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Short Communication

Magnetite nanoparticles immobilized Salen Pd (II) as a green catalyst for Suzuki reaction

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ABSTRACT

In this work, we described a methodology to immobilize Salen Pd (II) complex on the surface of magnetite nanoparticles. The palladium catalyst exhibited efficient catalytic activity in coupling reactions with aryl iodides or bromides and phenylboronic acid at 100 °C for 1–3 h under DMF/H_2O. Furthermore, the catalyst could be magnetically isolated with a permanent magnet and the yields achieved above 85% after reused at least 5 times.

1. Introduction

The palladium-catalyzed Suzuki and Heck reactions have been shown as an efficient method for the construction of C–C bonds and play an important role in pharmaceutical industry and organic synthesis [1,2]. High activity for coupling reaction can be achieved using homogeneous palladium catalysts. Therefore, it is not surprising that much efforts have been devoted to the development of homogeneous systems for this reaction, such as phosphine ligands [3], N-heterocyclic carbenes [4], bidentate ligands [5], pyridines [6], and simple amines [7]. Schiff bases are an important class of ligand and have been studied extensively. A few reports investigating the viability of Schiff-type ligands for coupling reactions exist, the Salen Pd (II) complex were found to act as efficient catalyst in coupling reactions [8–10].

However, many noble metals used in homogeneous system are quite expensive and it is difficult to separate the soluble catalyst from the reaction system. To address these problems, heterogenization of the homogeneous catalyst is a promising option. Thus, efforts have been made to immobilize them on diverse soluble and insoluble supports, such as inorganic solids [11–15], polymers [16,17], and nanoparticles [18–24]. Nowadays, magnetite nanoparticles, especially Fe_3O_4 nanoparticles have attracted increasing interest because of their unique physical properties including the high surface area, superparamagnetism, low toxicity and their potential applications in various fields [25–27]. The Fe_3O_4 nanoparticles are easily prepared and surface functionalized and they can be recycled from the solution by external magnetic field. Hence, the catalyst supported on Fe_3O_4 nanoparticles can be easily separated from the reaction system and reused [18,19,22,24]. In addition, the reported coupling reactions were mostly carried out in organic solvents, to begin with environmental benign, the development of highly efficient heterogeneous catalysts to facilitate coupling reaction in benign medium is highly desirable [16,20].

In this work, our interest in this area led us to explore the Salen Pd (II) complex immobilized onto the surface of magnetic nanoparticles, which can be sufficiently applied even for Suzuki reaction under environmentally friendly solvent, and then can be easily separated from the reaction mixture to reuse. Herein, we wish to describe the synthesis of reusable magnetite nanoparticles supported Salen Pd (II) complex and its catalytic activity in the Suzuki reaction.

2. Experimental

2.1. Characterization methods

Pd content of the catalyst was measured by inductively coupled plasma (ICP) on IRIS Advantage analyzer. FT-IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer with a DTGS detector, and samples were measured with KBr pellets. The size and morphology of the magnetic nanoparticles were observed by a Hitachi-600 electron microscope, with an accelerating voltage of 100 kV. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 10–80°. Magnetic measurements of samples were investigated with a Quantum Design vibrating

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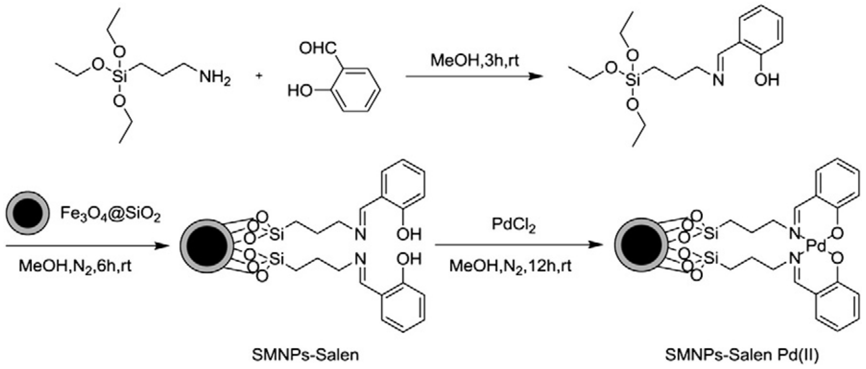


Scheme 1. Preparation of palladium catalyst.

sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 kOe.

2.2. Catalyst preparation

All chemicals were of analytical grade and used as received without further purification. The magnetite nanoparticles (MNPs) were synthesized according to the method reported previously [25]. The silica coated magnetite nanoparticles (SMNPs) were prepared through a reverse microemulsion method [26].

2.2.1. Preparation of Salen complex modified Fe_3O_4@SiO_2 (SMNPs-Salen)

At first, the Salen complex was synthesized by the following procedure [28]. 5.0 mmol (610.6 mg) of salicylaldehyde was added in 30 ml of absolute methanol, to which 3-aminopropyltrimethoxysilane (5.0 mmol, 1107.0 mg) was then added. After 3 h, 0.4 g of as-prepared Fe_3O_4@SiO_2 microspheres was then added and stirred for 6 h, the Fe_3O_4@SiO_2 immobilized Salen complex was obtained.

2.2.2. Preparation of palladium catalyst (SMNPs-Salen Pd (II))

For preparation of Fe_3O_4@SiO_2 nanoparticles immobilized Salen Pd (II), a solution of $PdCl_2$ (0.5 mmol, 88.5 mg) in absolute methanol (30 ml) was dropwise added to the above obtained solution of Fe_3O_4@SiO_2 immobilized Salen complex, and the mixture was stirred overnight. The resulting product was separated magnetically, washed with absolute ethanol 3 times and dried at 50 °C under vacuum.

2.3. Catalytic Suzuki reactions

In a typical procedure, aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), DMF/H_2O as solvent (5.0 ml, v/v = 1:1) and the catalyst were taken in a 10 ml round bottom flask. The mixture was stirred at 100 °C in an air atmosphere and for required time. After reaction completion, the catalyst was recovered magnetically by placing a magnet, and the solvent was evaporated to remove water. The products were collected and analyzed by GC (P.E. AutoSystem XL) or GC–MS (Agilent 6890 N/5973 N). The separated catalyst washed with absolute ethanol could be reused by addition of new portions substrate after drying at 50 °C under vacuum.

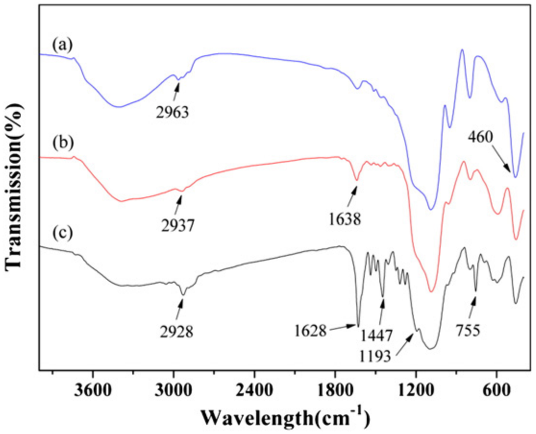


Fig. 1. FT-IR spectra of (a) SMNPs, (b) SMNPs-Salen and (c) SMNPs-Salen Pd (II).

3. Results and discussion

3.1. Catalyst preparation and characterization

The immobilization of the Salen Pd (II) complex onto the surface of SMNPs consists of the following steps as shown in Scheme 1. Palladium contents (analyzed by ICP-AES): 3.85 wt.%. Fig. 1 shows FT-IR spectra of SMNPs, SMNPs-Salen and SMNPs-Salen Pd (II). The observation of two broad bonds at around 460–590 cm^{-1} indicates the presence of magnetite nanoparticles. The silica coated magnetite nanoparticles are confirmed by observation of a broad band about 1000–1100 cm^{-1}. In Fig. 1(c), the subtractive spectra show bands at 1628 cm^{-1} and 1447 cm^{-1} due to C═N and C–O stretching vibrations. Some weak bands at 1400–1500 cm^{-1} assign to stretching vibrations of aromatic rings of Salen complex are observed, and that are not present in parent SMNPs. The bands at 2937 cm^{-1} and 1638 cm^{-1} upon reaction of Salen complex with Pd shifted to lower frequency (2928 cm^{-1}, 1628 cm^{-1}) indicate to form Pd complex. Also, weak bands at 755 cm^{-1} and 1193 cm^{-1} in Fig. 1(c) are characteristic of the presence of Pd and formation of SMNPs-Salen Pd (II) nanomaterials.

The TEM image in Fig. 2 shows that the SMNPs (Fig. 2(a)) and SMNPs-Salen Pd (II) (Fig. 2(b)) are of uniform spherical shape. However, aggregation gives rise to increasing the size of observed nanoparticles as seen in the TEM image (Fig. 2(b)).

The XRD pattern of palladium catalyst confirms the presence of crystalline Fe_3O_4 by the corresponding reflections of (220), (311), (400), (422), (511) and (440) crystal planes as indicated in Fig. 3. Comparing with XRD pattern of SMNPs (Fig. 3(a)) and SMNPs-Salen Pd (II) (Fig. 3(b)), immobilization palladium complex on the surface of Fe_3O_4 nanoparticles did not significantly affect the structure of nanoparticles.

Fig. 4 shows the magnetization curves of the samples. It can be seen that the saturation of the obtained catalyst decreases from 25 to 16 emu/g for the SMNPs. The superparamagnetic properties of the prepared SMNPs-Salen Pd (II) are attractive for their application.

3.2. Catalytic Suzuki reaction

In this study, we first tested SMNPs-Salen Pd (II) catalyst in the Suzuki reaction of iodobenzene with phenylboronic acid in DMF as a model reaction. The coupling reaction in the presence of 1.0 mol%

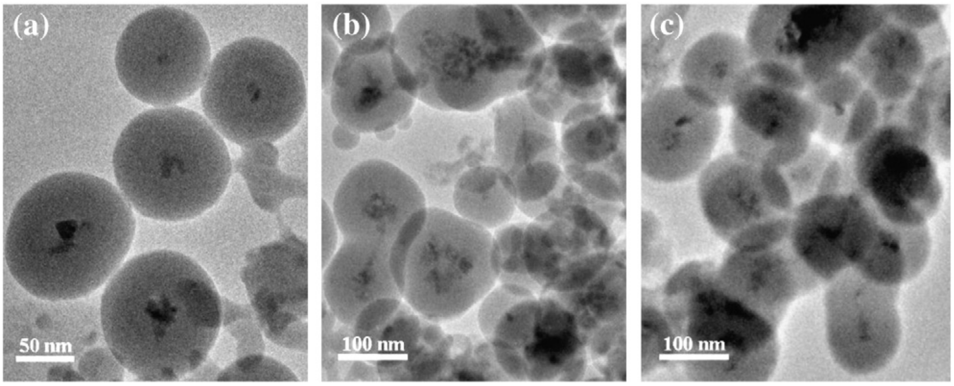


Fig. 2. TEM images of (a) SMNPs, (b) SMNPs-Salen Pd (II) and (c) SMNPs-Salen Pd (II) after the five cycles.

catalyst and K_2CO_3 as a base at 100 °C for 2 h afforded the corresponding product in excellent yield (entry 1). We next investigated the reaction in DMF/H_2O, as shown in Table 1, after 2 h heating, the best yields were obtained in the presence of 1.0–0.5 mol% catalyst at 100 °C (entries 2–3), when the loading of catalyst was decreased to 0.1 mol%, the yield was influenced (entry 4). Upon changing the temperature and time, the reactions were coupled well with only 0.5 mol% of catalyst at 100 °C for 1 h (entries 5–7). And then, we obtained the similar results under the same conditions in EtOH (entries 8–9). It is remarkable that 85% of yield was obtained in the presence of 0.5 mol% catalyst at 130 °C for 2 h in water (entry 11). The results were summarized in Table 1, the best catalytic activity of the catalyst was found in DMF/H_2O solvent together with K_2CO_3 for required time, the optimized condition was thus used for all further studies.

Further, we investigated the general applicability of SMNPs-Salen Pd (II) in the coupling of various aryl halides under the optimized condition. As summarized in Table 2, the coupling of deactivated aryl iodides proceeded smoothly at 100 °C for 1 h and the corresponding products obtained high yields (entries 1–6). We further explored the catalytic activity for the coupling of aryl bromides, lengthen reaction time to 3 h, aryl bromides and their derivatives efficiently reacted with phenylboronic acids, to yield Suzuki products in good to excellent yields (entries 7–12). It is worth to mention that aryl iodides and bromides bearing an electron-withdrawing group obtained excellent yields (entries 4, 10–11, and 14). Meanwhile, for aryl iodides and bromides with electron-donating groups such as $-CH_3$, $-OCH_3$ and –OH, good to highly yields were achieved (entries 2–3, 5–6, 8–9, and 13), however, the reaction of 4-bromoanilines was observed a moderate yield (85%) (entry 12). Besides, the protocol tolerated the presence of functional groups in the *-ortho* and *-meta* position of the aryl halides (entries 6 and 13–14). Then, in order to test the feasibility of this protocol for challenging substrates, we conducted the coupling of several aryl chlorides with phenylboronic acid, however, poor yields were obtained in the reactions with 0.5 mol% or 1.0 mol% under 100–130 °C for 6 h (entries 15–19). Interestingly, it is worth noting that the coupling of 4-chloroacetophenone possessing an electron-withdrawing group with phenylboronic acid gave the product in 43% yield in the presence of 0.5 mol% catalyst at 130 °C for 6 h (entry 19).

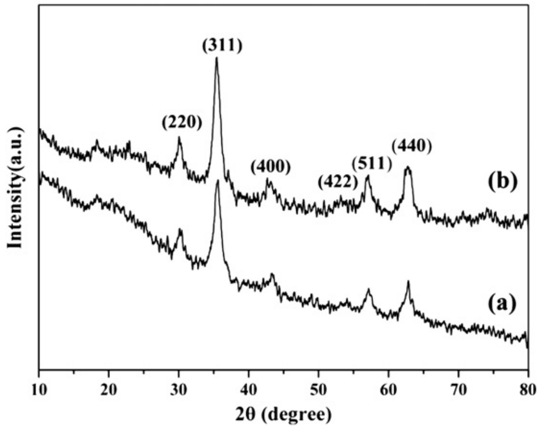


Fig. 3. XRD pattern of (a) SMNPs and (b) SMNPs-Salen Pd (II).

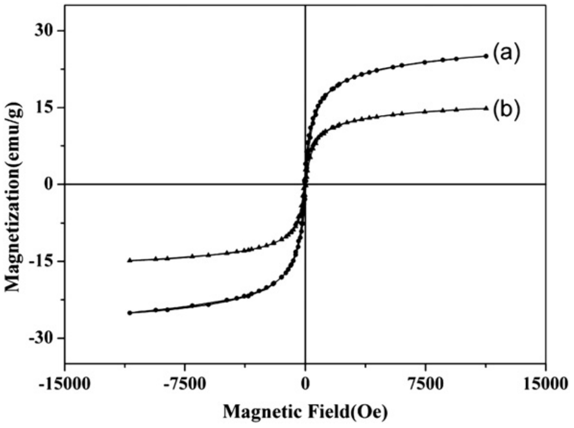
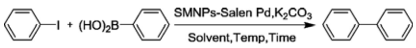


Fig. 4. Room temperature magnetization curve of (a) SMNPs and (b) SMNPs-Salen Pd (II).

Table 1
The Suzuki reaction of iodobenzene with phenylboronic acid using Pd catalyst.[a]

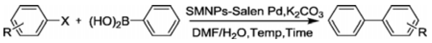


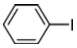
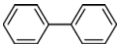
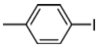
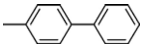
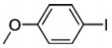
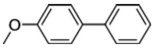
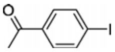
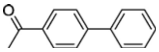
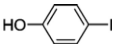
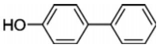
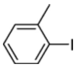
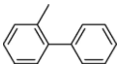
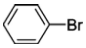
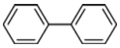
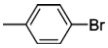
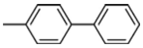
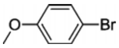
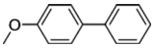
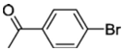
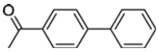
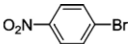
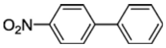
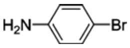
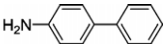
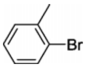
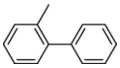
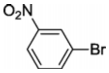
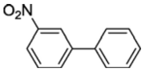
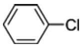
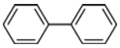
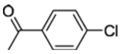
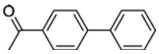
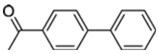
Entry	Solvent	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%)[b]
1	DMF	1.0	100	2	100
2	DMF/H_2O (v/v = 1:1)	1.0	100	2	100
3		0.5	100	2	100
4		0.1	100	2	64
5		0.5	100	1	100
6		0.5	100	0.5	73
7		0.5	80	1	46
8	EtOH	1.0	100	2	100
9		0.5	100	1	96
10	H_2O	0.5	100	2	41
11		0.5	130	2	85
12		0.5	130	1	62

[a] Reaction condition: iodobenzene (1.0 mmol), phenylboronic (1.5 mmol), K_2CO_3 (2.0 mmol), solvent (5.0 ml), Pd catalyst (0.1–1.0 mol%), and 100–130 °C.

[b] Yield was determined by GC analysis.

Table 2
The Suzuki reaction of aryl halides with phenylboronic acid using Pd catalyst.[a]

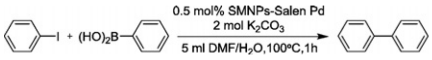


Entry	Aryl halide	Product	Temp (°C)	Time (h)	Yield (%)[b]
1			100	1	100
2			100	1	99
3			100	1	97
4			100	1	100
5			100	1	94
6			100	1	97
7			100	3	100
8			100	3	96
9			100	3	94
10			100	3	99
11			100	3	96
12			100	3	85
13			100	3	94
14			100	3	93
15			100	6	11
16			110	6	16
17			130	6	31
18			130	6	40[c]
19	 		130	6	43

[a] Reaction condition: aryl halide (1.0 mmol), phenylboronic (1.5 mmol), K_2CO_3 (2.0 mmol), DMF/H_2O (5.0 ml, v/v = 1:1), Pd catalyst (0.5 mol%), 100–130 °C.
[b] Yield was determined by GC analysis.
[c] The loading of Pd catalyst is 1.0% mol.

The recycling of the catalyst is an important issue in the heterogeneous reaction for commercial application. After the separation from reaction mixture by magnet, the catalyst has been reused in model reaction for five reaction cycles. As shown in Table 3, the yields were above 85% in all five reaction cycles and the decreased catalytic activity as recycling proceeded may be due to the significant loss of palladium. Metal leaching of the catalyst before and after reaction was studied by ICP-AES analysis. The Pd content was found to be 3.85 wt.% before reaction and 3.49 wt.% after five reaction cycles, which confirmed negligible Pd leaching. In addition, the isolated solution did not exhibit any further reactivity. Fig. 2(c) presents the TEM image of the catalyst after the five cycles. It can be seen that the morphology of recycled SMNPs-Salen Pd (II) does not go any drastic change, but aggregation is more obvious.

Table 3
Reuse of Pd catalyst in Suzuki reaction of iodobenzene with phenylboronic acid.



Time	1	2	3	4	5
Yield (%)	100	95	91	90	86

4. Conclusions

In conclusion, we successfully prepared the magnetite nanoparticles immobilized Salen Pd (II) complex which was assembled for highly efficient heterogeneous Suzuki reactions in DMF/H_2O. And then, the catalyst can be separated from the reaction system by using a magnet and the yields achieved above 85% after reused at least 5 times. It demonstrates a new strategy to introduce nanoparticles into functional coordination complexes through simple steps for multifunctional materials.

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