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Palladium supported on hollow magnetic mesoporous spheres as recoverable catalyst for one-pot reductive amination of aldehydes with nitroarenes under mild conditions

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ABSTRACT

We described here a method to stabilize Pd(0) on the surface of hollow magnetic mesoporous spheres (HMMS), with Fe_3O_4 nanoparticles embedded in the mesoporous shell. The catalyst was characterized by TEM, XRD and VSM. It was found that the catalyst showed a high activity for the one-pot direct reductive amination of aldehydes with nitroarenes in the presence of molecular hydrogen in ethanol, even at room temperature. Besides, the catalyst could be recovered in a facile manner from the reaction mixture and recycled six times without loss in activity.

1. Introduction

The amide is one class of most common intermediates in synthetic organic chemistry and biological chemistry. Amidation reaction is one of the most fundamental synthetic tools in modern organic synthesis [1]. However, the application scope of this method is still limited by some flaws, such as the demand on activated carboxylic acids, harsh conditions, and tedious workup [2]. The direct reductive amination of carbonyl compounds is still the most practical way to get target amines [3,4]. Numerous methods have been developed to achieve this transformation including biocatalytic [5], metal or metal oxide [6–8], dirhodium tetracarboxylate-catalyzed amidation reaction [9], catalytic hydrogenation [10], or use a reducing agent [11,12], PEG/oxidant system [13], etc. Unfortunately, there have been one or more drawbacks in these methods, such as poor stability, toxic byproducts and in acidic conditions. Therefore, development of facile, effective and more economical methods for the synthesis of amide has been attracting a great deal of attention.

It has been found that palladium nanoparticles (particularly with dimension less than 10 nm) exhibit unexpectedly high catalytic activities toward different types of reactions but do not display the property in bulk palladium [14–17]. In recent years, many attempts have been made to immobilize palladium nanoparticles on different solid supports for reductive amination of carbonyl compounds, such as polymers [18–20], metal oxide [21,22], and inorganic materials [23]. Hollow mesoporous silica spheres (HMS) with well-defined structures have received great interest, owing to their unique properties such as low toxicity, good compatibilities, low density, and very high specific surface area with abundant Si—OH bonds on the pore surface, which can provide high catalyst loading and homogeneous spherical morphologies [24–27]. Although these supported catalysts possess extremely high catalytic activity, the separation step becomes a more troublesome issue. To overcome the problem, magnetic nanoparticles (Fe_3O_4 nanoparticles) are used as the support materials because they have unique physical properties and can be easily separated from reaction mixture by using an external magnet due to the paramagnetic character of the support [28–34]. In addition, in the point of environmental and economic, the one-pot reductive amination of aldehydes with nitroarenes have gained more and more attention, since it avoids the isolation of the intermediary imine or iminium.

Based on above considerations, in this paper, we report our results about Pd immobile on mesoporous Fe_3O_4 (Pd/Fe_3O_4) catalyzed one-pot reductive amination reaction under a hydrogen atmosphere, even at room temperature (Scheme 1).

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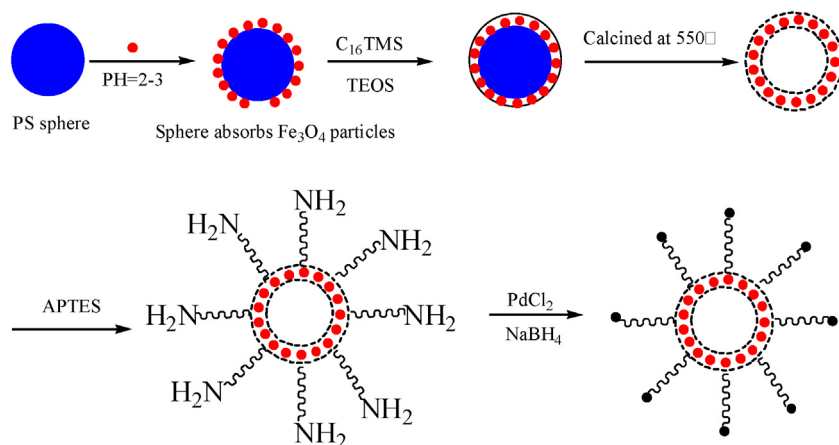
Scheme 1. Preparation of the catalysts.

2. Experimental

2.1. Synthesis of the hydrophobic magnetite nanoparticles (Fe_3O_4 NPs)

The Fe_3O_4 NPs were prepared using a published method with a slight modification [35]. First, 4.8 g of $FeCl_3 \cdot 6H_2O$, 2.0 g $FeCl_2 \cdot 4H_2O$ and 1.0 mL oleic acid were added to 40 mL of deionized water under vigorous stirring. Second, the mixture solution was purged with nitrogen gas for 30 min under nitrogen atmosphere. Third, the mixture solution was heated to 90 °C. Finally, 10 mL of ammonium hydroxide (28 wt%) was added rapidly to the solution, and it immediately turned black. The reaction was kept at 90 °C for 2.5 h. The black precipitate was obtained with the help of a magnet and dried at 323 K overnight.

2.2. Preparation of polystyrene latex with attached Fe_3O_4 nanoparticles

Briefly, carboxylic polystyrene (PS) latex was prepared by soap-free emulsion polymerization of St with AA [36]. 1.5 g Fe_3O_4 nanoparticles and 2.5 g negatively charged PS latex were dispersed in 84 mL and 60 mL hydrochloric acid solution (pH = 2.3), respectively. Then the latter suspension was added dropwise into the former under vigorous stirring at room temperature. After 6 h, the heteroaggregates, i.e. Fe_3O_4 nanoparticles attached on the surface of PS latex particles, were separated from the solution by an external magnet and washed several times with water until the pH value of the solution became close to 7.

2.3. Preparation of hollow magnetic mesoporous silica spheres (HMMS)

First, 2.0 g heteroaggregate of the PS latex and Fe_3O_4 nanoparticles were dispersed in a solution composed of 75 mL of ethanol, 5 mL of H_2O, and 3.8 mL of $NH_3 \cdot H_2O$ (28 wt%). After stirring for 10 min, 0.4 mL of TEOS and C_{16}TMS mixture with a molar ratio of 4.7:1 were added dropwise under vigorous stirring. Then, the reaction proceeded for 8 h at room temperature under strong stirring. The resultant particles were separated by centrifugation, purified by three cycles of magnetic separation/washing in ethanol, and dried at room temperature for 12 h. Finally, the as-prepared products were dried at 313 K overnight and calcined in air at 823 K for 7 h.

Hollow magnetic mesoporous silica spherical magnetite nanoparticles were synthesized via the versatile solvothermal reaction reported by Xia [37].

2.4. −NH_2 modify the surface of hollow magnetic mesoporous silica spheres (HMMS-NH_2)

Briefly, 1.0 g HMMS samples were dispersed in 80 mL ethanol solution, then, 2.5 g aminopropyltriethoxysilane (APTES) was dropped into the system. The mixture was refluxed for 24 h. After filtration, washing and drying, the functionalized HMMS was obtained and denoted as HMMS-NH_2.

2.5. Loading of Pd on aminopropyl-modified silica coated HMMS (HMMS-NH_2-Pd)

500 mg of HMMS-NH_2 samples were first dispersed in a 50 mL ethanol solution under ultrasonication for 0.5 h. The formed black suspension was ultrasonically mixed with 3.0 mmol of a $PdCl_2$ solution for 1 h, then an excess 0.01 M $NaBH_4$ solution was slowly dropped into the above mixture with vigorous stirring. After 2 h of reduction, the products were obtained with the help of a magnet, washed thoroughly with deionized water and then dried in a vacuum at room temperature overnight.

2.6. Typical procedure for catalytic reductive amination reactions

2.6.1. The catalyst for the reductive amination of different aldehydes with nitroarenes

1.0 mmol of the different aldehydes, 1.2 mmol of nitrobenzene and 20 mg of catalyst were added in 5 mL of ethanol at room temperature by ball milling under a hydrogen atmosphere. The reaction process was monitored by thin layer chromatography (TLC). After the reaction, the catalyst was separated by a small magnet placed at the bottom of the flask, and the conversion was estimated by GC (P.E. AutoSystem XL) or GC–MS (Agilent 6890 N/5973 N).

2.6.2. The catalyst for the reductive amination of aldehydes with different nitroarenes

20 mg of catalyst and 1.2 mmol nitroarene were added in 5 mL of ethanol. The resulting suspension was stirred under a hydrogen atmosphere and at room temperature for the specified period of time. After amine formation was completed, 1.0 mmol of aldehyde was added. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was separated from the reaction mixture with the aid of an external magnet. The conversion was estimated by GC or GC–MS.