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Superparamagnetic polymer composite microspheres supported Schiff base palladium complex: An efficient and reusable catalyst for the Suzuki coupling reactions

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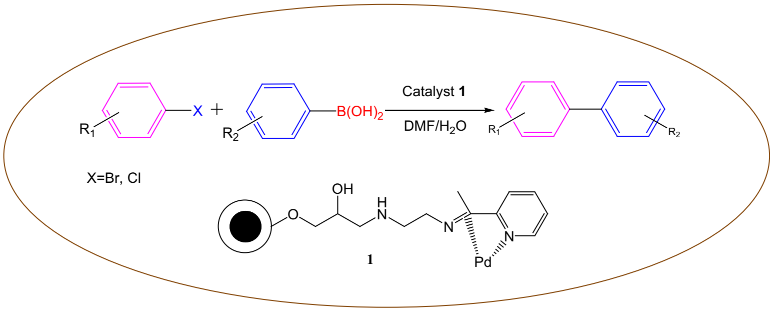
HIGHLIGHTS

- Fe_3O_4/P(GMA-AA-MMA) has been prepared successfully by soap free emulsion.
- Fe_3O_4/P(GMA-AA-MMA) was used to support Schiff base palladium complex.
- The novel catalyst exhibited efficient catalytic activity in the Suzuki reactions.
- The magnetic catalyst could be recovered by applying a permanent magnet quickly.
- The catalyst can be reused at least 7 times without obvious change in the activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Superparamagnetic polymer composite microspheres Fe_3O_4/P(GMA-AA-MMA) prepared by soap free emulsion polymerization were used to support Schiff base palladium complex. Fourier transform infrared (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM), X-ray photoelectronic spectrography (XPS) and thermal gravity (TG) studies have been used to characterize the supported magnetic Schiff base catalyst. The magnetic catalyst could provide excellent reactivity in the Suzuki coupling reactions of aryl halides with phenylboronic acids under mild condition. Meanwhile, the supported magnetic catalyst acted as a true heterogeneous catalyst in the Suzuki coupling reactions. Furthermore, the novel catalyst could be conveniently recovered by an external magnet and reused at least seven times without significant loss of its catalytic activity or Pd leaching.

1. Introduction

Palladium-catalyzed Suzuki–Miyaura cross-coupling reactions have been regarded as efficient and powerful tools for the formation of carbon–carbon bond in both academic and industrial laboratories [1–5]. Generally, the Suzuki cross-coupling reactions are frequently carried out in the presence of palladium catalyst containing well designed phosphine-based ligands, due to which can

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facilitate the corresponding transformation efficiently [6–8]. However, phosphine ligands have the defects including toxicity, air-sensitivity and high cost, which will limit their application to a large extent in the field of catalysis. Thus, it is still important to develop phosphine free ligands for the Suzuki reactions. In the past decades, a number of phosphine-free ligands including N-heterocyclic carbene [9–11], carbocyclic [12,13], thiols [14], imidazoles [15–17], anionic carbocyclic [18], pincer [19] and porphyrins ligands [20] have been developed. Among these phosphine free ligands, Schiff bases have been recognized as efficient and suitable ligands for palladium species, due to the versatility of the steric and electronic property, nontoxicity and simple preparation. Up to now, many active and well defined Schiff base palladium complexes have been developed and widely studied for the Suzuki reactions [21–25]. In 2009, Kantam and his co-workers have reported the successful synthesis of palladium (II) complexes of trifunctional amido/pyridyl carboxylate ligands and their catalytic activity for the Suzuki reactions [21]. Subsequently in 2012, Singh and his co-workers have reported the selenated Schiff base palladium complex, which showed high activity in the Suzuki coupling reactions of aryl halides with phenylboronic acids under mild condition [22]. Although these homogeneous Schiff base palladium catalysts have contributed to improve catalytic activity significantly as a result of electron-donating functionality, they often suffered from the separation of these expensive catalysts after the reactions have completed. Furthermore, these homogeneous catalysts often result in heavy metal contamination of the desired isolated products.

In order to overcome these problems mentioned above, immobilization of homogeneous Schiff base palladium complex onto solid materials has been extensively employed in the field of the Suzuki coupling reactions, since immobilized Schiff base palladium catalysts have the fewer of the drawbacks of homogeneous catalysts, such as the difficulties in recovery and regeneration. In recent years, many types of carriers, such as macromolecular polymers [26–28], mesoporous molecular sieve [29–31], magnetic nanoparticles (MNPS) [32–34], graphene oxide [35,36], metal organic framework (MOF) materials [37] were applied to support Schiff base palladium catalyst. However, a substantial decrease in activity and selectivity of the immobilized catalysts is frequently observed, since there are a number of challenges and obstacles such as leaching of palladium species from the supports, easy agglomeration of palladium particles and low utilization efficiency of Pd. It is thus desirable to develop more efficient and simple supported Schiff base palladium catalysts for the Suzuki coupling reactions.

During recent years, superparamagnetic polymer composite microspheres prepared by radical polymerization technology are now emerging as new promising support materials in the field of Pd-catalyzed Suzuki coupling reactions, due to their superparamagnetic property, nano-scale structure and various kinds of functional groups on polymer shell [38–40]. In 2005, Gao and his co-workers have prepared superparamagnetic polymer composite microspheres supported NHC complexes, which were efficient for Suzuki coupling reactions [38]. In 2014, magnetic polymer microspheres prepared by miniemulsion polymerization were used to support bulky N-heterocyclic carbene ligands for the Suzuki–Miyaura coupling reactions [39]. The novel magnetic catalyst showed high catalytic activity towards the Suzuki–Miyaura reaction of phenylboronic acids with aryl bromides in ethanol–water solution. In our previous work, superparamagnetic polymer composite microspheres prepared by an emulsifier free emulsion polymerization using DPE as a free radical control agent were also used as efficient support materials to contribute Suzuki coupling reactions significantly [40]. However, superparamagnetic polymer composite microspheres, to the best of our knowledge, have not been used as supports for immobilizing Schiff base palladium catalyst for the Suzuki reactions.

In continuation of our efforts to develop efficiently immobilized catalysts for Suzuki reactions, herein we would like to report on the first application of superparamagnetic polymer composite microspheres, prepared by soap free emulsion polymerization as the support material for the immobilization of Schiff base palladium complex. The supported magnetic catalyst can provide excellent reactivity in the coupling reactions of aryl halides with phenylboronic acids under mild condition. Furthermore, the novel magnetic catalyst can be conveniently recovered by an external magnetic field and reused at least five times without significant loss of its catalytic activity or Pd leaching.

2. Experimental

2.1. Characterization

All reagents were commercially available (J & K CHEMICA) and were directly used without further purification. The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. The magnetization curves of the samples were measured with a vibrating sample magnetometer (VSM) (model-155, Digital Measurement System, Inc.). X-ray photoelectronic spectrograph (XPS) was collected on a PHI-5400 instrument. The elemental contents of palladium in the supported catalyst were determined by Z-8000 atomic absorbance spectroscopy (AAS). The microscopic morphologies of Fe_3O_4, Fe_3O_4/P(GMA-MMA-AA), Fe_3O_4/P(GMA-MMA-AA)-Schiff base and Fe_3O_4/P(GMA-MMA-AA)-Pd were observed in a transmission Electron microscope was recorded by INOVA-400 spectrometer (Varian), DMSO-d_6 and $CDCl_3$ as solvents, and Tetramethylsilane (TMS) as internal standard. Melting points were taken with a XT4A (Beijing Keyi) micro melting point apparatus, the temperature is uncorrected.

2.2. Preparation of Fe_3O_4/P(GMA-AA-MMA) microspheres

Glycidyl methacrylate (GMA) (4.5 g), methyl methacrylate (MMA) (3 g) and acrylic acid (AA) (0.25 g) constituted the oil phase. Next water (75 mL) was added to the oil phase was added and homogenized at room temperature with an ultrasound mixer for 10 min. The mixture was then charged in a four necked flask equipped with a stirrer, a condenser. When the mixture was heated to 54 °C, 2.5 g of Fe_3O_4 magnetic nanoparticles (10%, w/w in water) that had been homogenized at room temperature with an ultrasound mixer for 10 min were added. Subsequently, while the mixture was heated to 70 °C, KPS (0.14 g) which had been dissolved in 10 mL water was added. The mixture was maintained at 80 °C for 12 h. The reaction mixture was cooled to room temperature and the resulting microspheres were washed with deionized water to remove the excess stabilizer and other impurities. Finally, the separated product was dried in a vacuum oven at 40 °C for 12 h to give yellow magnetic composite microspheres (abbreviated as Fe_3O_4/P(GMA-AA-MMA)). The epoxy group content in the magnetic composite microspheres, amounting to 2.5 mmol/g, which was determined by a modification of Jay's method [41].

2.3. Amination of Fe_3O_4/P(GMA-AA-MMA) microspheres

Fe_3O_4/P(GMA-AA-MMA) microspheres (0.1 g) were added to the solution of Ethylene Diamine (5 g) in DMF (100 mL). Then the mixture was stirred at 80 °C in a four necked flask at room temperature for 8 h. The amino-functionalized microspheres were washed with plenty of acetone, ethanol and H_2O, and then dried at 45 °C under vacuum for 24 h to give yellow Fe_3O_4/P(GMA-AA-MMA) microspheres supported ethylene diamine (abbreviated as Fe_3O_4/P