Catalysis Communications 11 (2010) 606–610

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Supported nanosized palladium on superparamagnetic composite microspheres as an efficient catalyst for Heck reaction

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ARTICLE INFO

Article history:
Received 14 July 2009
Received in revised form 22 December 2009
Accepted 5 January 2010
Available online 11 January 2010

Keywords:
Magnetic composite microspheres
Heck reaction
Palladium catalyst
Heterogeneous catalyst

ABSTRACT

A magnetically separable palladium catalyst has been easily synthesized by immobilizing palladium nanoparticles on the surface of superparamagnetic composite microspheres. It can promote Heck cross-coupling reactions efficiently without an inert atmosphere. The novel catalyst can be conveniently recovered by applying a permanent magnet externally and reused at least six times without significant loss of its catalytic activity.

1. Introduction

Immobilization of homogeneous catalyst on various support materials has been extensively employed in various fields since immobilized catalysts have fewer of the drawbacks of homogenous catalyst, such as the difficulties in recovery and regenerations [1–3]. However, a substantial decrease in activity and selectivity of the immobilized catalysts is frequently observed, due to the problem of slow diffusion rate of reactants to the surface anchored catalyst. Thus, in order to increase the diffusion rate, a method of utilizing nanoparticles as support materials is frequently used in this field [4,5]. This is because when the size of support materials is decreased to the nanometer scale, the surface area will increase dramatically and nanometer sized supports will even be dispersable in solution to form an emulsion. Therefore, reactants in solution have easy access to the active sites on the surface of nanoparticles, accordingly avoiding the problems encountered in many heterogeneous support matrixes, where a great portion of catalysts are present deep inside the matrix backbone and reactants have the limited access to the catalytic sites [6,7]. And until now, many nanomaterials such as nanotubes [8] and monolayer protected Au nanocluster (Au MPCS) [9] have been selected for supporting homogeneous catalyst because of their excellent properties. However, in this extreme case of immobilized systems, the same problems of isolation and recycling of nanocatalysts will also be encountered, due to the fact that nanoparticles, which include nanoscaled metal catalyst and support, are difficult to be separated from the reaction mixture [10,11].

Currently, a method used to address this problem is through the use of magnetic nanoparticles, due to that they can be easily recovered and separated by using an external magnetic field. So far, the reports on the magnetic nanoparticles as catalyst supports are mainly focused on Fe_3O_4 nanoparticles because they can be prepared by co-deposition method conveniently and have strong magnetic responsiveness [10–18]. Unfortunately, due to the high ratio of surface to volume and magnetization, magnetic nanoparticles are prone to aggregate, which will limit their applications. Thus, it is still important to develop a reliable synthetic route to highly efficient reusable catalysts [19]. Recently, superparamagnetic composite microspheres have received much attention in the fields of potential applications, such as magnetic bioseparation, enzyme immobilization, cell isolation, nuclei acid, protein purification and immunoassay because of their non-toxicity, good stability, high concentration of magnetite and functional groups [20–26]. These magnetic composite microspheres are usually composed of magnetic cores and polymer shells. Magnetic cores can respond to a magnetic field and retain no magnetization properties when the field is removed. While polymer shells can not only stabilize nanoparticles by preventing aggregation of inorganic cores, but provide favorable functional groups for immobilizing catalyst.

Herein, we would like to report the feasibility of using the new materials, which have been prepared by soap free emulsion polymerization, for supporting homogeneous catalyst. The Pd catalysts immobilized on superparamagnetic composite microspheres could be easily separated by using an external magnetic filed. In addition,

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doi:10.1016/j.catcom.2010.01.005

the magnetic supported catalyst could be reused at least six times without significant loss of its catalytic activity.

2. Experiments

2.1. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared via co-precipitation of Fe^{3+} and Fe^{2+} ions in the presence of NaOH. About 11.2 g $FeSO_4 \cdot 7H_2O$ and 16.3 g $FeCl_3 \cdot 6H_2O$ were dissolved in 200 ml of deionized water in a flask. This solution was stirred followed by adding 3 M NaOH solution quickly at 30 °C until the mixture reached a pH around 11. Then the mixture was heated to 80 °C for 30 min. The Fe_3O_4 nanoparticles were isolated from the solution by magnetic separation and washed with deionized water until pH 7 reached. Finally, the Fe_3O_4 nanoparticles were kept at room temperature.

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

Fe_3O_4 nanoparticles (2 g), KPS (0.1 g) and water (50 ml) constituted the aqueous phase. glycidyl methacrylate (GMA) (3.5 g), methyl methacrylate (MMA) (3 g) and acrylic acid (AA) (0.25 g) constituted the oil phase. The aqueous phase was homogenized at room temperature with an ultrasound mixer for 3 min, and then the oil phase was continuously added in an aqueous phase to disperse for 5 min. The mixture was then charged in a four necked flask equipped with a stirrer, a condenser, at 80 °C in a water bath under N_2 atmosphere for 10 h. The magnetic composite microspheres were collected by magnetic separation and washed with acetone and deionized water several times. Finally, the separated product was dried in a vacuum oven at 40 °C for 24 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 1.8 mmol g^{-1}, was determined by a modification of Jay's method [27].

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

To a solution of triethylene tetramine (10 ml) in DMF (100 ml), Fe_3O_4/P (GMA–AA–MMA) microspheres (5 g) were added. Then the mixture was stirred at 80 °C in the air for 8 h. The amino-functionalized microspheres were washed with plenty of ethanol, acetone 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 triethylene tetramine (abbreviated as Fe_3O_4/P (GMA–AA–MMA)–NH_2). The amino group content on the surface of Fe_3O_4/P (GMA–AA–MMA) microspheres was determined to be 2.3 mmol g^{-1} using volumetric method [28]. The nitrogen content was also confirmed by element analysis: N: 3.58; C: 42.43; H: 7.11%.

2.4. Preparation of Fe_3O_4/P (GMA–AA–MMA) supported palladium complex catalyst

To a solution of Fe_3O_4/P (GMA–AA–MMA)–NH_2 (2 g) in ethanol (50 ml), Pd $(OAc)_2$ (0.1 g) was added. And the mixture was stirred at 45 °C in the air for 24 h. Then the mixture was separated by using an external magnetic field and washed with ethanol (3 × 30 ml) and H_2O (3 × 30 ml), until no palladium in the filtrate can be detected by atomic absorption spectroscopy (AAS). Then the separated product was dried under vacuum at 60 °C for 24 h to give yellow magnetic composite microspheres supported palladium complex (abbreviated as Fe_3O_4/P (GMA–AA–MMA)–Pd(II)). Fe_3O_4/P (GMA–AA–MMA)–Pd(II) (2 g) was put into a solution of KBH_4 (0.05 g) in ethanol (50 ml) at 45 °C for 24 h, then washed with ethanol (3 × 30 ml) and Et_2O (3 × 30 ml) and dried under vacuum at 60 °C for 24 h to give yellow magnetic composite microspheres supported palladium complex catalyst (abbreviated as Fe_3O_4/P (GMA–AA–MMA)–Pd(0)) (Scheme 1). The palladium content in Fe_3O_4/P (GMA–AA–MMA)–Pd(0) catalyst was determined to be 4.57 wt% by AAS.

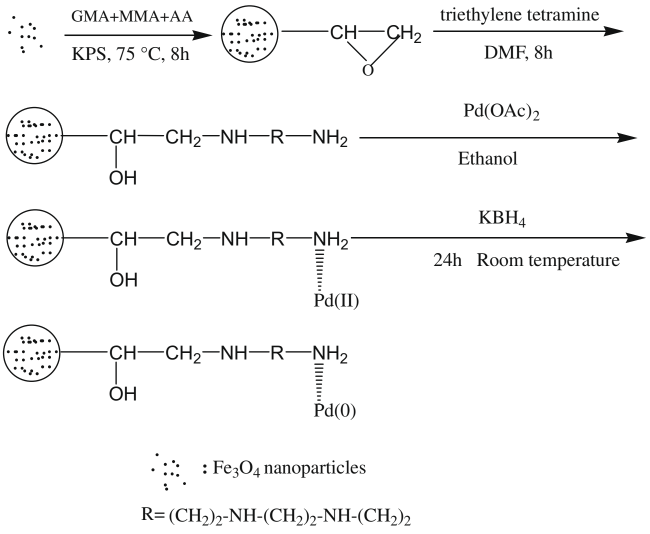
2.5. General procedures for Heck reactions and recovery of the supported magnetic catalyst

The novel magnetic supported catalyst (0.5 mol%), acrylic acid (7.5 mmol), aryl halides (5 mmol), base (10 mmol) and solvent (5 ml) were added into a round bottomed flask and stirred at 90–140 °C in atmosphere for 3–12 h. After the reaction mixture was cooled to room temperature, the catalyst was magnetically separated. The product was analyzed by HPLC to give corresponding yield. All the products have been identified by comparison of their IR, ^{1}H NMR and melting points with those reported previously (see Supporting information).

3. Results and discussion

3.1. Characterization of magnetic composite microsphere Fe_3O_4/P (GMA–AA–MMA) supported palladium complex

Fig. 1 shows the TEM images of the different samples. As shown in Fig. 1a, the Fe_3O_4 nanoparticles prepared by the chemical co-precipitation are quasi spherical with an average of 10 nm. Fig. 1b clearly displays that Fe_3O_4 nanoparticles have been successfully encapsulated into the polymer shell, and the dispersion of particles has been improved greatly, which can be explained by the steric hindrance between the polymer chains on the surface of the Fe_3O_4 nanoparticles. The dispersed Fe_3O_4/P (GMA–MMA–AA) microspheres with perfect sphere shaped morphologies consist of a dark core and a light shell. The dark inner corresponds to magnetic nanoparticles, while the light outer attributes to P (GMA–MMA–AA). Additionally, as shown in Fig. 1c and d, it can be seen that magnetic microspheres were not broken in the coordination process. Furthermore, as presented in Fig. 1d, it can be seen that the surface of the magnetic composite microsphere is very smooth and no other particles are found on the surface of polymer nanobead. This is a significant indication that the prepared Pd nanoparticles are highly dispersed around the surface of



Scheme 1. Preparation of Fe_3O_4/P (GMA–MMA–AA) composite microspheres and Fe_3O_4/P (GMA–AA–MMA)–Pd(0).