An efficient and reusable palladium nanocatalyst in C-C bond forming cross-coupling reactions

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INTRODUCTION

Palladium catalysts have been extensively studied in the synthetic organic chemistry particularly in C-C bond forming cross-coupling reactions. 1 Alternatively, palladium nanoparticles (Pd NPs) have attracted a remarkable interest in organic synthesis owing to the enhanced catalytic reactivity and lower catalytic loading. 2 Traditional stabilizers such as phosphines, amines and dendrimers are used for the preparation of NPs which often leads to agglomeration of NPs during the catalytic reaction. The Pd NPs stabilized by Pd-C covalent bond are much more stable than the traditional stabilizers. 3

RESULTS AND DISCUSSION

Palladium NPs were prepared by simple reduction of potassium tetrachloropalladate and 1,1′-binaphthyl-2,2′-bis(diazonium tetrafluoroborate) with sodium borohydride (Scheme 1). The palladium NPs are well characterized with FTIR, NMR, SEM, TEM, ICP-OES and XPS analysis. 4

Scheme 1. Synthesis of Pd NPs stabilized by Pd-C covalent bonds

This new class of Pd nanoparticles was efficiently used as reusable catalysts for C-C bond forming cross coupling reactions such as Heck, Suzuki–Miyaura and Sonogashira coupling reactions (Scheme 2).

Scheme 2. Pd NPs catalyzed cross-coupling reactions

<table>
<thead>
<tr>
<th>Substrate</th>
<th>cycles</th>
<th>recovery of Pd NPs</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R= CH$_3$; R'= H; X=I</td>
<td>1</td>
<td>95%</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>93%</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>90%</td>
<td>91</td>
</tr>
</tbody>
</table>

a) Suzuki-Miyaura cross-coupling reaction

b) Heck cross-coupling reaction

c) Sonogashira cross-coupling reaction

The Pd NPs are quantitatively recovered and reused for these reactions. After the catalytic reactions the NPs had same size and reactivity without any apparent agglomeration which was confirmed with SEM, TEM and ICP-OES analysis (Figure 1).

Figure 1. HRTEM images of Pd NPs before and after catalytic reactions.

CONCLUSION

In conclusion, we have synthesized a new class of stable Pd NPs stabilized by stable Pd-C(binaphthyl) covalent bond and were successfully utilized as recoverable and reusable catalysts for Suzuki, Heck and Sonogashira cross-coupling reactions.

ACKNOWLEDGEMENTS

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REFERENCES