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Synthesis and characterization of Schiff base complex of Pd(II) supported on superparamagnetic $Fe_3O_4@SiO_2$ nanoparticles and its application as an efficient copper- and phosphine ligand-free recyclable catalyst for Sonogashira–Hagihara coupling reactions

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ABSTRACT

Superparamagnetic nanoparticles functionalized with Schiff base complex of Pd (II) were simply synthesized by a two-step method. The catalyst was characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS),vibrating sample magnetometry (VSM), Fourier transform infrared (FT-IR), and N_2 adsorption–desorption isotherm analysis. Also, its Pd content was determined by Inductively Coupled Plasma (ICP) analyzer. The immobilized palladium complex was used as an efficient catalyst for copper- and phosphine ligand-free Sonogashira reaction of aryl halides with phenylacetylene. This catalyst shows notable advantages such as simplicity of operation, excellent yields, short reaction times, heterogeneous nature, easy magnetically work up and recyclability.

1. Introduction

The Sonogashira cross-coupling reaction is one of the most widely used carbon–carbon bond forming reactions in organic chemistry [1] and has been recently utilized as an efficient methodology to obtain conjugated oligomers [2] and polymers [3], symmetrical diynes [4–6], alkenyl-and arylacetylenes, substituted alkynes [7], material for nonlinear optical and molecular electronics [8]. The Sonogashira reaction has been usually performed using a palladium–phosphine ligand complex as catalyst in the presence of a catalytic amount of copper (I) salt and large excess of an amine under homogeneous conditions [1,9].

The conventional Sonogashira reaction has the following drawbacks: a) using environmentally unfriendly copper salts, b) generation of homocoupling products of the terminal alkynes by copper acetylides formed under reaction conditions. Although for resolving these problems, many copper-free Sonogashira coupling systems have been developed in the past few years [10] but due to significant cost of palladium salts used, difficulty in their recovery and tendency to contaminate organic Sonogashira products [11,12], significant efforts have been made to overcome these problems. One of the popular strategies for this goal has been immobilization of the homogeneous palladium catalysts and providing the corresponding heterogeneous catalysts, for example a zeolite-supported reaction system [13], $Pd(OAc)_2$/Agarose [14], Pd(dmba)Cl(PTA) [15], MCM-41-S-Pd(0) [16], CELL-Pd(0) [17], Pd^0-Mont [18], Pd–PPy [19], $Pd@Fe_3O_4$ [20], hollow Pd–Fe [21], palladium catalyst immobilized on $Fe_3O_4@SiO_2$ [22], polystyrene-anchored Pd(II) phenyldithiocarbazate complex [23], $Pd(OAc)_2$/2-aminodiphenyl–phosphine [24] and Si–PVI–Pd [25]. Although these methods are valuable, however, many of these procedures have significant drawbacks such as the tedious work up procedures, using of copper salts and phosphine ligands, long reaction times, high temperatures and low yields. It was also observed that non-functionalized superparamagnetic nanoparticles exhibited no activity in the reaction, indicating the necessity of the catalyst immobilization [20,21]. Thus, the development of a new procedure for the Pd-catalyzed Sonogashira reaction is still a desirable goal.

Nowadays, Fe_3O_4 nanoparticles, as magnetite nanoparticles, have attracted increasing interest because of their unique

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properties including a large surface-to-volume ratio, superparamagnetism, low toxicity, biocompatibility and their potential applications in various fields [26–30]. The Fe_3O_4 nanoparticles are easily synthesized [31] and functionalized by metal and organocatalysts and they can be easily separated from the reaction mixture by external magnetic field and reused [32–35].

Therefore, due to our interest in using silica coated iron oxide functionalized by Schiff base complex of metal ions [31], herein, we wish to prepare a Schiff base complex of palladium immobilized on superparamagnetic Fe_3O_4 nanoparticles, as a catalyst, to perform efficient Sonogashira cross-coupling between aryl halides and phenylacetylene under copper and phosphine ligand-free conditions. In addition, using the aforementioned methodology, catalyst separation becomes easier and cost effective with an external magnetic field.

2. Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All the solvents were distilled, dried and purified by standard procedures. NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was taken on a Shimadzu FT-IR 8300 spectrophotometer and the sample and KBr were pressed to form a tablet. The phase formation and crystallographic state of magnetic nanoparticles were determined by Bruker AXS D8-advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$). The size and morphology of the nanoparticles were observed using a Philips EM208 transmission electron microscope (TEM) with an acceleration voltage 100 kV. Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained on HITACHI S-4160. The BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2000 instrument at -196 °C. The magnetic properties of nanoparticles were measured on a BHV-55 vibrating sample magnetometer (VSM) and the hydrodynamic size of the particles was measured by dynamic light scattering (DLS) techniques, using a HORIBA-LB550 particle size analyzer. Pd loading and leaching test was carried out with an Inductively Coupled Plasma (ICP) analyzer (Varian, vista-pro). Determination of the purity of the substrate and monitoring of the reaction were accomplished by thin-layer chromatography (TLC) on a silica-gel polygram SILG/UV 254 plates. Elemental analysis was done on a 2400 series Perkin–Elmer analyzer. Melting points were determined on a Mel-Temp apparatus and are Uncorrected. Therefore, all of the products were characterized by FT-IR, ^1H NMR and ^{13}C NMR, and also by comparison with authentic samples.

2.1. General procedure

2.1.1. Preparation of $Fe_3O_4@SiO_2$ core–shell

The core–shell $Fe_3O_4@SiO_2$ nanospheres were prepared by a modified Stober method in our previous work [31].

2.1.2. General procedure for the preparation of the Schiff base ligands, [(OH)-salen]

To the solution of 3-aminopropyl (triethoxy)silane (1 mmol, 0.176 g) in 25 mL ethanol was added dropwise to the stoichiometric amount of salicylaldehyde (1 mmol, 0.122 g) in ethanol (25 mL). The yellow solution obtained, due to imine formation, was stirred at room temperature for 6 h. The resulting Schiff base ligand, as the bright yellow precipitate, was separated by filtration and washed with ethanol (5 mL) and then dried in vacuum. The crude product was recrystallized from ethanol to obtain the pure product in 98% yield (0.271 g). Anal. found (%): C, 58.36; H, 8.52; N, 4.48. Calc. for $C_{16}H_{27}NO_4Si$ (%): C, 59.04; H, 8.36; N, 4.30. 1H NMR (250 MHz, $CDCl_3$): $\delta = 0.7$ (t, 2H, CH_2, $J = 8.5$ Hz); 1.22 (t, 9H, CH_3, $J = 7.0$ Hz); 1.82 (m, 2H, CH_2); 3.59 (t, 2H, CH_2, $J = 6.5$ Hz); 3.81 (q, 6H, CH_2, $J = 7.0$ Hz); 6.85–6.96 (m, 2H, CH aromatic); 7.21–7.29 (m, 2H, CH aromatic); 8.33 (s, 1H, CH); 13.59 (s, 1H, OH). ^{13}C NMR (63 MHz, $CDCl_3$): $\nu = 7.94$, 18.32, 24.37, 58.43, 62.05, 117.03, 118.38, 118.81, 131.12, 132.05, 161.40 and 164.78 [31].

2.1.3. General procedure for the preparation of the Schiff base complex of palladium (II)

To the solution of the Schiff base ligand (2 mmol) in ethanol (25 mL) was added palladium acetates (1 mmol) and the mixture was reflux to complete the reaction. The progress of the reaction was monitored by TLC. After the completion of complex formation, a color change was observed. Resulting product was filtered and washed with ethanol. Schiff base complex of Pd(II): FT-IR (KBr pellets, cm^{-1}): 3000–30,850 (CH stretching), 2821–2979 (CH_2 stretching), 1621 (C=N), 1480–1600 (C=C), 1447, 1464 (CH_2 bending), 1389 (CH_3 bending), 1326 (C–O), 1139 (C–N), 1000–1150 (Si–O) and 525 (O–Pd).

2.1.4. General procedure for Schiff base complex of palladium ion functionalized magnetite@silica nanoparticles ($Fe_3O_4@SiO_2$/Schiff base/Pd(II))

$Fe_3O_4@SiO_2$ (2 g) was added to the solution of Schiff complex of palladium (1 mmol) in ethanol (10 mL) and the resultant mixture was under reflux for 12 h. The solvent was removed and the resulting solid was dried at 80 °C overnight. The product was washed with ethanol and water to remove no reacted species and dried at 80 °C for 6 h.

2.1.5. General procedure for the Sonogashira reaction using $Fe_3O_4@SiO_2$/Schiff base of Pd(II) magnetic nanocatalyst

To a mixture of the $Fe_3O_4@SiO_2$/Schiff base of Pd (II) nanocatalyst (0.7 mol%) and ArX (1.0 mmol) in DMF (5.0 mL) was added phenylacetylene (1.2 mmol) and triethylamine (2 mmol). The mixture was heated to 90 °C and the progress of the reaction was monitored by TLC. After completion of the reaction and separation of nanocatalyst with using magnetic field, 20 mL water was added and the mixture was extracted with Et_2O. The organic phase was washed with water (2 × 5 mL) and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography to give the desired cross-coupling products in excellent isolated yields.

3. Results and discussion

The $Fe_3O_4@SiO_2$ core–shell was synthesized by a modified Stober method [31] and then functionalized by the Schiff base complex of Pd(II), which had been obtained by the reaction between palladium(II) acetate and the Schiff base prepared from 3-aminopropyl (triethoxy)silane and salicylaldehyde, according to Scheme 1.

FT-IR spectra of Fe_3O_4, $Fe_3O_4@SiO_2$, Schiff base ligand, Schiff base complex of Pd(II) and $Fe_3O_4@SiO_2$/Schiff base/Pd(II) are shown in Fig. 1a–e.

For pure magnetic nanoparticles exhibit a strong band at 571 cm^{-1}, characteristic of the Fe–O vibration correlated to the magnetic core and the broad band around 3300 cm^{-1}, indicative of the presence of –OH groups on the nanoparticles surface (Fig. 1a). From the IR spectra presented in Fig. 1b, the absorption peak at 569 cm^{-1} belonged to the stretching vibration mode of Fe–O bonds in $Fe_3O_4@SiO_2$, the absorption peak presented at 1000–1150 cm^{-1}