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Magnetic Carbon-Supported Palladium Nanoparticles: An Efficient and Sustainable Catalyst for Hydrogenation Reactions

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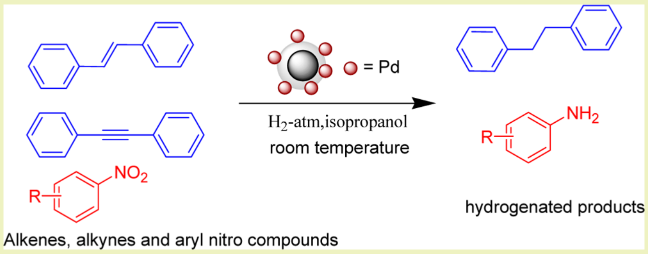
S Supporting Information

ABSTRACT: A magnetic carbon-supported Pd catalyst has been synthesized via in situ generation of nanoferrites and incorporation of carbon from renewable cellulose via calcination. The catalyst can be used for the hydrogenation of alkenes and reduction of aryl nitro compounds.



KEYWORDS: *Nano ferrites, Cellulose, Reduction, Alkenes, Nitro compounds, Magnetic separation*

INTRODUCTION

Catalytic hydrogenation is one of the most important and widely used transformations in synthesis.[1−3] The methods involving the use of molecular hydrogen and recyclable catalysts are often the most desired pathways to reduce an organic compound. Recovery and reuse of the precious metal catalyst has become significant not only in response to an economical concern but also from an ecological perspective due to growing environmental cognizance.[4−6] In general, the homogeneous catalysts give a high level of activity and selectivity due to their uniformity on a molecular level and solubility in the reaction medium. On the other hand, on an industrial scale, it is often very difficult and expensive to recover these catalysts from reaction mixtures. This is especially important due to the high costs of the catalysts and to avert the heavy metal contamination in pharmaceutically significant products for human use.[7] Consequently, in most of the industrial transformations, heterogeneous catalysts are preferred,[8] and immense efforts have been expanded in this area from the research scientists across the globe on heterogeneous catalyst. The active part of the catalyst remains on the sites over the surface of the porous supports, which results in diminished overall activity of the heterogeneous system.[9−13]

Nano catalysts have drawn attention due to their high surface-to-volume ratio.[14−16] Nanoparticles, being small, present close to a homogeneous experience thus bridging the gap between homogeneous and heterogeneous systems.[12−14] The most common problems associated with the nanocatalyst are its tedious filtration and centrifugation. Additionally, nanoparticles often undergo agglomeration without the addition of stabilizers, thereby diminishing their activity (by way of surface coating by the capping agent).[12] Therefore, efforts have been made to stabilize nanoparticles by immobilization on different solid supports such as polymers, silica, and zeolites.[17−20] However, many of these supports have serious limitations including the ease of their synthesis, along with their tiresome recovery using centrifugation or time-consuming filtration. A superb way of combining high surface area along with ease in recovery using an external magnet is via magnetic support for catalytic applications.[21−23] In continuation of our research toward the sustainable and versatile magnetic catalyst system,[12−15] we report a magnetic carbon-supported Pd heterogeneous catalyst system for the catalytic hydrogenation reactions.

The first step in our goal was to achieve easy and straightforward synthesis of a magnetic carbon-supported Pd catalyst (Scheme 1) via a step-wise addition of multiple reagents in one-pot. The magnetic nanoferrite (Fe_3O_4) was generated in situ via a hydrolysis method by stirring the solutions of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3$ in water in 1:1 ratio at pH 10 (adjusted using 25% ammonium hydroxide solution) followed by heating in a water bath at 50 °C for 1 h. The reaction temperature was brought to room temperature, and cellulose was added with stirring, which was continued for 6 h at room temperature. To this solution, $PdCl_2$ was added, and reaction mixture was further stirred for 8 h (Scheme 1). Magnetic cellulose-supported Pd materials were separated using an external magnet, washed with water, and calcinated at 450 °C for 3 h. The crystal structure was determined using X-ray diffraction (XRD) (Figure S1, Supporting Information); the major phases were Fe_3O_4, Pd, and C, which were compared with JCPDS patterns 01-075-0033, 01-088-2335, and 01-075-0444, respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 1a−c) were

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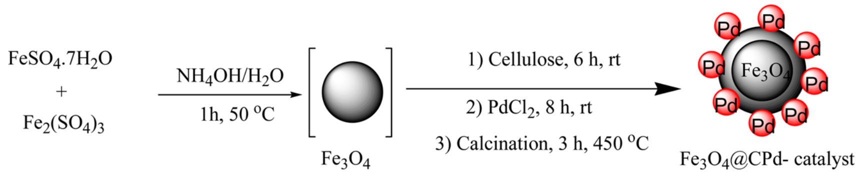
Scheme 1. Synthesis of Magnetic Carbon-Supported Pd Catalyst



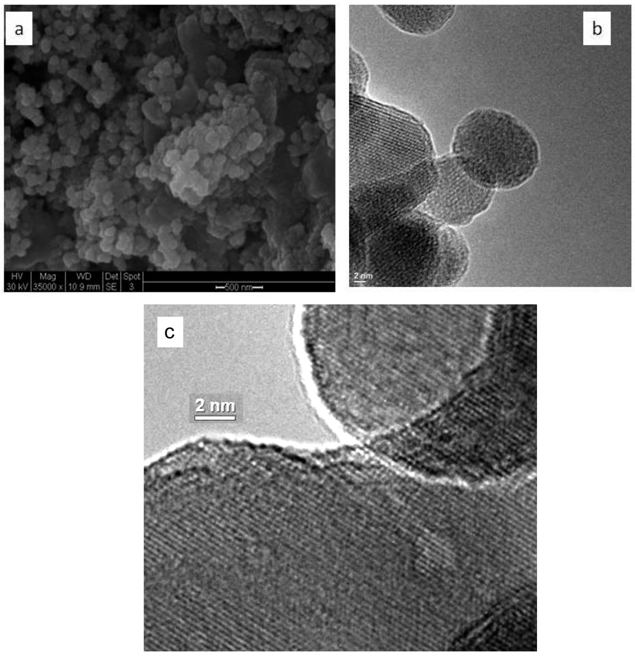
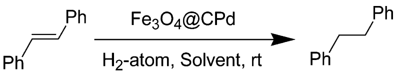


Figure 1. (a) SEM image and (b) TEM image of Fe_3O_4@CPd catalyst. (c) TEM image of Fe_3O_4@CPd particles with visible carbon coating.

conducted to determine the surface morphology. The SEM images showed the formation of spherical particles along with big aggregates. The TEM images indicated that the particle size ranges from 20 to 50 nm. The magnified TEM image of individual particles shows that each particle has been uniformly coated with a thin carbon layer (Figure 1c). The concentration of Pd (4.81 wt%) was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. The BET surface analysis of the catalyst showed a surface area of 175.71 m^2/g.

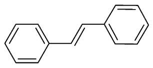
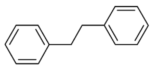
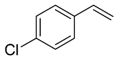
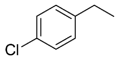
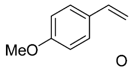
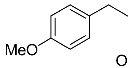
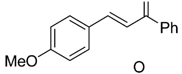
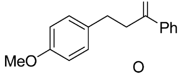
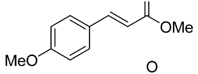
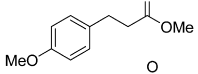
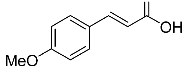
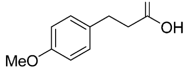
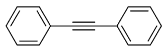
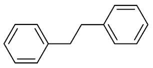
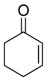
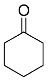
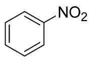
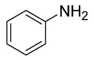
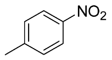
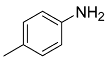
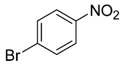
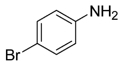
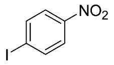
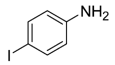
Initial experiments were performed to evaluate the catalytic activity of the Fe_3O_4@CPd catalyst for hydrogenation of stilbene (5 mmol) as a substrate (Scheme 2) using 1 atm of hydrogen and a varied amount (25, 50, and 100 mg) of Fe_3O_4@CPd catalyst in various solvents. The best result was obtained in isopropanol using 100 mg of catalyst when reaction was completed in 40 min at room temperature.

Scheme 2. Fe_3O_4@CPd Catalyzed Hydrogeneation of Alkene



The reaction progress was monitored by thin layer chromatography (TLC) and conversion estimated by gas chromatography (GCMS). After completion of the reaction, the catalyst was recovered using an external magnetic bar. The catalyst was then washed with acetone, dried at 50 °C, and reused for a subsequent cycle. In order to demonstrate the substrate scope and activity of the catalyst, the catalytic activity of Fe_3O_4@CPd was examined for various hydrogenation reactions (Table 1). We observed an efficient catalytic activity for the hydrogenation of a wide range of alkenes under 1 atm pressure of H_2 at room temperature (Table 1, entries 1–8). Cyclohexenone underwent efficient hydrogenation at room temperature (Table 1, entry 8). Diphenyl acetylene also underwent efficient hydrogenation at room temperature (Table 1 entry 7). Reactions were conducted to demonstrate the scope and activity of Fe_3O_4@CPd for hydrogenation of nitroarenes (Table entries 9–12); all the reactions proceeded smoothly to afford the corresponding amines. A comparative study with commercially available 10% Pd/C for the hydrogenation of nitro benzene (Table 1, entry 9) revealed that the

Table 1. Catalytic Hydrognetion of Alkenes and Nitroarenes Using Magnetic Carbon-Supported Fe_3O_4@CPd Catalyst

Entry	Substrate	Product	Times	Conversion[a]
1			40 min	>99%
2			35 min	>99%
3			35 min	>99%
4			60 min	>99%
5			60 min	>99%
6			60 min	>99%
7			40 min	>99%
8			60 min	>99%
9			40 min 300 min [b]	>99% >99%
10			40 min	>99%
11			40 min	>99%
12			40 min	>99%

[a] Reaction condition: 5 mmol of substrate, 100 mg of catalyst, isopropanol, H_2 1 atm, room temperature [b] Reaction was performed using 100 mg of 10% Pd/C

magnetic carbon ferrite surface provides the ideal environment for better conversions when compared with the commercially available 10% Pd/C catalyst. The commercial Pd/C catalyst requires 5 h for completion of the reaction, whereas the Fe_3O_4@CPd completes the reaction in 40 min with very low Pd loading under similar experimental conditions. It is clear from Table 1 that the catalyst finds high tolerance for many functional groups under a hydrogenation environment.

The recovery of the catalyst is of prime importance in sustainable organic synthesis, which is generally accomplished via laborious filtration or centrifugation techniques. Due to the magnetic nature of the nano-Fe_3O_4@CPd catalyst, it could be recovered easily using an external magnet. To attest to the applications of the developed heterogeneous magnetic system, the evaluation of the catalyst, recyclability, stability, and lifespan are very important. To affirm its reusability and durability, we carried out a set of experiments for the hydrogenation of 4-nitrobromobenzene using the recycled nano-Fe_3O_4@CPd catalyst. After the completion of the reaction, Fe_3O_4@CPd was recovered using an external magnet, washed with acetone, and dried at 50 °C. A fresh reaction was then setup using recovered Fe_3O_4@CPd and 4-nitrobromobenzene under hydrogen pressure and similar reaction conditions. The magnetic carbon-supported Pd catalyst could be used at least three times without any change in activity. ICP-AES analysis of the catalyst before and after the reaction was performed to calculate the Pd concentration. The initial concentration (4.81% of Pd) before the reaction was reduced to 4.75% after the reaction. No Pd metal was detected in the hydrogenation product, which confirmed negligible Pd leaching. The trifling Pd leaching may be due to a well-defined magnetic carbon-coated Pd catalyst (Scheme 1).

The TEM and SEM images of the catalyst taken after the third consecutive recycle did not show any unusual change in the morphology of the catalyst (Figures S2 and S3, Supporting Information), which favors retention of the catalytic activity during recycling experiments. It is always preferable to use an easily accessible, economic, and benign Pd catalyst, provided that the system works well and the catalyst could be recycled many times without leaching metal into the final product. All of the above conditions were satisfactorily met by the nano-Fe_3O_4@CPd catalyst.

EXPERIMENTAL SECTION

Synthesis of Magnetic Carbon-Coated Pd (Fe_3O_4@CPd). $FeSO_4{\cdot}7H_2O$ (2.78 g) and $Fe_2(SO_4)_3$ (4.0 g) were dissolved in 150 mL water in a 500 mL beaker. The pH of the solution was adjusted using NH_4OH. The reaction mixture was stirred for 1 h at 50 °C, and then it was cooled to room temperature. Cellulose (10 g) was then added, and stirring was continued for 6 h at room temperature. To this solution, $PdCl_2$ was added and further stirred for 8 h (Scheme 1). Magnetic cellulose-supported Pd materials were separated using an external magnet; the residual amount of catalyst sticking to magnetic bar was washed with mother liquor, separated, and combined with earlier portions. The catalyst was washed with water and calcinated at 450 °C for 3 h. XRD and TEM analyses of the catalyst confirmed the formation of carbon-coated magnetic nanoparticles Fe_3O_4@CPd, with a size range of 20−50 nm. The concentration of Pd (4.81 wt %) was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

Hydrogenation Using Magnetic Carbon-Supported Fe_3O_4@CPd Catalyst. Five mmol of substrate (alkene or aryl nitro compound) and 100 mg Fe_3O_4@CPd catalyst were placed in a 100 mL round-bottomed flask with a magnetic stirrer bar under a hydrogen atmosphere (1 atm of H_2) at room temperature in 25 mL of isopropanol. The reaction was continuously stirred at room temperature. The progress of the reaction was monitored using GCMS and TLC at regular intervals of time. After completion of the reaction, the catalyst was allowed to deposit over the magnetic stirring bar and was separated using an external magnetic bar for reuse. Most of the time, the products were isolated by simple concentration under reduced pressure.

CONCLUSION

A novel magnetic carbon-supported Pd catalyst has been synthesized, which can be readily prepared in multigram quantities in aqueous media. A naturally abundant biopolymer (cellulose) has been utilized for the generation of magnetic carbon. The active catalyst efficaciously catalyzed the hydrogenation of alkenes, alkynes, and aryl nitro compounds. Because of the magnetic nature of the catalyst, it can be retrieved using an external magnet, which eliminates the requirement of catalyst filtration after completion of the reaction.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed preparative procedure and SEM and TEM of the recovered catalyst after the reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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