

Pd and Au Immobilized On Amine-Functionalized Magnetite Nanoparticles: A Novel and Highly Active Bimetallic Catalyst for Hydrogenation

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Abstract: A novel heterogeneous Au-Pd bimetallic catalyst stabilized by amine-functionalized magnetite nanoparticles was synthesized by anchoring palladium and gold by a facile one-pot template-free method combined with a metal adsorption–reduction procedure. A highly efficient and recyclable heterogeneous bimetallic catalyst exhibits excellent catalytic activity for various aromatic nitro compounds and unsaturated compounds to their corresponding products under a H₂ atmosphere at room temperature. The catalyst was found to be highly stable and passes hot filtration test successfully. The catalyst was characterized by FTIR, AAS, XRD, SEM and TEM. In addition, the catalyst can be easily separated and recovered with an external permanent magnet, and the reuse experiment shows that it can be used consecutively five times without significant loss in catalytic activity.

Keywords: Au-Pd/Fe₃O₄-NH₂, heterogeneous catalysis, reduction, recyclability, selectivity

1. Introduction

Catalytic hydrogenation of nitrobenzene and its derivatives is an industrially important transformation, as anilines are widely used raw materials for the production of methylene diphenyl diisocyanate, rubber chemicals and intermediates of dyes and pharmaceuticals. This reaction is mainly performed in liquid-phase and vapour-phase processes and requires high temperature and high pressure to improve the conversion of nitrobenzene (1). So the exploration of new catalytic systems that can effectively catalyze the hydrogenation processes under mild reaction conditions has received a great attention in the past years (2).

Numerous methodologies have been reported in the literature, for example, Pd, Rh, Pt, Ni, Ir, Co and their complexes, [3(a-d)] hydrides of Sn, Se, Te, B; [4(a-b)] sodium dithionite [5] and sodium borohydride [6] have also been reported to be useful for the hydrogenation of nitro compounds. However, some of these systems suffer from their own limitations: handling of reagents, strict reaction conditions, temperature maintenance, long reaction time, cost and poor yields of the desired product. Therefore, the development of a mild and selective organic transformation still attracts a great deal of attention from organic chemists.

Recently, breakthrough in Au and Pd catalysis provided new opportunities for reduction and hydrogenation chemistry [7]. Bimetallic nanoparticles are of greater interest than monometallic ones for improving the catalytic properties due to synergetic effects between two elements [8]. The advantage of bimetallic catalysts is attributed not only to electronic interaction between the two metals but also to the complex structure of bimetallic nanoparticles [9]. Several studies tested different bimetallic nanoparticle structures, such as core–shell structure [10], cluster-in-cluster structure [11], and single-alloy structure [12]. However, these catalysts are generally prepared by multistep procedures and further require high

temperatures and strong reductants during their preparation.

We herein report a recyclable Au-Pd nanoparticles supported on amine-functionalized magnetite nanoparticles [13] prepared from readily available reagent, like HAuCl₄ and Pd(OAc)₂ and its applications in selective hydrogenation of aromatic nitro compounds at room temperature under a H₂ atmosphere.

2. Materials and Methods

Ferric chloride hexahydrate (FeCl₃·6H₂O, >99%) as a single iron source, anhydrous sodium acetate, ethylene glycol, 1, 6-hexanediamine and ethanol. All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

HAuCl₄ and Pd(OAc)₂ were purchased from Merck (Germany) and Aldrich Chemical Company. All melting points were determined on a Perfit melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker DPX-200 NMR spectrometer (200 MHz) in CDCl₃ using tetramethylsilane as an internal standard and IR spectra were recorded on Perkin-Elmer FTIR spectrophotometer using KBr discs. Mass spectral data was recorded on Bruker Esquire 3000 (ESI). Thermal analysis was carried out on Linseis Thermal Analyser with heating rate of 10 °C/min. SEM was recorded using Jeol make T-300 Scanning Electron Microscope and Transmission Electron Micrographs (TEM) in a H7500 Hitachi. The amount of Au and Pd was determined on GBC Avanta-M Atomic Absorption Spectrometer manufactured by GBC Scientific agencies.

2.1 Synthesis of amine-functionalized magnetite nanoparticles: ($\text{Fe}_3\text{O}_4\text{-NH}_2$)

Amine-functionalized magnetite nanoparticles were synthesized via the versatile solvothermal reaction reported by Li.[14] Typically, a solution of 6.5 g 1,6-hexanediamine, 2.0 g anhydrous sodium acetate and 1.0 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a ferric source in 30 mL ethylene glycol was stirred vigorously at 50 °C to give a transparent solution. The solution was then transferred into a Teflon-lined autoclave and maintained at 200 °C for 6 h. The magnetite nanoparticles were then thoroughly rinsed with deionized water and ethanol to effectively remove the solvent and unbound 1,6-hexanediamine, and then vacuum dried at 50 °C to obtain a black powder for further use. During each rinsing step, the nanoparticles were separated from the supernatant by using a magnetic force.

2.2 Loading of Pd and Au on amine-functionalized magnetic nanoparticles: ($\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Au-Pd}$)

500 mg of as-synthesised Fe_3O_4 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 mM of a $\text{Pd}(\text{OAc})_2$ and HAuCl_4 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. The weight percentage of Pd and Au in the $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Pd}$, as determined by atomic absorption spectroscopic (AAS) analysis, was 8.43 wt%.

Several bimetallic catalysts with different Au/Pd molar ratios were prepared by varying the concentrations of HAuCl_4 and $\text{Pd}(\text{OAc})_2$, and labeled by the Au/Pd molar ratio. For instance $\text{Au}(1)\text{Pd}(1)/\text{Fe}_3\text{O}_4\text{-NH}_2$ corresponds to the $\text{Fe}_3\text{O}_4\text{-NH}_2$ supported catalyst prepared by sol-immobilization method with an Au/Pd molar ratio of 1:1. The catalytic activities of these catalysts were studied on the selective hydrogenation of aromatic nitro compounds. The most active catalyst ($\text{Au}(1)\text{-Pd}(1)/\text{Fe}_3\text{O}_4\text{-NH}_2$) was employed to study the scope of the substrates.

2.3 General procedure for the hydrogenation of aromatic nitro compounds ($\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Au-Pd}$ catalyst for hydrogenation reaction)

In a typical experiment, 1 mmol of the reagent was dissolved in 5mL ethanol with 20 mg of catalyst under a H_2 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 reaction vessel and the residue was washed with hot ethyl acetate (3×10 mL) followed by distilled water (200 mL). The organic layer was washed with water and dried over anhydrous Na_2SO_4 . The conversion was estimated by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6,890N/5,973N). Thereafter, the catalyst was washed three times with ethanol and dried at room temperature for the next cycle. The structures of the products were confirmed by spectral data and comparison with authentic samples obtained commercially or prepared

according to the literature methods. The catalytic reactions were repeated, and even after 5 cycles, there was no deterioration in the catalytic efficiency.

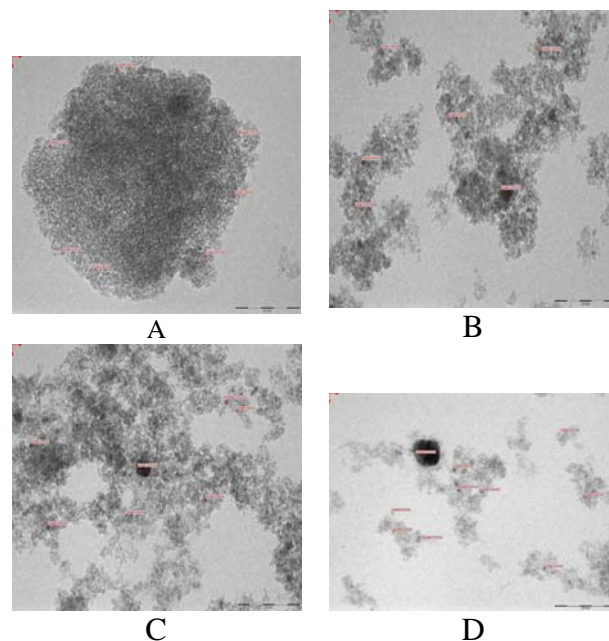
3. Results and Discussion

3.1 Characterization of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Au-Pd}$

The characterization of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Au-Pd}$ was done on the basis of simultaneous thermal analysis (TGA), Fourier transform infrared spectroscopy (FTIR), atomic absorption spectroscopy (AAS), X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

3.2 Transmission electron microscopy studies

TEM observations were performed to examine the mean particle size and size distribution of bimetallic ($\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Au-Pd}$) catalysts. The images are shown in Fig. 1. The bimetallic Au-Pd nanoparticles (10.3 ± 2.2 nm) for the catalyst prepared by the solvothermal method were much smaller than both Au (20.42 ± 3.85 nm) and Pd (23.51 ± 3.42 nm) monometallic nanoparticles, suggesting the chemical combination of Au and Pd to form the bimetallic nanoparticles rather than physical combination and are nearly mono-disperse. The TEM images in Fig. 1 shows that the $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-Pd}$ catalyst didn't change considerably after attachment of the gold and palladium onto the surface of the magnetic nanoparticles. Unambiguous evidence of gold and palladium particles on $\text{Fe}_3\text{O}_4\text{-NH}_2$ is provided via Energy-Dispersive X-ray spectroscopy (EDX), indicating a highly dispersed Au and Pd phase on the support. TEM images (Figure 1) showed the uniform distribution of gold and palladium onto surface of $\text{Fe}_3\text{O}_4\text{-NH}_2$



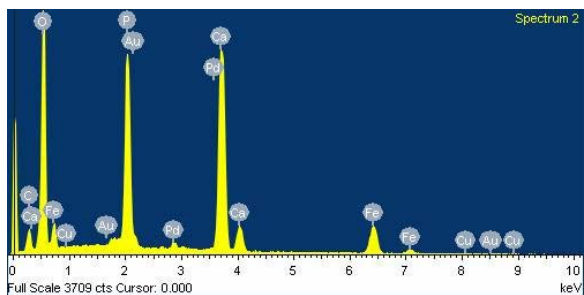


Figure 1: TEM images of bimetallic Au-Pd/Fe₃O₄-NH₂ catalyst with corresponding nanoparticles size distributions. Insets: (a) Au-Pd/ Fe₃O₄-NH₂ (b) Au/ Fe₃O₄-NH₂ (c) Pd/ Fe₃O₄-NH₂ (d) recycled Au-Pd/ Fe₃O₄-NH₂ (e) EDX spectra of the catalysts containing Au and Pd with the Cu, Ca and Fe signal because of the copper grid holder and support Fe₃O₄-NH₂

3.3 Thermogravimetric Analysis

Thermal analysis curve for the Au-Pd/Fe₃O₄-NH₂ showed initial weight loss up to 100 °C which may be due to the loss of residual water trapped onto the surface of Fe₃O₄-NH₂. Further, a negligible weight loss (0.29%) was observed up to 395 °C. Thus, catalyst is stable up to 395 °C and hence, it is safe to carry out the reaction below 395 °C.

3.4 Fourier Transform Infra-Red Spectroscopic Studies

In FTIR spectra, strong absorption peaks at 473, 569, 602, 3572 cm⁻¹ and weak intensity peaks at 1412 and 2924 cm⁻¹ were observed. Further, wide absorption bands also appear at 1047 and 3421 cm⁻¹ (Figure 2). IR spectrum of Fe₃O₄-NH₂ Au-Pd, indicating that plenty of 1,6-hexanediamine molecules are immobilized on the surface of the nanoparticles. The peaks at 1047, 1412, 3421 and around 2924 cm⁻¹ correspond to C–N stretching, C–H symmetric blending vibration, N–H stretching vibration and C–H stretching models of the alkyl chain, respectively.

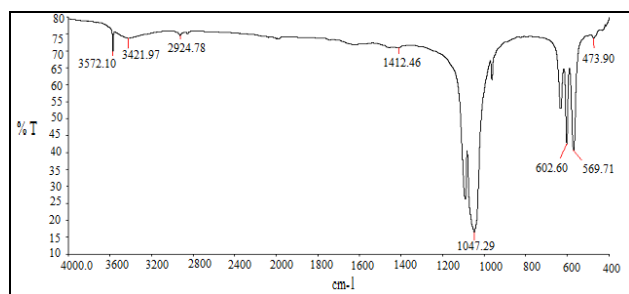


Figure 2: FTIR spectra of Au-Pd/ Fe₃O₄-NH₂

3.5 X-Ray Diffraction Studies

The XRD (Figure 3) showed reflection patterns corresponding to $2\theta = 38.3^\circ$, 44.6° which were attributed to Au and $2\theta = 33.8^\circ$ which corresponds to Pd. The diffraction peaks of the bimetallic catalyst at 38.6° located

between Au(1 1 1) and Pd(1 1 1) is assigned to the Au–Pd stable alloy phase.

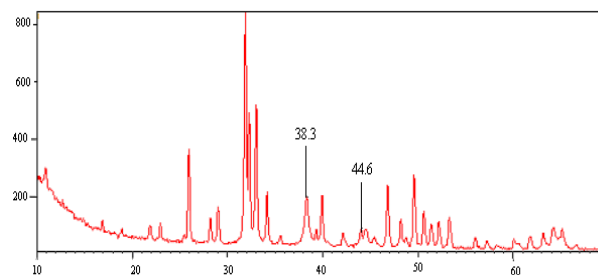


Figure 3: XRD spectra of Au-Pd/ Fe₃O₄-NH₂

3.6 Atomic Absorption Spectroscopy

The amount of gold and palladium loaded onto the surface of hydroxyapatite was determined by AAS analysis. The catalyst was stirred in dil. HNO₃ and then subjected to AAS analysis. It was found that Au-Pd/ Fe₃O₄-NH₂ contained 0.02461 g of Au and Pd per gram of the catalyst.

3.7 Scanning Electron Microscope Studies

The physical form of the catalyst was characterized by using Scanning Electron Microscope. SEM image of Au-Pd/ Fe₃O₄-NH₂ shown in (Figure 4) indicates that it is a homogeneous powder.

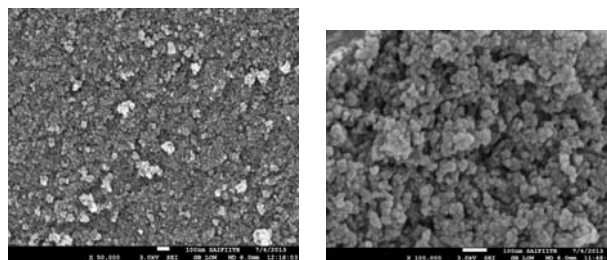


Figure 4: SEM images of Au-Pd/HAP/SI

3.8 Catalyst Testing for the Selective Hydrogenation of Aromatic Nitro Compounds

The reaction conditions for catalytic selective hydrogenation of aromatic nitro compounds were optimized by selecting nitrobenzene as the test substrate and Au-Pd/ Fe₃O₄-NH₂ as the heterogeneous catalyst. For the optimization of the solvent, the reaction was carried out in polar and non-polar solvents (Table 1). Among toluene, ethanol and water, best results in term of yield, reaction times and selectivity were observed in ethanol. Thus, ethanol was selected as the solvent for selective hydrogenation of aromatic nitro compounds. The reaction with the test substrate was also carried out using different molar ratios of the catalyst (Table 1) and found that 2.5 mol% of Au and Pd in Au-Pd/ Fe₃O₄-NH₂ was efficient to carry out the reaction with good selectivity.

Table 1: Effect of solvents and catalyst loading on Au-Pd/ Fe₃O₄-NH₂-catalyzed hydrogenation of aromatic nitro compounds

Effect of solvent			Effect of catalyst loading		
Entry	Solvent	Yield (%) ^b	Entry	Catalyst (mol% Au and Pd)	Yield (%) ^b
2	Toluene	20	2	1	65
2	Water	15	2	1.5	70
2	Ethanol	95	2	2	85
			2	2.5	95
			2	3	95

^aReaction conditions: nitrobenzene (1 mmol), Au-Pd/ Fe₃O₄-NH₂ (0.2 g, 2.5 mol%), ethanol (5 mL), at room temp in H₂ atmosphere.

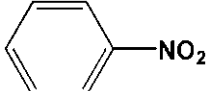
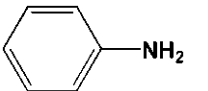
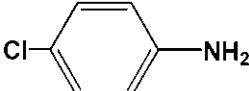
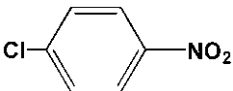
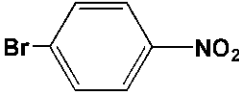
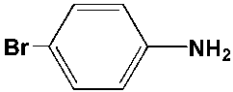
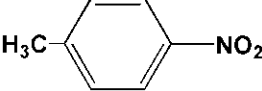
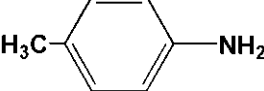
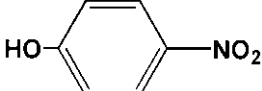
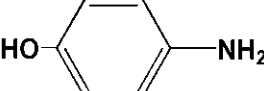


^bYield refer to column chromatography yield.

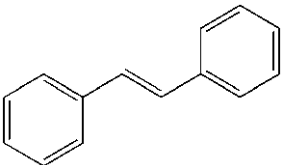
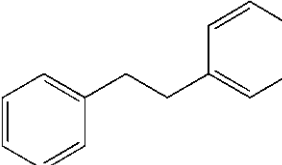
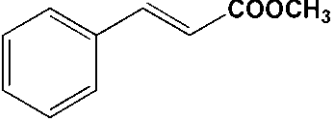
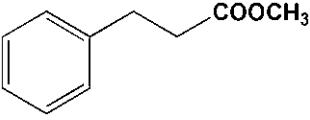
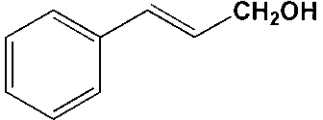
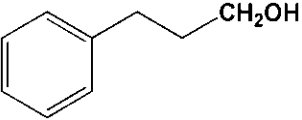
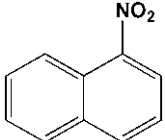
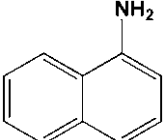
In order to study the generality of the developed protocol, different aromatic nitro compounds with substituted electron-donating and electron-withdrawing substituents were chosen and good to excellent results were obtained. All the substrate gave good results (Table 2).

3.9 Catalyst Testing for Hydrogenation Reaction of Aromatic Nitro Compounds

Initially, the catalytic activity of Fe₃O₄-NH₂-Au-Pd was tested for the hydrogenation of a variety of aromatic nitro compounds to their corresponding products. The reactions were carried out in ethanol at room temperature under H₂ atmosphere. Detailed observations of all the reactions are given in Table 3. We observed that the catalyst was very active for the hydrogenation reaction under such mild conditions, since the amine groups are known to enhance the catalytic activity of Pd and Au. A satisfactory yield (>95%) was still obtained even after the catalyst had been reused five times. The recyclability of the catalyst can be attributed to the efficient stabilisation of the active Au and Pd species by the amine groups on the magnetite surface.

Table 3: Hydrogenation of various aromatic substrates using Fe₃O₄-NH₂-Au-Pd as the catalyst

Entry	Substrate	Product	Time/min	Yield ^b (%)
1			50	95
2			45	98
3			45	95
4			50	97
5			60	98
6			120	92

7			50	95
8			50	98
9			70	98
10			75	96

^aReaction conditions: The reactions were carried out by stirring a mixture of aromatic nitro compounds (1 mmol), Au-Pd/Fe₃O₄-NH₂ (0.2 g, 2.5 mol%), and ethanol (5 mL) at room temperature in H₂ atmosphere.

^bYield refer to column chromatography yield.

To determine the role of Au-Pd/Fe₃O₄-NH₂ for selective reduction of aromatic nitro compounds, the test reaction was also carried out in the absence of the catalyst. The reaction didn't proceed in the absence of the catalyst, thus, indicating that Au-Pd/Fe₃O₄-NH₂ is catalyzing the reduction.

3.10 Heterogeneous Catalysis and Recyclability

To rule out the contribution of homogeneous catalysis, hot filtration test was carried out for these reduction reactions. After 40% conversion of the test substrate (Table 2, entry 2), the reaction mixture was filtered and liquid phases were transferred to another flasks and allowed to react under the reaction conditions, but no further conversion was observed. The second point was the deactivation and recyclability of the catalyst, which becomes more important in case of reduction reactions. To test this, series of five consecutive runs were carried out with the same test substrate. It was found that there occurred a very little drop in the activity of the catalyst which may be attributed to the microscopic changes on the structure of the catalyst.

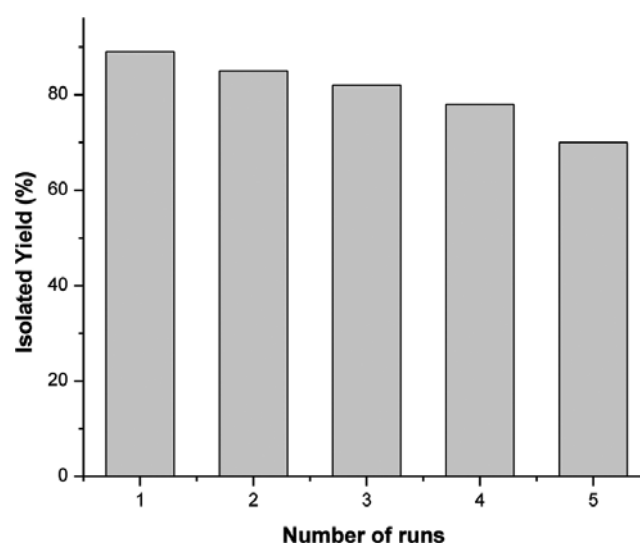


Figure 6: Recyclability of Au-Pd/Fe₃O₄-NH₂ catalyst

4. Conclusion and Future Implications

In conclusion, Au-Pd/Fe₃O₄-NH₂ as a bimetallic heterogeneous catalyst for selective reduction of carbon-carbon double bond in α,β -unsaturated ketones and hydrogenation reaction of aromatic nitro compounds has been explored successfully without affecting the double bond in acetonitrile and ethanol respectively under H₂ atmosphere at room temperature. The alloying of gold with palladium leads to a more enhancement in activity with the simultaneous retention of selectivity over monometallic gold and palladium. The mild reaction conditions, high yield of products, ease of work-up, compatibility with various functional groups, and the ecologically clean selective procedure will make the present methodology a useful and important addition to the present methodologies for the selective hydrogenation reactions. The designs of alternative synthesis techniques should inject "greenness" into the three aspects of organic transformation, specifically: (i) utilizing green oxidants, (ii) employing clean solvents, and (iii) designing environmentally benign catalysts with high activity and selectivity, is of supreme importance.

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