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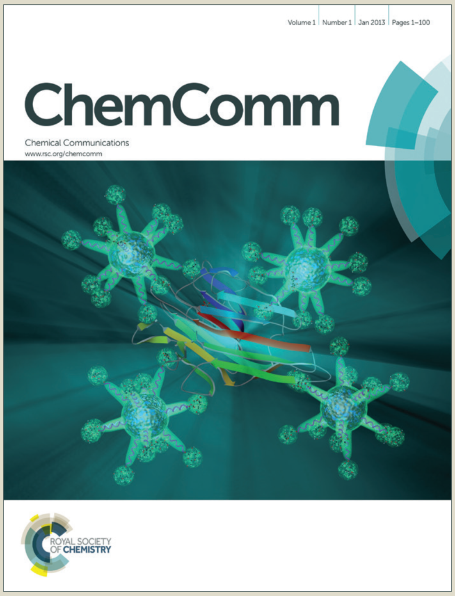

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ARTICLE TYPE

in situ Formation of Well-dispersed Palladium Nanoparticles Immobilized in Imidazolium-based Organic Ionic Polymers

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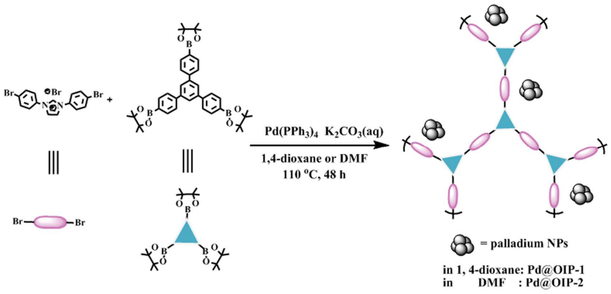
A new strategy for *in situ* generation of well-dispersed palladium nanoparticles (NPs) immobilized in imidazolium-based organic ionic polymers was presented. Without extra addition of palladium species, the as-synthesized ionic polymers showed excellent catalytic activity and good reusability in hydrogenation of nitroarenes.

The synthesis of palladium nanoparticles (NPs) immobilized on porous supports has attracted extensive interests in heterogeneous catalysis.[1] The catalytic activity of palladium NPs is known to depend on their size and degree of dispersion. Much effort has been devoted to embedding palladium NPs into porous materials containing coordination groups, which can offer potential for the control of particle size and prevention of NPs aggregation.[2] In the context, porous organic polymers (POPs) are a new promising class of porous materials owing to their unique features,[3] such as high stability, flexible synthetic strategy and ready functionality.[4] Coordination groups of metal precursors can be easily introduced into POPs to enhance the interactions between the polymers and metals. Very recently, POPs containing metal-binding sites have been successfully employed as stabilizers of palladium NPs in heterogeneous catalysis, high catalytic activity and recyclability have been shown because the synergetic effects of coordination and steric interactions in POPs endow palladium NPs unique performances.[5] Imidazolium-based ionic compounds are proposed to stabilize palladium NPs not only through electrostatic interaction, but also by binding to NPs surface,[6] resulting in the decrement of palladium leaching from the NPs surface.[7] Recently, some imidazolium-based POPs have been synthesized, and their application in gas absorption[8] and heterogeneous catalysis[9] were reported. However, the study of POPs containing imidazolium linkages as the stabilizer of palladium NPs has not been explored.

Suzuki-Miyaura cross-coupling reaction has been a common method for the synthesis of POPs.[9a, 10] It has been reported that palladium NPs may be *in situ* generated during catalytic reaction and are subsequently stabilized by imidazolium groups,[7a] this process avoids the use of reductive reagents in comparison with traditional impregnation and coprecipitation methods. However, in most cases, palladium species are leached during the reaction and purification process of POPs, which makes it difficult to take advantage of palladium species in the preparation of POPs. The development of a new approach to make full use of palladium will be of great significance owing to high price and source scarcity of palladium. In our continuous efforts to develop highly efficient and recyclable catalytic protocols,[11,12] herein, we present a facile approach for synthesis of well-dispersed palladium NPs in organic ionic polymers (OIPs).



Scheme 1 Synthesis of Pd@OIP-1 and Pd@OIP-2 (❀= palladium NPs).

Pd@OIP-1 and Pd@OIP-2 were *in situ* generated in the preparation of OIPs through Suzuki-Miyaura cross-coupling reaction of 1,3-bis(4-bromophenyl)imidazolium bromide and 1,3,5-tri(4-pinacholatoborolanephenyl)benzene in 1,4-dioxane and DMF, respectively (Scheme 1). After the reaction, the precipitate was filtered and successively washed with DMF, deionized water and methanol to remove any possible residues. The resultant reddish brown powder was further treated by Soxhlet extraction in CH_2Cl_2 and dried in vacuo at 80 °C for 12h to give the target product. Both Pd@OIP-1 and Pd@OIP-2 are insoluble in water and common organic solvents. It should be mentioned that Pd@OIP-1 and Pd@OIP-2 were synthesized under the identical conditions except for the difference of reaction media, but ICP analyses show that the palladium content in Pd@OIP-1 and Pd@OIP-2 are 0.39 and 0.95 mmol/g,

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† Electronic Supplementary Information (ESI) available: experimetal details, solid-state ^{13}C NMR spectra, IR spectra, TGA curves, SEM images and PXRD patterns of Pd@OIP-1 and Pd@OIP-2, as well as NMR spectra for catalytic products. See DOI: 10.1039/b000000x/

respectively. Higher palladium content in Pd@OIP-2 is probably ascribed to easier reduction of palladium(II) species in DMF than in 1,4-dioxane during the cross-coupling reaction,[13,14] which is favorable for the formation palladium NPs.

To determine the chemical structure of Pd@OIP-1 and Pd@OIP-2, solid-state ^{13}C NMR and IR were conducted. In solid-state ^{13}C NMR spectrum of Pd@OIP-1 (Fig. S1, †ESI), the weak peak at 114 ppm corresponds to 4,5-positioned carbon of imidazolyl rings, other peaks at 139, 135 and 127 ppm may be ascribed to carbon of phenyl rings and 2-positioned carbon of imidazolyl rings.[10a,15] Solid-state ^{13}C NMR spectrum of Pd@OIP-2 is similar to that of Pd@OIP-1 except for the disappearance of the peak at 135 ppm, which is probably overlapped by the adjacent peaks. It was reported that the interactions between supported palladium NPs and aromatic groups can decrease the regularity of the polymer networks, and ultimately results in broadening of the peaks in solid-state ^{13}C NMR spectra. As a result, the difference of solid-state NMR spectra between Pd@OIP-1 and Pd@OIP-2 presumably results from different loading amount of palladium NPs.[16] However, FTIR spectra between Pd@OIP-1 and Pd@OIP-2 are almost identical with each other (Fig. S2, †ESI). Thermogravimetric-mass spectrometric (TG-MS) analyses show that Pd@OIP-1 and Pd@OIP-2 are stable up to 200^{o}C (Fig. S3, †ESI). Initial weight losses of 2.8% and 3.2% before 150^{o}C in Pd@OIP-1 and Pd@OIP-2 are ascribed to the presence of water molecules captured in the polymers, which are confirmed by ion current at m/z=18, respectively.

The porosities of Pd@OIP-1 and Pd@OIP-2 were studied by N_2 adsorption/desorption at 77 K (Fig. S4, †ESI). The specific surface areas of Pd@OIP-1 and Pd@OIP-2 are 5.9 and 60.4 m^2 g^{-1}, respectively, which are lower than the reported imidazolium-based POPs.[9] Scanning electron microscopy (SEM) images show that both Pd@OIP-1 and Pd@OIP-2 are composed of irregular granular particles, and the granules of Pd@OIP-2 are much smaller than that of Pd@OIP-1 (Fig. S5a and 5b, †ESI), which is ascribed to the solubility difference of the ionic polymers in DMF and 1,4-dioxane. Ionic polymers is more inclined to precipitate in low polar 1,4-dioxane, finally resulting in the formation of large particles.[12c,17]

The existing state of surface palladium on Pd@OIP-1 and Pd@OIP-2 was investigated by X-Ray photoelectron spectroscopy (XPS). As shown in Fig. S6 in ESI, Pd 3d region is divided into two spin-orbital pairs, indicating the presence of two types of the surface-bound palladium species. The binding energy peaks at 340.8 (Pd $3d_{5/2}$) and 335.5 eV (Pd $3d_{3/2}$) are assigned to Pd(0) species, while the peaks at 342.4 (Pd $3d_{5/2}$) and 337.1 eV (Pd $3d_{3/2}$) correspond to Pd(II) species, which probably result from the oxidation of Pd(0) during air contact.[18] The ratios of Pd(0)/Pd(II), which are estimated by their ratio of relative peak areas, are 2.94 and 2.85 in Pd@OIP-1 and Pd@OIP-2, respectively.

Transmission electron microscope (TEM) images reveal that palladium NPs possess uniform size distribution, and their average diameters in Pd@OIP-1 and Pd@OIP-2 are 2.80±0.41 nm and 3.07±0.48 nm, respectively (Fig. 1). It should be mentioned that their particle size is smaller than imidazolium-immobilized palladium NPs in organic-inorganic hybrid materials.[7] A high magnification TEM image of Pd@OIP-2 (Fig. 1d, inset) shows visible lattice fringes of 0.23 nm, corresponding to the *d*-spacing of Pd (111) plane. The diffuse rings in the selected-area electron diffraction (SAED) pattern of Pd@OIP-2 show the refection of crystalline palladium (Fig. 1d, inset). The lack of the diffuse rings or spots in Pd@OIP-1 (Fig. 1b, inset) illustrates the amorphous nature of its palladium NPs. Powered X-ray diffraction (XRD) patterns (Fig S7, †ESI) further confirm the existence of palladium lattice in Pd@OIP-2. The strong peak at 2θ=44.1^{o} is ascribed to (111) lattice spacing, while the weak peaks at 2θ=68.2 and 82.1^{o} are assigned to (220) and (311) lattice spacing of palladium, respectively.[7c] On the contrary, palladium NPs in Pd@OIP-1 turn out to be amorphous, suggesting that the reducing ability of solvents are important factors in determination of nucleation and crystal growth rate of palladium in catalytic reaction.[19] Incidentally, the broad reflection peak at 2θ=10~35^{o} indicates that Pd@OIP-1 and Pd@OIP-2 have no long-range frameworks owing to the kinetically- controlled irreversibility of Suzuki-Miyaura reaction. High-annular dark-field scanning TEM (HAADF-STEM) and Energy-dispersive X-ray (EDX) clearly demonstrate the homogeneous distribution of palladium NPs throughout Pd@OIP-1 and Pd@OIP-2 (Fig. S8 †ESI)).

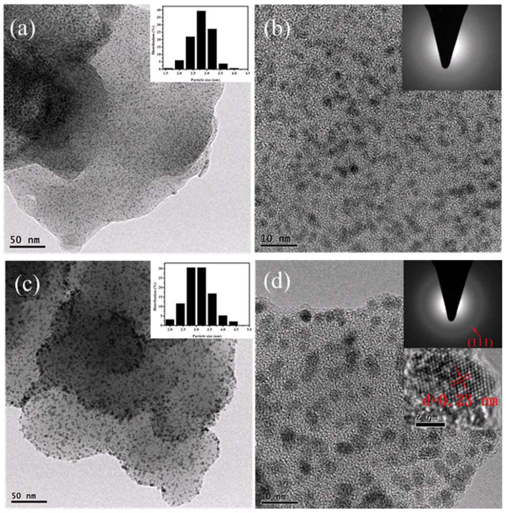


Fig. 1 TEM images of (a, b) Pd@OIP-1 and (c, d) Pd@OIP-2.

The catalytic performances of Pd@OIP-1 and Pd@OIP-2 were evaluated using hydrogenation of nitrobenzene at 25 ^{o}C. As shown in Fig. S9 in ESI, Pd@OIP-1 afforded a full conversion of nitrobenzene to aniline in 20 min, while Pd@OIP-2 almost gave a quantitative conversion to aniline in 10 min. The higher catalytic activity of Pd@OIP-2 is probably ascribed to its higher specific surface area and smaller granular particles than Pd@OIP-1, which provide more opportunities for contact between substrates and active sites in the polymers. On the other hand, the exposed (111) palladium facets in Pd@OIP-2 are also responsible for the higher catalytic activity.[20] The control experiment was also performed in the absence of Pd@OIP-1 and Pd@OIP-2, and no aniline was detected under the same conditions.

Besides activity, reusability is also an important performance in heterogeneous catalytic systems. Recycling experiment was further examined using Pd@OIP-2 as a precatalyst in hydrogenation of nitrobenzene without the addition of extra palladium. After the first run of hydrogenation was finished, ICP analysis shows palladium leaching into the solvent is only 0.20 ppm. Interestingly, no obvious efficiency loss was detected after the reaction was performed for five runs (Fig. 2). However, the selectivity of aniline is decreased to 88% in the sixth run with the total conversion of nitrobenzene. SEM image reveals that granular particles of Pd@OIP-2 are well maintained after consecutive six runs (Fig. S5c, †ESI). TEM analysis shows that the average diameter of the palladium NPs after sixth run reaction in Pd@OIP-2 was increased to 4.78±1.01 nm, but no obvious aggregation of NPs was observed (Fig. 3). Noteworthily, *d*-spacing of Pd (111) plane stays visible after the recycling reaction (Fig. 3b, inset), indicating that palladium NPs are well stabilized in polymers.

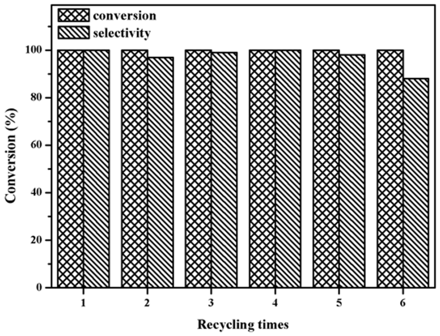


Fig. 2 Reusability of Pd@OIP-2. Reaction conditions: nitrobenzene (0.5 mmol), $NaBH_4$ (2.5 mmol), [Pd] (1 mol%), H_2O (2.5 mL), 25 °C, 15 min.

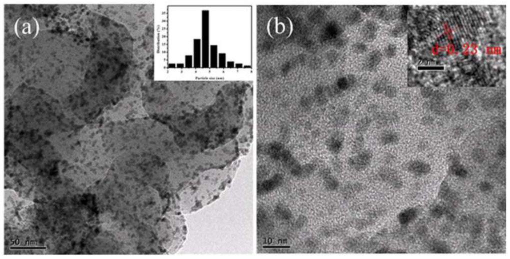
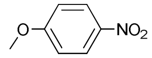
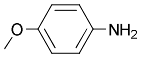
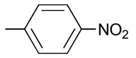
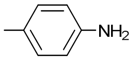
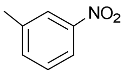
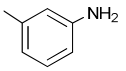
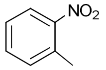
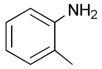
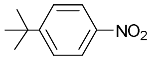
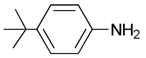
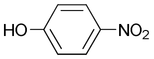
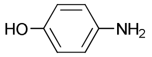
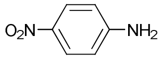
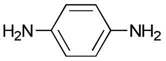
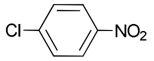
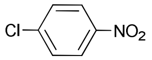
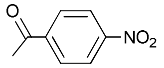
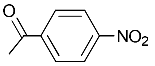
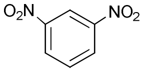
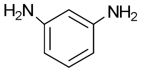


Fig. 3 TEM images of Pd@OIP-2 after consecutive six runs.

The excellent catalytic activity of Pd@OIP-2 encouraged us to further explore the generality of the catalytic system, and several nitroarenes with different steric and electronic characters were tested. To ensure high conversion and selectivity of most substrates, the hydrogenation reactions were performed in a mixed solvent of H_2O and THF (9:1 in volume) for 1.5 h at 25 °C (Table 1). The substrates bearing electron-donating groups, such as 4-nitroanisole, 4-nitrotoluene, 3-nitrotoluene and 2-nitrotoluene, provided the full conversion and selectivity to corresponding products (entries 1-4). The steric hindrance at *ortho*- *meta*- and *papa*-position of nitrotoluene has no obvious effect on the catalytic reaction. In contrast, 4-*t*-Butylnitrobenzene gave rise to 4-*t*-butylaniline in 99% GC yield and 96% selectivity due to its bulky steric effect (entry 5). Functional groups, such as –OH and –NH_2, could be well tolerated in this catalytic system (entries 6 and 7). However, 4-nitrochlorobenzene gave a 90% yield for 4-chloroaniline and 10% yield for dechlorinated product of aniline (entry 8). This tendency toward dehalogenation was often observed in palladium-catalyzed hydrogenation of aryl halides (entry 9).[2c] Interestingly, 4-nitroacetophenone gave 1-(4-aminophenyl)ethanol as the sole product in 2.5h, in which thecarbonyl group was reduced into hydroxyl (entry 9). It should be mentioned that the catalytic system is also reactive for hydrogenation of 1,3-dinitrobenzene, and the corresponding dianiline was obtained in a 98% isolated yield (entry 10).

Table 1 Reduction of nitroarenes.[a]

Entry	Reactant	Product	Conv. (%)[b]	Select. (%)[b]
1			100(99)	100
2			100(91)	100
3			100(98)	100
4			100(98)	100
5			99(88)	96
6			100(99)	100
7			100(99)	100
8			100-	90
9[c]			100(94)	100
10			100(98)	100

[a] Reaction conditions: nitroarene (0.5 mmol), $NaBH_4$ (2.5 mmol), [Pd] (1 mol%), in 2.5 mL H_2O/THF (9:1, v/v) at 25 °C, 1.5 h; [b] conversion and selectivity were determined by GC, isolated yields were given in parentheses; [c] 2.5h.

In summary, a facile approach for *in situ* generation of palladium NPs supported in imidazolium-based porous organic ionic polymers was developed. The ionic polymers were synthesized through Suzuki cross-coupling reaction, in which the concomitant formation of well-dispersed palladium NPs with small size and narrow size distribution were observed. Through judicial selection of reaction solvents, the size of the polymers, palladium content and the size of palladium NPs could be regulated. The excellent catalytic performances and recyclability of Pd@OIP-2 were observed in hydrogenation of nitroarenes without an extra addition of palladium species. This study not only provides a new method for fabrication of well-dispersed metal NPs supported in porous organic polymers, but also opens a new avenue to make full use of the noble metals involved in synthetic reactions.

Notes and references

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