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¹Palladium 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.

Keywords: hollow magnetic mesoporous spheres, Pd (0), one-pot direct reductive amination, aldehydes, nitroarenes

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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, etc. [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/Fe₃O₄) catalyzed one-pot reductive amination reaction under a hydrogen atmosphere, even at room temperature (Scheme 1).

2. Experimental

2.1 Synthesis of the hydrophobic magnetite nanoparticles (Fe₃O₄ NPs)

The Fe₃O₄ NPs were prepared using a published method with a slight modification. [35] First, 4.8 g of FeCl₃•6H₂O, 2.0 g FeCl₂•4H₂O 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 Fe₃O₄ nanoparticles

Briefly, carboxylic polystyrene (PS) latex was prepared by soap-free emulsion polymerization of St with AA. [36] 1.5 g Fe₃O₄ 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. Fe₃O₄ 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 Fe₃O₄ nanoparticles were dispersed in a solution composed of 75 mL of ethanol, 5 mL of H₂O, and 3.8 mL of NH₃.H₂O (28 wt %). After stirring for 10 min, 0.4 mL of TEOS and C₁₆TMS 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 nanoparticleswere

synthesized via the versatile solvothermal reaction reported by Liao. [37]

2.4 -NH₂ modify the surface of hollow magnetic mesoporous silica spheres (HMMS-NH₂)

Briefly, 1.0 g HMMS samples were dispersed in 80 mL ethanol solution, then, 2.5 g aminopropyltriethoxysilane (APTES) was droped into the system. The mixture was refluxed for 24 h. After filtration, washing and drying, the functionalized HMMS was obtained and denoted as HMMS-NH₂.

2.5 Loading of Pd on aminopropyl-modified silica coated HMMS (HMMS-NH₂-Pd)

500 mg of HMMS-NH₂ 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 PdCl₂ solution for 1 h, then an excess 0.01 M NaBH₄ 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 6,890 N/5,973 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.

Characterization

XRD measurement was performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source in the 20 range of 10–70°. The size and morphology of the magnetic nanoparticles were observed by a Tecnai G2 F30 transmission electron microscopy and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporated in air at room temperature. Magnetic measurement of HMMS, HMMS-NH₂ and HMMS-NH₂-Pd was investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from -15 to 15 kOe.

Results and discussions

Catalyst preparation and characterization



Scheme 1 Preparation of the catalysts

The preparation of the HMMS-NH₂-Pd catalyst follows the steps described in Scheme 1. Firstly, HMMS were prepared. Secondly, the functionalization of the silica coated HMMS with 3-(2-aminoethylamino) propyltrimethoxysilane. Thirdly, Palladium chloride was supported on the surface of HMMS, and the palladium chloride reduced to palladium particles with sodium borohydride. The amount of Pd in the obtained catalyst was found to be 4.04 wt % based on ICP analysis.



Fig. 1 TEM images of (a, b) HMMS, (c, d) HMMS-NH₂-Pd

Fig. 1a shows the typical TEM image of HMMS nanoparticles. As can be seen from the image, the average diameter of the as-synthesized spherical particles was about 350 nm and they were nearly monodisperse. Fig. 1b is HRTEM image of a single HMMS. HMMS can be observed from the picture and the wall thickness is about 30 nm. The TEM image in Fig. 1c shows that the HMMS-NH₂-Pd catalyst didn't change considerably after attachment of the palladium onto the surface of the hollow magnetic silica sphere. It can also be concluded that the palladium particle size distribution was centered at 7-8 nm in Fig. 1d.



Fig. 2 XRD patterns of (a) HMMS, (b) HMMS-NH₂ and (c) HMMS-NH₂-Pd

Unambiguous evidence of palladium particles on HMMS-NH₂ is provided via X-ray powder diffraction analysis (XRD). The XRD pattern of the HMMS shows characteristic peaks of magnetite nanoparticles and the sharp, strong peaks confirm the products are well crystallized. The XRD results revealed their high crystallinity, which is coincident with the results reported by Frank Caruso [39]. Fig. 2c shows that apart from the original peaks, the appearance of the new peaks at $2\theta = 40.1$ and 46.5 is attributed to the Pd species. The results from XRD imply that the Pd nanoparticles have been successfully immobilized on the surface of magnetic nanoparticles. The average crysallite size, calculated using Scherrer's equation, is about 9 nm and the crystallite size nearly matches with the average particle size seen in the TEM analysis. The elemental composition of the HMM-NH₂-Pd samples was determined by EDX analysis. The result shown in Fig. 3 reveals that the as-prepared products contain Fe, Si, Pd, Cu, C and O. Among these elements, Cu C and O are generally influenced by the copper network support films and their degree of oxidation, Si, O, Fe and Pd signals result from the HMMS and Pd particles which form the products.



Fig. 3 EDX spectrum of HMMS-NH₂-Pd

Fig. 4 shows the XPS spectrum of the synthesized HMMS-NH₂-Pd catalyst. Peaks corresponding to oxygen, carbon, nitrogen, palladium, silicon, and iron are observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out.



Fig. 4 XPS spectrum of the elemental survey scan of HMMS-NH₂-Pd

In Fig. 5 the Pd binding energy of HMMS-NH₂-Pd exhibits two strong peaks centered at 339.7 and 335.5 eV, which are assigned to Pd 3d3/2 and Pd 3d5/2, respectively. Interestingly, there is no the oxidation state of Pd species in the figure. In the

experiment we used the amount of reducing agent is ten times for palladium. Pd(II) would be reduced into Pd(0) completely, which is in favourable to amination reaction. So the oxidation state of Pd species is hard to find in the figure. On the basis of above analysis, it can be concluded that the XPS data further identified the hollow mesoporous structure of the synthesized HMMS-NH₂-Pd.



Fig. 5 XPS spectrum of the HMMS-NH₂-Pd showing Pd 3d5/2 and Pd 3d3/2 binding

energies.

Magnetic measurements were carried out by employing vibrating sample magnetometer (VSM) at room temperature. The magnetization curves measured for HMMS, HMMS-NH₂ and HMMS-NH₂-Pd are compared in Fig. 6. There was no hysteresis in the magnetization for the three tested nanoparticles. It can be seen that the values of the saturation magnetization were 63.64 emu/g for HMMS, 50.84 emu/g for HMMS-NH₂ and 37.65 emu/g for HMMS-NH₂-Pd respectively. The decrease of the saturation magnetization suggests the presence of some palladium particles on the surface of the surface of the magnetic supports. Even with this reduction in the saturation magnetization, the catalyst still can be efficiently separated easily from the

solution with the help of an external magnetic force. Meanwhile, the figure also shows



the photograph of the catalyst being pulled magnetically.

Fig. 6 Room temperature magnetization curves of (a) HMMS, (b) HMMS-NH₂ and (c)

HMMS-NH₂-Pd

Catalytic activity for one-pot reductive amination of aldehydes with nitroarenes

In the first step of experiments, the reductive amination of benzaldehyde with nitrobenzenewas compared with various reaction conditions. Based on the reaction yields and environmental consideration, ethanol was proved to be superior to the other alcohols [38]. As can be seen in Table 1, increasing the reaction time from 6 to 10 h resulted in a little decrease of reaction yield (entries 3-5). The main by-products are Benzenamine, N-(phenylmethylene)- (C₁₃H₁₁N), Benzenemethanamine, N-ethyl-N-phenyl- (C₁₅H₁₇N), and Methanone, diphenyl-, oxime (C₁₃H₁₁NO). Benzenamine, N-(phenylmethylene)- is more than others, which is about 2%. Therefore, all of the following experiments were performed using the optimized reaction conditions.



Table 1 Optimization of reaction conditions.^a

a Reaction conditions: benzaldehyde (1.2 mmol), nitrobenzene (1 mmol), catalyst (0.76 mol%), and solvent (5 mL) at room temperature under a H_2 atmosphere.

b Yield was determined by GC analysis.

Under the optimized reaction conditions, the scope of the reaction was explored with structurally different aldehydes and nitroarenes. As shown in Table 2, various

aldehydes were reductively aminated with nitrobenzene in ethanol at room temperature and under a hydrogen atmosphere. It could be seen that there was no remarkable electron withdrawing and steric effects for the aromatic aldehydes during this reaction, although benzaldehydes are with o-, m-, and p-substituents (entries 1–8). We also found that 2-methoxybenzaldehyde and mutil-substituent benzaldehyde had low yields (entries 9, 12, 13), this was probably due to the relatively large steric hindrance. Besides, aliphatic aldehydes, regardless of whether they were linear or R-branched, underwent the reductive amination rapidly and gave the products in excellent yields nearly without the formation of any side products (entries 14–16).

On the contrary, commercial 10% Pd/C was used to this reaction, the reaction result showed that the yield was only 17% (Entry 1), at the same time, the catalyst can be reused 6 times without loss in activity. As we all know, the HMMS-NH₂-Pd catalyst is hollow mesoporous spheres, which has a higher specific surface area than Pd/C catalyst. The Pd NPs may disperse into the catalyst. Meanwhile the Pd/C catalyst in the reaction easily form hydroxylamine compound, then the content main product would decreased.

Table 2 HMMS-NH₂-Pd catalyst for the reductive amination of different aldehydes with nitrobenzene.^a







a Reaction conditions: aldehyde (1 mmol), nitrobenzene (1.2 mmol), Pd/Fe₃O₄ catalyst (0.76 mol%), and ethanol (5 mL) at room temperature under a H_2 atmosphere.

b Yield was determined by GC analysis.

c catalyst with of 10% Pd/C.

d Yield after 6 runs.

Table 3 shows the results obtained for reactions carried using benzaldehyde with different nitrobenzenes. Unsubstituted (Table 2, entry 1) as well as substituted 4-methyl, 2-methyl, 4-chlorine, 4-Bromine, 4-methoxy nitrobenzenes obtained the desired product in high yields, except for nitromethane (Table 3 Entry 6), which only achieved 45%. This is maybe due to the $-CH_3$ does not have π - π conjugated. It was

observed that all of these reactions have nearly no formation of side products.

Table 3 HMMS-NH₂-Pd catalyst for the reductive amination of aldehydes with

	NO ₂ +	CHO catalyst		Ŏ
Entry	nitroarenes	Product	Time/h	Yield/% ^b
1	NO ₂	NH Ph	6	95
2	NO ₂	NH Ph	6	90
3		CI Ph	6	85
4	Br NO ₂	H Ph	6	80
5	NO ₂	Br ~ H Ph	6	92
6	H_3CO \sim CH_3NO_2	H ₃ CO Ph CH ₃ NH	6	45

different nitroarenes.^a

a Reaction conditions: benzaldehyde (1 mmol), nitroarenes (1.2 mmol), Pd/Fe₃O₄ catalyst (0.76 mol%), and ethanol (5 mL) at room temperature under a H_2 atmosphere.

b Yield was determined by GC analysis.

Conclusions

In conclusion, we describe here a method to stabilized Pd (0) on the surface of hollow magnetic mesoporous spheres (HMMS), with Fe_3O_4 nanoparticles embedded in the

mesoporous shell. The simple catalyst exhibits high activity for one-pot reductive amination undermild conditions. The simple catalyst exhibits high activity even after six cycles. These advantages make this methodology attractive for the development of large-scale industrial synthesis.

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Highlights

The synthesized HMMS-NH₂-Pd shows excellent catalytic activity in amination reaction with over 97% yield in 6h.

The catalyst can be recycled 6 times without loss activity.

The catalysts can be easily recovered by using an external magnet.