



Recyclable Palladium Catalysts for Suzuki Cross-Coupling Reaction

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Two magnetic palladium catalysts *i.e.*, Pd/Fe₃O₄/CB (carbon black) and Pd/Fe₃O₄/RGO (reduced graphene oxide), are prepared for Suzuki coupling reaction. The catalysts are characterized by FTIR, XRD and SEM. It shows that both Pd and Fe₃O₄ are well dispersed on the carbon black and reduced graphene oxide supports. The catalytic activity of Pd/Fe₃O₄/RGO catalyst is much higher than that of Pd/Fe₃O₄/CB catalyst for Suzuki coupling reaction of phenylboronic acid and bromobenzene, which indicates that the catalyst support reduced graphene oxide enhances the catalytic activity of Pd. Furthermore, the Pd/Fe₃O₄/RGO catalyst can be easily separated by an external magnet and reused for 8 times without obvious loss of its catalytic activity, which shows that the recyclability of the magnetic catalyst is good.

Keywords: Pd catalyst, Fe₃O₄, Graphene, Suzuki cross-coupling reaction, Recyclability.

INTRODUCTION

Graphene (GR) and graphene oxide (GO) have attracted more and more attention for their two-dimensional structure and excellent electronic conductivity¹ and have been applied in various areas, such as drug carrier^{2,3}, cellular imaging⁴, membrane construction⁵, *etc.* Except for its high specific surface area and stability⁶, graphene oxide has a good number of functional groups on the surface, such as hydroxyl (-OH), epoxy group (-O-) and carbon-carbon double bonds (-C=C-)⁷, which can be good chelating agents with metal ions. There are various noble metal nanoparticles that have been loaded on reduced graphene oxide (RGO) support, such as silver^{8,9}, gold^{10,11}, platinum^{12,13} and palladium^{14,15}.

In the field of catalysis, Pd nanoparticles are especially important for their extensive catalytic applications in organic synthesis such as Suzuki coupling reaction¹⁶⁻¹⁹, Heck coupling reaction^{20,21} and Sonogashira coupling reaction²². However, it is difficult to recycle the Pd nanoparticles from the reaction system. Recently, magnetic Fe₃O₄ nanomaterials have been widely used as separation materials²³⁻²⁷. They not only simplify the separation procedure, but also enhance the recycling performance.

In the present paper, carbon black (CB) and reduced graphene oxide (RGO) are used as substrates to load with both Fe₃O₄ and Pd nanoparticles, respectively. Magnetic catalysts, Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO, are synthesized for the Suzuki coupling reaction. The effect of the catalyst support on the catalytic activity is studied.

EXPERIMENTAL

Preparation of Pd/Fe₃O₄/CB: Preparation of Fe₃O₄/CB: First, FeCl₃·6H₂O (0.541 g, 2 mmol) and FeCl₂·4H₂O (0.199 g, 1 mmol) were dissolved in 1 g carbon black (Vulcan XC-72R)/40 mL water. Then, ammonia (25-28 %, 5 mL) was added dropwise into the solution under vigorous stirring and the solution turned black slowly. The mixture solution was then moved into a autoclave and maintained at 180 °C for 6 h to form Fe₃O₄ nanocrystals. After being cooled down to room temperature, the products were separated by an external magnet and washed with water and alcohol for 3 times. Finally, the products were oven-dried at 60 °C for 4 h.

Preparation of Pd/Fe₃O₄/CB: The as-prepared Fe₃O₄/CB was first dissolved in 100 mL ethanol solution. The aqueous solution of PdCl₂ (10 mL, 1 × 10⁻⁴ M) was added to the mixture solution and then transferred in a 250 mL glass flask and refluxed at 90 °C for 6 h. After being cooled down to room temperature, the black products were separated by an external magnet and washed with ethanol for 3 times and dried at 60 °C for 4 h.

Synthesis of Pd/Fe₃O₄/RGO: Graphene oxide was prepared by oxidation of graphite flakes according to the method described by Hummers and Offeman²⁸. Briefly, graphite (3 g) was stirred in concentrated sulfuric acid (70 mL) at room temperature and sodium nitrate (1.5 g) was added. After 16 h of stirring, the mixture was cooled to 0 °C and potassium permanganate (9 g) was added. Then after being stirred for 6 h, the whole batch was carefully poured into a

beaker filled with ice-cold water. Subsequently, hydrogen peroxide (3 %) was added in excess and the mixture was stirred overnight and then filtered. The products were washed with a mixture of HCl/H₂O₂ (1:1, 5 %) for 3 times and then filtered with water and centrifugated until the supernatant did not show anymore precipitation with AgNO₃ solution and oven-dried at 60 °C for 4 h.

Preparation of the Fe₃O₄/GO: Graphene oxide (1 g) was dissolved in 40 mL water by ultrasonication for 0.5 h, then FeCl₃·6H₂O (0.541 g, 2 mmol) and FeCl₂·4H₂O (0.199 g, 1 mmol) were added. Then, ammonia (25-28 %, 5 mL) was added dropwise into the solution under vigorous stirring and the solution turned black slowly. The mixture solution was then moved into a autoclave and maintained at 180 °C for 6 h to form Fe₃O₄ nanocrystals. After being cooled down to room temperature, the products were separated by an external magnet and washed with water and alcohol for 3 times. Finally, the products were oven-dried at 60 °C for 4 h.

Preparation of the Pd/Fe₃O₄/RGO: The as-prepared Fe₃O₄/GO was first dissolved in 100 mL ethanol solution. The aqueous solution of PdCl₂ (10 mL, 1 × 10⁻⁴ M) was added to the mixture solution and then transferred in a 250 mL glass flask and refluxed at 90 °C for 6 h. After being cooled down to room temperature, the black products were separated by an external magnet and were washed with ethanol for 3 times and dried at 60 °C for 4 h.

Procedure of the Suzuki cross-coupling reaction: C₆H₅Br (0.785 g, 5 mmol) was added to a stirred mixture of C₆H₇BO₂ (0.732 g, 6 mmol), Na₂CO₃ (1.06 g, 10 mmol) or K₃PO₄ (2.12 g, 10 mmol), DMF (10 mL) and H₂O (10 mL), followed by Pd/Fe₃O₄/CB (0.87 g) or Pd/Fe₃O₄/RGO (0.87 g). The mixture was then stirred at 95 °C in oil bath for 5 h and then extracted with ether (3 × 10 mL). The solvent of the combined organic extraction was removed under reduced pressure and the product was analyzed by GC.

Catalyst recycling in the Suzuki cross-coupling reaction: After the Suzuki cross-coupling reaction finished, the Pd catalyst was separated by an external magnet. The Pd catalyst was washed with distilled water (10 mL) for 3 times and absolute ether (10 mL) for 3 times. Then the Pd catalyst was dried at 60 °C for the use of next Suzuki reaction.

RESULTS AND DISCUSSION

Characterization of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO:

Fig. 1A shows the FTIR spectra of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO catalysts. The band at 3400 cm⁻¹ is attributed to O-H stretching vibration. The band at 1620 cm⁻¹ is attributed to C=C stretching vibration. The bands at 1380 and 1060 cm⁻¹ are attributed to C-OH stretching vibration. The band at 580 cm⁻¹ is attributed to Fe-O vibration. Comparing with the FTIR spectrum of Pd/Fe₃O₄/CB, the 1620 cm⁻¹ band of Pd/Fe₃O₄/RGO is greatly enhanced. It indicates that the percentage of C=C double bonds in Pd/Fe₃O₄/RGO is much higher than that in Pd/Fe₃O₄/CB.

The XRD patterns of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO are shown in Fig. 1B. The peaks at 30.1°, 35.6°, 43.3°, 53.5°, 57.0° and 62.7° are assigned to the (220), (311), (400), (422), (511) and (440) crystallographic planes of Fe₃O₄, respectively.

The peaks at 40°, 46.6° and 67.9° are assigned to the (111), (200) and (220) crystallographic planes of Pd, respectively. It can also be seen that the crystallinity of Pd and Fe₃O₄ in reduced graphene oxide is better than that in carbon black. The SEM images of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO are shown in Fig. 2. It can be seen that Pd and Fe₃O₄ nanoparticles are well dispersed on carbon black and reduced graphene oxide supports. Both Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO suspensions are attracted to the sidewall of a glass vessel when a magnet is placed beside them (inset of Fig. 2), indicating that the magnetisms of the catalysts are very strong.

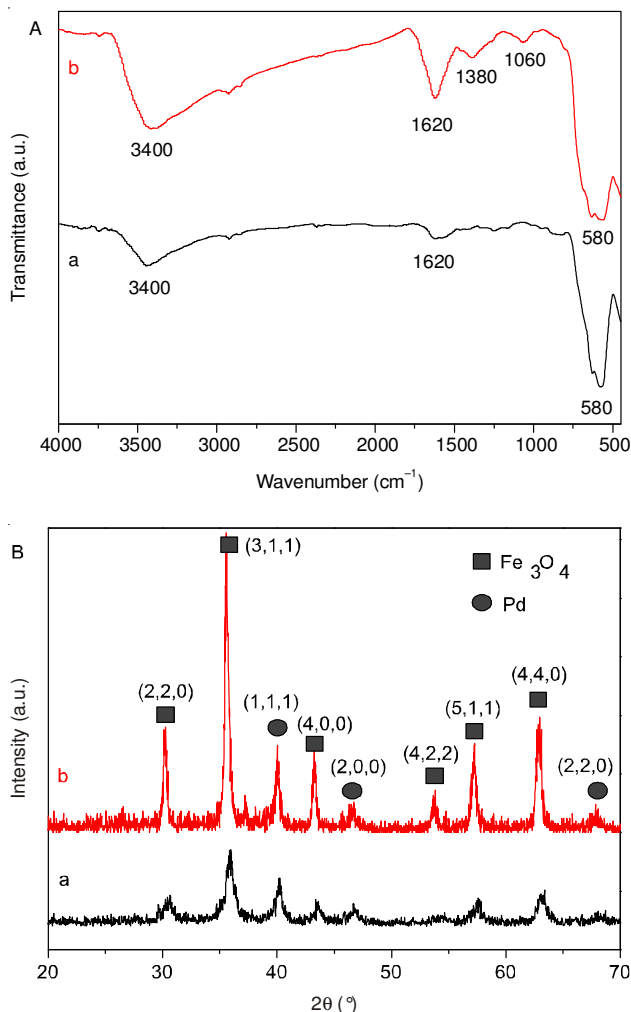


Fig. 1. (A) FTIR spectra of Pd/Fe₃O₄/CB (a) and Pd/Fe₃O₄/RGO (b). (B) XRD patterns of Pd/Fe₃O₄/CB (a) and Pd/Fe₃O₄/RGO (b)

Optimizing reaction conditions of Suzuki reaction:

Normally, Suzuki reactions are carried out in a mixture of an organic solvent and an aqueous inorganic base under an inert atmosphere. When Suzuki reactions are performed under aerobic conditions, activation by phosphine ligands is usually required. In the present paper, Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO catalysts with 1 mol % Pd loading are investigated to catalyze Suzuki reaction in DMF/water mixture solvent containing Na₂CO₃ under aerobic conditions, without any pre-activation. To optimize the reaction conditions, a series of experiments with different reaction times and different alkali electrolytes are carried out (Table-1).

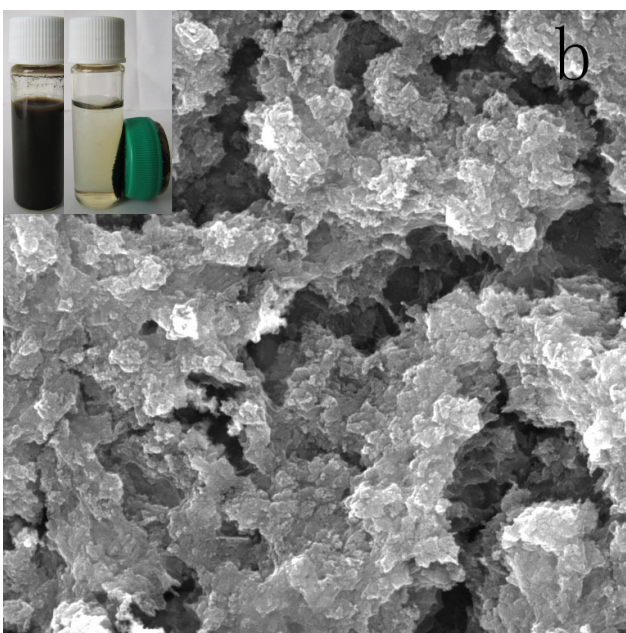
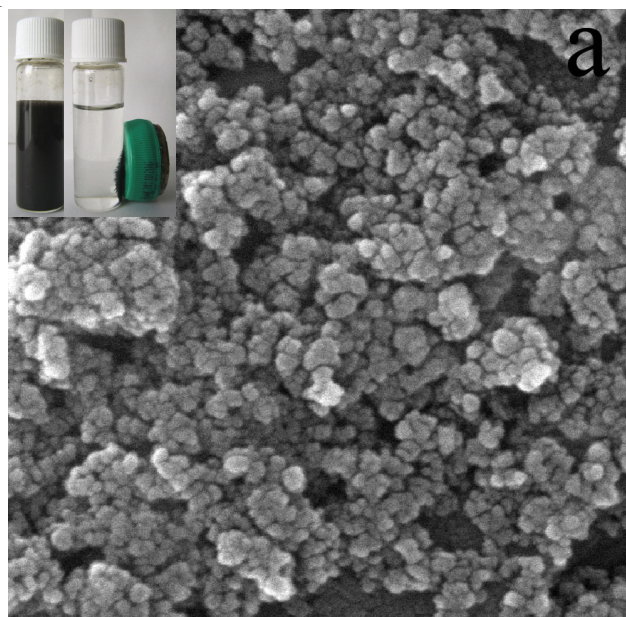


Fig. 2. SEM images of the catalysts Pd/Fe₃O₄/CB (a) and Pd/Fe₃O₄/RGO (b). Inset: Photographic images of suspended Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO in aqueous solution before and after placing a magnet beside them

It shows that the Suzuki reaction is accomplished in 5 h. The catalysts in Na₂CO₃ alkali electrolyte are more catalytically active than that in K₃PO₄ alkali electrolyte, which indicates that the alkaline strength enhances the biphenyl yield. The results also show that the catalytic activity of Pd/Fe₃O₄/RGO is much higher than that of Pd/Fe₃O₄/CB. The biphenyl yield is about 99 % when Pd/Fe₃O₄/RGO catalyst is used in Na₂CO₃ alkali electrolyte for 5 h. However, when Pd/Fe₃O₄/CB catalyst is used at the same conditions, the biphenyl yield is only 72 %.

Suzuki reaction catalyzed by Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO: The catalytic activities of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO for the formation of biaryl carbon-carbon bonds are investigated using the Suzuki reaction of phenylboronic acid with bromobenzene. The gas chromatograph traces for

TABLE-1
ACTIVITIES OF Pd/Fe₃O₄/CB AND Pd/Fe₃O₄/RGO CATALYSTS FOR SUZUKI COUPLING REACTION ON DIFFERENT CONDITIONS

Entry	Catalyst	Alkali	Time/h	Yield (%)
1	Pd/Fe ₃ O ₄ /CB	K ₃ PO ₄	2.5	39
2	Pd/Fe ₃ O ₄ /CB	K ₃ PO ₄	5	46
3	Pd/Fe ₃ O ₄ /CB	K ₃ PO ₄	10	57
4	Pd/Fe ₃ O ₄ /CB	Na ₂ CO ₃	2.5	60
5	Pd/Fe ₃ O ₄ /CB	Na ₂ CO ₃	5	72
6	Pd/Fe ₃ O ₄ /CB	Na ₂ CO ₃	10	79
7	Pd/Fe ₃ O ₄ /RGO	K ₃ PO ₄	2.5	65
8	Pd/Fe ₃ O ₄ /RGO	K ₃ PO ₄	5	75
9	Pd/Fe ₃ O ₄ /RGO	K ₃ PO ₄	10	80
10	Pd/Fe ₃ O ₄ /RGO	Na ₂ CO ₃	2.5	91
11	Pd/Fe ₃ O ₄ /RGO	Na ₂ CO ₃	5	99
12	Pd/Fe ₃ O ₄ /RGO	Na ₂ CO ₃	10	99

C₆H₅Br, biphenyl and the final product are shown in Fig. 3. It shows that the GC peak of pure C₆H₅Br is located at t = 1.25 min (Fig. 3a). The GC peak of biphenyl is located at t = 3.35 min (Fig. 3b). The GC peak at t = 0.90 min is attributed to the solvent ether. Fig. 3c and 3d show the GC traces of the Suzuki reaction products catalyzed by Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO, respectively. The high GC peaks at t = 3.35 min are

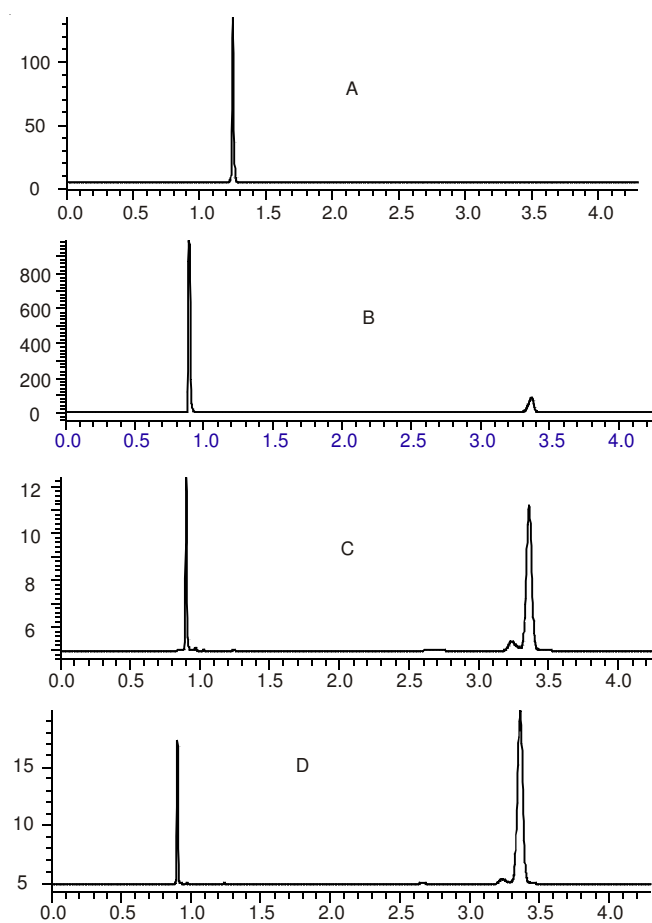


Fig. 3. GC traces for C₆H₅Br (a), biphenyl in ether (b), the final products catalyzed by Pd/Fe₃O₄/CB (c) and Pd/Fe₃O₄/RGO (d)

attributed to biphenyl and the little GC peaks at $t = 3.25$ min are attributed to the by-product of Suzuki reaction. The conversion ratios of biphenyl catalyzed by Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO are 98 and 99 %, respectively, indicating that both of the two catalysts have high selectivity on the Suzuki reaction.

The yields of corresponding biphenyl using different Pd loading capacities of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO catalysts are shown in Fig. 4A. The yield of biphenyl first increases when Pd mol % loading increases from 0.3 to 1 %. Further increase of Pd mol % loading does not increase the yield of biphenyl. The optimal Pd mol % loading that showing the highest catalytic activity is 1 %. It can also be seen that that the catalytic activity of Pd/Fe₃O₄/RGO is about 20 % higher than that of Pd/Fe₃O₄/CB, which indicates that reduced graphene oxide promotes the catalytic activity of Pd.

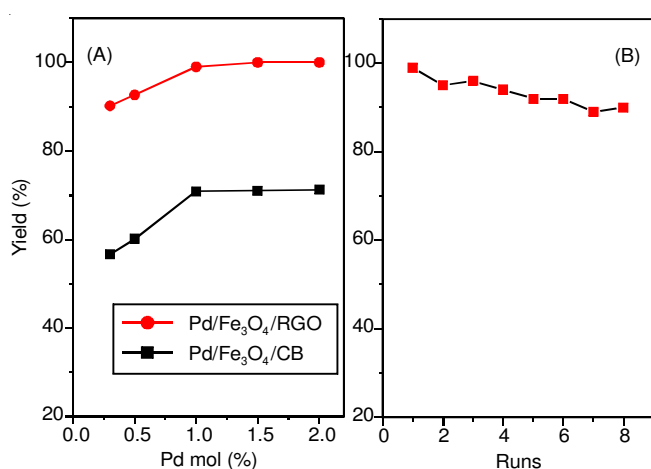


Fig. 4. (A) Yields of the Suzuki reaction between C₆H₇BO₂ and C₆H₅Br using different Pd loading capacities of Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO catalysts. (B) Plot of the product yield vs. number of runs in the Suzuki coupling reaction using Pd/Fe₃O₄/RGO catalyst

Catalyst recyclability: To demonstrate the recyclability of Pd/Fe₃O₄/RGO catalyst, the Suzuki coupling reaction of phenylboronic acid and bromobenzene is carried out, with the product extracted with ether. The Pd/Fe₃O₄/RGO catalyst is separated by an external magnet for the next use. As shown in Fig. 4B, the Pd/Fe₃O₄/RGO catalyst can be reused 8 times without obvious loss of its catalytic activity, demonstrating its excellent recyclability and lifetime.

Conclusion

In summary, two magnetic palladium catalysts, Pd/Fe₃O₄/CB and Pd/Fe₃O₄/RGO, were prepared and characterized for Suzuki coupling reaction. The Pd/Fe₃O₄/RGO catalyst showed higher catalytic activity than Pd/Fe₃O₄/CB, indicating that reduced graphene oxide promotes the catalytic activity of Pd. The Pd/Fe₃O₄/RGO catalyst can be easily separated by an external magnet and reused for 8 times without obvious loss

of its catalytic activity. The Pd/Fe₃O₄/RGO catalyst exhibited an excellent catalyst with high activity and good reusability for Suzuki coupling reaction.

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