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Palladium–polypyrrole nanoparticles-catalyzed Sonogashira coupling

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Palladium nanoparticles were encapsulated into polypyrrole globules *via* one-step one-pot redox reaction between tetraamminepalladium(II) dichloride and pyrrole in water. Such a material is an active catalyst for the Sonogashira coupling of iodo- and bromoarenes.

In recent years there has been a growing interest in preparation of Pd nanoparticles for application in various reactions of C–C bond formation.[1–5] Since heterogeneous catalysis occurs on metal surface, nanoparticles are much more reactive than traditional supported transition metal catalysts due to their high surface-to-volume ratio.[2] The use of nanoparticles provides a bridge between homogeneous and heterogeneous catalysis integrating their advantages.

Recently, a non-template one-step method for synthesis of palladium nanoparticles encapsulated into polypyrrole (PPy) globules *via* direct redox reaction between palladium(II) acetate and pyrrole monomer in acetonitrile[6] or between tetraamminepalladium(II) dichloride and pyrrole monomer in water[7] has been proposed. Such formation of nanocomposites during redox-polymerization of heterocyclic monomer in the presence of metal ions is a promising-for-catalysis approach. It allows one to avoid addition of surface stabilizers (as it is often the case in preparation of stable nanosize systems) since thus formed conducting polymer matrix itself stabilizes nanoparticles and prevents their aggregation. This formation of the metal surface free of adsorbates provides higher catalytic activity of Pd nanoparticles.

Pd/PPy nanocomposites prepared in water previously showed very high catalytic activity in direct C–C coupling[7] and in the Suzuki–Miyaura coupling of haloarenes with aryl boronic acids or sodium tetraphenylborate.[8] The aim of this work was to broaden the scope of using Pd/PPy in cross-coupling exemplified in the Sonogashira reaction.[9–16] Although many catalytic systems for this reaction have been reported (see refs. 9–11,17–19 and the literature cited therein), the search for new efficient catalytic systems is still an active research area.

The general protocol for preparation of polymer globules with incorporated Pd nanoparticles in aqueous medium was described previously.[7,8] For the synthesis of the required material, in this work 1 mM tetraamminepalladium(II) dichloride and 300 mM pyrrole mixed aqueous solution was used. After the redox reaction between the monomer and the palladium precursor was complete, the sedimented composite was rinsed several times with water and acetonitrile and dried *in vacuo* under inert atmosphere. According to TEM data (Figure 1), the synthesized composite had a structure which was similar to that described earlier.[7,8] One can see that the resulting powder is composed of polypyrrole globules with diameter of ~50–60 nm and Pd nanoparticles of 1.5–2 nm in size distributed inside the whole polymer volume. The content of Pd was 35 wt%.

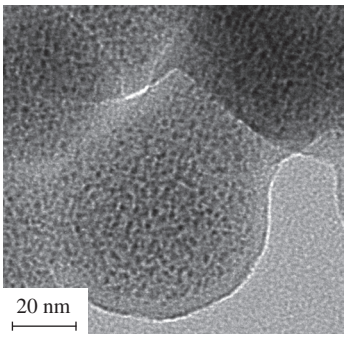
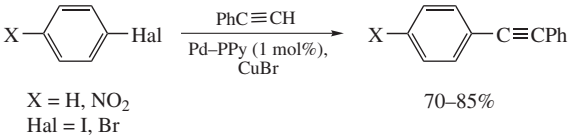


Figure 1 TEM image of Pd/PPy composite.

The Sonogashira coupling was carried out under argon atmosphere in NMP. This solvent, along with DMF or DMSO proved to be efficient since it allows overcoming the incompatibility of lipophilic organic substrates and inorganic salts used as bases. In our case, sodium carbonate (5-fold excess relatively to the haloarene) was shown to be the most efficient base. For testing, iodobenzene and bromobenzene, as well as their *p*-nitro derivatives were chosen. For catalytic applications, the suspension of Pd/PPy in NMP was prepared using ultrasonication.† The amount of Pd/PPy nanocomposite used for each catalytic experiment was estimated to provide 1 mol% of palladium (as calculated *vs*. the starting haloarene). As co-catalyst, CuBr (2 mol%) was used.

Phenylacetylene was used as a model terminal alkyne in 1.5 molar excess relatively to haloarene (Scheme 1). The reaction mixture was vigorously stirred at 100 °C under argon atmosphere for 4 h. Afterwards, it was analyzed using GCMS with naphthalene as internal standard. Both iodo- and bromoarenes were active; the yields of arylacetylenes were sufficiently good. In addition to the coupling product, a certain amount of the starting haloarene was detected.



X = H, NO_2
Hal = I, Br

70–85%

Scheme 1

† 0.5 mg of Pd/PPy (1 mol%) was suspended in 2 ml of NMP using ultrasonication (42 kHz, 170 W) for 15 min.

Table 1 The Sonogashira reaction between PhC≡CH (0.3 mmol) and ArHal (0.2 mmol) in the presence of Na_2CO_3 (1 mmol), Pd/PPy (1 mol%), CuBr (2 mol%), NMP, 100 °C, 4 h.

Haloarene	Yield of ArC≡CPh (%)	Starting haloarene[b] (%)
PhI	70	30
PhBr	66 (76[a])	32 (22[a])
p-$NO_2C_6H_4Br$	78	19
p-$NO_2C_6H_4I$	85	15

[a] 6 h. [b] The amount of the starting aryl halide detected in the reaction mixture.

Surprisingly, the impact of the side reaction of oxidative dimerization of phenylacetylene was rather small (~1–3%). Meanwhile it should be mentioned that the amount of dimerization product is extremely sensitive to the presence of even traces of dioxygen in the reaction mixture and may achieve 40% under aerobic conditions.

Prolongation of the reaction up to 6 h allowed one to raise the yield of the product up to 76% but still ~20% of bromobenzene remained unreacted. Since the catalyst does not lose its activity for more than 12 h of processing[8] the further increase in the reaction time could bring about complete conversion of haloarene to the cross-coupling product, taking into account that the impact of competitive oxidative coupling of alkyne does not grow substantially. The results obtained are given in Table 1.

One of the modern tendencies in improvement of the traditional Sonogashira coupling is the search for a copper-free procedure. Unfortunately, our Pd/PPy nanocomposite was inefficient in the absence of Cu^I additives. Even in the case of active *p*-nitrophenyl iodide, the processing at 120 °C in NMP for 6 h gave no cross-coupling product, whereas only starting haloarene was detected in the reaction mixture.

Thus, the Pd/PPy composite in combination with Cu^I salt demonstrates a catalytic activity in the cross-coupling reaction for both iodo- and bromoarene derivatives. Exploration of capabilities of the new Pd nanocatalyst which is available *via* an operationally simple and reproducible procedure will be further extended. The scope of substrates will be broadened including various halogens and substituents in benzene ring. This work is in progress.

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