mmol), benzene iodine (1.0 mmol), Pd–Pol nanocomposite (0.1–15 mol-%) and 3.0 mL of solvent under air at room temperature.

It was shown in our investigation, that in the synthesis of **1**, Pd–Pol nanocomposite presents a reusable heterogeneous catalyst. Table 3 demonstrates changes in its catalyst efficiency for eight successive cycles of the use. If to be limited to 90% yield of **1** as acceptable for the practical use, the catalytic system can be reused six times without considerable loss of the catalytic activity. After six cycles, the catalytic activity of Pd–Pol nanocomposite begins to decrease more noticeably. We believe that the decrease in catalytic activity is caused by the loss of palladium particles from the polymeric matrix surface, which can take place as a result of recovery procedure as well as during liquid phase Suzuki–Miyaura synthesis. After eight cycles, palladium content of nanocomposite is about 26 wt-%.

Table 3. Reusability of Pd–Pol nanocomposite catalyst in synthesis of **1**¹

Cycle number	Isolated yield of 1 /wt-%
1	92
2	90
3	91
4	92
5	91
6	90
7	87
8	85

¹After completion of a previous cycle, the catalyst was recovered by a procedure, described in Experimental Section, and then used again in the next cycle.

By investigating Mott-Schottky processes for obtaining **2** (Scheme 2), different solvents also were scanned to find their effect on the activity of the catalyst (Table 4). Product **2** was obtained in excellent yields in all solvents but the best results was obtained for water. Thus, Pd–Pol nanocomposite also can be used as effective catalyst for Mott-Schottky reduction of nitrobenzene to aniline.

Further, the Mott-Schottky model process was performed at room temperature catalyzed by different amounts of Pd–Pol nanocomposite catalyst (Table 5). As can be seen from Table 5 (Entries 2–4), the Mott-Schottky reaction could still finish in 3h, being catalyzed by 1–8 mol-% Pd–Pol, with almost the same yields of 92–94 wt-%, as in the case of 11 mol-% of the catalyst (Entry 1).

Table 4. Effects of solvents on the catalytic activity of Pd–Pol in Mott-Schottky reduction of nitrobenzene to aniline^{1, 2}

No	Solvent	Time/h	Isolated yield of 2 /wt-%
1	MeOH	4	88
2	EtOH	5	87
3	MeOH/H ₂ O (1:1)	3	90
4	EtOH/H ₂ O (1:1)	3.5	92
5	H ₂ O	3	94

¹ All reactions were performed with nitrobenzene (1.0 mmol) and Pd–Pol nanocomposite (1.14 mg, 1 mol-%). The reaction mixture were suspended in deionized water (5.0 mL) by sonication for 2 min, after what formic acid (215μl, 5.0 mmol) was added to the solution and then the reaction mixture was stirred at 25°C for a certain time.

² The structure of 2 was confirmed by GC-MS spectrometry.

Table 5. Different amounts of Pd–Pol nanocomposite catalyst in synthesis of 2¹

No	Catalyst loading/mol-%	Synthesis duration/h	Isolated yield of 2 /wt-%
1	11	3	91
2	8	3	93
3	4	3	92
4	1	3	94
5	0.75	6	88
6	0.3	9	86
7	0.15	14	85

¹ All reactions were performed with nitrobenzene (1.0 mmol) and Pd–Pol nanocomposite (1.14 mg, 1 mol-%). The reaction mixture were suspended in deionized water (5.0 mL) by sonication for 2 min, after what formic acid (215μl, 5.0 mmol) was added to the solution and then the reaction mixture was stirred at 25°C for a certain time.

Our model experiments, concerned about the synthesis of 2 by using Pd–Pol nanocomposite catalyst, show that it can be used as a reusable heterogeneous catalyst too. Table 6 demonstrates changes in its catalyst efficiency for nine successive cycles of the use. If to be limited to 90% yield of as acceptable for the practical use, the catalytic system can be reused eight times without considerable loss in the catalytic activity. After nine cycles, the catalytic activity of Pd–Pol nanocomposite begins to decrease also more noticeably. We believe that the reason of decrease in catalytic activity is the loss of palladium particles from the polymeric matrix surface, which can take place as a result of recovery procedure as well as during Mott-Schottky catalytic reaction. After eight cycles, palladium content of nanocomposite is about 27 wt-%.

Table 6. Reusability of Pd–Pol nanocomposite catalyst in synthesis of 2¹

Cycle number	Isolated yield of 2 / wt-%
1	94
2	92
3	93
4	90
5	91
6	92
7	91
8	90
9	89

¹ After completion of a previous cycle, the catalyst was recovered by a procedure, described in Experimental Section, and then used again in the next cycle.

Conclusions. In summary, we obtained a new catalyst for green Suzuki–Miyaura cross-coupling and Mott-Schottky nitrobenzene reduction processes. The catalyst presents Pd nanoparticles, supported on nitrogen-containing polymer matrix. It demonstrated valuable catalyst qualities such as: a) high catalytic activity; b) low catalytic loading; c) easily recoverable for further usage; d) cheapness; e) resistance to oxidation on air and different solvents include water action. By using this catalyst, Suzuki–Miyaura cross-coupling and catalytic Mott-Schottky nitrobenzene reduction processes proceed in aerobic conditions and without any ligands at room temperature in water with relatively short reaction time.

Experimental Section

CAUTION: The prepared palladium(II) poly-5-vinyltetrazolate and poly-5-vinyltetrazole are energetic compounds with increased sensitivities against heat. Although we had no problems in synthesis, the use of safety equipment such as leather gloves, face shield and use of Teflon spatulas is mandatory.

Materials and Physical Techniques. All reagents and solvents were obtained from commercial sources and used without purification. Infrared spectra were recorded on a Nicolet Thermo Avatar 330 FT-IR system over the 400–4000 cm^{-1} range in SiC cavities. The TG and DSC curves were obtained using a Netzsch STA429 thermoanalyzer in a dynamic nitrogen atmosphere (heating rate $10^\circ\text{C}\cdot\text{min}^{-1}$, aluminium oxide, mass 1–3 mg, and temperature range from room temperature up to 500°C). The scanning electron microscopy (SEM) images were obtained on a LEO-1420 equipment. XRD powder data were collected on a diffractometer Empyrean (PANalytical, Netherlands) using $\text{CuK}\alpha$ radiation (Ni filter). XRD powder pattern of the standard compound LaB6 was also registered to determine instrumental broadening, used for obtaining copper crystal sizes. The NMR spectra were recorded in CDCl_3 on a Bruker Avance 600 NMR spectrometer. Gas chromatography mass-spectrometry investigation was carried out with a spectrometer Shimadzu GCMS-QP2010 Plus.

Synthesis of poly-5-vinyltetrazole. Poly-5-vinyltetrazole was obtained through polymer-analogous transformation of polyacrylonitrile [13]. Polyacrylonitrile (25 g) was dissolved in DMF (250 mL). Then to resulting solution was added a mixture of sodium azide (32 g) and ammonium chloride (27 g). The reaction mixture was stirred at 100°C for 25 h. After that the solution was diluted with water, and the resulting mixture was added to a solution of hydrochloric acid (0.7 mole/L). The obtained product was filtered out, washed with water, and dried in vacuum oven for 8 h.

Preparation of palladium(II) poly-5-vinyltetrazolate and Pd–Pol nanocomposite. For synthesis of Pd–Pol nanocomposite, poly-5-vinyltetrazole (6.5 g) was dissolved in aqueous solution of sodium hydroxide (200 mL, 1.2 wt-%). The resulting solution of sodium poly-5-vinyltetrazolate was added to aqueous solution of palladium(II) chloride (100 mL, 5.3 wt-%). The reaction mixture was stirred at room temperature for 2 h. After that the solution was filtered through the cellulose membrane. The obtained precipitate of palladium(II) poly-5-vinyltetrazolate was washed with water and ethanol and dried in a vacuum oven for 4 h. Further, this salt was subjected to thermolysis in a muffle oven at 280°C for 5 min to give Pd–Pol nanocomposite. IR: $\tilde{\nu} = 3374, 2180, 2134, 2031, 1534, 1497, 1409, 1376, 1362, 1294, 1250, 996 \text{ cm}^{-1}$.

General procedure for Suzuki–Miyaura cross-coupling reaction. 1,1'-Biphenyl was obtained in 10 mL round bottom flask by mixing benzene boronic acid (1.0 mmol), benzene iodine (1.0 mmol), Pd–Pol nanocomposite (5.7 mg, 5 mol-%) and 3 mL of deionized water. The resulting mixture was stirred at room temperature for 5h, and the reaction was monitored by gas chromatography-mass spectrometry (GC-MS) until the starting reagents disappeared. After the completion of the reaction, the mixture was filtered, and the mother solution was evaporated. The solid residue was recrystallized from 2-propanol to give colorless needle crystals with m.p. 70°C . ^{13}C NMR: 140.8, 128.4, 126.8, 126.7; MS: EI (75 eV), 154 (100.0) [M+], 128 (3.3), 115 (3.5), 76 (10.3), 63 (3.7), 51 (4.8).

General procedure for Mott-Schottky catalytic hydrogenation of nitrobenzene. Nitrobenzene (1.0 mmol) and Pd–Pol nanocomposite (1.14 mg, 1 mol-%) were suspended in deionized water (5.0 mL) by sonication for 2 min, after what formic acid (215 μl , 5.0 mmol) was added to the solution and then the reaction mixture was stirred at 25°C for a certain time. The resulting mixture was stirred

at room temperature for 3h. The product was extracted with ethyl acetate (3 × 5 ml) and dried over anhydrous magnesium sulfate. The reaction was monitored by gas chromatography-mass spectrometry (GC-MS) until the starting reagents disappeared. MS: nitrobenzene (EI (75 eV)), 123 (52.7), 78 (6.7) [M+], 77 (100.0) [M], 65 (12.0), 50 (13.0); aniline (EI (70 eV)), 94 (14.2) [M+], 93 (100.0), 92 (22.1), 66 (50.0), 65 (24.0).

Recovering procedure of Pd–Pol nanocomposite catalyst. After completion of a previous cycle of the synthesis of **1** or **2**, the Pd–Pol nanocomposite catalyst was recovered by the following procedure. It was filtered over a Teflon membrane (PTFE, 0.2 mm pore size), washed with ethyl alcohol and kept in THF at 50°C for 10 min. Then the catalyst was filtered out and dried on air, becoming ready for the use in the next cycle.

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