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Resin-trapped gold nanoparticles: An efficient catalyst for reduction of nitro compounds and Suzuki-Miyaura coupling

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ABSTRACT

Gold in nanoparticle form shows good catalytic activity in contrast to bulk form and is finding applications in a variety of organic reactions. The present investigation describes direct deposition of gold nanoparticles onto commercially available resin by sorption reduction method. Uniformly dispersed nanoparticles of 3–8 nm dimensions were characterized by UV–visible spectroscopy, XRD, SEM and TEM, etc. The AuNPs were found to be remarkably stable and active catalysts for the selective reduction of nitro group under mild reaction conditions and microwave-assisted ligand-free Suzuki-Miyaura cross-coupling reaction between aryl halides and phenylboronic acid. Calculated rate constant (2.5×10^{-2} s^{-1}) for the reduction of 4-nitrophenol is among the best reported in the literature. The versatility of both the protocols is demonstrated by taking a number of substrates.

1. Introduction

Today, noble metals are being used as catalysts in the synthesis of a variety of important organic compounds. An efficient, recyclable and cost-effective synthesis of noble metal nanocatalysts is of great importance as it allows effective utilization of these expensive metals. Two key factors that determine the catalytic performance of such nanocatalysts are the particle size and the supports used for the dispersion of the noble metals [1]. Small size of the particles enhances their surface area and hence the number of reactive sites. On the other hand, choice of support plays a crucial role in the accessibility to catalytic sites. In the last few decades, gold nanoparticles (AuNPs) have been used in many areas of research including electronics, biomedicines, optics, and catalysis due to their strong optical, electrical, and chemical properties, as well as their biocompatible nature. Catalytic activity has been extensively reviewed in many reactions of both, industrial and environmental importance [2]. To facilitate catalyst recovery, AuNPs are usually dispersed onto solid matrices to prepare heterogeneous AuNP catalysts. According to the literature [3–8], various materials have been used as supporting matrices, including carbon nanotubes, silica, titania, ceria alumina, polymers, etc. Amongst them, alumina is one of the most frequently used supports owing to its remarkable properties such as high surface area, porous structure and good mechanical strength [9,10]. The impregnation method is a general strategy for the heterogenization of AuNPs [11,12]. How-ever, the resultant catalysts often suffer from a significant loss of catalytic activity during recycling because of weak interactions between the AuNPs and supporting matrices. To overcome these disadvantages, much effort has been paid to the development of new methodologies for the heterogenization of AuNPs. Yang et al. [13] have used of an organic gel based on polymeric phloroglucinol carboxylic acid and formaldehyde to support gold nanoparticles. Li et al. [14] have synthesized stable AuNPs encapsulated in a silica dendrimer organic–inorganic hybrid support as a recyclable catalyst for the oxidation of alcohols. Ohno et al. employed high density poly (methyl methacrylate) brushes to increase dispersion of gold nanoparticles [15]. Miyamura et al. [16] have reported polystyrene supported AuNPs as a catalyst for the aerobic oxidation of alcohols to aldehydes and ketones under atmospheric conditions.

We have earlier synthesized palladium nanoparticles supported on Amberlite XAD-4 and found that the resulting catalyst was not only stable and recyclable but also showed catalytic activity comparable to colloidal nanoparticles [17,18]. This prompted us to study the catalytic behavior of other metals on this support. In the present work, we have evaluated the catalytic activity of resin-trapped AuNPs toward reduction of nitro compounds and the Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acid.

2. Experimental

2.1. Materials and instruments

All chemicals used were of the analytical grade or of the highest purity grade available. Gold chloride was purchased from

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Aldrich. Aryl halides and aryl nitro compounds were purchased from Aldrich or Merck. Dichloromethane (DCM), diethyl ether (Et_2O), NaOH and $NaBH_4$ were purchased from Finar Chemicals. Amberlite XAD-4 (surface area $725\,m^2\,g^{-1}$ mesh size 20–40) was purchased from Aldrich. Water used in all experiments was purified by the Millipore-Q system. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO_3 (aqua regia) prior to use.

CEM benchmate microwave reactor was used for microwave heating. UV–visible absorption spectra were acquired on a Jasco V-570 UV–visible spectrophotometer. X-ray diffraction was recorded on SEIFERT FPM, XRD 7 using Cu Kα radiation ($\lambda = 1.5418$) and filter of nickel. Scanning Electron Microscopy (SEM) image of the bead was taken on a Leo 1430 VP Electron Microscope after coating it with palladium. High resolution transmission electron microscopy (HR-TEM) pictures were taken using a Hitachi (H-7500) instrument. The swollen resin beads were milled and a drop of alcoholic suspension was placed onto a 200 mesh carbon coated copper grid. It was then dried to evaporate the solvent and used for microscopy. GC–MS measurements were carried on Perkin-Elmer USA Auto system XL. ^{1}H NMR spectra were recorded on a Bruker Advance II 400 NMR spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were carried out on a HJY Ultima-2 instrument: power 1000 W, nebulizer flow 1.29, nebulizer pressure 2.96, wave length 242.795 nm. LOD (limit of detection) as determined by signal to noise ratio was found to be 0.25 mg/L.

2.2. Preparation of resin supported gold nanoparticles (resin-AuNPs)

The resin supported gold nanoparticles were synthesized by a method developed in our lab. Amberlite XAD-4 beads (5.0 g) were washed repeatedly with hot water to remove salts, swollen in ethanol and then equilibrated with 10 mL of 1 mmol solution of gold chloride in ethanol. After 1 h, excess solution was drained and the metal was reduced by passing cold aqueous $NaBH_4$ ($0.1\,mol\,dm^{-3}$) solution. The resin particles were further washed with water to remove excess reagent and stored in ethanol.

2.3. Reduction of nitro compound by resin-AuNPs

In a typical reduction protocol, 100 mg of catalyst was added to 20 mL of methanol/water (1:1) solution containing 0.5 mmol of nitro compound and 5 mmol of $NaBH_4$. The mixture was vigorously stirred at 40 °C. The reaction was monitored by Thin Layer Chromatography (TLC) and reaction mixture was quenched by extracting the organic derivatives with ethyl acetate. The solvent was evaporated under vacuum to give crude product of corresponding amine compound. Further purification was done through column chromatography. The products were confirmed by their melting points and ^{1}H NMR spectroscopy.

2.4. Suzuki-Miyaura coupling catalyzed by resin-AuNPs

Into a 10 mL vial, phenylboronic acid (1.5 mmol), aryl iodide (1.0 mmol), sodium hydroxide (3.0 mmol), ethanol (2.0 mL), water (1.0 mL) and catalyst (200 mg wet resin) were taken and heated in a CEM microwave (140 °C, 300 w) for 12 min. The reaction was quenched by filtering the hot solution in 10 mL of cold water. The resulting solution was extracted with Et_2O/DCM (2 × 5 mL). The combined extracts were dried over anhydrous $MgSO_4$ and the solvents were removed under vacuum. The crude products were then recrystallized from appropriate solvent and characterized by ^{1}H NMR.
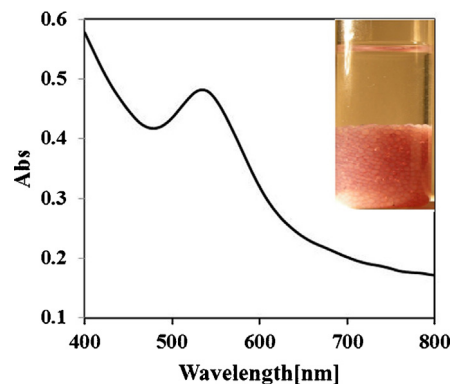

Fig. 1. UV–visible spectrum for the resin-AuNPs, inset: picture of resin-AuNPs. Beads taken with lateral illumination.

3. Results and discussion

3.1. Synthesis and characterization of resin supported AuNPs

Amberlite XAD-4 is a neutral, non-functional, hydrophobic, macroporous, commercial and cross-linked polystyrene resin. The resin is chemically and mechanically stable and there is no interference with the reaction conditions. While the presence of ligands/functional groups on a resin can control the size and stability of the nanoparticles, they have a negative influence from the catalytic activity point of view i.e. reducing the interaction of catalytic sites with the substrate. Hence, it seemed prudent to use the resin as a support for nanoparticle synthesis. The resin beads turn pink on impregnation of gold nanoparticles and since no other stabilizing agent was used it is assumed that the nanoparticles are trapped in the polymer network and stabilized solely by the steric factor/electrostatic interaction of the benzene rings.

AuNPs exhibit strong surface plasmon resonance (SPR) absorption band that is absent in the spectrum of the bulk metal. This band is dependent on the size, shape and aggregation of AuNPs. Therefore, UV–visible spectroscopy is a useful tool to estimate nanoparticle size, concentration, and aggregation level. In the present case, the resin-AuNPs beads were milled with ethanol and the solution centrifuged for 10 s. The supernatant solution was analyzed by spectrophotometer against a blank prepared from similarly treated resin beads. The SPR band maximum for AuNPs was thus observed at 535 nm which is characteristic of gold nanoparticles (Fig. 1). The red shift observed in the SPR band at 535 nm (Mie theory predicts SPR at 510–515 nm for gold particles of 3–8 nm as measured by TEM) can be due to stabilization of the nanoparticles by the π electron cloud of the benzene ring [19].

The XRD pattern of the powdered resin beads is shown in Fig. 2. The resin particles did not show any peak, only a broad hump was observed, which indicated the amorphous nature of the polymer matrix. When these beads were impregnated with gold nanoparticles, characteristic peaks of gold at $2\theta = 38.5$ and 44.2 (JCPDS No. 04-0784) were observed, corroborating the immobilization of the nanoparticles onto the resin beads. The bands were identified as (1 1 1) and (2 0 0) reflections corresponding to the fcc lattice of gold nanoparticles [20]. The broad nature of the bands was also indicative of the nanosize of the particles.

SEM image of the resin beads did not show any particles or agglomerations on the surface (Fig. 3). Thus, we inferred that all the particles are trapped inside the matrix of the resin. TEM was used to study the shape and size of nanoparticles. TEM pictures of AuNPs taken after milling the beads (Fig. 4) showed spherical nanoparticles embedded in polymer matrix. The size of the nanoparticles varies between 3 and 8 nm. To determine the amount of gold loaded