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Magnetically palladium catalyst stabilized by diaminoglyoxime-functionalized magnetic Fe_3O_4 nanoparticles as active and reusable catalyst for Suzuki coupling reactions

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ABSTRACT

A Pd supported on diaminoglyoxime (DAG)-functionalized Fe_3O_4 (Fe_3O_4/DAG/Pd) hybrid materials was fabricated for the first time. In this fabrication, DAG played an important role as a capping agent. The immobilized palladium catalyst was an efficient catalyst without added phosphine ligands for the Suzuki cross-coupling reaction of several aryl halides with phenylboronic acid in aqueous phase at room temperature. The yields of the products were in the range from 70% to 98%. The prepared heterogeneous nanocatalyst was characterized by XRD, XPS, EDS, FT-IR, ICP, FESEM, VSM and TEM. Interestingly, the novel catalyst could be recovered in a facile manner from the reaction mixture by applying an external magnet device and recycled eight times without any significant loss in activity.

1. Introduction

The biaryl moiety is an important structural motif in a great number of biologically active compounds and functional molecules [1]. Such molecules include the natural product biphenomycin [2], the pharmaceuticals valsartan, telmisartan, felbinac, losartan, and imatinib [3], the agrochemical boscalid [4], and liquid crystals for LCD screens [5]. Biaryls can be synthesized by using Pd-catalyzed Suzuki [6], Negishi [7], Kumada [8], Hiyama [9], and Stille [10] reactions. The Suzuki reaction has become part of the standard toolbox of organic chemists. The importance of the reaction is also reflected by the fact that one of the inventors, Akira Suzuki, was awarded with the Nobel Prize in Chemistry in 2010.

Development of this reaction is greatly dependent on the reactivity of the palladium catalyst. Generally, catalysts are divided into two groups: Most examples are homogeneous systems and the others are heterogeneous systems. Despite the observed beneficial effects with homogeneous catalyst, problems associated with the separation and recovery of the expensive active catalyst, limit their use in industrial and synthetic applications. In light of this, continuous efforts are now being made to carry out the reactions with heterogeneous system to aid recovery, recyclability and reuse of the catalyst. Immobilization of homogeneous catalysts on various insoluble supports (especially porous materials with high surface areas) can lead to simplify catalyst recycling via filtration or centrifugation. But, a substantial decrease in the activity of the immobilized catalyst is frequently observed due to the loss of the catalyst in the separation processes and/or diffusion factors. In the attempt to resolve such problems, nanoparticles (NPs) have used as alternative soluble matrixes for supporting homogeneous catalysts. When the size of the support materials is decreased to the nanometer scale, the surface area of NPs will increase dramatically. As a consequence, NPs could have higher catalyst loading capacity and higher dispersion than many conventional support matrixes, leading to the improved catalytic activity of the supported catalysts. However, conventional separation methods may become inefficient for support particle sizes below 100 nm. The incorporation of magnetic NPs (MNPs) into supports offers a solution to this problem. The renewed interest in synthesis of magnetic nanoparticles (MNPs) is due to their technological applications such as data storage, biological imaging, and biomedicine [11–15]. One of the attractive features of MNPs is the possibility of fast and

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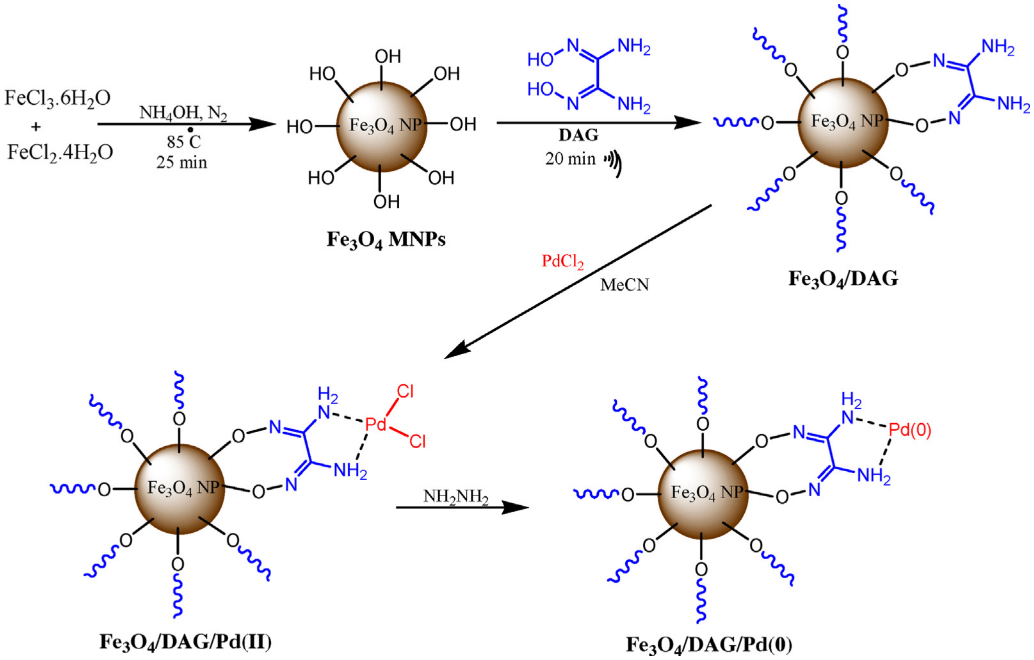

Scheme 1. Preparation of Fe_3O_4/DAG/Pd nanocatalyst.

cost-efficient separation by applying an external magnetic field, which makes them as the ideal candidates for practical use in catalysis process. This new direction in catalysis galvanized the academic research and lead to the development of a great number of magnetic-based catalysts, especially magnetite (Fe_3O_4) that found application in the various reactions [16–25]. Several accounts about synthesis, characterization and application of Fe_3O_4 MNPs utilized in the coupling reaction have been reported in the literature [26–37].

It should be noted that magnetostatic interactions between particles, makes Fe_3O_4 particles susceptible for agglomeration. On the other hand, the oxidation of Fe^{2+} causes depletion of magnetism of Fe_3O_4. Thus, in order to decrease the agglomeration degree and increase the oxidation resistance, effective coating of magnetite particles is essential. Several molecules have been used to coat on the surface of MNPs. In recent years, modified magnetic nanoparticles have received a lot of attention as support for preparation of noble metal nanoparticles. However, most of these techniques require many reaction steps to introduce functional groups to the magnetic surface and they use organosilica precursors as organic shell in order to prepare a suitable support for trapping metal nanoparticles [38–43]. The organosilane precursors not only involve complicated synthesis and purification method, but also are very expensive and toxic. Therefore, from both environmental and economic points of view, preparation of the modified magnetic nanoparticles via a simple method and without using organoalkoxysilane compounds is highly desirable. In this study, diaminoglyoxime (DAG), which is inexpensive and nontoxic materials, was used as good candidate for incorporation of palladium nanoparticles.

In continuing our efforts toward the development of efficient and environmentally benign heterogeneous catalysts [44–47], herein, we will report a simple preparation of palladium nanoparticles incorporated into Fe_3O_4/diaminoglyoxime nanocomposite as a new magnetically recoverable heterogeneous catalyst. The synthesized Fe_3O_4/DAG/Pd nanocomposites exhibited efficient catalytic activities for various Suzuki cross-coupling reactions. The Fe_3O_4 nanocrystal was used as a support of Pd nanoparticles, as well as enhancing the dispersion of catalysis active sites and improving its catalytic activity. More importantly, the synthesized Fe_3O_4/DAG/Pd nanocomposite presented good magnetic property, and could be easily separated from the reaction mixture by using a magnet. By utilizing this property, it could be reused for seven cycles without losing its catalytic activity, indicative of a potential application in industry.

2. Experimental

2.1. Preparation of the magnetic Fe_3O_4 nanoparticles (MNPs)

Naked Fe_3O_4 nanoparticles were prepared by chemical coprecipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1. Typically, $FeCl_3·6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2·4H_2O$ (2.147 g, 0.0108 mol) were dissolved in 100 mL deionized water at 85 °C under N_2 atmosphere and vigorous mechanical stirring (500 rpm). Then, 10 mL of 25% NH_4OH was quickly injected into the reaction mixture in one portion. The addition of the base to the Fe^{2+}/Fe^{3+} salt solution resulted in the formation of the black precipitate of MNPs immediately. The reaction continued for another 25 min and the mixture was cooled to room temperature. Subsequently, the resultant ultrafine magnetic particles were treated by magnetic separation and washed several times by DI water.

2.2. Preparation of the Fe_3O_4/DAG

The obtained MNPs powder (500 mg) was dispersed in 50 mL ethanol/water (volume ratio, 1:1) solution by sonication for 20 min, and then DAG (250 mg) was added to the mixture. After mechanical agitation at 40 °C for 5 h, the suspended substance was separated with centrifugation. The settled product was re-dispersed in ethanol by sonication and then was isolated with magnetic decantation for 5 times. The precipitated product (Fe_3O_4/DAG) was dried at room temperature under vacuum.

2.3. Preparation of the Fe_3O_4/DAG/Pd(0)

The Fe_3O_4/DAG (500 mg) were dispersed in CH_3CN (30 mL) by ultrasonic bath for 30 min. Subsequently, a yellow solution of $PdCl_2$