



Ligand-Free Polymeric Catalysts for Suzuki, Sonogashira and Heck Cross-Coupling Reactions: Influence of Support Hydrophobicity

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In this study, new data are presented on the behavior of Pd nanoparticles (NPs) stabilized in naphthalene-based polymers containing different functional groups (hydroxyl, sulfonate, and nitro groups) in cross-coupling reactions (Suzuki, Sonogashira, and Heck). Polymers were synthesized by the direct knitting strategy using naphthalene or naphthol as the monomers and iron chloride as the polymerization catalyst with following sulfonation or nitration. The resulting polymeric materials were used to support the formation of Pd NPs. It was shown that the sizes of Pd NPs depend on the relative hydrophobicity of the polymeric environment. All the catalytic materials were shown to be highly active and selective: using low amounts of catalysts (0.2 mol.% of Pd with respect to an aryl halide) in environmentally benign solvents (ethanol, dimethyl sulfoxide) and in the absence of any ligands and co-catalysts more than 90 % conversion was achieved in 60 min in the case of Suzuki and Sonogashira cross-coupling. Catalytic activity was found to go through a maximum corresponding to the sizes of Pd NPs of about 10 nm. The Heck cross-coupling required the use of N,N-dimethylformamide as a solvent and the addition of triethylamine, which allowed achieving more than 80 % aryl halide conversion for 3 h.

1. Introduction

In the last decades, the interest in porous organic polymers has been continuously increasing (Yuan and Zhu, 2019). Porous aromatic polymers (PAPs) are characterized by their simplicity of synthesis, low cost, and the possibility of using readily available monomers (Tan and Tan, 2017). PAPs possess high stability, large specific surface area (SSA), and the ability to regulate the nature and concentration of functional groups, which, in turn, can be used in catalysis to immobilize metal complexes and nanoparticles (NPs).

Pd-catalyzed reactions are the most widespread ones. Cross-coupling reactions of Suzuki, Sonogashira, and Heck are of particular interest (Ashraf et al., 2023). These reactions are complicated by various processes, such as aggregation, dissociation, and leaching of Pd, which can contribute to the decrease in its activity and selectivity (Eremin and Ananikov, 2017). This is due to the continuous transformation of various forms of palladium: Pd(II) compounds, clusters, and Pd(0) NPs (Kashin and Ananikov, 2013). Unlike the Suzuki cross-coupling, the Heck and Sonogashira reactions are more sensitive to the presence of ligands that stabilize the active forms of Pd in a solution (Schmidt et al., 2008), and are also complicated by the fact that they usually require the participation of co-catalysts – Cu(I) or amines (Chinchilla and Nájera, 2011).

In spite of numerous polymers reported in the literature, PAPs are promising supports for the development of catalysts for cross-coupling reactions. The increase of catalytic activity in the absence of ligands, co-catalysts, and phase-transfer agents in environmentally friendly solvents would benefit the atom economy and environmental safety of the process. Among the solvents typically used in cross-coupling reactions, water, ethanol (EtOH), and isopropanol can be considered as green; dimethyl sulfoxide (DMSO) can be recommended at high temperatures, while N,N-dimethylformamide (DMF) is toxic and undesirable (Byrne et al., 2016).

Functionalized PAPs can prevent the leaching and aggregation/sintering of metal NPs. One of the ways to obtain functionalized PAPs is to use monomers containing functional groups. Another approach is the introduction of substituents into aromatic rings after the resulting polymer is obtained. In the framework of this study, the synthesis of amorphous PAPs based on naphthalene and 1-naphthol was carried out. Naphthalene is a well-known monomer for polymer synthesis (Teng et al., 2020), which allows for high polymer yield (Wang et al., 2017). Functionalization of naphthalene-based polymer by SO₃H- and NO₂-groups was provided. The synthesized PAPs were used to create Pd-containing catalysts for the Suzuki, Sonogashira and Heck cross-coupling. The dependence of catalytic activity on the sizes of palladium NPs formed during the reduction of catalysts was investigated for the first time.

2. Experimental

2.1 Polymer synthesis and characterization

Polymer synthesis was carried out by the direct knitting method (Gu et al., 2021): cross-linking the monomer with methylal according to the procedure described elsewhere (Tan and Tan, 2017). In a typical experiment, 60 mmol of anhydrous FeCl₃, 20 mL of 1,2-dichloroethane (1,2-DCE) were placed in a three-necked round-bottomed flask with a magnetic stirrer (300 rpm), and 20 mmol of monomer (naphthalene or 1-naphthol) were added. After that, 60 mmol or 120 mmol of methylal was slowly added at a stirring (1,000 rpm). The mixture was kept at 45 °C (5 h) and then at 80 °C (19 h). The resulting naphthalene- (Nap) or 1-naphthol-based (Nap-OH) polymer was purified from FeCl₃ and 1,2-DCE by methanol extraction for 24 h and dried under vacuum at 40 °C (24 h). The Nap was also sulfonated (Dalla Valle et al., 2020) and nitrated (Philippides et al., 1993) that resulted in increase of oxygen content on the surface (according to the data of X-ray photoelectron spectroscopy, XPS) from about 4 at.% (in the case of Nap) up to 8 at.% and 11 at.% in the case of sulfonated (Nap-SO₃H) and nitrated (Nap-NO₂) samples. In the case of Nap-OH the oxygen content on the polymer surface was about 7 at.%.

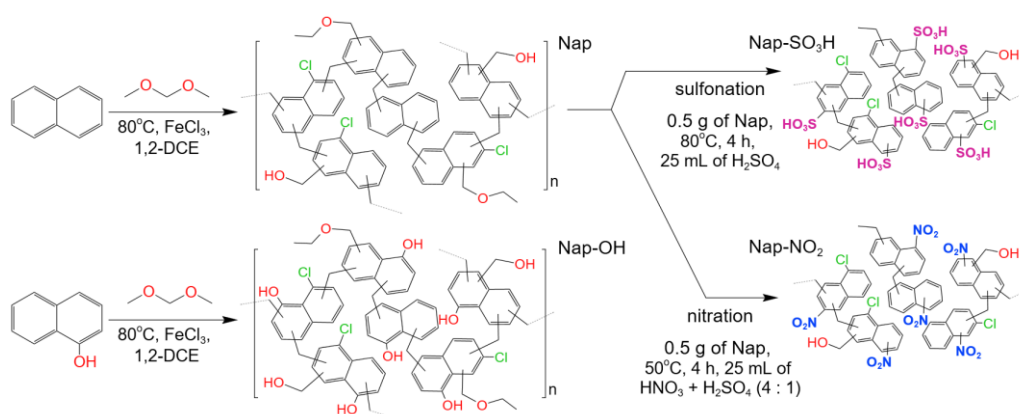


Figure 1: The scheme of the polymers synthesis and functionalization

The resulting polymers were characterized by the low-temperature nitrogen physisorption (Table 1).

Table 1: Comparison of the polymers

Monomer	Content of methylal, mmol	SSA (BET model), m ² /g	Total pore volume, cm ³ /g	Micropore volume, cm ³ /g
Nap	120	757	0.602	0.234
Nap-OH	60	489	0.645	0.155
Nap-SO ₃ H	120	627	0.436	0.217
Nap-NO ₂	120	358	0.283	0.113

As it can be seen (Table 1), the polymer samples have a micro-mesoporous structure, and the SSA varies from 358 m²/g (for the nitrated polymer) up to 757 m²/g (for the polymer without any additional functional groups). It is obvious that after the sulfonation and nitration, the SSA of the Nap decreased by 1.2 and 2.1 times, which can be due to the partial destruction of methylene bridges between the neighboring aromatic rings. A detailed description of used characterization methods (XPS and low-temperature nitrogen physisorption) can be found elsewhere (Nikoshvili et al., 2020).

2.2 Catalyst synthesis and characterization

The synthesis of Pd-containing catalysts was carried out by the impregnation method. In a typical experiment, 0.5 g of polymer was impregnated with 3 mL of palladium precursor solution ($\text{Pd}(\text{CH}_3\text{COO})_2$) in tetrahydrofuran. The samples were then dried in air at 65 °C. The following samples were obtained: 1 %-Pd/Nap, 1 %-Pd/Nap-OH, 1 %-Pd/Nap-SO₃H, and 1 %-Pd/Nap-NO₂. The palladium content was confirmed by X-ray fluorescence analysis (XFA).

All the synthesized catalysts were reduced with hydrogen. The reduction was carried out in an EtOH medium at a temperature of 0–5 °C using NaBH₄ (0.1 mol/L) as a hydrogen source. The reduced samples (1 %-Pd/Nap-R, 1 %-Pd/Nap-OH-R, 1 %-Pd/Nap-SO₃H-R, and 1 %-Pd/Nap-NO₂-R) were dried for 24 h at 65 °C and stored in air. After the reduction, Pd(0) NPs were formed, the sizes of which were estimated by scanning transmission electron microscopy (STEM). A detailed description of XFA and STEM methods can be found elsewhere (Nikoshvili et al., 2020).

2.3 Reaction procedure

The Suzuki reaction proceeded between 4-bromanisole (4-BrAn) and phenylboronic acid (Figure 2) in the presence of a base (NaOH) under mild conditions (atmosphere – air, 60°C, solvent – mixture of EtOH and H₂O) selected earlier (Sapunov et al., 2023). In a typical experiment, 4-BrAn (1 mmol), phenylboronic acid (1.5 mmol), NaOH (2 mmol), and a solvent (5 mL of H₂O and 15 mL of EtOH) were added to a three-necked flask and left for 60 min at a stirring (900 rpm). Then a catalyst was introduced (0.2 mol.% Pd with respect to 4-BrAn) and 10 mL of EtOH. The duration of the reaction was 60 min.

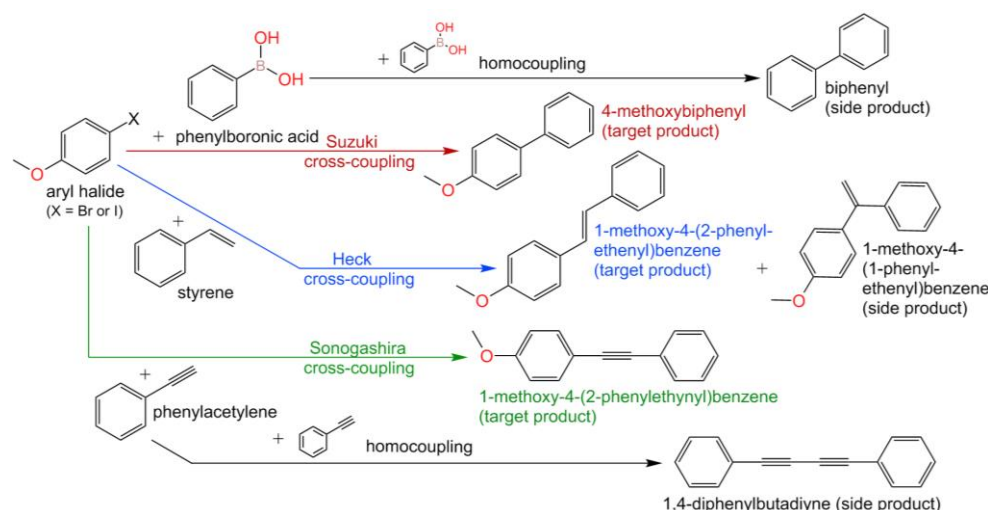


Figure 2: Generalized scheme of the cross-coupling reactions

The Sonogashira reaction between 4-iodanisole (4-IAn) and phenylacetylene (Figure 2) was carried out in a DMSO medium under Ar at a temperature of 90 °C and a stirring rate of 900 rpm selected earlier (Nikoshvili et al., 2021). Pd concentration with respect to 4-IAn was 0.2 mol.%. Additives of sodium acetate (1.5 mmol) and tetrabutylammonium bromide (TBAB) – 10 mol.% – were used as stabilizers of active forms of Pd. The reaction duration from the moment of the addition of phenylacetylene or a catalyst (see below) was 60 min.

Heck reaction between styrene and 4-IAn was carried out in DMF medium at a temperature of 120°C and a stirring rate of 900 rpm in an argon atmosphere using 0.2 mol.% of Pd. Note that, unfortunately, no catalytic activity was revealed in the DMSO medium. Additives of sodium acetate (1.5 mmol), TBAB (10 mol.%), and triethylamine (Et₃N, 3 mmol) were used. The duration of the reaction from the moment of the addition of styrene or a catalyst was 180 min.

In the reactions of Sonogashira and Heck cross-coupling, the order of reagents introduction is important (Nikoshvili et al., 2021). While testing the preliminarily reduced samples, 4-IAn, sodium acetate, TBAB (and also Et₃N in the case of Heck reaction) were first introduced into the reactor, and then (after 30 min) phenylacetylene or styrene was added. In the case of the initial (unreduced) catalysts, all reagents were added simultaneously, while the catalyst was added 30 min later.

In each catalytic experiment, samples of the reaction mixture were periodically taken and analyzed via GC-MS (Shimadzu GCMS-QP2010S) equipped with a capillary column HP-1MS (100 m × 0.25 mm i.d., 0.25 μm film thickness). The concentrations of the reaction mixture components were calculated using the internal standard

calibration (diphenylamine was used as an internal standard). Catalytic activity was defined as the tangent of the slope of the initial part on the kinetic curves of aryl halide conversion, and related to the amount of Pd.

3. Results and discussion

3.1 Catalyst characterization

STEM study of the reduced catalysts revealed (Figure 3) that in the following series of polymeric supports: Nap, Nap-OH, Nap-SO₃H, and Nap-NO₂, the mean diameter of Pd NPs formed after the reduction in EtOH medium decreases, which is likely due to the corresponding increase of oxygen content and the decrease of relative hydrophobicity of the naphthalene-based polymers.

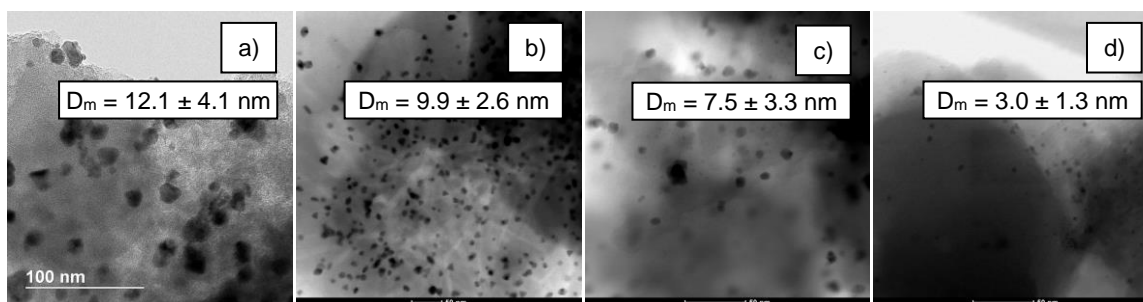


Figure 3: Bright-field STEM images of 1 %-Pd/Nap-R (a) (scale 100 nm), 1 %-Pd/Nap-OH-R (b) (scale 50 nm), 1 %-Pd/Nap-SO₃H-R (c) (scale 50 nm) and 1 %-Pd/Nap-NO₂-R (d) (scale 50 nm).

3.2 Catalytic testing

As a result of testing the developed catalytic systems in the Suzuki reaction, it was found (Table 2) that the initial (unreduced) samples allow for achieving high values of 4-BrAn conversion (up to 98 %) and the share of target cross-coupling product up to 93 %. The observed catalytic activity was in correlation with the relative hydrophobicity (oxygen content) of the polymeric supports (Figure 4a). The same tendency was found for the Sonogashira reaction: catalytic activity of the initial (unreduced) samples increased while decreasing the polymer hydrophobicity. It should be noted that in most cases, high selectivity (the share of target product in the mixture of both target and side products) was observed at up to 98-100 %.

Regarding the preliminarily reduced catalysts containing well-defined Pd NPs, the conversion of 4-BrAn in the Suzuki reaction varied from about 70 % up to 93 %, with the share of the target product 68-91 %. It was found (Figure 4b) that the dependence of catalytic activity on the mean diameter of Pd NPs goes through the maximum corresponding to the value of about 10 nm (the sample 1 %-Pd/Nap-OH-R). In the reaction of Sonogashira cross-coupling, the highest activity was also found, at 1 %-Pd/Nap-OH-R.

In one of the recent studies on the Heck cross-coupling (Redón et al., 2022) it was revealed that under process conditions (catalyst concentration – 3.5×10^{-5} mmol, 120 °C, solvent – DMF, base – Na₂CO₃, reaction duration 10 h) the calculated threshold size of Pd NPs allowing for high activity is 27 nm. It was proposed that larger NPs appear to be more readily available for catalysis as compared to smaller ones that do not undergo significant leaching. At the same time, Redón et al. (2022) postulated the mechanism of “cocktail”-type catalysis (Eremin and Ananikov, 2017), when NPs dissolved and then re-precipitated and participated in the reaction. Interestingly, the lowest conversion rates were achieved while using DMSO as a solvent at 200 °C. Presumably, the high temperature led to a decrease in the share of Pd(II), and DMSO likely contributed to the agglomeration of NPs by provoking their precipitation and removal from the reaction mixture.

Complexity of the observed behaviour of Nap-based catalytic systems is likely caused by several factors: (i) the sizes of Pd NPs – vertex and edge palladium atoms more easily undergo leaching in case of larger NPs; (ii) availability of Pd species for the reagents – polymer porosity and swelling ability; (iii) affinity of Pd precursor (Pd(CH₃COO)₂) to the polymeric environment; (iv) mutual combination of polymer properties (relative hydrophobicity) and solvent nature (polarity, ability to serve as a ligand for dissolved palladium species). For example, in the case of the Sonogashira reaction, it can be noted that some samples (i.e. based on Nap and Nap-OH) with higher activity allow lower conversion of 4-IAn for the same reaction time that can be due to their faster slowdown during a single experiment in contrast to the samples based on Nap-SO₃H and Nap-NO₂.

Two catalysts (based on Nap-OH and Nap-SO₃H) were chosen for the testing in the Heck reaction (Table 2). The highest activity was found for the sample 1 %-Pd/Nap-SO₃H-R.

Table 2: Results of catalytic testing of synthesized catalysts in the Suzuki, Sonogashira, and Heck reactions

Catalyst	Conversion of aryl halide, %	Selectivity (or share of the target product), %	Activity, mol (ArHal)/(mol(Pd)*min)
Suzuki reaction			
Initial catalysts			
1 %-Pd/Nap	90	96	14.9
1 %-Pd/Nap-OH	92	96	41.1
1 %-Pd/Nap-SO ₃ H	96	96	64.0
1 %-Pd/Nap-NO ₂	98	96	77.0
Reduced catalysts			
1 %-Pd/Nap-R	81	98	12.6
1 %-Pd/Nap-OH-R	93	97	31.2
1 %-Pd/Nap-SO ₃ H-R	73	97	9.5
1 %-Pd/Nap-NO ₂ -R	70	97	10.7
Sonogashira reaction			
Initial catalysts			
1 %-Pd/Nap	86	99	27.1
1 %-Pd/Nap-OH	81	98	36.9
1 %-Pd/Nap-SO ₃ H	82	99	49.0
1 %-Pd/Nap-NO ₂	87	96	53.2
Reduced catalysts			
1 %-Pd/Nap-R	75	98	38.5
1 %-Pd/Nap-OH-R	93	100	63.9
1 %-Pd/Nap-SO ₃ H-R	88	99	21.4
1 %-Pd/Nap-NO ₂ -R	93	96	16.8
Heck reaction			
Initial catalysts			
1 %-Pd/Nap-OH	92	90	4.0
1 %-Pd/Nap-SO ₃ H	15	91	1.3
Reduced catalysts			
1 %-Pd/Nap-OH-R	18	91	1.1
1 %-Pd/Nap-SO ₃ H-R	82	89	7.5

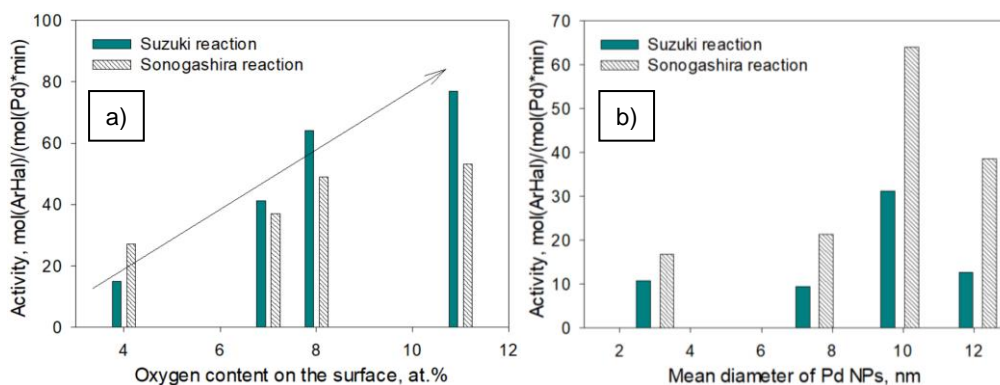


Figure 4: Dependence of catalytic activity on the oxygen content on the surface of the polymers for the initial (unreduced) catalysts (a) and on the sizes of Pd NPs for the reduced samples (b)

4. Conclusions

In the framework of this study, Pd-containing catalysts based on amorphous PAPs synthesized via one-step cross-linking of Nap or Nap-OH by the Friedel-Crafts reaction were synthesized with the following sulfonation or nitration. It was shown that, depending on the presence of functional groups in the polymer, Pd NPs of various mean diameters (from 3 nm up to 12 nm) can be formed during the liquid-phase reduction in polar medium (EtOH). For the first time, by the example of Suzuki and Sonogashira cross-coupling reactions proceeding under mild conditions in environmentally safe solvents (EtOH, DMSO) in the absence of phase-

transfer agents and co-catalysts, the dependence of catalytic activity on the mean diameter of Pd NPs was found to pass through a maximum corresponding to ~10 nm. For the initial (unreduced) samples containing palladium acetate, catalytic activity in Suzuki and Sonogashira reactions was found to depend on the relative hydrophobicity of the polymers. In the case of the Heck reaction, no dependencies were found, possibly due to the more complex reaction mechanism involving amines. In general, the behavior of ligandless polymer-based catalytic systems is very complex. It depends on many factors, including the rates of Pd dissolution and precipitation and the combination of polymer and solvent polarities. The observed dependences can be useful for targeting the design of catalytic supports for further optimization of ligand-free catalytic systems.

Acknowledgments

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