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Reusable functionalized polysiloxane-supported palladium catalyst for Suzuki–Miyaura cross-coupling

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ABSTRACT

Palladium catalyst, obtained in the reaction of $PdCl_2$(cod) with poly[(3-N-imidazolopropyl)methylsiloxane-co-dimethylsiloxane], was used in the Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid. Catalytic reactions, performed at 40–80 °C in water or 2-propanol/water mixture, led to high yields of 2-methylbiphenyl with TOF up to 25,000 h^{-1}. In recycling experiments, excellent results were obtained in eight subsequent runs. With application of microwave heating, more than 95% of product was formed under mild conditions and short time. XRD, TEM, and XPS methods evidenced the presence of Pd(0) nanoparticles bonded to the polysiloxane support. Their important role in the catalytic process was indicated by the results of mercury poisoning test.

1. Introduction

Heterogenized catalysts supported on polymers or porous oxides have been attracting more and more attention because of the increasing environmental requirements [1–11].

In this context, the expected advantage of immobilization consists in efficient separation of the catalyst and its recycling in the next run. This diminishes the cost of the catalytic process and, in addition, makes it possible to minimize the metal content in the final organic product. This aspect is very important when pharmaceutical applications of products are considered.

One of the strategies used for the preparation of active catalysts containing metal ions covalently attached to the support is the functionalization of the surface with organic ligands such as phosphines, pyridines, amines, or mercapto groups [1–3,12].

It can be expected that the covalent attachment of the metal to the support offers some advantages, mainly higher stability under catalytic conditions, with regard to metals supported on porous materials. Moreover, functionalization of the support with coordinating groups provides better control over the distribution of the metal on the surface, which is important for catalytic activity and selectivity.

Palladium complexes anchored on differently functionalized polymers have been used in catalysis [13], including Suzuki–Miyaura reaction [14]. Pd(0) stabilized on polyvinylpyrrolidone [15], polyvinylpyridine [16] or other polymers have been widely applied [17]. However, very few reports have presented the application of imidazole-functionalized polymers [18] or silicas [19] as catalyst supports.

Recently, it has been shown that Pd(II) complexes with coordinated imidazole ligands exhibit high catalytic activity in the Suzuki–Miyaura reaction with 100% of the cross-coupling product formed at 60 °C in 1 h [20]. At the same time, polysiloxane-supported palladium has recently been successfully used in the Heck reaction [21,22]. Therefore, we decided to examine the catalytic activity of palladium supported on imidazole-functionalized polysiloxane in the Suzuki–Miyaura reaction with the expectation to obtain a highly active and recyclable catalyst. It is also worth noting that polysiloxanes are chemically resistant, non-toxic materials and imidazole functionality plays an important role in many biological systems. Thus, imidazole-substituted polysiloxanes could be considered as potentially biodegradable materials although their high antibacterial potency should be also mentioned in this context [23].

2. Results and discussion

2.1. Structural studies

Coordination of palladium to poly[(3-N-imidazolopropyl)methylsiloxane-co-dimethylsiloxane] (P1) resulted in a change of composition and decrease in N, C, and H amounts in comparison

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with P1. The Pd/N ratio, calculated from the N and Pd contents, indicated that there were *ca*. 3.5 imidazole groups per one palladium ion. The most probable structure of C1, containing palladium bonded to two imidazole groups and two chloride ions, is shown in Fig. 1.

In is worth noting that palladium acted as a cross-linking agent, which was observed during the synthesis of C1, when solid C1 precipitated after the addition of the solution of $PdCl_2$(cod) to the liquid polymer. Because of the very low solubility of C1 in common solvents, CP MAS ^{13}C and ^{29}Si NMR spectra were measured in the solid state. The obtained parameters of ^{13}C were similar to those determined in a $CDCl_3$ solution of polymer P1; however, only one broad signal was found in the ^{29}Si CP MAS spectrum of C1 instead of two signals found for P1 in solution.

The XPS spectrum of catalyst C1 exhibited two dominating peaks (*ca*. 83%) of Pd 3d at BE 338.3 eV (Pd $3d_{5/2}$) and 342.6 eV (Pd $3d_{3/2}$), typical for Pd(II), and assigned to palladium bonded to two imidazole nitrogen atoms and two chlorides. Such interpretation was confirmed by comparison with the spectrum of the complex $[(mim)_3PdCl]Cl$ (mim = 1-methylimidazole), which showed two peaks at BE 338.0 eV (Pd $3d_{5/2}$) and 343.3 eV (Pd $3d_{3/2}$). The small difference in the BE values (0.3 eV) between the two spectra can be related to the fact that in C1 two nitrogen atoms are bonded to palladium, whereas in $[(mim)_3PdCl]Cl$ three nitrogen atoms are present in the first coordination sphere (Fig. 2 and Table 1).

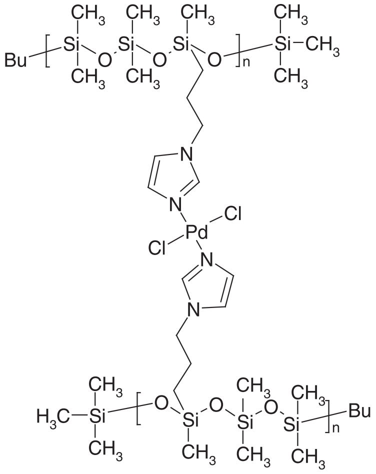


Fig. 1. The proposed structure of catalyst C1.

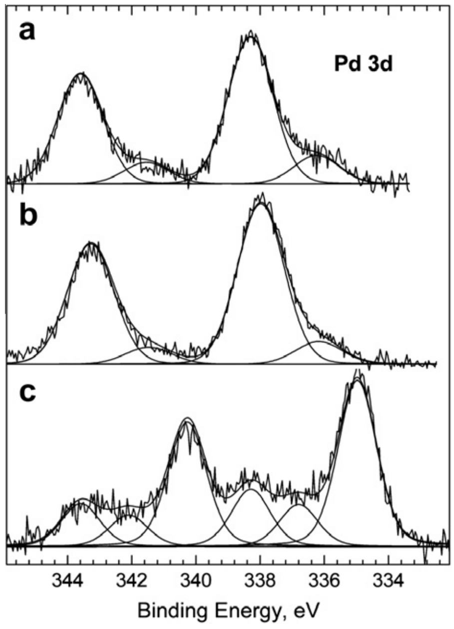


Fig. 2. XPS spectra Pd 3d of: (a) C1, (b) [(mim)3PdCl]Cl, (c) C1 isolated after Suzuki–Miyaura reaction.

Table 1
XPS data Pd 3d.

		Amount (%)	BE Pd $3d_{3/2}$ (eV)	BE Pd $3d_{5/2}$ (eV)
C1	N_2–Pd–Cl_2	82.8	343.6	338.3
	PdO	17.2	341.5	336.2
$[(mim)_3PdCl]Cl$	N_3–Pd–Cl	89.1	343.3	338.0
	PdO	10.9	341.5	336.2
C1 after Suzuki–Miyaura reaction	Pd(0)	61.5	340.3	335.0
	N_2–Pd–Cl_2	22.9	343.6	338.3
	Pd–Br	15.6	342.1	336.8

The second form of palladium observed in the XPS spectra of C1 and $[(mim)_3PdCl]Cl$ in *ca*. 17% and 11%, respectively, was PdO characterized by BE 336.2 and 341.5 eV. The presence of some amounts of PdO can be explained by air oxidation of palladium at the surface.

XPS spectra of catalyst C1 and the complex $[(mim)_3PdCl]Cl$ in the N 1s region show two lines indicating the presence of differently surrounded nitrogen atoms, namely imidazole nitrogen bonded to palladium (Pd–N, BE 399.4 eV) and free imidazole nitrogen (N, BE 400.8 eV). In the XPS spectrum of $[(mim)_3PdCl]Cl$, the ratio of the surface areas of these peaks, Pd–N/N, was 5:5, as expected if all imidazole ligands were bonded to palladium. In case of catalyst C1, the Pd–N/N ratio was 4:6, in agreement with earlier supposition that not all imidazole groups are involved in the formation of bondings with palladium.

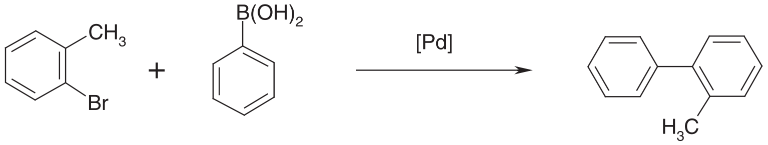
3. Studies of the Suzuki–Miyaura reaction

3.1. Catalytic activity of catalyst C1

The Suzuki–Miyaura reaction of 2-bromotoluene with phenylboronic acid was selected as a model catalytic reaction for catalyst C1 (Scheme 1).

The first tests of the activity of catalyst C1 were performed at 40 °C over 1 h using 2-propanol as solvent. Under these conditions, 43% of 2-methylbiphenyl was formed. Next, the catalyst was separated, washed, and reused in four subsequent runs. The yield of the product ranged from 56% to 76% in the fifth reaction, which indicates the high stability of the catalyst under reaction conditions. In the next experiment, the reaction time was prolonged to 3 h, which resulted in the yield increasing to 82%. When microwave heating was applied instead of conventional heating, even better results were obtained and yields of 90–100% were found after 1 h in three subsequent runs with the same sample of C1 (Table 2).

In further investigations, a screening of solvents was performed in the temperature range 60–110 °C. At 60 °C, the Suzuki–Miyaura reaction in 2-propanol proceeded, as expected, with a higher yield than at 40 °C, and in the second run, the highest yield, 100%, was achieved. In subsequent reactions performed with the recycled C1 catalyst, the yield of 2-methylbiphenyl decreased to 43% in the fifth reuse (Table 2). Very good results were obtained at 80 °C; however, like before, the yield was lower in the fifth run (63%). Following the rules of green chemistry, we attempted to use water as an inexpensive, non-toxic, and non-flammable sol-



Scheme 1. Suzuki–Miyaura reaction under studies.

Table 2
Results of Suzuki–Miyaura reaction with catalyst C1.[a,b]

Solvent	Reaction conditions	Run				
		1	2	3	4	5
2-Propanol	40 °C, 1 h	43	56	72	63	76
	40 °C, 3 h	68	82			
	40 °C, 1 h, MW	90	90	100		
2-Propanol	60 °C, 3 h	56	100	79	35	43
	80 °C, 3 h	89	92	98	83	63
Water	110 °C, 3 h	76	88	60	73	
2-Propanol/water 4/1	60 °C, 3 h	82	58	32	16	
2-Propanol/water 1/1	40 °C, 1 h, MW	80	86	92	82	68
2-Propanol/water 1/1	60 °C, 3 h	100	93	93	97	96
2-Propanol/water 1/1	60 °C, 1 h, MW	96	92	99	98	98

[a] The yield of 2-methylbiphenyl obtained in subsequent runs;
[b] The amount of biphenyl (homocoupling product) decreased from *ca.* 4% in the first run to maximum 1% in the subsequent runs.

vent in the Suzuki–Miyaura reaction [24]. The results were quite good: At 60 °C, the cross-coupling product was formed with 40% yield, whereas at 110 °C the yield increased to 88% in the second run (Table 2).

The application of a 4:1 2-propanol/water mixture produced poorer results than with neat 2-propanol, whereas a 1:1 mixture of 2-propanol/water turned out to be the best solvent in the studied system. In addition, the reaction was successfully performed at a relatively low temperature, 60 °C. It was possible to obtain a high yield of 2-methylbiphenyl in eight successive Suzuki–Miyaura reactions using the same sample of catalyst C1 (Fig. 3). High yields, over 90%, were seen in seven runs, while in the eighth one the yield decreased to 70.5%.

An important criterion to assess the efficiency of the catalytic process is the amount of palladium in the organic product. To estimate palladium content, the Suzuki–Miyaura reaction was performed at 60 °C in 2-propanol/water (1:1) mixture. After 1 h, catalyst was separated by filtration and used for the second run. 2-Methylbiphenyl was extracted from a residue with hexane, which was next removed *in vacuo*. The amount of palladium found in product, using ICP method, was as low as 0.6 ppm in the first and 0.2 ppm in the second run.

Further experiments confirmed a high activity and stability of catalyst C1 also under microwave conditions. The results obtained in a series of experiments performed in a 2-propanol/water (1:1) mixture at 60 °C over 1 h were comparable with those obtained with conventional heating over 3 h (Fig. 3). In both cases, it was possible to perform eight successive runs with high yield of the product. The decrease in product yield observed after the fifth run can be related to some decomposition of the catalyst or the loss of material during separation procedure, but alternatively palladium leaching should also be considered.

Only slightly lower yields were obtained when catalyst C1 was used at 40 °C with microwaves in 2-propanol/water (1:1) mixture. In this case, the yield of 2-methylbiphenyl obtained after 1 h was higher than in 2-propanol only, and five efficient recycling runs were successfully carried out (Table 2). The maximum yield, 92%, was obtained in the third run. An increase in the reaction yield in subsequent runs can be explained by the transformation of C1 to the more active form, namely Pd(0) nanoparticles supported on the polymer.

3.2. The effect of C1 amount on catalytic activity

To follow the influence of the amount of palladium on the yield of the Suzuki–Miyaura reaction, a series of experiments were performed in 2-propanol over 15 min in 80 °C. The [Pd]/[2-bromotoluene] ratio was changed by changing the amount of C1 or by applying different amounts of organic substrates. In order to compare the obtained results, the TOF (h^{-1}) values were calculated

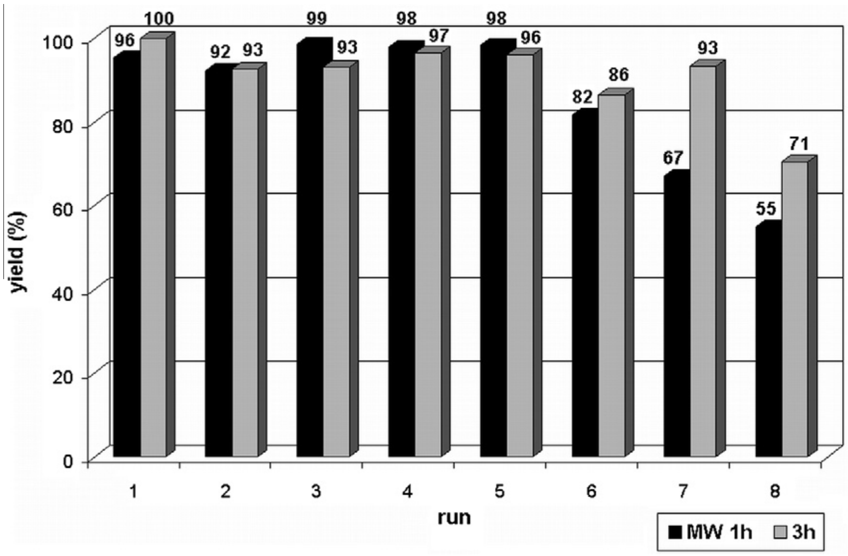


Fig. 3. Results of Suzuki–Miyaura reaction with catalyst C1 in recycling experiments.

(Table 3). It is worth noting that the 15-min reaction time was, in most cases, suitable to obtain over 90% yield of 2-methylbiphenyl. It was found that the optimal amount of catalyst C1 was 6×10^{-7} mol, enabling the formation of 98.6% of the product, the corresponding TOF value being 6573 h^{-1}. Application of smaller or larger amounts of catalyst C1 led to poorer results. According to the literature, such non-linear dependence of the reaction yield on the catalyst amount was frequently observed, also in reactions catalyzed by palladium nanoparticles [25,26].

Using the same optimal amount of catalyst C1 (6×10^{-7} mol), the reactions were performed with higher excesses of the substrates to demonstrate that TOF as high as 25,173 can be reached. It is important to point out that in a blank experiment performed under the same conditions but without C1, 2-methylbiphenyl was not formed.

3.3. The Suzuki–Miyaura reaction with other substrates

The scope of the Suzuki–Miyaura reaction catalyzed by catalyst C1 was evaluated by reacting phenylboronic acid with different aryl bromides as substrates. High conversion to the cross-coupling product was found for 4-bromotoluene and 2-bromoanisole. Lower yield was obtained when 2-bromobenzaldehyde or 2-bromoacetophenone was used. Application of microwave conditions made it possible to react the less reactive 4-chlorotoluene and 1-chloro-4-nitrobenzene (Table 4).

3.4. Filtration test

In order to check whether immobilized or leached palladium was responsible for the observed catalytic activity, the hot filtration test was performed [6]. The Suzuki–Miyaura reaction in 2-propanol/water (1:1) at 60 °C was stopped after 5 min, when conversion of 2-bromotoluene reached 56%. Next, the solution was separated from the catalyst by filtration, and the reaction continued for 60 min. After that time, the yield of the product increased to 100%, indicating that the solution had contained some catalytically active palladium. In fact, when the catalytic reaction was finished, some black precipitate was seen in the solution. It was, however, impossible to judge whether there was palladium black formed from soluble palladium species or palladium bonded to polymer P1 that was not separated from the solution during the first filtration.

In the second experiment, a StratoSpheres SPE resin (Varian) designed for removing of metal species from the solution was used to separate palladium from the reaction mixture after 5 min. The reaction then continued with the remaining solution, and the final yield of 2-methylbiphenyl was 50% after 60 min, close to that noted after 5 min (56%). The small decrease in the product yield was probably caused by fact that some amount of 2-methylbiphenyl remained on the resin after filtration. Thus, in this case, the reaction stopped because probably all palladium was removed, both supported on the polymer and soluble.

It is also worth to note that palladium content found in the C1 catalyst recovered after Suzuki–Miyaura reaction was always higher than in the as-prepared sample, and consequently, palladium analysis could not be used for estimation of the palladium leaching.

To obtain more information about the nature of the catalytically active species, the mercury test was performed [6,27].

Table 3
Results of Suzuki–Miyaura reaction with different amounts of catalyst C1.

Amount of Pd (mol)	[Pd]/[2-bromotoluene]	Yield[a] (%)	TOF (h^{-1})
1×10^{-5}	0.01	83.5	334
5×10^{-6}	0.005	93.1	745
6×10^{-7}	0.0006	98.6	6573
6×10^{-7}	0.0003	95.7	12,760
6×10^{-7}	0.00015	94.4	25,173
3×10^{-7}	0.0003	83.2	11,093

[a] GC determined as conversion of 2-bromotoluene.

Table 4
Results of Suzuki–Miyaura reaction with catalyst C1 and different aryl halides.

Substrate	Yield[a] (%)
2-Bromotoluene	100
4-Bromotoluene	100
2-Bromoanisole	97
2-Bromobenzaldehyde	45
2-Bromoacetophenone	13
4-Chlorotoluene	10[b]
1-Chloro-4-nitrobenzene	16[b]

[a] GC determined as conversion of aryl halide.

[b] 1 h, 60 °C, with microwaves.

3.5. Mercury test

Two experiments were performed using 500-fold excess of Hg(0) relative to palladium in the Suzuki–Miyaura cross-coupling in a 2-propanol/water mixture. In the first case, Hg(0) was introduced at the beginning, together with other reactants, whereas in the second experiment, Hg(0) was added after 5 min of reaction. Analysis of the products showed 100% and 98% yield of the product in both cases. Thus, the reaction was not inhibited by Hg(0), indicating small, if any, influence of free Pd(0) nanoparticles on the reaction course. Consequently, immobilized palladium nanoparticles can be considered as the main catalytically active form.

3.6. Catalytic activity of catalyst C2

In reactions catalyzed by C1, performed in 2-propanol at 40 °C and at 60 °C, an increase in reaction yield was noted in the second run, compared with the first reaction, which produced 56–68% of the cross-coupling product. In the second reaction, a higher yield, 82% or 100%, was obtained. These observations suggest that the catalytically active species, presumably a Pd(0) catalyst, was slowly formed under the conditions applied. In fact, when prereduced catalyst C2, containing supported Pd(0) nanoparticles, was used, a high yield, 90%, was seen already in the first reaction performed at 60 °C in 2-propanol. This result, indicating, as expected, the higher catalytic activity of Pd(0) compared with Pd(II), prompted us to perform structural studies of C1 isolated after the catalytic reaction.

3.7. Structural studies of catalyst C1 recovered after the Suzuki–Miyaura reaction

Analysis of the composition of catalyst C1a, namely C1 separated from the reaction mixture after one run of Suzuki–Miyaura, showed some changes in the amounts of N, C, and H and a remarkable increase in palladium content from 7.6% to 12.0%. When C1 was reduced with hydrazine to form C2, an increase in palladium content even up to 31.5% was observed. This can be explained by the reformation of the liquid polymer P1 during formation of Pd(0) nanoparticles.

The XRD diffractograms of C1 before and after reduction are shown in Fig. 4. In the spectrum of C1, containing Pd(II), there is a broad line at *ca.* $2\theta = 20°$, originating from polymer P1 (Fig. 4a).

The sample of C1 separated after the Suzuki–Miyaura reaction performed in 2-propanol (Fig. 4b) and in 2-propanol/water (Fig. 4c) showed a new signal at $2\theta = 40.1°$, characteristic for crystallites of Pd(0). The average diameter of Pd(0) nanoparticles was 4.7 nm and 6.2 nm, respectively. Slightly bigger Pd(0) nanoparticles, 6.7 nm, were found in the sample of C2a, obtained by reduction in C1 with hydrazine in methanol (Fig. 4d).

The application of the TEM method allowed us to collect more structural data for the catalysts under study. The samples of C1 separated after the Suzuki–Miyaura reaction in 2-propanol and in 2-propanol/water (1:1) contained uniformly distributed Pd(0) nanoparticles of *ca.* 4 nm in diameter. Fig. 5 shows typical TEM pictures and size analyses of both materials. A similar distribution and size of Pd(0) nanoparticles were also found for catalyst C2 (Fig. 5c) with the maximum at 4.1 nm. TEM analysis of C2a, obtained by the reduction in C1 in methanol using a higher concentration of hydrazine, revealed aggregates ranging from tens to hundreds of nanometers, formed by individual Pd(0) nanoparticles.

The XPS Pd 3d spectrum of catalyst C1a, separated after the Suzuki–Miyaura reaction, differs from that measured for the freshly prepared C1 and contains three forms of palladium species. The dominating lines, observed at BE = 335.0 eV (Pd $3d_{5/2}$) and 340.3 eV (Pd $3d_{3/2}$), are typical for Pd(0). The relatively low BE values can indicate a high dispersion of palladium nanoparticles on polymer P1. The content of Pd(0) was estimated as 61%. The presence of lines at 338.3 and 343.6 eV confirmed that reduction in palladium was not complete, and 23% of the starting C1 remained unaffected. The third form of palladium, with BE = 336.8 eV and 342.1 eV, was identified as Pd–Br containing form (16%) [28]. The formation of such species in the Suzuki–Miyaura reaction with 2-bromotoluene as a substrate is expected (Fig. 2 and Table 1).

The SEM method was used to obtain more information about structural changes in the catalyst during its reduction. The sample for analysis was prepared by treating C1 with KOH in 2-propanol under reflux. SEM micrographs showed that the as-prepared C1 contained spongy and more regular fragments, whereas after reduction only spongy-type structures remained. Table 5 sets out the collected EDS data determined for both samples as average values from five measurements. In line with the conclusions from ICP analysis, the amount of palladium increased during reduction. At the same time, the contents of C, O, and Si, the main components of the polymer, decreased. This can be explained by some solubilization of polymer P1 during palladium reduction and the formation of Pd(0) nanoparticles attached to the polymer. The Cl/Pd atomic ratio determined by EDS spectroscopy decreased remarkably, from 2.8 in the as-prepared C1 to 0.7 as a result of C1 reduction with KOH in 2-propanol. As expected, during this process, Pd(0) nanoparticles were formed with simultaneous removal of chloride ions.

4. Experimental

4.1. General

TEM measurements were performed using a FEI Tecnai G^2 20 X-TWIN electron microscope with LaB_6 catode providing 0.25 nm resolution. To the small sample of catalyst, 2 cm^3 of methanol was added and the resulted mixture was ultrasonically treated

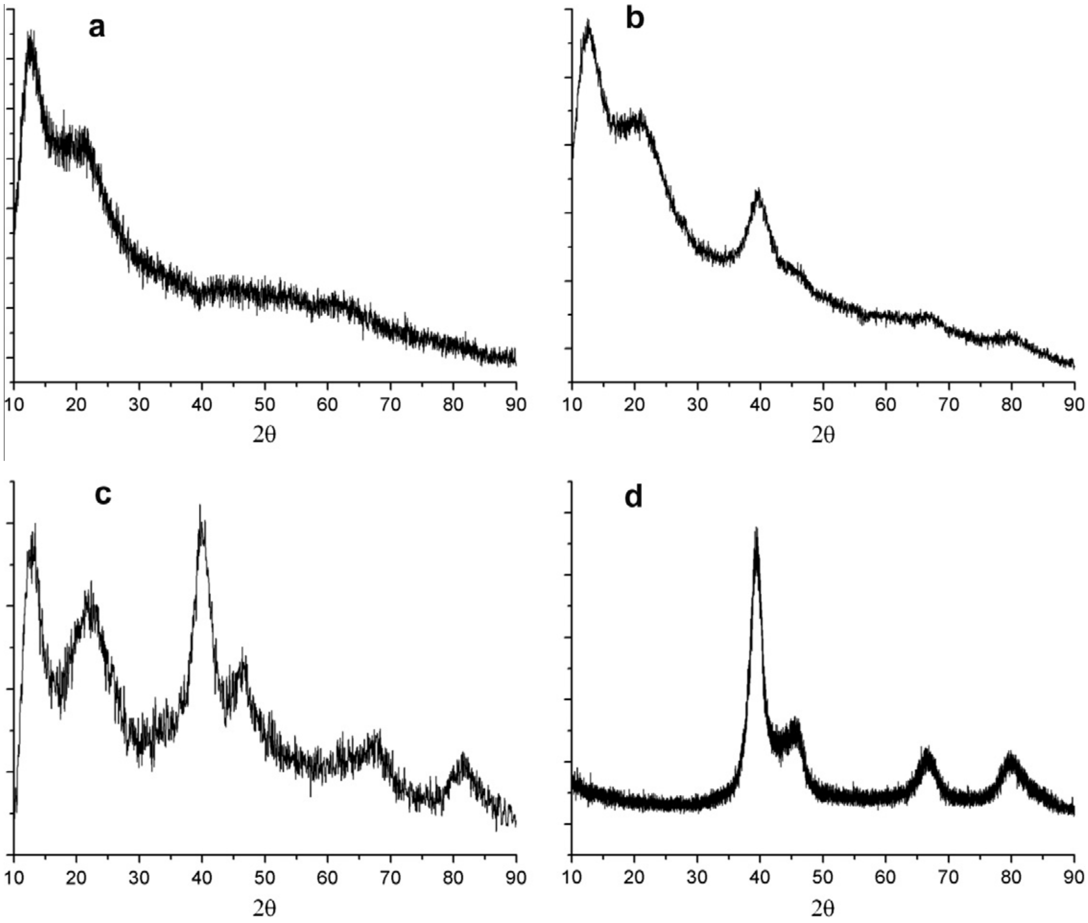


Fig. 4. XRD pictures of: (a) C1 as prepared, (b) C1 after Suzuki–Miyaura reaction in 2-propanol, (c) C1 after Suzuki–Miyaura reaction in 2-propanol/water 1/1, (d) C2a (C1 reduced with hydrazine in methanol).

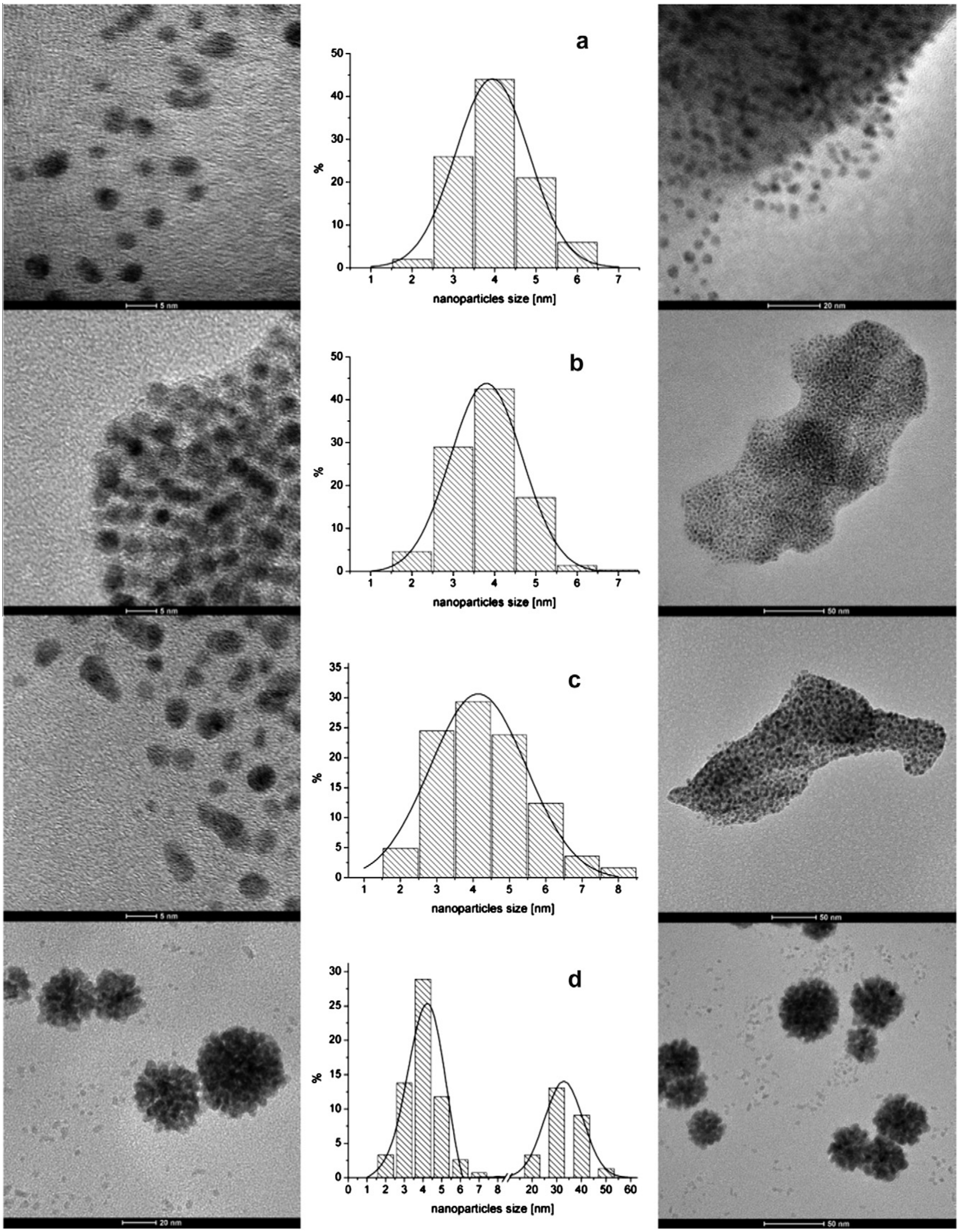


Fig. 5. TEM pictures and Pd(0) nanoparticles size distribution of: (a) C1 after Suzuki–Miyaura reaction in 2-propanol, (b) C1 after Suzuki–Miyaura reaction in 2-propanol/water 1/1, (c) C2 (C1 reduced with hydrazine in 2-propanol), (d) C2a (C1 reduced with hydrazine in methanol).

for 5 min. Specimens for TEM studies were prepared by putting a droplet of a colloidal suspension on a copper microscope grid followed by evaporating the solvent under IR lamp for 15 min. The mean particle diameter and size distributions were calculated by counting at least 400 particles from the enlarged micrographs.

Table 5
EDS data (%) for catalyst C1 (as prepared) and C1 after reaction with KOH in 2-propanol under reflux.

Element	C1	C1 after reaction with KOH in 2-propanol
C	46.4	13.8
O	16.9	8.3
Pd	4.1	25.0
Cl	11.6	17.4
Si	4.0	0

X-ray powder diffraction (XRD) measurements were performed using BRUKER D8 Advance diffractometer.

XPS spectra were obtained with a SPECS XPS System equipped with a hemispherical PHOIBOS analyzer and Mg-Kα radiation source operated at 250 W under a residual pressure better then 5×10^{-10} mbar. The analyses were carried out under fixed analyzer transmission (FAT) with a constant pass energy of 10 eV in a high-resolution scans. For charge compensation, a flood gun was used. Additionally, the raw data were corrected for substrate charging with the binding energy of the Si 2p (101.9 eV) on silicate support as a reference. The samples were analyzed as pressed powders mounted on a double-sided adhesive tape. The measured spectra were fit by a least-squares procedure to a product of Gaussian–Lorentzian functions after subtraction of background noise by Shirley method. The concentration of each element was calculated using SpecLab software.

GC-FID and GC/MS spectra of organic products were obtained using HP 5890 (Hewlett Packard) instrument with mass detector 5971 A. Capillary column HP 5 was used with non-polar liquid phase containing 95% of dimethyl- and 5% of diphenyl-polysiloxane.

ICP measurements of palladium content were performed using spectrometer ARL model 3410. Before analysis, weighted samples of palladium catalyst were mineralized with 2 cm^3 of aqua regia, left for 7 days and diluted next to 10 cm^3 with distilled water.

4.2. Synthesis of palladium catalysts

Palladium complexes $[(mim)_3PdCl]Cl$ [29] and $PdCl_2(cod)$ [30] were obtained according to literature methods.

Poly[(3-N-imidazolopropyl)methylsiloxane-co-dimethylsiloxane], P1, was obtained according to literature method [23].

^{1}H NMR ($CDCl_3$) δ 0.05 (m, 3H, $SiC\underline{H}_3$); 0.43 (b.m., 2H, $SiC\underline{H}_2$); 1.75 (b.m., 2H, $SiCH_2C\underline{H}_2$); 3.86 (t, 2H, $C\underline{H}_2N$); 6.86 (s, 1H, $NC\underline{H}CH$); 7.05 (s, 1H, $NCHC\underline{H}$); 7.46 (s, 1H, $NC\underline{H}N$) ppm.

^{13}C NMR ($CDCl_3$) δ 0.54 (s, 1C, $Si\underline{C}H_3$); 1.11 (s, 2C, $\underline{C}H_3Si\underline{C}H_3$); 14.18 (s, 1C, $Si\underline{C}H_2$); 25.00 (s, 1C, $SiCH_2\underline{C}H_2$); 49.51 (s, 1C, $\underline{C}H_2N$); 118.64 (s, 1C, $N\underline{C}H$); 129.39 (s, 1C, $NCH\underline{C}H$); 137.03 (s, 1C, $N\underline{C}HN$) ppm.

^{29}Si NMR ($CDCl_3$) δ −20.95 (b.m., 1Si, $(CH_3)_2\underline{Si}O$); −23.05 (b.m., 1Si, $CH_3\underline{Si}CH_2$) ppm.

Found: C, 41.2; N 8.4; H 7.9.

M = 23,600 g/mol.

4.3. Synthesis of catalyst C1

Siloxane polymer P1 (0.10405 g) was dissolved in 1 mL of $CHCl_3$, and in another flask, a solution containing 0.02683 g of $PdCl_2(cod)$ in 2 mL $CHCl_3$ was prepared. The solution of the palladium complex was slowly added dropwise to the stirred solution of P1. When the entire amount of the solution was added, the product started to precipitate. Stirring continued for 30 min, after which time the product was filtered off and dried *in vacuo*.

Found: C 34.9; N 6.9; H 5.5; Pd 7.6.

^{13}C CP/MAS NMR δ 1.4 (m, 3C, $Si\underline{C}H_3$); 14.1 (s, 1C, $Si\underline{C}H_2$); 24.9 (s, 1C, $SiCH_2\underline{C}H_2$); 50.9 (s, 1C, $\underline{C}H_2N$); 120.3 (s, 1C, $N\underline{C}H$); 128.9 (s, 1C, $NCH\underline{C}H$); 139.3 (s, 1C, $N\underline{C}HN$) ppm.

^{29}Si CP/MAS NMR δ −19.3 (b.m., 2Si, $(CH_3)_2\underline{Si}O$, $CH_3\underline{Si}CH_2$) ppm.

4.4. Synthesis of catalyst C2

Catalyst C1 (0.1 g) and 2-propanol (2 mL) were added to a Schlenk tube, which was then introduced into an oil bath preheated to 60 °C. Next, 1 mL of hydrazine solution in 2-propanol (containing 0.2 mL of 80% hydrazine hydrate in 10 mL of 2-propanol) was added. The resulting solution was heated at 60 °C for 30 min, the color of the solution changing from yellow to black. Next, the solution was cooled down and evaporated to dryness *in vacuo*.

Found: C 17.5; N 14.7; H 4.8; Pd 31.5.

4.5. Synthesis of catalyst C2a

Catalyst C1 (0.1 g) and methanol (2 mL) were added to a Schlenk tube, which was then introduced into an oil bath preheated to 60 °C. Next, 0.5 cm^3 of hydrazine solution in methanol (containing 1 mL of 80% hydrazine hydrate in 10 mL of methanol) was added. The color of the solution changed from yellow to black. The resulting solution was heated at 60 °C for 30 min, cooled down, and evaporated to dryness *in vacuo*.

4.6. The Suzuki–Miyaura reaction procedure

Suzuki–Miyaura reactions were performed in a Schlenk tube. Weighed amounts of the solid reactants: phenylboronic acid (1.1 mmol; 0.135 g), KOH (1.95 mmol; 0.112 g), catalyst (1.064 mg Pd), and liquids: 2-bromotoluene (1 mmol; 0.118 mL) and 5 mL of solvent (2-propanol, 2-propanol/water mixture, or water) were introduced to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber tap and introduced into an oil bath preheated to 40 °C, 60 °C, or 80 °C. The reaction mixture was magnetically stirred at a given temperature for 1 h or 3 h and after this time cooled down. Next, organic products were separated by extraction with hexane (4 mL, 3 mL, and 3 mL). In the first extraction, 3 mL of water was added in order to facilitate the separation of phases. The combined extracts (10 mL) were GC-FID analyzed with dodecane (0.076 mL) as an internal standard to determine the conversion of 2-bromotoluene.

4.7. Separation of the catalyst and recycling

When the Suzuki–Miyaura reaction was finished, 1 mL of water was added to the reaction mixture in order to facilitate solubilization of side products. Next, all liquid components were transferred to another Schlenk tube using a U-shaped glass bridge equipped with a glass fit. The solid catalyst left in the first Schlenk tube was washed twice with 2-propanol and used in the next catalytic run with new portions of the reactants.

4.8. Application of StratoSpheres SPE resin for palladium removal

Palladium was removed from the post-reaction mixture using StratoSpheres™ resin (PL3582-CM89, Varian) with thiol groups.

5. Conclusions

It was demonstrated that palladium supported on siloxane polymer functionalized with imidazole groups efficiently catalyzes Suzuki–Miyaura reaction in environmentally friendly solvents such as water or a 2-propanol/water mixture. Very good results were obtained using conventional heating as well as microwave energy. The catalyst showed very good recyclability, demonstrated by the performance of eight successive runs with only a slight decrease in catalytic activity in the last one. Another advantage of the catalyst under study is its high activity at low temperatures, 40 or 60 °C. Excellent activity was demonstrated by the achievement of a high yield of the cross-coupling product and by high TOF values, *ca.* 25,000 h^{-1}.

The studies of the catalyst separated after the Suzuki–Miyaura reaction showed the presence of Pd(0) nanoparticles bonded to the polymer. During palladium reduction, some of the polymer was lost (polymer P1 without palladium is liquid) and the palladium content increased. The relatively mild and slow reduction in palladium took place under the Suzuki–Miyaura conditions, and consequently, palladium content increased from 7% to 12%. In contrast, application of a strong reducing agent, hydrazine, resulted in a *ca.* 40% loss of mass, and the final palladium content increased to 35%. When more hydrazine was used in methanol, agglomeration of nanoparticles started to occur.

On the basis of the experimental data, we propose that Pd(0) supported on siloxane polymer, formed under the reaction conditions, is the main catalytically active form. This conclusion is additionally corroborated by an experiment involving the application of pre-formed supported Pd(0) nanoparticles, in which high yield of the product was found.

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