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Synthesis and Applications of Palladium-Coated Poly(vinylpyridine) Nanospheres

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Monodisperse poly(4- and poly(2-vinylpyridine) nanospheres in the 500 nm diameter range were prepared by emulsifier-free emulsion polymerization techniques under free radical initiation of the respective monomers with 4 wt % divinylbenzene as the cross-linking agent. The size, integrity, and nature of the nanospheres were investigated by Scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray analysis, Auger spectroscopy, and Fourier-transform infrared spectroscopy measurements. The rigid and highly stable nanospheres with exposed pyridine nitrogen on the surface serve as an excellent support for Pd^0 nanoparticles in the range of 1−4 nm. The Pd-coated nanospheres were also characterized by transmission electron microscopy and inductively coupled plasma mass spectrometry measurements. Four weight percent palladium-coated nanospheres serve as good catalysts for Suzuki-, Heck-, and Stille-type coupling reactions for carbon−carbon bond formation.

Introduction

Noble metal colloids stabilized by synthetic polymers and their catalytic properties were described by Nord and co-workers as far back as the 1940s.[1] The synthesis of catalytically active metal colloids by aqueous alcohol reduction of metal salts in the presence of protective polymer was first reported by Hirai and co-workers.[2] They have a characteristic high surface-to-volume ratio, and consequently large fractions of the metal atoms that are exposed at surfaces are accessible to reactant molecules and available for catalysis. They are often coated with an organic shell to prevent them from agglomeration.[3] The colloidal particles of 1−3 nm mean diameter with narrow size distributions have shown high activity and selectivity for the hydrogenation of olefins and dienes,[2,4] hydration of acrylonitrile,[5a] and light-induced hydrogen generation from water.[5b] Supported polymer-stabilized noble metal colloids on supports have great potential for environmental and industrial processes, but many established methods suffer from complex steps for the immobilization and reduced catalytic activity.[6] These synthesis routes are based on a two-step process involving synthesis of metal colloids and immobilization via covalent interaction or ligand coordination between the protective polymers and supports.

Recently, palladium dispersions containing small metal particles (20−80 Å) have been of increasing scientific interest as a colloidal catalyst for organic C−C bond formation reactions.[7,8] Palladium-catalyzed carbon−carbon bond reactions are gaining prominence in organic synthesis for their remarkable chemo-, regio-, and stereoselectivities, mild reaction conditions, and high efficiency. Several challenges, however, remain for chemical practitioners to grapple with when performing a palladium-catalyzed process at scale. First, the relatively high price of palladium complexes, albeit in catalytic amounts, contributes significantly to the overall cost of production. Second, removal of ligands and byproducts derived from using palladium as homogeneous catalyst often complicates workup and product isolation.[9] To address these concerns, several heterogeneous palladium catalysts with either carbon/graphite as supports[10] or a silica/alumina supported[11,12] or poly-

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meric resin supported[13] system have been developed over the last two decades with varying degrees of success. Most of these resin-bound ligand systems bind the Pd atoms or particles through phosphine ligands, attached to 1−2% cross-linked polystyrene, a system that requires several demanding synthetic transformations and expensive reagents to prepare.[14,15] In most cases additional free ligands such as PPh_3 have to be added to stabilize the polymer−phosphine−Pd complexes.[16] Addition of soluble ligands, however, increases the chance for metal to leach out of the system through disproportionation between the polymer-bound and free phosphines, which often leads to reduced activity as compared to the similar homogeneous systems.[17] An easily prepared, air- and moisture-stable, and recyclable solid system is highly desirable in all-important Pd-catalyzed C−C bond formation reactions.

In the present study, a new approach of making a palladium metal colloid based heterogeneous catalyst system has been developed by involving preparation of high surface area poly(vinylpyridine) submicrometer beads followed by their subsequent derivatization with palladium colloids in common Pd-catalyzed C−C coupling reactions. For the first time, we report here the preparation and characterization of poly(-4- and poly-(2-vinylpyridines) by emulsifier-free dispersion polymerization. We also report the preparation and characterization of palladium colloids on poly(vinylpyridine) nanospheres by scanning and transmission electron microscopy (SEM, TEM), energy-dispersive X-ray (EDX), analysis, Fourier-transformed infrared (FTIR) spectroscopy, and inductively coupled plasma mass spectrometry (ICP-MS), together with their catalytic properties in simple organic C−C coupling reactions (Heck, Suzuki, and Stille couplings).

Experimental Section

All polymer syntheses were carried out in a 1 L reaction kettle. The kettle was fitted with a condenser, a nitrogen inlet valve, and a mechanical stirring apparatus. The mechanical stirrer used was the IKA Eurostar power control-visc. Analysis was carried out on the Cambridge 360 scanning electron microscope at 10 kV, and the Perkin-Elmer Philips 660 scanning Auger multiprobe spectrometer. SEM samples were prepared by placing a drop of sample diluted with water or ethanol on a glass plate and allowing it to air-dry. The sample was then sputter-coated with gold. Auger samples were prepared by placing a very dilute drop of sample onto a silicon wafer and allowing it to air-dry. The vinylpyridines and divinylbenzene used were purchased from Aldrich. The vinylpyridines were vacuum distilled from calcium hydride to remove the inhibitor and traces of moisture. The divinylbenzene was vacuum distilled to remove the inhibitor. Potassium persulfate was purchased from Aldrich and used as received. All TEM samples were prepared by placing a drop of sample (diluted with water or ethanol) on top of a copper sample grid and drying it in air. All TEM analyses were performed using a Philips EM 420 electron microscope at 120 kV accelerating voltage equipped with a KEVEX EDX analyzer. UV−vis spectroscopy was performed on a Hewlett-Packard HP8453 model spectrometer. The average size of colloids was calculated by averaging the size of over 50 particles from the TEM picture.

Synthesis of Poly(vinylpyridine) Nanospheres. A 1 L reaction kettle, equipped with a condenser, gas inlet, and mechanical stirring apparatus, containing 700 mL of water was heated to 80 °C, stirred at 300 rpm, and degassed with N_2 for 1 h. After 1 h, the gas flow was turned off, and 73 mL of vinylpyridine (0.673 mol) and 4 mL of divinylbenzene (∼4 mol %) were added to the water. The reaction was stirred for 20 min to bring the monomer and cross-linking agent to the temperature, followed by the addition of 0.6 g (3 mmol) of potassium persulfate dissolved in 20 mL of water as the initiator. The milky reaction mixture was stirred at 300 rpm and 80 °C for 4 h and then stopped. The reaction was cooled to room temperature, and then the nanospheres were vacuum filtered using a coarse filter frit. The resulting polymer was then characterized via scanning electron microscopy to determine the size and integrity of the nanospheres and Auger spectroscopy to analyze the surface of the nanospheres. SEM showed uniform nanospheres of ∼500 nm (±10%). Auger spectroscopy showed a nitrogen peak at 379 eV (corresponding to KLL transition).

Palladium Colloidal Preparation. *(a) Citrate Reduction. A* 50 mL sample of an aqueous 0.393 mM solution of potassium hexachloropalladate(IV) was heated to reflux (110 °C). A 1% solution of sodium citrate (6 mL) was added. Continued refluxing for 4 h gave a dark brown colored solution, which was filtered off and characterized as palladium colloids.

(b) Ethanol Reduction. Palladium(II) chloride (12 mg, 0.066 mmol) was dissolved in 25 mL of ethanol and 25 mL of water. To the solution was added poly(vinylpyrrolidone) (PVP-K30, 290 mg, 2.64 mmol as monomer units), and the solution was allowed to reflux (100 °C) overnight in an inert atmosphere. In yet another similar experiment poly(vinyl alcohol) (PVA-K30, 116 mg, 2.64 mmol as monomer units) was added instead of poly(vinylpyrrolidone), to check the activity vis-à-vis the colloidal protecting group. In both cases, the resulting dark brown solution was characterized to be monodisperse palladium colloids.

Immobilization of Pd Nanoparticles on PVP Nanospheres. The palladium colloids used for the surface derivatization of PVP nanospheres were in the size range of 1−4 nm and were bearing different surface stabilizing groups (citrate ion, poly(vinylpyrrolidone), or poly(vinyl alcohol)). In all the cases, immobilization was done by adsorption from aqueous/ethanolic colloidal solution onto dispersed PVP nanospheres. For this purpose 0.5 mL (∼10.0% solid suspension concentration) of PVP nanopheres was suspended in 5 mL of water or ethanol in a 30 mL centrifuge tube followed by addition of 5 mL of prefabricated colloidal particles. The resulting mixture was centrifuged and the supernatant decanted followed by at least two washings with water or ethanol. The sequence was repeated until the colloids were exhaustively deposited as observed by the absence of the brown-black color of the colloids in the supernatant during subsequent wash steps (as confirmed by the UV−vis spectrum of the supernatant).

Palladium-Derivatized PVP-Based Catalysis. A 100 mL three-necked flask equipped with a thermometer and a reflux condenser was charged with 1-bromo-4-nitrobenzene (0.99 mmol), *n*-butylacrylate (1.4 mL, 9.9 mmol), triethylamine (0.2 mL, 1.5 mmol), and *N,N*-dimethylacetamide (DMA, 10 mL). To this was added 10 mg (0.4 mol % palladium with respect

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to 1-bromo-4-nitrobenzene) of PVP−Pd through a funnel, and the catalyst was allowed to disperse by allowing it to stir for about 20 min. After this, the reaction mixture was heated to 130−140 °C. To monitor the reaction, 0.2 mL samples were taken in regular intervals, diluted with CH_2Cl_2, filtered with a 0.2 μm filter, and analyzed by thin-layer chromatography (1:1 mixture of CH_2Cl_2/Et_2O), gas chromatography, and mass spectrometry. *E*/*Z* selectivity of the reaction was determined by gas chromatography (as well as TLC in a 1:1 mixture of CH_2Cl_2 Et_2O as solvent) by comparing the retention time of the product (*E*)-*n*-butyl-4-nitrocinnamate against the *E*-isomer prepared by acid esterification of 4-nitrocinnamic acid (predominately in the trans geometry) and 1-butanol. The completion of the reaction was determined when no reactant (1-bromo-4-nitrobenzene) was left as analyzed by GC−MS.

For the Suzuki-type coupling reactions, essentially the same procedure was used at the same scale except for the following modification in the reactants. With 0.99 mmol of 1-bromo-4-nitrobenzene, 1.5 equiv of phenylboronic acid, 3 equiv of Na_2CO_3 (2 M in H_2O, degassed or otherwise) or NEt_3, and 10 mg (0.4 mol % palladium with respect to 1-bromo-4-nitrobenzene) of PVP−Pd catalyst were allowed to react at 125 °C in DMA as solvent. In this case also, the reaction was monitored in the same manner except that the organic phase was dried over $MgSO_4$ before TLC or GC−MS was performed. For the PVP−Pd based catalysis of Stille-type coupling, almost the same procedure as described above for the Heck reaction was employed with the following modifications. With 0.25 mmol of 1-bromo-4-nitrobenzene, 1.5 equiv of trimethylphenyltin was reacted in DMA at 130 °C in the presence of 10 mg (1.5 mol % palladium with respect to 1-bromo-4-nitrobenzene) of PVP−Pd catalyst. In this case too, products were analyzed using TLC and GC−MS. In all the above cases blank experiments were performed under exactly the same conditions, i.e., with all the reactants, solvent, and temperature, in the absence of the catalysts to ensure the role of catalysts in the above-mentioned reactions. Also a similar method of palladium derivatization as well as catalysis was performed with commercially available amine-functionalized Polybead 1.0 μm latex microspheres (Polysciences, Inc.).

Results Discussion

Poly(vinylpyridine) nanospheres have been successfully synthesized using 4-vinylpyridine and 2-vinylpyridine as monomers. The nanospheres were cross-linked using ∼4 mol % divinylbenzene. This percentage of cross-linking was chosen because it decreases the solubility and swelling of the polymer beads while maintaining the monodisperse character of the nanospheres. Three types of nanospheres have been synthesized using vinylpyridines. These include poly(4-vinylpyridine), poly(2-vinylpyridine), and the copolymer poly(2-vinylpyridine-*co*-4-vinylpyridine). All nanospheres were ∼500 nm in diameter and showed uniformity in shape and monodispersity in size (Figure 1). Varying the reaction conditions does not appear to affect the size of the beads, although temperatures too high or low do affect the spherical integrity. Reaction times, temperature, and stirring rates were all varied and the beads still retained the monodisperse character of ∼500 nm. Auger spectroscopy showed a nitrogen peak at 379 eV, supporting the presence of nitrogen on the surface of the nanospheres (Figure 2).

Application of PVP Nanospheres. Figure 3 shows the palladium coverage of PVP nanospheres after adsorption from polymer-protected preprepared solution. As is obvious from the TEM micrographs, the coverage is highly uniform in terms of both the particle size and the support size. A strong palladium−pyridine lone pair interaction leads to a stronger binding of these beads to the palladium nanoparticles by displacing the surface stabilizing groups (i.e., poly(vinylpyrrolidone), poly(vinyl alcohol), etc.) used initially to make the colloids. ICP-MS analysis suggests a palladium loading of 4 wt % on these nanospheres. What can be argued about the coverage is not in terms of the weight percent of loading but the particle size of the catalyst itself, which is 1−4 nm, which means that more surface palladium atoms (which are the catalytically active sites) are available for catalysis as compared to using bulk palladium as catalyst, resulting in high activity per gram of supported catalysts.

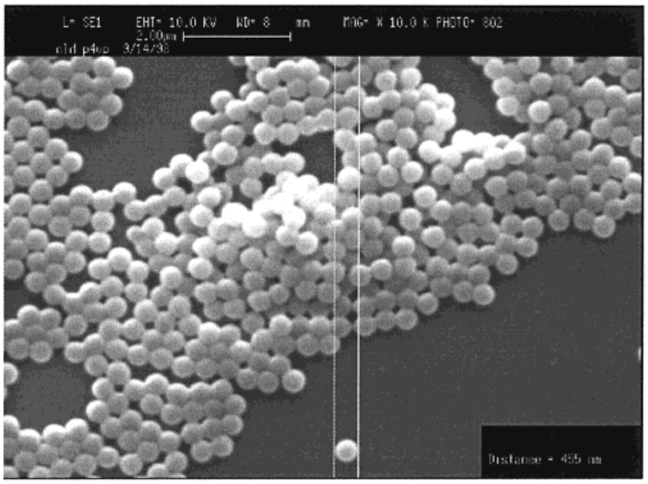

Figure 1. SEM micrograph of 4-vinylpyridine beads showing the size and shape uniformity magnification 10000 × (reproduced at 83% of original size).

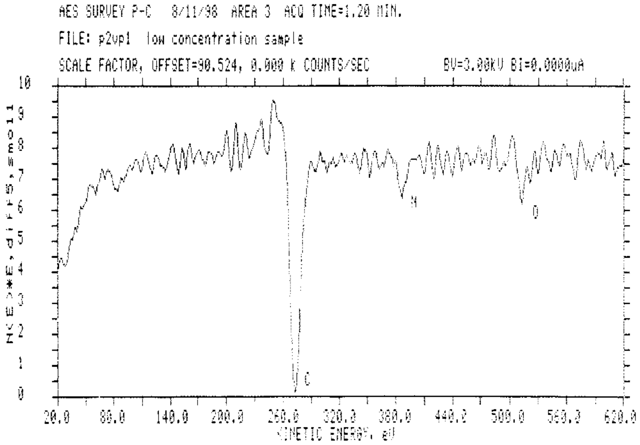

Figure 2. Auger analysis of 4-vinylpyridine beads.

Scheme 1 lists the types of three important reactions that were investigated to test the catalytic activity of supported palladium nanoparticles. In all the cases, complete conversion to the product was observed. In case I (Heck), the reaction was complete in 4 h with no reactants remaining as observed by GC−MS. The *E*:*Z* ratios was found to be 99:1. In case II (Suzuki), the reaction was complete in less than 6 h with complete conversion to the product when 2 M Na_2CO_3 was used as base, while the conversion was only 50% if NEt_3 was used as base. In the case of Stille coupling (case III), 100% conversion was achieved in 4 h. In all the cases, experiments without catalysts yielded no products, under identical conditions. Also, in all cases under

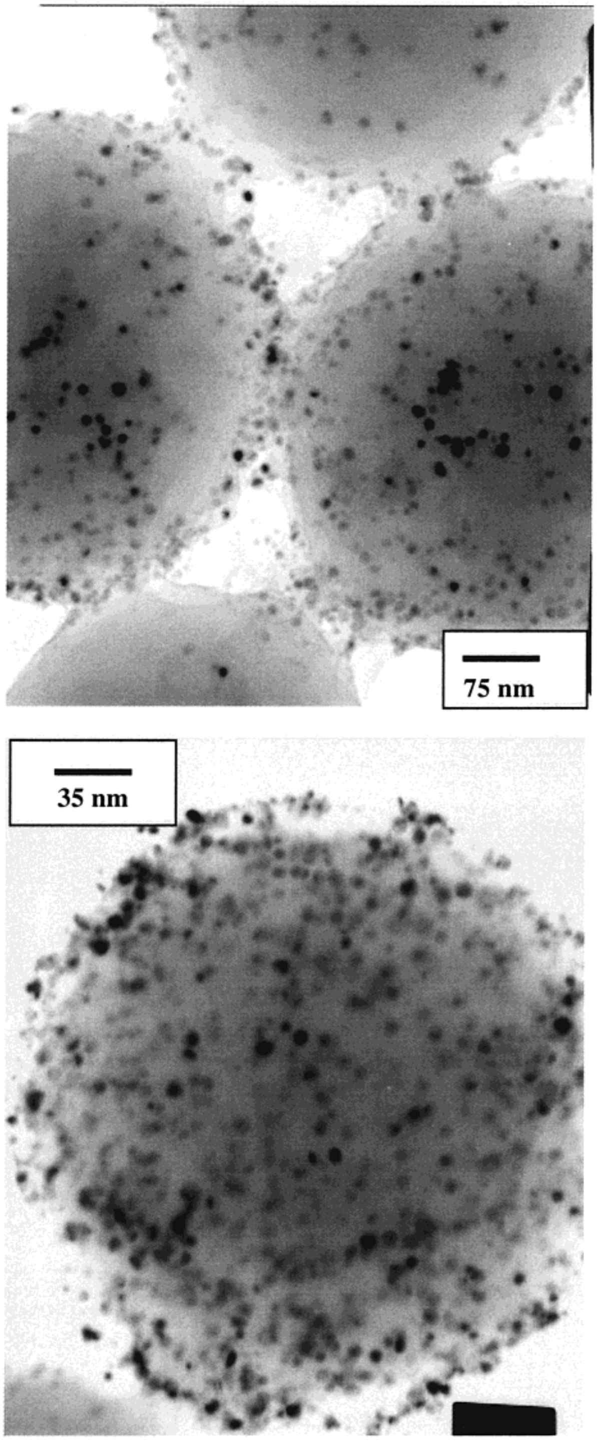

Figure 3. TEM micrographs showing the surface coverage of 4-vinylpyridine microbeads with colloidal palladium nanoparticles (magnification: (a, top) 175000×; and (b, bottom) 230000×).

identical experimental conditions, no products were observed when Pd supported on Polybead amino nanospheres was used as catalyst, although the Polybead amine samples showed similar coverage of palladium nanoparticles by TEM.

It has been previously reported that the reactivity of colloidal nanoparticles is affected by the nature of the surface stabilizing groups.[18] In our case, however, similar activity was found in the case of colloids stabilized by citrate, polypyrrolidone, or poly(vinyl alcohol). In all these cases the concentration of stabilizing groups was optimized to give maximum coverage without agglomeration on the surface of nanospheres. The catalyst was found to be air-stable and was stored in air for more than six months, and it did not show any decrease in activity with time. The substrate (PVP microspheres) was also found to be very stable, as evidenced by TEM and SEM as well as EDX analysis; it

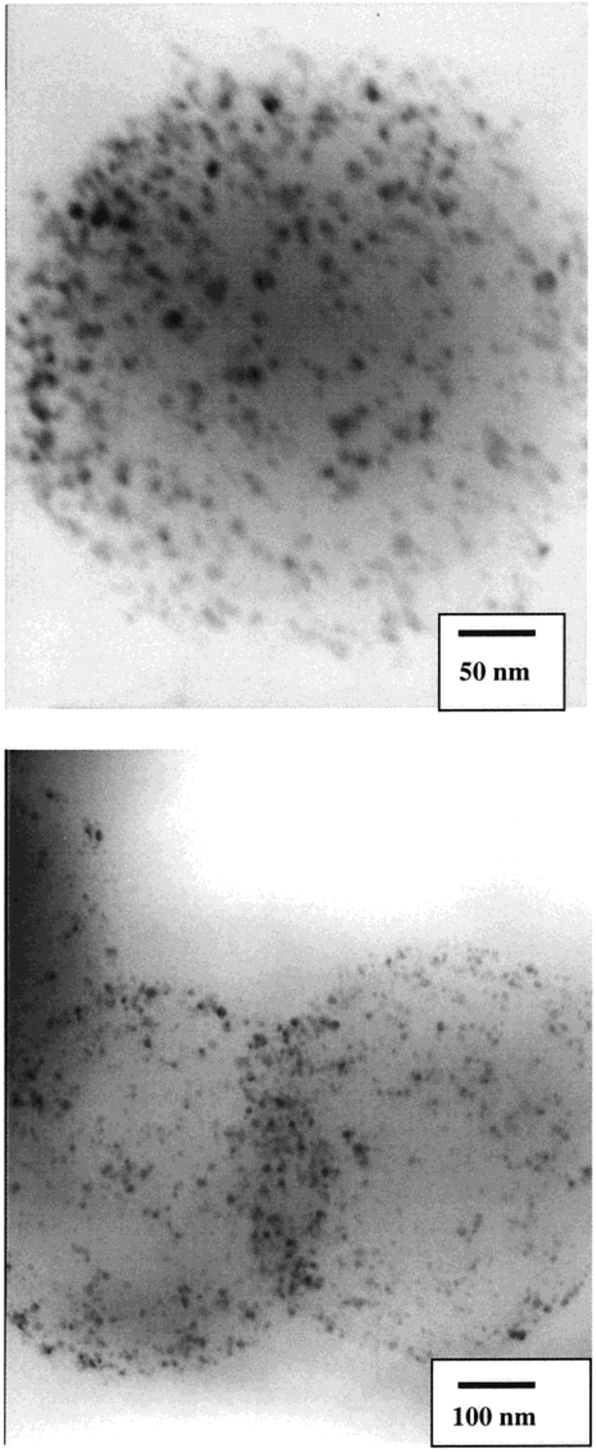

Figure 4. TEM micrographs showing PVP−Pd coverage under the reaction conditions (as in Scheme 1): (a, top) before and (b, bottom) after the reaction (magnification: (a) 230000×; (b) 135000×).

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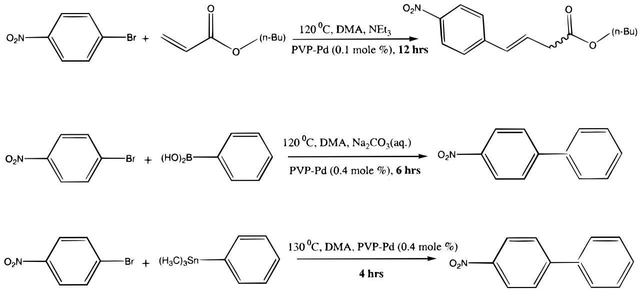
Scheme 1. Schematics of the Representative Catalysis Reactions Performed Using PVP−Pd Catalysts



does not tend to agglomerate and can be dried and resuspended in common organic solvents (DMA, toluene, etc.) without any significant swelling. Figure 4 shows the palladium coverage on PVP microspheres, before and after the reaction (Heck reaction, temperature 135 °C). Thus, it is clear that they do not have any substantial palladium loss or swelling under the relatively harsh experimental conditions. Similar stability of palladium colloids prepared in block copolymer micelles of polystyrene−poly(4-vinylpyridine) has been reported by Klingelhofer et al.[19] However, coverage and palladium loading over beads are relatively higher compared to those of their system.

A cross-linker concentration of 4 mol % divinylbenzene was chosen as this concentration reduces the swelling of the polymer while maintaining the spherical integrity and the monodisperse character of the nanospheres. Also, the fact that amine-functionalized Polybead microspheres failed to catalyze the above reactions under our conditions itself suggests a role of metal−support (i.e., palladium−pyridine nitrogen) interaction in the catalysis. However, further investigations are needed to conclude definitely about the role of the support. Some initial investigations with “deactivated” or “unactivated” substrates under identical conditions showed much lower activity for the coupling product, which warrants more careful studies with respect to the role of palladium nanoparticles,[18,20] in the catalysis as well as the metal−support interaction.[13,21] Further investigations are also underway to explore a whole range of Pd-catalyzed C−C coupling reactions as well as to understand some mechanistic aspects.

Conclusion

Poly(vinylpyridine) nanospheres have been synthesized using the emulsifier-free emulsion polymerization technique. These nanospheres are highly uniform in size and shape. Currently the modification of the polymeric bead preparation process is underway to synthesize beads with larger diameters or make beads with more desirable surface properties (i.e., supporting other metal particles, etc.) by using a suitably functionalized coploymer. Poly(vinylpyridine) nanospheres were used as a stable support for dispersing polymer-stabilized palladium nanoparticles by a one-step adsorption from colloidal solution. These supported palladium nanoparticles were then tested for their catalytic activity in C−C bond formation, in some very common activated systems. They were found to be highly active at a mole ratio of catalyst <0.5 mol % for the substrates that were employed in the studies. The obvious advantage of the PVP−Pd-based catalytic system is its high activity, air and temperature (up to 150 °C) stability, stability in a number of organic solvents, ease of separation, and high dispersion of catalyst particles. Further studies on the catalytic activity of these Pd-coated beads in other organic reactions as well as their reusability are underway.

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