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Catalysts of Suzuki Cross-Coupling Based on Functionalized Hypercrosslinked Polystyrene: Influence of Precursor Nature

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ABSTRACT. This paper describes synthesis of Pd-containing catalysts of Suzuki cross-coupling based on amino-functionalized hypercrosslinked polystyrene at variation of Pd precursor nature $(PdCl_2, PdCl_2(CH_3CN)_2 \text{ or } PdCl_2(PhCN)_2)$. The investigation of the influence of palladium oxidation state (Pd(II) or Pd(0)) and form $(Pd_n \text{ clusters or } Pd \text{ nanoparticles})$ on the rate of Suzuki cross-coupling of 4-bromoanisole and phenylboronic acid is discussed. Developed catalysts are shown to allow achieving conversion of 4-bromoanisole higher than 98% at mild reaction conditions. Independently of the precursor nature, Pd(II) is mainly responsible for observed catalytic activity. However, preliminary reduction of catalysts with H₂ results in formation of a large number of Pd_n clusters, the contribution of which in Suzuki reaction becomes predominant.

KEYWORDS. Suzuki cross-coupling; palladium; hypercrosslinked polystyrene; phenylboronic acid; 4-bromoanisole.

INTRODUCTION. Palladium-catalyzed Suzuki cross-coupling between aryl halides and arylboronic acids is one of the most widespread and effective methods of synthesis of biaryl, which are in turn important semi-products in synthesis of pharmaceuticals, ligands and polymers¹⁻³. There are more than three hundred various commercial compounds which can react Suzuki and huge diversity of Pd-containing catalysts⁴. The latter include:

(i) homogeneous Pd complexes⁵⁻⁷;

(ii) so-called ligandless catalysts containing Pd²⁺ or Pd⁰, which are Pd salts^{8,9}, Pd deposited on inorganic supports¹⁰⁻¹², Pd deposited on carbon¹²⁻¹⁵ or non-functionalized polymers¹⁶⁻

²⁰, Pd nanoparticles (NPs) stabilized in magnetically separable nanocomposites^{21,22};

(iii) Pd immobilized via ionic or covalent interactions on ligand-containing polymers (including functionalized dendrimers²³, carbon nanotubes²⁴, graphenes²⁵, resins²⁶⁻²⁹ and other polymers³⁰⁻³²) or on magnetic NPs with anchored ligands^{31, 33-36}.

Besides, one of the routes to Pd catalyst synthesis, which has recently attracted attention of scientific community and is worth to be mentioned, is so-called "green" synthesis of Pd NPs using plant extracts³⁷⁻⁴⁰, containing both stabilizing and reducing compounds, or microorganisms⁴⁰⁻⁴². Catalytic systems obtained via "green" approach were found to allow high yields of coupling products (more than 95%) at mild reaction conditions in aqueous medium and recyclability potential.

Among the polymeric materials acting as supports for Pd NPs or complexes, nitrogencontaining polymers are the most prospective ones^{30,31,43-46} due to the possibility of nitrogen to coordinate metal species and thus to prevent their leaching. However, in order to achieve appropriate catalytic activity, good swelling of polymeric matrix should be provided⁴⁴. Recently, hypercrosslinked polystyrene (HPS) was shown to be promising support for Pd NPs for different

catalytic applications^{47,48}. HPS can swell in virtually any solvent⁴⁹, reveals high mechanical and thermal stability⁵⁰, and allows controlling metal NPs growth due to the existence of rigid nanocavities.

The first application of HPS bearing amino-groups (Macronet MN100 type) for the development of the catalysts of Suzuki cross-coupling was reported by Lyubimov et al.⁵¹. Recently, we have shown that catalytic activity of Pd/MN100 system can be increased via modification of the procedure of catalyst synthesis, which allowed us to obtain small Pd NPs (about 2-4 nm in diameter) and Pd_n clusters revealing high activity in Suzuki cross-coupling⁵².

In this paper we discuss in more detail the role of Pd precursor nature in provision of observed activity of the developed Pd/MN100 catalysts in Suzuki reaction. Three types of precursors and their transformations inside the polymeric matrix of MN100 during the catalyst synthesis and testing were investigated: PdCl₂, PdCl₂(CH₃CN)₂, and PdCl₂(PhCN)₂. Catalytic properties of synthesized Pd/MN100 samples were evaluated in Suzuki cross-coupling of 4-bromoanisole (4-BrAn) and phenylboronic acid (PBA) to yield 4-methoxybiphenyl (4-MBP) (biphenyl, formed as a result of PBA homocoupling, was the side product (see Figure 1)).



Figure 1. Scheme of Suzuki Cross-Coupling of 4-BrAn and PBA

EXPERIMENTAL SECTION.

Materials. HPS Macronet MN100 (Purolite Int., UK) bearing amino-groups was washed with distilled water and acetone and dried under vacuum as described elsewhere⁵³. 4-Bromoanisole (4-BrAn, \geq 98%) was purchased from Merck KGaA. 4-Methoxybiphenyl (4-MBP, >99%) was purchased from Tokyo Chemical Industry Co. Ltd. Phenylboronic acid (PBA, 95%), diphenylamine (99%), biphenyl (99.5%), palladium(II)chloride (PdCl₂, 99%), bis(acetonitrile)palladium(II)chloride (PdCl₂(CH₃CN)₂, >99%), bis(benzonitrile)palladium(II)chloride (PdCl₂(PhCN)₂, 95%), tetrahydrofuran (THF, \geq 99.9%), ethanol (EtOH, \geq 99.8%), methanol (MeOH, 99.8%), sodium chloride (NaCl, \geq 99%), sodium carbonate (Na₂CO₃, \geq 99.5%) and sodium hydroxide (NaOH, \geq 98%) were obtained from Sigma-Aldrich. All chemicals were used as received. Distilled water was purified with an Elsi-Aqua

water purification system.

Catalyst Synthesis. Series of Pd-containing HPS-based catalysts was synthesized via wetimpregnation method according to the procedure described elsewhere⁵³. In a typical experiment, 1 g of pretreated, dried and crushed (<63 μ m) granules of MN100 were impregnated with 2.8 mL of the THF solution of precursor (PdCl₂(CH₃CN)₂ or PdCl₂(PhCN)₂) of a certain concentration. The Pd-containing polymer was dried at 70°C, treated with 2.7 mL of Na₂CO₃ solution (concentration 0.07 mol/L) and dried until the constant weight was achieved. After that the catalyst was washed with distilled water till neutral pH and dried at 70°C.

In the case of PdCl₂, the synthesis procedure was similar, but the complex solvent THF/MeOH/H₂O was used (at a ratio of 8 : 1 : 1) instead of pure THF or pure water (see e.g. ref. 51). Besides, NaCl (1.5 molar excess with respect to palladium chloride) was added to the

precursor solution in order to obtain Na₂PdCl₄ that has better solubility in comparison with pure PdCl₂.

Thus the following catalysts were synthesized (see Table 1, palladium content was confirmed by the elemental analysis):

Table 1. Pd Content in Pd/MN100 Samples

Sample designation	Pd precursor	Pd content, ± 0.05 wt.%
Pd/MN100-1	PdCl ₂	2.25
Pd/MN100-2	PdCl ₂ (CH ₃ CN) ₂	1.54
Pd/MN100-3	PdCl ₂ (PhCN) ₂	2.05

Besides, for all the synthesized catalyst preliminarily reduction in hydrogen flow at 275°C for 2 h was carried out (the catalysts were designated as Pd/MN100-1-R, Pd/MN100-2-R and Pd/MN100-3-R, respectively).

Catalytic Testing. Testing of HPS-based catalysts was carried out in a 60 mL isothermal glass batch reactor at vigorous stirring at a temperature of 60°C. The total volume of liquid phase was 30 mL. EtOH/water mixture at the volumetric ratio of 5 : 1 was used as a solvent. NaOH was used as a base at the quantity of 1.5 mmol. In each experiment the quantity of 4-BrAn was equal to 1 mmol, 1.5 molar excess of PBA was used. Catalyst loading in each experiment was 50 mg. Before the catalyst addition in the reactor, in each experiment the blank test (duration of 60 min) was carried out in order to ensure that the reaction not proceeded at the absence of catalyst.

Samples of reaction mixture were periodically taken and analyzed via GC-MS (Shimadzu GCMS-QP2010S) equipped with a capillary column HP-1MS ($30 \text{ m} \times 0.25 \text{ mm}$ i.d., 0.25 µm

film thickness). Helium was used as a carrier gas at pressure of 74.8 kPa and linear velocity of 36.3 cm/s. Oven temperature was programmed: $120^{\circ}C (0 \text{ min}) \rightarrow 10^{\circ}C/\text{min} (160^{\circ}C) \rightarrow 25^{\circ}C/\text{min} (300^{\circ}C) \rightarrow 300^{\circ}C (2.4 \text{ min})$. Temperature of injector, interface and ion source was $260^{\circ}C$, range from 10 up to 500 m/z. The concentrations of the reaction mixture components were calculated using the internal standard calibration method (diphenylamine was used as an internal standard).

Catalytic activity was defined as $R = N_{4-BrAn} \times N_{Pd}^{-1} \times \tau^{-1} \times X$, where N_{4-BrAn} and N_{Pd} are number of moles of 4-BrAn and Pd, respectively; *X* is conversion of 4-BrAn, and τ is the reaction time for achieving of conversion *X*.

Catalyst Characterization. Pd/HPS catalysts were characterized by liquid nitrogen physisorption, X-Ray Fluorescence Analysis (XFA), X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM).

Liquid nitrogen physisorption was carried out using Beckman Coulter SA 3100 (Coulter Corporation, USA). Prior to the analysis, samples were degassed in Becman Coulter SA-PREP at 120°C in vacuum for 1 h. Weight of each sample was above 0.1 g. The following models were used for calculation of specific surface area (SSA) and pore size distribution: Langmur, Brunauer-Emmett-Teller (BET), t-Plot, Barrett-Joyner-Halenda (BJH). Pore size distribution was measured in the range of 3-200 nm. Microporosity was estimated using t-plot model.

X-ray fluorescence analysis (XFA) was carried out to determine the Pd content. It was performed with a Zeiss Jena VRA-30 spectrometer (Mo anode, LiF crystal analyzer and SZ detector). Analyses were based on the Co K α line and a series of standards prepared by mixing 1 g of polystyrene with 10-20 mg of standard compounds. The time of data acquisition was constant at 10 s.

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X-ray photoelectron spectroscopy (XPS) data were obtained using Mg K α (hv = 1253.6 eV) radiation with ES-2403 spectrometer (Institute for Analytic Instrumentation of RAS, St. Petersburg, Russia) equipped with energy analyzer PHOIBOS 100-MCD5 (SPECS, Germany) and X-Ray source XR-50 (SPECS, Germany). All the data were acquired at X-ray power of 250 W. Survey spectra were recorded at an energy step of 0.5 eV with an analyzer pass energy 40 eV, and high resolution spectra were recorded at an energy step of 0.05 eV with an analyzer pass energy 7 eV. Samples were allowed to outgas for 180 min before analysis and were stable during the examination. The data analysis was performed by CasaXPS.

Transmission electron microscopy (TEM) characterization was provided using a JEOL JEM1010 instrument at electron accelerating voltage of 80 kV. Samples were prepared by embedding the catalyst in epoxy resin with following microtomming at ambient temperature. Images of the resulting thin sections (*ca*. 50 nm thick) were collected with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

RESULTS AND DISCUSSION. The results of catalytic testing of both the unreduced samples and the samples treated in hydrogen flow are presented in Table 2 and in Figure 2. It is noteworthy that for the unreduced Pd/MN100 catalysts (Table 2, #1-3), the data on the mean diameter of Pd NPs are provided after the 1st run in Suzuki reaction due to the fact that in some cases no NPs were found in the freshly prepared samples.

As it can be seen, the catalytic activity of unreduced samples is quite different depending on the Pd precursor nature (the highest yield of 4-MBP was found for MN100 impregnated with PdCl₂(CH₃CN)₂ (Table 2, #2; Figure 2 (a))), but it seems that there is no dependence on the mean diameter of palladium NPs observed after the catalytic use in Suzuki reaction. In the case

of the catalysts preliminarily reduced in H₂ flow, the best results regarding to the 4-MBP yield were observed for Pd/MN100-3-R (Table 2, #6; Figure 2 (b)) impregnated with PdCl₂(PhCN)₂, though catalytic activity of Pd/MN100-3-R, calculated with respect to palladium content, was the same as for Pd/MN100-2-R. Surprisingly, the lowest yield of 4-MBP (44.7%) was found for Pd/MN100-1-R in spite of the formation of relatively small Pd NPs.

		Mean diameter	Conversion	Yield of 4-	Yield of	
N	Sample	of Pd NPs, nm	of 4-BrAn,	MBP,	BP,	R, $\pm 0.1 \text{ min}^{-1}$
		(TEM data)	$\pm 0.5\%$ *	$\pm 0.5\%$ *	$\pm 0.5\%$ *	
		Multimodal NP				
		size distribution				
1	DJ/MN1100 1	(see Fig. 3 and	64.2	62.6	1.6	1.0
1	Pd/MIN100-1	Fig. 4) with	04.2	02.0	1.0	1.0
		aggregates up to				
		19.3 nm in size				
2	Pd/MN100-2	4.3 ± 1.2	98.4	93.1	5.3	2.4
3	Pd/MN100-3	3.7 ± 2.1	82.0	79.5	2.5	1.4
4	Pd/MN100-1-R	2.5 ± 0.7	45.1	44.7	0.4	0.7
5	Pd/MN100-2-R	2.8 ± 0.6	58.4	57.5	0.9	1.2
6	Pd/MN100-3-R	3.2 ± 1.9	63.8	62.5	1.3	1.1

Table 2. Results of Testing of Pd/MN100 Catalysts

* After 60 min of reaction duration

Figure 3 shows TEM images of the Pd/MN100 samples: after the 1st use in Suzuki reaction (Figure 3 (a), (b) and (c)) and preliminarily reduced in hydrogen flow (Figure 3 (d), (e) and (f)). Obviously in the case of Pd/MN100-1 catalyst synthesized while using PdCl₂ as a precursor, rather big particles and irregular aggregates were formed after the Suzuki reaction (Figure 3 (a)) that is likely due to the tendency of PdCl₂ to form chains of [PdCl₂]_n and to aggregate. This observation is in consistent with previously reported data⁵³. Earlier we have shown that huge Pd

NPs (more than 35 nm in diameter) can be formed during liquid-phase *in situ* reduction in the reaction of selective hydrogenation of triple bond⁵³.



Figure 2. Kinetic Curves Obtained While Using Unreduced (a) and Preliminarily Reduced (b) Pd/MN100 Samples in Suzuki Cross-Coupling of 4-BrAn and PBA

From the data presented in Figure 4 (a) it can be also seen that the sample Pd/MN100-1 has multimodal particle size distribution with the particle sizes up to 19.3 nm. In the case of catalyst Pd/MN100-2 synthesized while using PdCl₂(CH₃CN)₂ as a precursor, mean diameter of Pd NPs formed after cross-coupling of 4-BrAn and PBA was 4.3 ± 1.2 nm (see Figure 3 (b)). It is noteworthy that in the case of this catalyst there is also visible fraction of small Pd NPs with the sizes below 2 nm (Figure 4 (a)), which can be responsible for the observed activity in Suzuki reaction. For the catalyst Pd/MN100-3 impregnated with PdCl₂(PhCN)₂, Pd NPs with mean diameter of 3.7 ± 2.1 nm were formed (see Figure 3 (c)). In this case, broader particle size distribution can be noted, and, in contrast to Pd/MN100-2, additional slight mode can be found in the range of Pd NP sizes of 7-11 nm (see Figure 4 (a)).





Figure 3. TEM Images of Pd/MN100 Samples Taken After the 1st Run in Suzuki Cross-

Coupling (a, b, c) and Preliminarily Reduced in Hydrogen Flow (d, e, f)



Figure 4. Comparison of Particle Size Distributions for the Samples Taken after the 1st Run in Suzuki Cross-Coupling (a) and for the Samples Preliminarily Reduced in Hydrogen Flow (b)

For the preliminarily reduced samples (Figure 3 (d), (e) and (f)), the treatment in hydrogen flow at 300°C allowed formation of Pd NPs with the diameters of about 2-3 nm independently on the precursor nature. Thus considering the NP sizes it is not possible to explain observed difference in catalytic behavior of the catalysts of Pd/MN100-R series. Moreover, for the most active Pd/MN100-3-R the broadest particle size distribution can be seen (Figure 4 (b)) that contradicts to the data of catalytic testing.

That is why we used other analysis methods (low-temperature nitrogen physisorption and XPS) in order to find if there any additional explanation to the observed results.

The results of low-temperature nitrogen physisorption are shown in Table 3. The BET SSA of MN100 after impregnation with Pd precursors changed slightly indicating that negligible blockage of pores took place after incorporation of Pd compound.

The only exception was $PdCl_2(PhCN)_2$, the impregnation of which resulted to the noticeable drop of BET SSA from 724 m²/g to 530 m²/g that is likely due to the existence of relatively large benzonitrile ligand, which blocks mainly micropores of HPS and is eliminated during the reduction in hydrogen flow.

	SSA	, m ² /g	Micropore volume, mL/g		
Sample —	BET	t-plot	(t-plot model)		
MN100	724	189 ^{a)} ; 603 ^{b)}	0.48		
Pd/MN100-1	669	159 ^a); 566 ^b)	0.41		
Pd/MN100-1-R	747	165 ^a); 643 ^b)	0.45		
Pd/MN100-2	706	130 ^a); 599 ^b)	0.41		
Pd/MN100-2-R	698	118 ^{a)} ; 603 ^{b)}	0.39		
Pd/MN100-3	530	128 ^a); 444 ^b)	0.33		
Pd/MN100-3-R	710	146 ^{a)} ; 627 ^{b)}	0.42		

Table 3. SSA of MN100 and Pd/MN100 Catalysts

^{a)} external SSA

^{b)} SSA of micropores

XPS data revealed that the surface of freshly prepared Pd/MN100 catalysts contains chlorine, carbon, oxygen, nitrogen and palladium which match the combination of the Pd precursor and HPS. In the case of the catalysts examined after the use in the Suzuki reaction, the surface of samples was found to contain also sodium, boron and bromine in the quantities less than

0.6 at.%, which indicates that during the reaction negligible adsorption of the reaction mixture components in HPS has occurred.

Composition of palladium species found on the catalyst surface according to the high resolution Pd 3d spectra (for details see Supporting Information, Figure S1-S9) as well as corresponding values of the binding energy of Pd $3d_{5/2}$ is shown in Table 4. Binding energy of pure PdCl₂(CH₃CN)₂ was found to be equal 338.7 eV.

Table 4. Chemical States of Pd Found as a Result of Modelling of the Pd 3d Band on theSurface of Pd/MN100 Samples

		Pd Content	Compo-		
C 1 -	Pd	4 1	.:	Chemical State	$E_{b} \pm 0.1$,
Sample	Precursor	on the	sition,	of Pd ^{54,55}	eV Pd 3dep
	Treeuisor	Surface, at.%	at.%	0110	ev , 1 u 5 u _{5/2}
			69.8	$PdCl_2$	337.8
Pd/MN100-1		0.45	14.6	Pd^0	335.0
			15.6	Clusters Pd _n	336.1
	D4C1	1 43	43.5	PdCl ₂	337.8
Pd/MN100-1-			32.9	$\mathbf{P}\mathbf{d}^0$	335.2
after the 1 st use	I del2	1.75	52.)	1 u	555.2
			32.6	Clusters Pd _n	336.5
	-		28.0	PdCl ₂	337.7
Pd/MN100-1-R		0.33	49.5	Pd^{0}	335.0
			22.5	Clusters Pd _n	336.1
Pd/MN100-2	PdCl ₂ (CH ₂ CN) ₂	0.34	29.2	PdCl ₂ (CH ₃ CN) ₂	338.6
1 W/1911 1 0 0 - 2		0.54	55.8	PdCl ₂	337.7

			15.0	Clusters Pd _n	336.1
	-		1.2	PdCl ₂ (CH ₃ CN) ₂	338.8
Pd/MN100-2-	0.60		50.0	PdCl ₂	337.7
after the 1 st use		0.60	0.3	Pd^{0}	335.2
			48.5	Clusters Pd _n	336.1
	-		15.1	PdCl ₂ (CH ₃ CN) ₂	338.8
		0.21	7.10	PdCl ₂	337.7
Pd/MN100-2-K			35.8	Pd^{0}	335.2
			42.0	Clusters Pd _n	336.4
			73.3	PdCl ₂	337.8
Pd/MN100-3		0.32	18.2	Pd^0	335.0
			8.5	Clusters Pd _n	336.
	-		48.0	PdCl ₂	337.2
Pd/IVIIN100-3-	PdCl ₂ (PhCN) ₂	0.51	39.5	Pd^{0}	335.2
after the 1 st use			16.1	Clusters Pd _n	336.2
	-		21.1	PdCl ₂	337.
Pd/MN100-3-R		0.21	38.0	Pd^{0}	335.2
			40.9	Clusters Pd _n	336.2

The existence of PdCl₂ in freshly prepared catalysts can be ascribed to the removal of acetonitrile and benzonitrile ligands in PdCl₂(CH₃CN)₂ and PdCl₂(PhCN)₂, respectively, due to partial or complete hydrolysis of the precursor inside the HPS matrix during the impregnation process.

Besides, on the surface of the samples impregnated with $PdCl_2$ and $PdCl_2(PhCN)_2$, Pd(0) NPs (binding energy of 335.0 eV) and small Pd_n clusters (binding energy of 336.1 eV) were also found that can be due to the partial reduction of Pd during the catalyst synthesis (Table 4).

It should be mentioned that no products of chemical interaction of palladium with aminogroups of MN100 were found. Nitrogen of synthesized catalysts with binding energy of N 1s equal to 400.0 ± 0.1 eV was revealed to belong to the amino-groups of MN100.

For all the catalysts, after the first use the percentage of Pd(II) decreased in 1.5-1.7 times. These changes were in line with an approximately 2-3-fold increase of the total percentage of Pd_n clusters and Pd NPs (see the data of TEM study). It is noteworthy that in the case of the catalyst Pd/MN100-2 impregnated with PdCl₂(CH₃CN)₂ no Pd NPs were found in freshly prepared sample. Moreover, after the first use of Pd/MN100-2 in Suzuki reaction the percentage of Pd_n clusters increased in 3.2 times, while the percentage of Pd NPs was negligible (only 0.3at.%). This observation is in accordance with TEM data (see Figure 3 (b)) revealing that even after the reaction, only few NPs can be found in the catalyst impregnated with PdCl₂(CH₃CN)₂ though the particle size distribution was quite similar to other two samples (Figure 4 (a)). This fact can explain higher activity of Pd/MN100-2 catalyst in comparison with other HPS-based samples.

Such interplay between different forms of Pd participating in Suzuki reaction is typical for cross-coupling processes. In this relation, two mechanisms were proposed³: (i) heterogeneous (when low-coordinate Pd atoms of NPs are responsible for catalytic activity, and adsorption of aryl halide on Pd NP surface is necessary step); (ii) homogeneous (when leached Pd is the most active one). So depending on the catalyst type (unreduced, containing Pd(II), or preliminarily reduced in hydrogen flow, containing Pd(0) NPs), one of two mechanisms can prevail. It should

be noted that small Pd clusters formed *in situ* are likely the most active Pd species¹⁴ participating in cross-coupling reactions according to the mechanism of (ii) type.

For the most promising sample – Pd/MN100-2, the shift of mean diameter of Pd NPs, which were formed at the first run in Suzuki reaction, to the higher values observed at the second run (from approximately 4 nm up to *ca*. 7 nm) as well as broadening of particle size distribution were shown during one of our previous studies⁵². Thus so-called Ostwald ripening likely took place due to the redistribution between different forms of Pd and transformation of the part of Pd(0) belonging to small clusters to Pd(II) followed by precipitation of Pd(II) on Pd NPs. While for the preliminarily reduced Pd/MN100-2-R sample, slight decrease of the mean diameter of Pd NPs was found (from 2.8 nm to 2.4 nm) after the first use in Suzuki cross-coupling accompanied by the increase of the share of Pd clusters on the catalyst surface. That can be due to the partial transfer of Pd(0) to Pd(II) and its further partial reprecipitation.

It should be also noted that after the Suzuki cross-coupling the surface content of Pd increased for all the samples that was likely due to the process of Pd leaching, which resulted in migration of Pd from the polymer volume to its surface. At the same time the total content of Pd in the catalysts taken after the first run in Suzuki cross-coupling decreased by about 0.4-0.5 wt.% independently on the precursor nature for all the unreduced samples, and by 0.1-0.2 wt.% for the catalysts preliminarily reduced in hydrogen flow.

We tried to find any correlation between the content of different forms of Pd on the surface of synthesized unreduced catalysts taken after the reaction and observed conversion of 4-BrAn. It is obvious that the lower the content of Pd NPs the higher the conversion (Figure 5 (a)), but as for other Pd forms it seems that there is no dependence. However, assuming that Pd(II) can serve as an effective source of Pd clusters formed quickly *in situ* and being the most active catalytic

specie in the case of unreduced samples, it was found that there is straight correlation between the conversion of 4-BrAn and the ratio of Pd(II) to the sum of Pd_n clusters and Pd NPs on the catalyst surface: the higher this ratio the higher the reaction rate (Figure 5 (b)).



Figure 5. Dependence of Conversion of 4-BrAn on the Pd Composition on Catalyst Surface (a) and on the Ratio of Pd(II) to the Sum of Pd_n Clusters and Pd NPs (b)

In the case reduced catalysts, all the above mentioned forms of Pd were found (Pd(II), Pd_n clusters and Pd NPs) that means that incomplete reduction took place, which can be ascribed to the influence of the HPS polymeric matrix (Table 4).

While taking in account the same assumption as in the case of unreduced catalysts, it was found that the opposite correlation took place (Figure 6 (a)): the higher the Pd(II) content the lower the conversion. Thus it can be concluded that the active specie was either Pd_n clusters or Pd NPs. We proposed Pd_n clusters to be responsible for observed catalytic activity. As it can be seen from Figure 6 (b) there is strong correlation between the ratio of Pd_n clusters to Pd NPs on the catalyst surface, and indeed small clusters of palladium were the main active form.

 That is why there was no dependence between the data of TEM (see Figure 4 (b)) for the preliminarily reduced Pd/HPS catalysts and observed difference in conversion of 4-BrAn (Table 2).



Figure 6. Dependence of Conversion of 4-BrAn on the Ratio of Pd(II) to the Sum of Pd_n Clusters and Pd NPs (a) and on the Ratio of Pd_n Clusters to Pd NPs

CONCLUSIONS. Pd-containing catalysts based on amino-functionalized HPS of MN100 type were shown to be promising for Suzuki cross-coupling: 98.4% conversion of aryl halide was achieved for the freshly prepared (unreduced) Pd/MN100-2 catalyst impregnated with PdCl₂(CH₃CN)₂. This Pd precursor resulted in better catalytic activity among the unreduced samples that was likely due to the less hydrolysis and precipitation of PdCl₂(CH₃CN)₂ in comparison with PdCl₂ and PdCl₂(PhCN)₂, which in turn caused the absence of Pd NPs in the case of Pd/MN100-2. However, independently of the precursor nature, Pd(II) was assumed to be the direct source of the main catalytically active form of Pd (Pd clusters formed *in situ*) in the case of unreduced sample. For the samples, which were preliminarily reduced in hydrogen flow, the use of the HPS support allowed formation of a large number of Pd NPs as well as of Pd_n

clusters, and the latter were found to be responsible for the observed activity of reduced Pd/MN100 catalysts in cross-coupling of 4-BrAn and PBA.

ASSOCIATED CONTENT

Supporting Information. The data of XPS analysis are presented. Survey spectra and high resolution spectra of Pd 3d for all the catalysts discussed in the paper (freshly prepared; taken after the Suzuki reaction; and preliminarily reduced in hydrogen flow) are shown in Figures S1-S9.

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Notes

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ABBREVIATIONS

NP, nanoparticle; HPS, hypercrosslinked polystyrene; 4-BrAn, 4-bromoanisole; PBA,

phenylboronic acid; 4-MBP, 4-methoxybiphenyl.

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