

Research Article

Pd Nanoparticles Stabilized by Hypercrosslinked Polystyrene Catalyze Selective Triple C-C Bond Hydrogenation and Suzuki Cross-Coupling

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This paper describes the synthesis of Pd-containing catalysts based on nonfunctionalized hypercrosslinked polystyrene via impregnation with Pd acetate. Developed Pd nanoparticulate catalyst allowed achieving conversion of aryl halide up to 90% in Suzuki cross-coupling reaction under mild conditions and at the absence of phase-transfer agents. During the selective hydrogenation of triple C-C bond of 2-methyl-3-butyn-2-ol, up to 96% selectivity with respect to corresponding olefinic alcohol was found at 95% conversion. The influences of the procedure of catalyst synthesis like precursor decomposition and reductive activation method on Pd nanoparticle formation are discussed.

1. Introduction

Metal nanoparticles (NPs) have unique catalytic properties due to a high ratio of surface-to-total atoms allowing a high number of reactive sites [1]. Catalytic properties of NPs depend on their size, size distribution, and environment provided by support [2, 3]. The most important issue arising while developing nanoparticulate catalysts is control over NP sizes and morphology as well as prevention of their aggregation and leaching. Besides, low-cost, reproducible, and scalable synthetic approaches to the synthesis of catalytic NPs are of great importance [4]. Among the diverse catalytic materials, supported metal NPs are the most widely studied and extensively employed in industrial processes [5]. In particular, reactions catalyzed by Pd NPs are widespread in fine organic synthesis and the polymer-supported are one of the

most prospective [6]. For understanding of the behavior of polymer-based palladium catalyst, the role of support should be carefully analyzed since the formation of NPs in nanostructured polymeric environment controls over NP size and size distribution stabilizing them but also may strongly influence the surface of NPs [6]. There are several approaches to the synthesis of Pd NPs using polymers: (i) formation of colloid metal NPs stabilized by block copolymer micelles; (ii) formation of metal NPs in ultrathin polyelectrolyte layers or brushes; and (iii) formation of metal NPs into the cavities (pores) of 3D polymeric networks [7, 8]. Among numerous supports, rigid nanostructured polymers such as hypercrosslinked polystyrene (HPS) can be considered the most promising. Recently, we have shown that the HPS of MN100 type bearing amino groups can be used as a support for

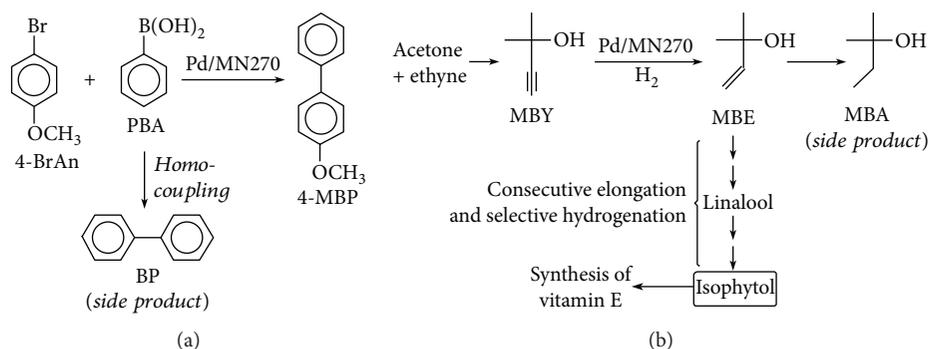


FIGURE 1: Reaction schemes of Suzuki cross-coupling of 4-BrAn and PBA (a) and selective hydrogenation of MBY (b).

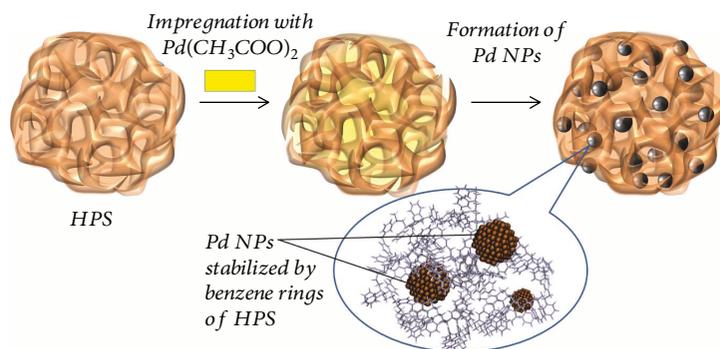


FIGURE 2: General scheme of Pd/HPS catalyst synthesis.

palladium NPs and clusters to catalyze effectively Suzuki reaction [9] and selective hydrogenation of triple bond in alkynols [10].

This work is devoted to the study of Pd-containing catalysts synthesized via impregnation of nonfunctionalized HPS of MN270 type by Pd acetate. We aimed at answering the questions regarding Pd NP formation and catalytic behavior of the Pd/MN270 system, in particular, (i) does the chosen combination of palladium precursor and the polymer support of the reduction step really matter, and (ii) does alkali metal addition to the catalyst composition improve catalytic properties of Pd/MN270 in C-C triple bond hydrogenation as it was observed [8] for Pd/MN100 catalytic system?

2. Materials and Methods

2.1. Materials. HPS Macronet MN270 (Purolite Int., UK) was washed with distilled water and acetone and dried under vacuum as described elsewhere [11]. 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%) (internal standard), biphenyl (BP, 99.5%), 2-methyl-3-butyn-2-ol (MBY, $>99\%$), 2-methyl-3-buten-2-ol (MBE, $>97\%$), 2-methyl-2-butanol (MBA, $>96\%$), tetrahydrofuran (THF, $\geq 99.9\%$), toluene (99.8%), ethanol (EtOH, $\geq 99.8\%$), sodium carbonate (Na₂CO₃, $\geq 99.5\%$), and sodium hydroxide (NaOH, $\geq 98\%$) were obtained from Sigma-Aldrich. Palladium acetate (Pd(CH₃COO)₂, Pd content 47.68%) was purchased from JSC “Aurat” (Moscow, Russian Federation).

All chemicals were used as received. Distilled water was purified with an Elsi-Aqua water purification system.

2.2. Catalyst Synthesis. HPS-based Pd-containing catalyst with calculated metal loading 1.5 wt.% was synthesized via conventional wet impregnation according to the procedure, which we described earlier elsewhere [9–12]. In a typical experiment, 1 g of pretreated (washed with distilled water and then with acetone), dried, and crushed ($<70\ \mu\text{m}$) granules of HPS was impregnated with 2.7 mL of the Pd(CH₃COO)₂ THF solution (concentration 0.058 mol/L). The Pd-containing polymer was dried at 70°C, treated with 2.7 mL of Na₂CO₃ aqueous solution (concentration 0.035 mol/L), and dried until a constant weight was achieved. The catalyst was washed with distilled water until neutral pH and dried at 70°C. Catalyst was designated as Pd/MN270-NaW, where “Na” indicates treatment with sodium carbonate and “W” indicates washing until neutral pH. The aim of treatment with Na₂CO₃ was the decomposition of Pd precursor and acceleration of Pd precipitation in the form of PdO or Pd NPs inside the HPS pores. The catalyst was tested in Suzuki cross-coupling between 4-BrAn and PBA (Figure 1(a)) and selective hydrogenation of the C-C triple bond of MBY (Figure 1(b)). The reactions are industrially important, for example, as a semiproduct of fragrant synthesis and fat-soluble vitamins [13]. It is important to underline that catalyst was used either as synthesized or after preliminary gas-phase reduction (Figure 2) in hydrogen (flow rate 100 mL/min, temperature 300°C, 2 h). In the latter case, the catalyst was designated as Pd/MN270-NaW-H₂. Additionally, in the case of MBY hydrogenation, the in situ treatment

with hydrogen at reaction conditions during 60 min (liquid-phase reduction) was applied in order to ensure the formation of Pd NPs before the reaction starts.

2.3. Catalyst Testing. Catalytic testing of synthesized HPS-based samples was carried out in a 60 mL isothermal glass batch reactor installed in a shaker at vigorous stirring (more than 800 two-sided sharing per minute), which avoids external diffusion limitation. The internal diffusion limitations were also excluded via crashing of HPS up to the size less than 70 μm . The total volume of liquid phase was 30 mL. A recirculating bath (LOIP LT 100, Saint-Petersburg, Russia) was used to stabilize the reaction temperature within $\pm 1^\circ\text{C}$ with water as a heating medium.

Liquid-phase hydrogenation of MBY was carried out at 90°C using toluene (30 mL) as a solvent. The reactor in this case was connected to a gasometrical burette for on-line hydrogen consumption control. At the beginning of each experiment, the temperature was set and allowed to stabilize (ca. 30 min), the reactor was charged with catalyst (Pd quantity was 0.0019 mmol), and hydrogen was then introduced for liquid-phase catalyst activation during 60 min. Then MBY (17.85 mmol) was introduced and the reaction started. Samples of the reaction mixture were analyzed via GC (Kristallux 4000 M) equipped with FID and capillary column ZB-WAX (60 m \times 0.53 mm i.d., 1 μm film thickness). Retention times for MBY, MBE, and MBA are 3.81 min, 2.52 min, and 2.39 min, respectively. Helium was used as a carrier gas. The concentrations of the reaction mixture components were calculated using an absolute *calibration* method.

Suzuki cross-coupling was carried out in the same set-up but under an inert atmosphere (nitrogen). Mixture of EtOH and water (EtOH: H₂O vol. ratio = 5) was used as a solvent (30 mL). In each experiment, the quantity of 4-BrAn was equal to 1.00 mmol with a 1.5 molar excess of PBA. Pd quantity was 0.0066 mmol. Before the catalyst addition in the reactor (time “zero,” $t = 0$ for the reaction), in each experiment, the control experiment (duration of 60 min) was carried out in order to ensure that the reaction does not take place in the absence of a catalyst. A noninvasive liquid sampling system allowed a controlled removal of aliquots (0.1–0.5 cm³) from the reactor by the syringe and analyzed via GC-MS (Shimadzu GCMS-QP2010S) equipped with a capillary column HP-1MS (30 m \times 0.25 mm i.d., 0.25 μm film thickness). Helium was used as a carrier gas. The concentrations of the reaction mixture components were calculated using the internal standard (diphenylamine) *calibration* method. Retention times for 4-BrAn, BP, diphenylamine, 4-MBP, and PBA are 3.05 min, 4.58 min, 6.05 min, 6.31 min, and 9.67 min, respectively.

2.4. Catalyst Characterization

2.4.1. X-Ray Photoelectron Spectroscopy (XPS). XPS data were obtained using Mg K α ($h\nu = 1253.6$ eV) radiation with an 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 an X-ray power of 250 W. Survey spectra were recorded at an energy step of 0.5 eV with analyzer pass energy 40 eV, and high resolution spectra were recorded at an energy step of 0.05 eV with 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.

2.4.2. Transmission Electron Microscopy (TEM). Pd NP sizes were evaluated by TEM using a JEOL JEM1010 instrument at an electron accelerating voltage of 80 kV. Samples were prepared by embedding the catalyst in epoxy resin following microtoming (ca. 50 nm thick) at ambient temperature. Images were obtained with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

2.4.3. Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy. DRIFT spectra were recorded in the range of 4000–500 cm⁻¹ with the step 4 cm⁻¹ using an IRPrestige-21 spectrophotometer equipped with a DRS-8000 diffuse reflectance accessory (Shimadzu, Japan). The material of the mirror of the optical system of DRS-8000 was used as a background.

3. Results and Discussion

3.1. Catalyst Characterization. TEM investigation of Pd/MN270-NaW showed that independently of the reduction method (gas-phase reduction in hydrogen flow or liquid-phase reduction in situ, which was also applied along with the H₂ gas-phase reduction in the case of MBY hydrogenation), impregnation of MN270 with Pd(CH₃COO)₂ results in the formation of relatively small Pd NPs with a mean diameter of ~3–5 nm (see Figures 3(b) and 3(d)). Interesting in the catalyst taken after the reaction of Suzuki cross-coupling, Pd NPs with a mean diameter of 3.7 ± 0.7 nm were found (Figure 3(a)) being about the same as in the case of preliminarily reduced sample (see Figure 3(c)). This observation also shows the ability of HPS of controlling to some extent the process of Pd NP formation probably as a result of the transmetalation step involved in a mechanism [14] of Suzuki cross-coupling.

For as-synthesized catalysts, the XPS data revealed that the surface of all the samples contains chlorine (remained in a traces after the HPS synthesis), carbon, oxygen, and Pd. The following components were found on the surface of unreduced catalysts: Pd(CH₃COO)₂, PdO, small Pd_n clusters ($n \leq 13$) [15], and Pd NPs. The presence of PdO in the catalyst composition is due to the precursor decomposition during the catalyst synthesis and/or to the partial oxidation of the surface of Pd NPs since the catalysts were synthesized and stored in air. It is worthy to note that the HPS structure remains stable during the impregnation with Pd acetate as well as during the catalyst reduction (see the results of DRIFT spectroscopy in Supporting Materials, Figure S1). Values of binding energy of Pd 3d_{5/2} obtained from high resolution spectra (Figure S2) of differently synthesized samples are presented in Table 1.

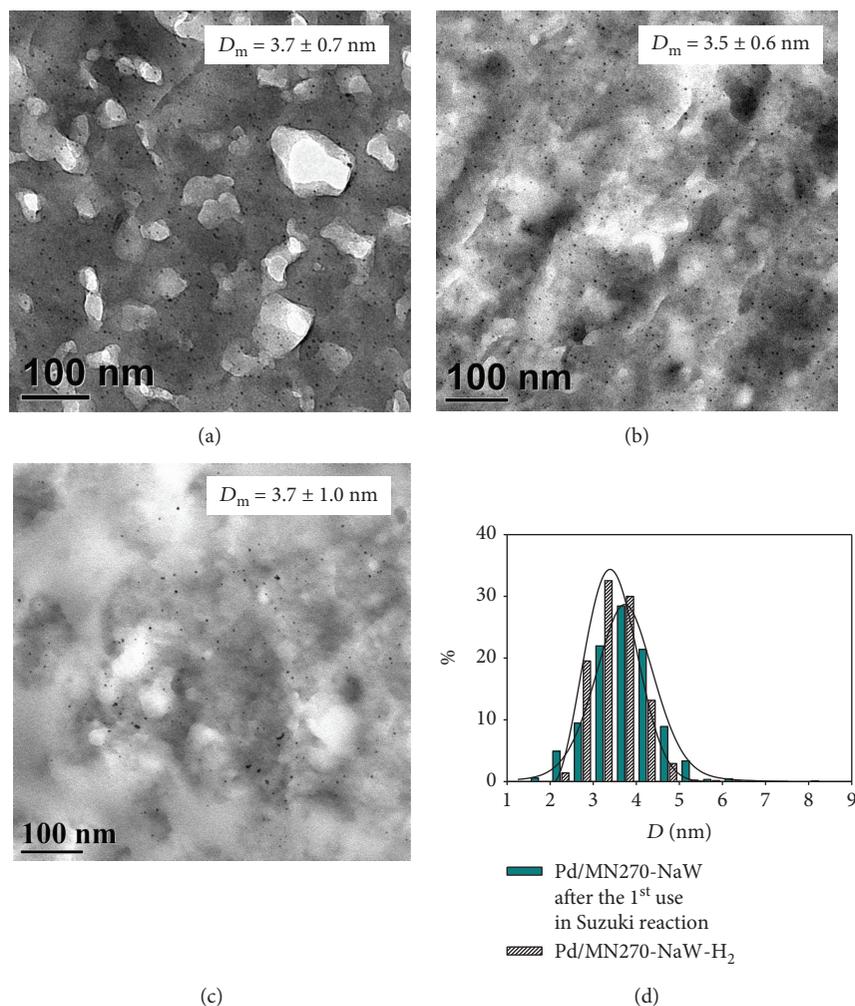


FIGURE 3: TEM images of Pd/MN270-NaW (taken after the first use in Suzuki reaction (a), preliminarily reduced in hydrogen flow (b), and taken after liquid-phase reduction in situ at conditions of MBY hydrogenation (c)) and comparison of NP size distributions (d).

As it can be seen from the XPS data (Table 1), preliminarily treatment of the catalyst with sodium carbonate accelerates the precursor decomposition and formation of metal NPs during the subsequent reduction in hydrogen flow. The fact that mainly PdO is on the surface of reduced Pd/MN270-NaW- H_2 can be ascribed to the partial oxidation of NP surface after exposition of the catalyst in air. We believe that since PdO is positioned on the particle surface, it is more accessible for XPS analysis than Pd(0).

3.2. Suzuki Cross-Coupling. Results of catalytic testing of Pd/MN270-NaW and Pd/MN270-NaW- H_2 samples in a model reaction of Suzuki cross-coupling of 4-BrAn and PBA (Figure 1(a)) are presented in Figure 4. After 1 h of reaction, conversion of 4-BrAn reached 90.0% and 79.4% for Pd/MN270-NaW and Pd/MN270-NaW- H_2 , respectively. Selectivity to 4-MBP was about the same for both samples: 97.8% and 98.1% with BP formed as by-product.

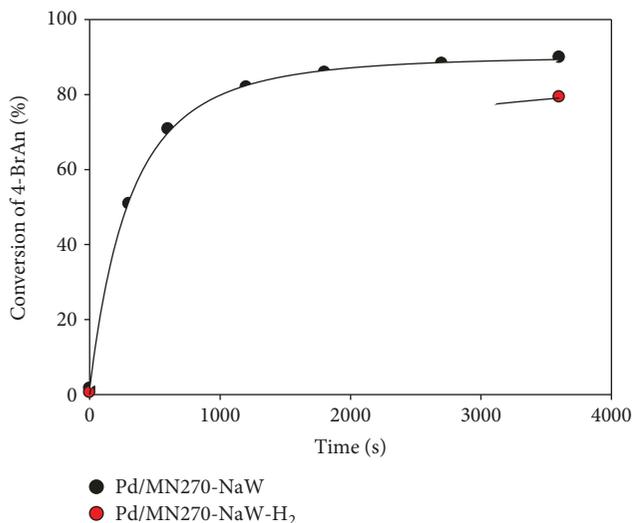
Generally, it is accepted that virtually any form of Pd (Pd^{2+} , Pd(0) in clusters or NPs) can catalyze the cross-coupling since this process involves the cycle of Pd

oxidation-reduction during catalysis [17]. Recently, we have shown [9] that 98.4% conversion of 4-BrAn can be achieved after 1 h using unreduced HPS of MN100 type impregnated with $PdCl_2(CH_3CN)_2$ and containing about 85% of Pd(II) without any bulk Pd(0) corresponding to NPs. In the case of Pd/MN100, the process of NP formation is relatively slow, possibly due to the strong interaction of MN100 with Pd salt. In contrast, for Pd/MN270-NaW, a fast Pd precipitation in the form of numerous NPs takes place (see Figure 3(a)) and conversion of 4-BrAn reached only 90%. The reduction of Pd/MN270-NaW in gaseous hydrogen diminished further the catalyst efficiency allowing conversion only about 80% after 1 hour of reaction.

At the same time, to the best of our knowledge, for preliminarily reduced catalysts [9], Pd NPs serve as a source of catalytic species at the beginning of the reaction and are responsible for observed activity. Taking into account this fact, it is not surprising that in the case of Pd/MN270-NaW- H_2 , for which the formation of small Pd NPs (3.5 nm) in H_2 medium occurs relatively fast, 4-BrAn conversion reached 79.4% that is in 1.4 times higher in

TABLE 1: XPS data for Pd/MN270 and Pd/MN270-NaW samples.

Chemical state of palladium	Surface Pd content (at %) and the corresponding binding energy (eV) [16]			
	Pd/MN270	Pd/MN270-H ₂	Pd/MN270-NaW	Pd/MN270-NaW-H ₂
Pd(CH ₃ COO) ₂	58 (338.8)	30 (338.3)	29 (338.6)	—
PdO	25 (337.3)	28 (337.3)	22 (337.1)	60 (337.4)
Pd NPs	7 (335.0)	20 (335.0)	13 (335.0)	13 (335.0)
Pd _n clusters	10 (335.9)	22 (336.0)	36 (335.9)	27 (335.8)

FIGURE 4: Kinetic curves of 4-BrAn conversion obtained while using Pd/MN270-NaW and Pd/MN270-NaW-H₂ in Suzuki cross-coupling.

comparison with a reported earlier result for preliminarily reduced MN100-based sample, for which conversion of 4-BrAn was only about 58% [9].

3.3. Hydrogenation of MBY. Results of testing of Pd/MN270-NaW in MBY hydrogenation (Figure 1(b)) are presented in Figure 5. As it can be seen, MBY hydrogenation occurs according to the classical Langmuir-Hinshelwood kinetics observed for triple bond semihydrogenation [18, 19] with slight induction period. These results suggest that Pd NPs were mostly formed (during H₂ liquid-phase reduction of Pd/MN270-NaW at conditions of MBY hydrogenation) and probably are responsible for observed catalytic activity.

Recently, we have found that the presence of alkali metals strongly influences the behavior (activity and selectivity) of hydrogenation catalysts synthesized while using chloride-containing Pd salt [10]. Moreover, the sample treatments after impregnation with sodium carbonate accelerates precursor decomposition rendering Pd oxide and Pd NPs (see the results of XPS data). In order to verify if this treatment is necessary, we compared the activity of Pd/MN270 and Pd/MN270-H₂ with that of Pd/MN270-NaW and the results are presented in Table 2.

As it can be seen from Table 2, the sodium carbonate treatment of the Pd catalyst prepared with HPS of MN270 type by impregnation with Pd acetate as a precursor has

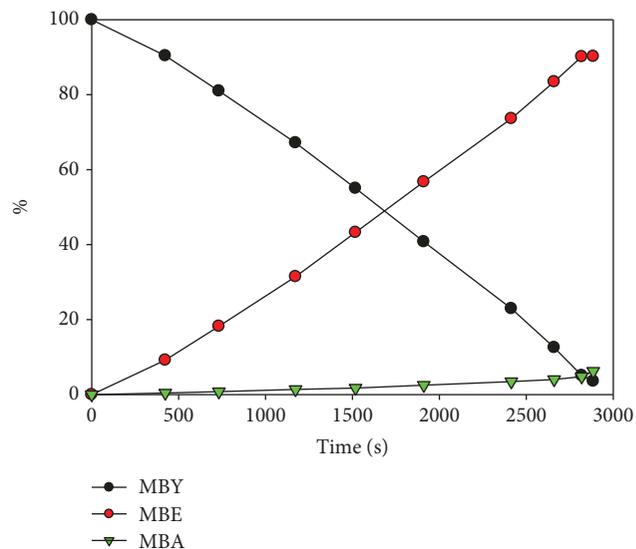


FIGURE 5: Kinetic curves obtained while using Pd/MN270-NaW in MBY hydrogenation.

TABLE 2: Results of testing of HPS-based catalysts in MBY hydrogenation: influence of reduction method and treatment of the catalyst with Na₂CO₃.

Catalyst	Selectivity, $\pm 0.5\%$ (calculated at MBY conversion 95%)	Catalytic activity R , molMBY/ (molPd*s)
Pd/MN270-NaW	94.6	3.2
Pd/MN270	95.2	3.7
Pd/MN270-H ₂	96.0	3.1
Pd/MN270-H ₂ without preliminarily liquid- phase reduction	95.4	3.4

almost no influence on the observed activity (R). The selectivity also remains the same with the value of about 95-96% at 95% of MBY conversion. That means that Pd NPs responsible for catalysis are easily formed under reaction conditions as well as during gas-phase reduction in hydrogen flow (see also TEM data). Moreover, for the sample Pd/MN270-H₂, it was also shown that its pretreatment in-situ is not necessary (see Table 2 and Figure 6), which is also proven by linear dependence of hydrogen uptake on MBY conversion.

Thus, the procedure of catalyst synthesis based on impregnation of MN270 with Pd(CH₃COO)₂ can be

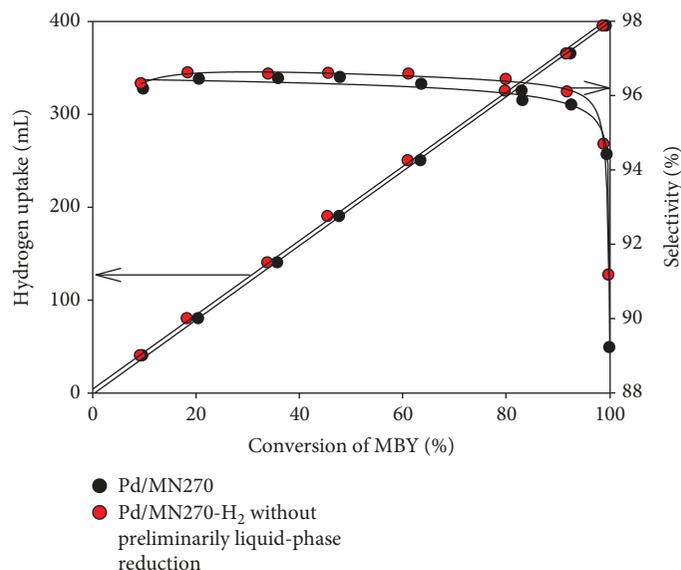


FIGURE 6: Influence of reduction method on selectivity to MBE and hydrogen uptake.

simplified, because such combination of HPS type and palladium precursor allows easy formation of Pd NPs *in situ* under reaction conditions without any additional treatment. It is important to underline that activity of Pd/MN270 catalyst is about 35% higher as compared to industrial Lindlar catalyst (2%-Pd/CaCO₃, 2.4 molMBY/molPd*s), which presents comparable (94.6%) selectivity to MBE.

4. Conclusions

Formation of Pd NPs of about 3-4 nm and relatively narrow particle size distributions were shown to proceed very fast in nonfunctionalized HPS of MN270 type after impregnation by Pd acetate and be independent on reduction method with molecular hydrogen (gas-phase at 300°C or liquid-phase *in situ* under reaction conditions at 90°C). Moreover, in contrast to analogous catalysts impregnated with chloride-containing palladium salts, the Pd/MN270 sample does not need any pretreatment with alkali metal compounds (such as Na₂CO₃) simplifying the catalyst synthesis. Pd NPs stabilized within MN270 catalyze effectively Suzuki cross-coupling allowing 90% conversion of 4-BrAn and have about 35% higher activity as compared to industrial Lindlar catalyst in selective hydrogenation of MBY.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Supplementary Materials

Figure S1: normalized DRIFT spectra of initial MN270 and Pd/MN270-NaW (as synthesized and reduced in H₂ flow). Figure S2: high resolution spectra of Pd 3d of freshly prepared Pd/MN270 (a) and Pd/MN270-NaW (b) and reduced in H₂ flow Pd/MN270-H₂ (c) and Pd/MN270-NaW-H₂ (d). (*Supplementary Materials*)

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