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Heterogeneous Suzuki Cross-Coupling Reaction Catalyzed by Magnetically Recyclable Nanocatalyst

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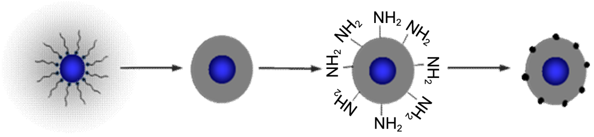
The Suzuki cross-coupling reactions proceeded in excellent yields when it was catalyzed by magnetically recyclable nanocatalyst. This nanocatalyst provided very high catalytic activity with low loading level (1 mol %), because the palladium nanoparticles were so small in size (~2 nm) and located on the surface of the nanocomposite. It was also easily recovered from the reaction mixture using a magnet and reused for six consecutive cycles.

Key Words : Heterogeneous catalysis, Magnetic separation, Nanoparticles, Palladium, Suzuki cross-coupling

Introduction

Suzuki cross-coupling reaction catalyzed by palladium is one of the most important $C(sp^2)$-$C(sp^2)$ bond formation reactions in the laboratory and the chemical industries.[1-3] Many catalytic Suzuki reactions using palladium nanoparticles (NPs) have been successfully demonstrated. These catalysts NPs present high surface-to-volume ratio characteristic.[4-6] However, most of the Pd NPs catalysts are proved to be of somewhat limited use due to the challenges in separating and reusing the expensive catalysts.[7-9] Most heterogeneous systems require a filtration or centrifugation step or a tedious workup of the final reaction mixture to recover the catalyst. Furthermore, the unprotected Pd NPs are usually unstable and coagulation is inevitable during the catalytic reactions.[10-12] The immobilization of catalysts NPs on solid supports has therefore attracted a lot of attention to circumvent recycling and instability probelms.[13-16] The catalyst NPs grafted or immobilized on the surface of the supports also provide accessible diffusion to reagents, and result in more effective chemical reactions.[17,18] Among the various nanostructured materials, magnetic NPs have attracted growing interest owing to their unique properties and potential applications in various fields, including isolation and recycling of expensive catalysts NPs.[19-21] Magnetic separation provides a convenient method for removing and recycling magnetized species by applying an appropriate magnetic field. This approach prevents the agglomeration of the catalyst NPs during recovery and increases the durability of the catalysts.[22-25] Herein, we report a simple method for the fabrication of magnetically recyclable nanocatalyst with excellent catalytic activity for Suzuki cross coupling reaction. This nanocatalyst provides high catalytic efficiency, due to the small size and location of active Pd NPs sites on the surface of the silica layer nanocomposite. The overall synthetic procedure is represented in Scheme 1.



Scheme 1. Synthetic procedure leading to the magnetically recyclable nanocatalyst.

Experimental

Water was deionized by a Nano Pure System (Barnsted). The chemicals used in this work were purchased at the highest possible grade from Aldrich. Transmission electron microscope (TEM) images were obtained using a JEOL EM-2010 microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy was collected using Al Kα source (Sigma probe, VG Scientifics). Inductivity coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7500 Japan) was used for the elemental analysis. Magnetic NPs were readily synthesized using a previously reported method.[26] In a typical synthesis of iron oleate complex, 10.8 g of iron chloride ($FeCl_3 \cdot 6H_2O$, 40 mmol) and 36.5 g of sodium oleate (120 mmol) was dissolved in a mixture solvent composed of 80 mL ethanol, 60 mL distilled water and 140 mL hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 h. Then, the upper organic layer containing the iron-oleate complex was washed three times with distilled water in a separatory funnel. After washing, hexane was evaporated off, resulting in iron-oleate complex in a waxy solid form. 36 g (40 mmol) of the synthesized iron-oleate complex and 5.7 g of oleic acid (20 mmol) were dissolved in 200 g of 1-octadecene at room temperature. The reaction mixture was heated to 300 °C with a constant heating rate of 3.3 °C min^{-1}, and kept at that temperature for 1 h. The resulting solution containing the nanocrystals was cooled to room temperature, and 500 mL of ethanol was added to the solution to precipitate the nanocrystals. The nanocrystals were separated by centrifugation and dispersed in chloroform. Iron oxide NPs were then coated with a thin layer of silica and the surface of nanocomposite could be easily functionalized. Finally Pd NPs were decorated on the surface of nanocomposite. In a typical synthesis, 0.2 g of synthesized Fe_3O_4 NPs was dispersed in 100 mL cyclohexane containing 5 g igepal® CO-520. To this solution, 2 mL aqueous ammonia was directly added. Tetraethoxysilane (TEOS 2 mL) was then rapidly added and the solution vigorously stirred at room temperature for 7 h to obtain silica coated iron oxide NPs. After ageing, the amine functionalized silica shell was formed by the addition 3-aminopropyl triethoxy silane (0.4 mL) for 2 h. The product was isolated by centrifugation, washed with ethanol and dispersed in 10 mL ethanol. While vigorous stirring, 200 mg palladium(II) acetate dissolved in chloroform was added dropwise, and the mixture was stirred for 2 h at room temperature to produce magnetically recyclable nanocatalyst. The color of the mixture changed from orange to deep black indicating the reduction of the $Pd(OAc)_2$ by amine functions. The efficiency of the designed nanocatalyst was verified in Suzuki cross-coupling reactions. General procedure for catalytic test using the nanocatalyst is as follows. Solvent dimethylformamide (DMF)/H_2O (3:1), aryl halide (0.5 mmol), aryl boronic acid (0.6 mmol), K_2CO_3 (2 mmol), nanocatalyst (1 mol %), and a small stirring bar were added to a round-bottom flask (25 mL). The flask containing reaction mixture was placed in an oil bath (100 °C) and stirred under air atmosphere. After completion of reaction, the mixture was cooled to room temperature and the nanocatalyst was separated using a magnet. The separated nanocatalyst was washed several times with DMF. Finally the products were analyzed by a gas chromatography mass spectrometer (GC-MS).

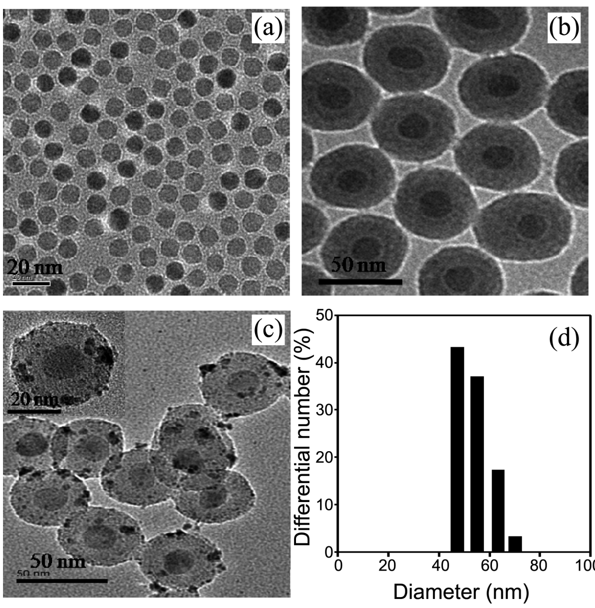


Figure 1. (a) TEM image of Fe_3O_4 NPs. (b) TEM image of silica coated magnetic NPs. (c) TEM image of magnetically recyclable nanocatalyst. (d) DLS diagram of magnetically recyclable nanocatalyst.

Results and Discussion

The Pd loading amount in the magnetically recyclable nanocatalyst was measured by ICP-AES. The intermediates and the final nanocatalyst materials were characterized by TEM, XPS, EDX, and CHN analysis. The TEM image of the magnetic iron oxide NPs (Figure 1(a)) shows that they are uniform and spherical with size of 18 nm. The TEM image of the silica-coated magnetic NPs reveals that the silica coating is uniform, with a thickness of about 20 nm (Figure 2(b)). As shown in Figure 1(c), the TEM image of the Pd NPs on silica layer surface reveals that they have an average size of ~2 nm. The overall size of magnetically recyclable nanocomposite was observed to be ~45 nm by TEM. The dynamic light scattering (DLS) measurements showed the hydrodynamic diameter of the nanocomposite to be around 55 nm (Figure 1(d)). The existence of Pd NPs on the silica layer of nanocomposite was confirmed by XPS analysis (Figure 2(a)). EDX data ascertained the composition of magnetically recyclable nanocatalyst (Figure 2(b)).

We first investigated the use of various solvents and bases in order to find the most appropriate conditions for the heterogeneous Suzuki cross-coupling reaction of iodobenzene with phenylboronic acid using 1 mol % of the catalyst. A remarkable increase in activity was observed with mixture of DMF and H_2O (3:1) as solvent and K_2CO_3 being selected

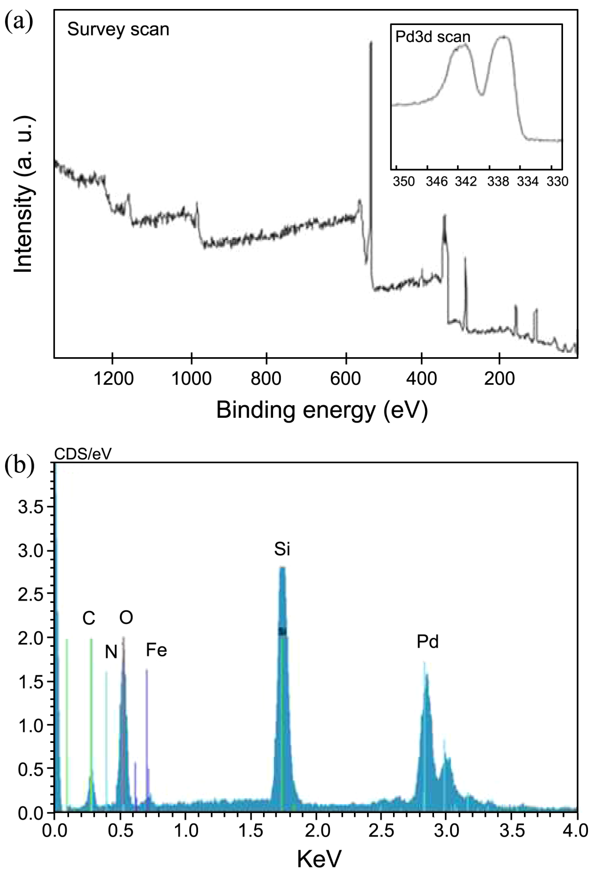
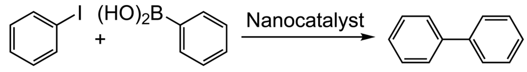


Figure 2. (a) XPS analysis of magnetically recyclable nanocatalyst. The inset shows the Pd 3d scan. (b) EDX spectrum of the nanocatalyst.

Table 1. Effect of solvents on the Suzuki reaction of iodobenzene and phenylboronic acid[a]



Entry	Solvent	Yield (%)[b]
1	DMF/H_2O (3:1)	97
2	DMF/H_2O (2:1)	87
3	DMF/H_2O (1:1)	70
4	DMA/H_2O (3:1)	91
5	DMF	39
6	DMA	28
7	H_2O	0

[a]Aryl iodide (0.5 mmol), phenylboronic acid (0.6 mmol), nanocatalyst (1 mol %), K_2CO_3 (2 mmol), 100 °C, 4 h. [b]Yields were determined by gas chromatography mass spectrometry (GC-MS) analysis using internal standard (decane).

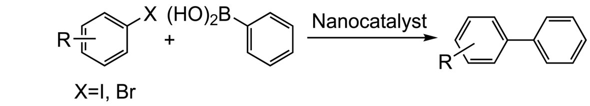
as the base of choice. The yield of this heterogeneous catalytic reaction proved to be significantly solvent-dependent (Table 1).

After finding the optimized conditions, to extend the application of the magnetically recyclable nanocatalyst, the coupling of several representative arylhalides with phenylboronic acid was carried out. As shown in Table 2, the reaction of aryliodides and bromides with phenylboronic acid gave almost quantitative yields in 4 and 8 h, respectively.

We further examined the reaction of various arylboronic acids with iodobenzene in DMF/H_2O, as shown in Table 3. Generally, in a Suzuki reaction, the hydrolysis of arylboronic acids occurs and causes the yield to be decreased.[27] However, the reactions of the arylboronic acids with iodobenzene using the magnetically recyclable nanocatalyst (1 mol %) were performed successfully. For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. The coupling of iodobenzene with phenylboronic acid using the magnetically recyclable nanocatalyst was chosen as a model reaction.

The durability of the nanocatalyst is an important factor for practical applications. To verify this issue, we investigated magnetic separation and recycling of the magnetically recyclable nanocatalyst in the Suzuki cross-coupling reaction of iodobenzene with phenylboronic acid under the optimal conditions. Upon completion of the reaction, the catalyst was easily separated using a magnet, washed several times with DMF and reused in the next reaction. The nanocatalyst was successfully reused for six consecutive cycles (Figure 3). There was very small decrease of catalytic activity of the nanocatalyst. ICP-AES analysis of the reaction solution after the six cycles of reaction and magnetic separation of the nanocatalyst showed that 0.4% of Pd species remained in the solution. The catalytic activity decay seems to result from the loss of nanocatalysts during the steps of washing and magnetic separation for consecutive reusing of the nanocatalysts.

Table 2. Heterogeneous Suzuki cross-coupling reaction of aryl halides with phenylboronic acid[a]



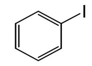
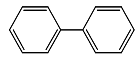
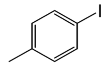
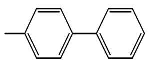
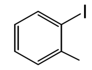
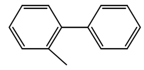
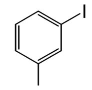
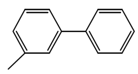
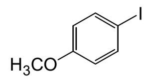
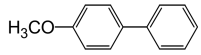
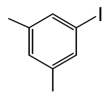
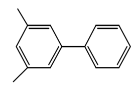
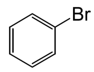
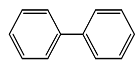
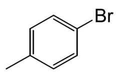
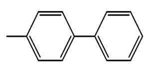
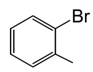
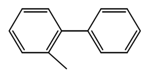
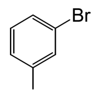
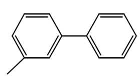
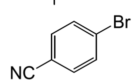
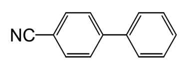
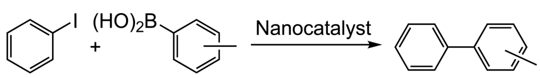
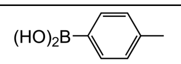
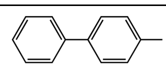
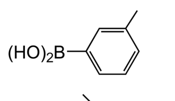
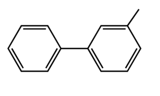
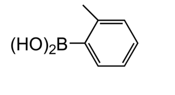
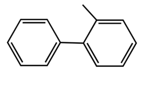
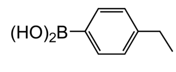
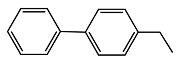
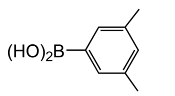
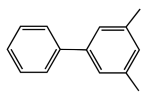
Entry	Aryl halide	Product	Time (h)	Yield (%)[b]
1			4	97
2			4	95
3			4	92
4			4	95
5			4	91
6			4	91
7			8	95
8			8	94
9			8	90
10			8	93
11			8	92

Table 3. Heterogeneous Suzuki cross-coupling reaction of aryl iodide with aryl boronic acids[a]



Entry	Arylboronic acid	Product	Yield (%)[b]
1			95
2			93
3			91
4			93
5			92

[a]Aryl iodide (0.5 mmol), aryl boronic acid (0.6 mmol), nanocatalyst (1 mol %), K_2CO_3 (2 mmol), DMF/H_2O (3:1), 100 °C, 4 h. [b]Yields were determined by GC-MS analysis using internal standard (decane).

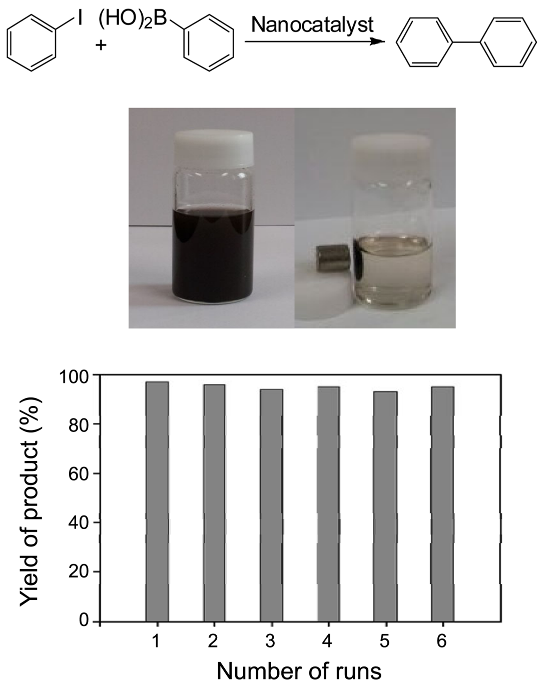


Figure 3. Suzuki reaction results for magnetic recycling of the nanocatalyst.

Conclusion

In summary, we have developed a new magnetically recyclable and efficient nanocatalyst for the Suzuki cross coupling reactions. This nanocatalyst with low palladium loading (1 mol %) provided efficient catalytic activity for successful Suzuki cross-coupling reactions due to small size and location of catalyst NPs on the surface of the nanocomposite. Facile magnetic recycling of the catalyst is another notable feature of this reaction as it eliminates the work-up procedure for catalyst separation and recovery after completion of the reaction. The nanocatalysts could be reused for six consecutive cycles in Suzuki cross-coupling reaction of iodobenzene with phenylboronic acid. We expect this novel magnetically recyclable nanocatalyst to find applications in many other important catalytic processes.

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