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Synthesis and catalytic activity of a poly(*N*,*N*-dialkylcarbodiimide)/palladium nanoparticle composite: a case in the Suzuki coupling reaction using microwave and conventional heating†

Yubiao Liu, Chalermchai Khemtong and Jun Hu*
Department of Chemistry, The University of Akron, Akron, OH 44325, USA. E-mail: jhu@uakron.edu

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Poly(*N*,*N*-dialkylcarbodiimide) was found to be an effective polymeric ligand system for preparing and stabilizing palladium nanoparticles (1–5 nm). The composite material prepared *in situ* was found to be a robust catalyst for the Suzuki coupling reaction under microwave or regular heating.

Recently we reported that poly(*N*,*N*-dialkylcarbodiimide), a helical backbone synthetic polymer,[1] is useful for synthesizing and stabilizing transition metal nanoparticles.[2] The unique supramolecular chirality of the polymer and the remarkable stability of the resulting nanocomposites prompted us to study the catalytic activities of such new materials. While polymers have been used to stabilize colloidal metal nanoparticles, only few of them are useful as polymeric ligands to provide optimum stability and catalytic activity. We examined the synthesis, stability and catalytic activity of poly(*N*,*N*-dihexylcarbodiimide)/palladium nanoparticle composite (PDHC–Pd). We report herein the remarkable catalytic activity and stability of PDHC–Pd in the Suzuki coupling reaction. In addition, we report that the catalyst is compatible with microwave heating, which greatly accelerates the coupling reaction.

The Suzuki coupling reaction is a powerful synthetic method for preparing biaryls from arylboronates and aryl halides.[3] Homogeneous transition metal catalysts such as $Pd(PPh_3)_4$ are most effective in terms of mild reaction conditions, high yields and shorter reaction times.[4,5] Polymer stabilized colloidal palladium nanoparticles have also been reported as catalysts for the Suzuki coupling reaction.[6] Poly(*N*-vinyl-2-pyrrolidone),[7] polyoxometalates,[8] dendrimers and block copolymers have been used as supporting matrices for stabilizing the colloidal nanoparticles.[9] In addition, nanosize palladium hollow spheres have also been described as active catalysts.[10] The most important potential advantage of using colloidal nanoparticles for the Suzuki coupling is to recover and reuse the catalysts. However, most of these procedures require prolonged reaction times at elevated temperatures and suffer lower yields. Furthermore, the reported catalytic activity of the recovered catalysts is too low for them to be reused for practical organic synthesis.[7b] Microwave heating has recently been used as a method for increasing the reaction rates of the Suzuki coupling reaction with homogenous catalysts.[11] The combination of using metal nanoparticles and microwave heating in Suzuki coupling reaction was unprecedented.

From a mechanistic point of view, the most active catalytic species in the nanoparticle catalyzed Suzuki coupling reactions may be the polymeric coordination complexes rather than the heterogeneous nanoparticles themselves. Examinations of the morphology of the used nanoparticles in our lab and published by others,[7b] indicated that: (1) there was an equilibrium between nanoparticles and dissolved metal atoms in the reaction which led to the dissolution of smaller nanoparticles and the growth of larger ones; (2) the larger nanoparticles were catalytically inactive. We found the selection of the polymer ligand for the catalyst to be critical for achieving optimum activity. Poly(*N*,*N*-dialkylcarbodiimide) is a more weakly coordinating ligand than the prevailing polymers that have been used in these Suzuki couplings. For the reactive intermediates in the catalytic processes, the weaker coordination results in higher activity of the catalysts. For the nanoparticles, more weakly coordinating ligands are less corrosive, and therefore the more slowly the redistribution of the nanoparticles to the larger size occurs in the reactions.

The nanoparticles were prepared by $NaBH_4$ reduction of H_2PdCl_4 in a two phase mixture of poly(*N*,*N*-dihexylcarbodiimide), toluene and water.† The light yellow $PdCl_4^{2-}$ ion was visible in the organic layer before the reduction. Presumably, $PdCl_4^{2-}$ was extracted into the organic phase by ion-pairing with the protonated guanine units of the polymer backbone. Subsequent reduction of the metal ions produced the PDHC–Pd nanocomposite. The reduction reaction can be monitored by UV–vis absorption spectroscopy. The peak at 376 nm of the organic phase before reduction was assigned to the ligand-to-metal charge transfer transition of the $PdCl_4^{2-}$ ion. This band disappeared after the formation of the palladium nanoparticles. A broad increase in the absorption coefficient from the ultraviolet to the visible region in the spectrum indicated the formation of the palladium nanoparticles.[12]

The particle size and size distribution of the palladium nanoparticles formed in the composite was analyzed with transmission electron microscopy (TEM). As shown in Fig. 1, narrowly dispersed palladium nanoparticles were produced in the one-pot synthesis. The average size of the palladium nanoparticles is about 3 nm and they are roughly spherical. Little change in the size of the nanoparticles was observed as the molecular weight (M_w) of the polymer used in the synthesis was varied from 42 000 to 84 000. The PDHC–Pd catalyst displayed remarkable colloid stability in storage and in the catalytic reactions. For example, they were found to be stable on the lab shelf for months without any aggregation or precipitation.

The catalytic activity of PDHC–Pd was examined in the Suzuki coupling reaction.† As shown in Table 1, nearly quantitative yields of biphenyl products for various substrates were observed in almost all cases. The catalytic activity was preserved in the presence of a

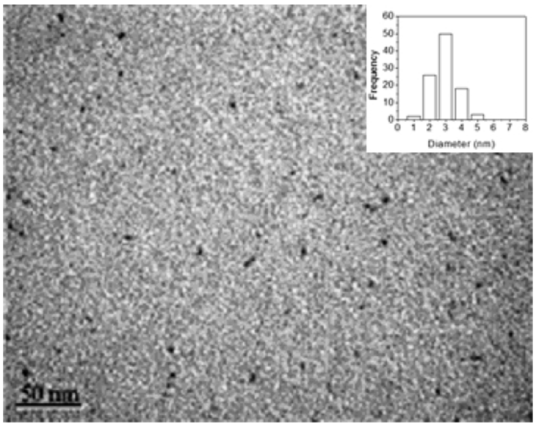

Fig. 1 TEM analysis of palladium nanoparticles stabilized by poly(*N*,*N*-dihexylcarbodiimide) (bar = 50 nm).

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† Electronic supplementary information (ESI) available: experimental details and UV–vis spectrum. See http://www.rsc.org/suppdata/cc/b3/b313210m/

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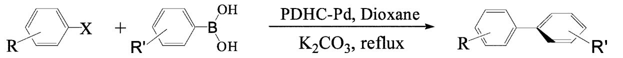
Table 1 Product yields for Suzuki cross coupling reaction catalyzed by PDHC-Pd nanoparticles



Entry	R	X	R′	Amount of catalyst (wt% wrt halide)	Time/h	Isolated yield (%)
1	H	I	H	0.5	20	97[d]
2	H	I	H	0.5	40 min	95[e]
3	H	Br	H	0.5	23	98
4	Br	Br	H	0.5	24	95
5	[a]		H	0.5	18	84
6	[b]		H	0.5	19	90
7	H	I	HCO	0.5	20	99
8	H	I	H[c]	0.5	20	98

[a] 5,5′-Dibromo-2,2′bithiophene. [b] 3,5-Dibromopyridine. [c] $Pd(PPh_3)_4$ as catalyst. [d] The yield from the first run, 2nd run yields 93% with TON 1600, 3rd run yields 95%, 4th run yields 92% and fifth run yields 90%. [e] Microwave heating of the first run.

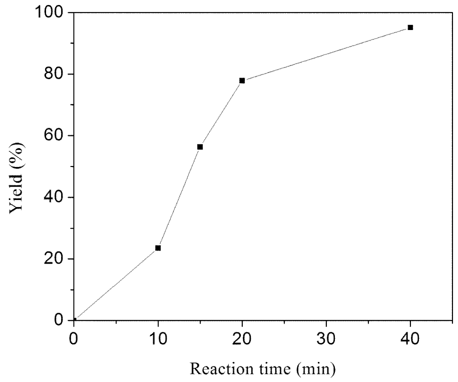


Fig. 2 Isolated yields of Suzuki coupling reactions of phenylboronic acid and iodobenzene *vs.* reaction time.

thio-containing substrate which is known to poison colloidal Pd nanoparticle catalysts (entry 5). No obvious difference in the catalytic activity of PDHC–Pd was observed when aryl iodides or aryl bromides were used in the reactions. The turnover number of the catalyst in the reactions was estimated to be over 1600 from the substrate and catalyst ratios of the reactions. A distinctive advantage of the polymer/nanoparticle composite over homogeneous catalysts such as $Pd(PPh_3)_4$ (entry 8) is that the catalyst can be easily recovered by precipitation and filtration. The recovered catalysts were found to be reactive in the coupling reactions even after five reaction–recovery cycles (entry 1). While colloidal metal catalysts tend to aggregate even in a single run of the Suzuki coupling reaction,[7] no significant aggregation of nanoparticles in PDHC–Pd was observed in most of the reactions. A small amount of black precipitate was observed in the coupling reaction between 5,5′-dibromo-2,2′-bithiophene and phenylboronic acid (entry 5), presumably due to the poisoning of the catalyst by the thiophene moiety.

The PDHC–Pd catalyzed Suzuki coupling reaction between phenylboronic acid and iodobenzene was also examined under microwave heating conditions (entry 2). Excellent conversions were achieved in about 40 min microwave irradiation. No palladium black was observed in the reaction. In comparison, the same coupling reaction required about 20 hours refluxing to achieve the same degree of conversion (Fig. 2). The catalyst can also be recycled for several times in the microwave heating experiments. The activity of the recycled catalyst is shown in Fig. 3. With 40 min microwave heating in each cycle, we observed lower yields for each of the consecutive reaction cycles, indicating a significant decrease in the catalytic activity of the recycled PDHC–Pd for the Suzuki coupling reaction when microwave heating was employed. Narayanan *et al.* have observed a similar decrease in the catalytic activity of polyvinylpyridine stabilized Pd nanoparticle catalyzed Suzuki coupling reactions.[7b] Most likely the intensive heating of the nanoparticles by microwave irradiation promoted the size redistribution of the catalyst during the reactions. However, we obtained good yields of the coupling reactions with PDHC–Pd even after five recycles.

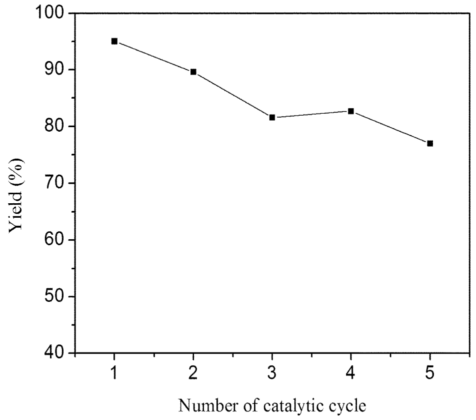


Fig. 3 Isolated yields of Suzuki coupling reactions of phenylboronic acid and iodobenzene *vs.* number of recycles of the catalyst under microwave heating at 100 °C for 40 min.

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