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Carbon-coated magnetic palladium: applications in partial oxidation of alcohols and coupling reactions†

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A carbon-coated magnetic 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 oxidation of alcohols, amination reaction and arylation of aryl halides (cross-coupling reaction).

Introduction

The oxidation of alcohols and olefins to carbonyl compounds and coupling of aryl halides are some of the most important transformations in synthetic organic chemistry because of their use in a wide range of pharmaceutically important products, agro-chemicals, and fragrances.^{1,2} Conventionally, oxidation is carried out using stoichiometric amounts of oxidants such as chromium and manganese compounds which generate copious amounts of hazardous metal waste.^{3–6} Due to the increasing environmental consciousness, persistent efforts are being made to develop environmentally benign catalysts for common oxidation and coupling reactions; various heterogeneous catalyzed protocols are now available.^{7–13} There have been many heterogeneous supports utilized for the immobilization of metal complexes and metal nanoparticles such as metal oxides, silica, natural and unnatural polymers, silicates and mesoporous carbon.^{7–13} Among these, Ru hydroxide and Pd supported on magnetic nanoferrite (Fe_3O_4), and Pd nanoparticles supported on SBA-15 have shown promise.^{14,15} However, most systems can be useful for the oxidations of only activated substrates or require larger quantities of additives such as bases and electron transfer mediators thus limiting their applications.^{6–15} Recently, the use of nano- $\gamma\text{-Fe}_2\text{O}_3$ for the oxidation of alcohols with high selectivity has been reported.¹⁶ The activity of magnetic catalyst was further improved by immobilization of Pd over dopamine-modified magnetic ferrites;¹⁷ however, this effort requires several synthetic manipulations. In continuation of our efforts^{18–27} in the development

of a sustainable and active catalyst system, we now report a versatile carbon-coated magnetic Pd catalyst for the common oxidation and coupling reactions.

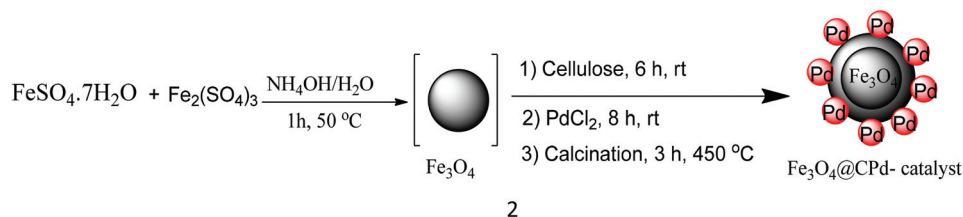
The first step in the accomplishment of this goal was the straightforward synthesis of the carbon-coated magnetic Pd catalyst (Scheme 1) by sequential addition of reagents in one pot. The magnetic nanoferrite (Fe_3O_4) was generated *in situ* via the hydrolysis method by stirring the solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ 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 (TEM image, ESI, Fig. 1†). The reaction mixture was cooled down to room temperature and cellulose was added with vigorous stirring which was continued for 6 h under ambient conditions. To this solution, PdCl_2 was added and stirring was continued for another 8 h (Scheme 1). Magnetic cellulose supported Pd materials were separated using an external magnet (TEM image, ESI, Fig. 2†), washed with water and calcinated at 450 °C for 3 hours. The crystal structure was determined by X-ray diffraction (XRD) (Fig. 2). 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) (Fig. 1a and b) were conducted to determine the surface morphology. The SEM images showed the formation of spherical particles along with big aggregates. The TEM images indicated the particle size of Fe_3O_4 @CPd ranging from 20 to 50 nm. The weight percentage of Pd was found to be 4.81% by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. Surface analysis of the catalyst showed a BET surface area of 175.71 $\text{m}^2 \text{g}^{-1}$.

The initial experiments were performed to test the catalytic activity of the Fe_3O_4 @CPd catalyst for oxidation of benzyl alcohol (10 mmol) as a substrate (Scheme 2), using 1.2 equivalents of hydrogen peroxide and 100 mg of Fe_3O_4 @CPd; conversion with very high TON (816), with >99% selectivity (Table 1, entry 1) was observed.

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Scheme 1 Synthesis of the carbon-coated magnetic $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst.

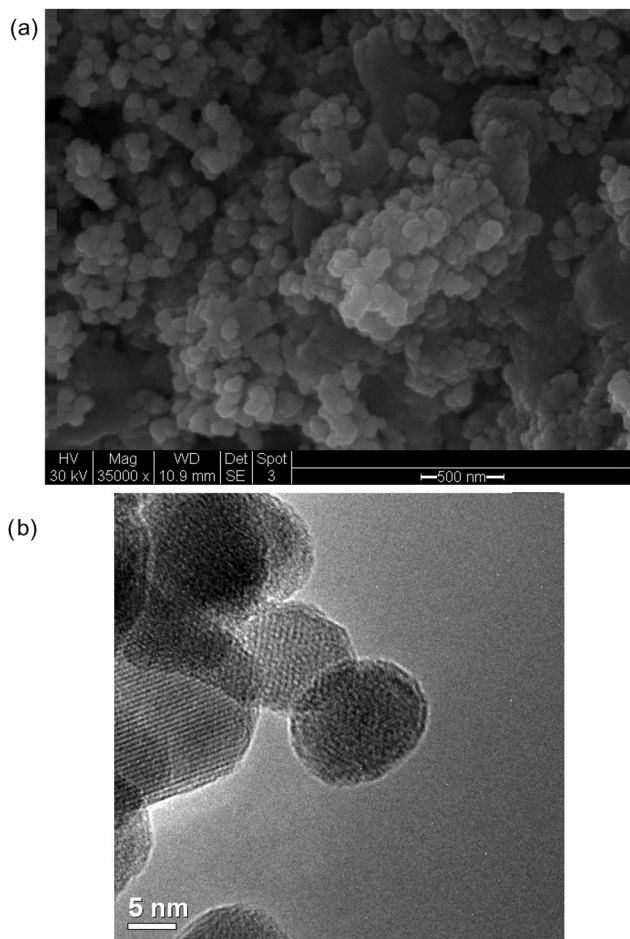


Fig. 1 (a) SEM image and (b) TEM image of the $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst.

The catalyst was then evaluated for the general scope and a variety of alcohols (Table 1) were investigated as substrates; impressive turnover numbers were observed for aromatic alcohols (entries 1–7), heterocyclic alcohols (entry 6) as well as aliphatic alcohols (entry 7). However, in the case of hexanol, relatively low TON may be attributed to its less reactivity. In all the reactions, the salient and distinctive feature was high selectivity using a very low amount of catalyst (0.01 mol% of Pd). This method may find applications in large-scale preparations where it is required that an alcoholic group is selectively oxidized to an aldehyde without any over-oxidation.

Arylation and amination of aryl halides is an important transformation and a method of choice for the synthesis of

fascinating molecules of biological importance;^{28–33} biaryls and *N*-aryl functionality is widely distributed in several biologically important natural products and pharmaceuticals. The Suzuki coupling and Buchwald–Hartwig amination using the palladium catalyst has been well explored.^{34–38} However, many of these methods involve the use of toxic and complex organic ligands which are often air-sensitive, expensive and many reactions require longer reaction times.^{27–40} In recent years, greater emphasis is placed on the development of sustainable heterogeneous catalysts and the ease of recyclability, especially using biodegradable polymers. We evaluated our iron-cellulose derived $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst for Suzuki and Buchwald–Hartwig amination reactions; the arylation of aryl halides could be easily performed using boronic acid within 30 min under microwave (MW) irradiation conditions. The reaction outcome did not alter due to the presence of electron donating and electron withdrawing groups; all the substrates (Table 2, entries 1–7) gave similar desirable results. The catalyst is also useful for the amination of aryl halides (Table 3, entries 1–4); amination of 4-nitro-1-bromobenzene with various amines proceeded smoothly to deliver the corresponding aryl amines in quantitative yields (Table 3, entries 1–4).

Separation and recovery of the catalyst is of paramount importance in sustainable organic synthesis which is generally achieved by tedious filtration or centrifugation with reduced efficiency. In our catalytic system, due to the magnetic nature of the nano- $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst, it can be recovered easily using an external magnet. For practical applications of heterogeneous systems, the life time of the catalyst and its level of reusability are significantly important factors. To clarify this issue, we established a set of experiments for the oxidation of benzyl alcohol using the recycled nano- $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst. After the completion of the reaction, the catalyst was recovered using an external magnet, washed with acetone, and dried at 60 °C for 20 min. A new reaction was then performed with fresh reactants and H_2O_2 , under the same reaction conditions. The carbon coated magnetic $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst could be used at least 3 times without any change in activity (ESI, Table 1†). Metal leaching was studied by ICP-AES analysis of the catalyst before and after the reaction; the Pd concentration was found to be 4.81% before the reaction and 4.77% after the reaction; no Pd metal was detected in the oxidation product which confirmed negligible Pd leaching. The trifling Pd leaching may be due to the well defined magnetic carbon coated Pd catalyst (Scheme 1). This non-covalent anchoring minimizes deterioration and metal leaching and allows efficient catalyst

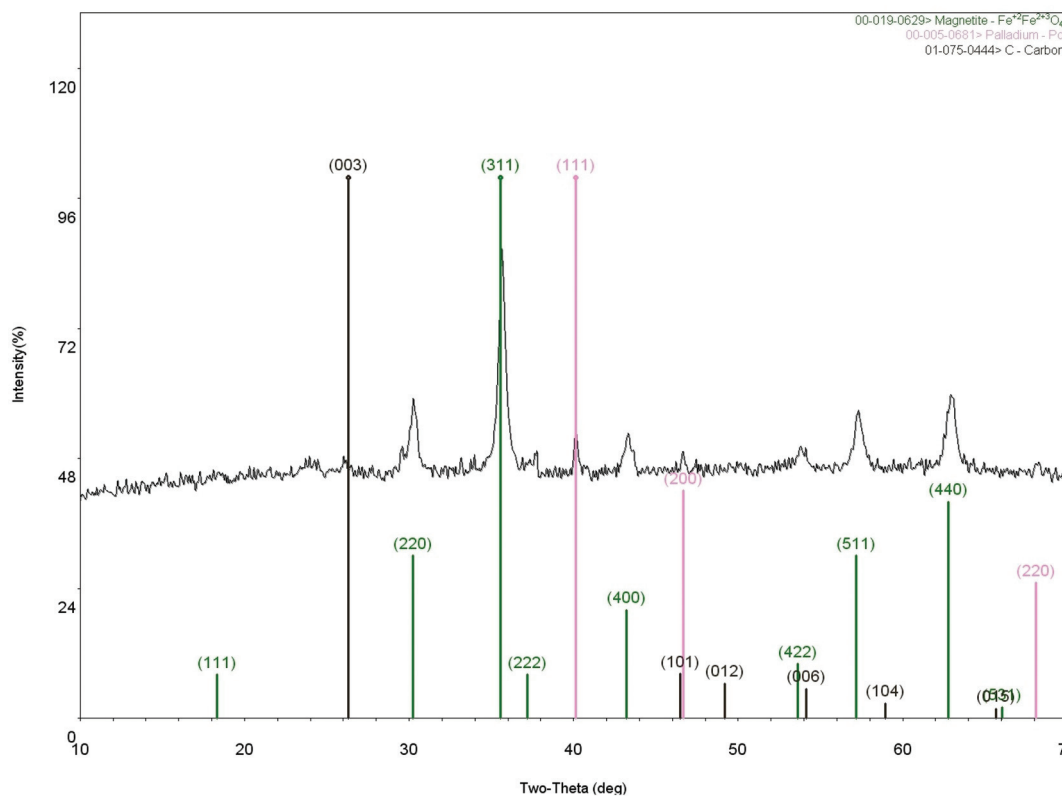
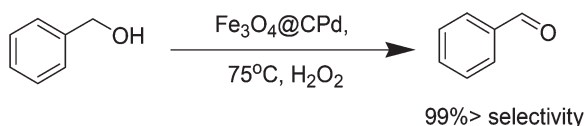


Fig. 2 XRD pattern of the $\text{Fe}_3\text{O}_4\text{@CPd}$ catalyst.



Scheme 2 $\text{Fe}_3\text{O}_4\text{@CPd}$ catalysed oxidation of benzyl alcohol.

recycling. The absence of metal deterioration in recycling experiments for C–N coupling also confirms the effectiveness and reusability of the catalyst.

The TEM and SEM images of the catalyst taken after the third cycle of the reaction did not show significant change in the morphology of the catalyst (ESI, Fig. 3 and 4†), which indicates the retention of the catalytic activity after recycling. It is always preferable to use a more accessible, economic Pd catalyst, provided that the process works at high TON and that the catalyst leaves no remnants of the metal in the final product, since metal contamination is highly regulated by the pharmaceutical industry. All the above conditions were well satisfied by our recyclable magnetic carbon supported Pd catalyst.

Conclusion

A novel magnetic carbon-supported Pd catalyst has been synthesized, which can be readily prepared in multi gram quantities in aqueous media. A naturally abundant biopolymer

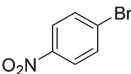
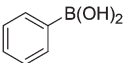
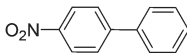
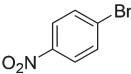
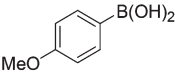
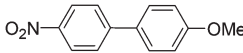
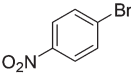
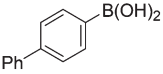
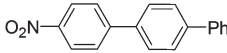
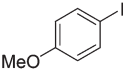
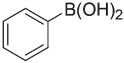
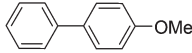
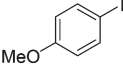
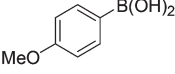
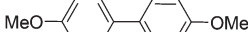
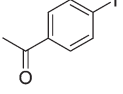
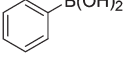
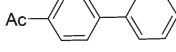
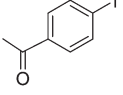
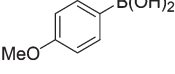
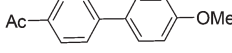
Table 1 Catalytic oxidation of alcohols using the carbon-coated magnetic $\text{Fe}_3\text{O}_4\text{@CPd}$ catalyst^a

Entry	Substrate	Product	TON
1			923
2			942
3			932
4			913
5			903
6			923
7			644

^a Reactions were carried out with 10 mmol of alcohol, H_2O_2 (1.2 equiv.), 100 mg (0.0104 mol% of Pd) of $\text{Fe}_3\text{O}_4\text{@CPd}$ nanocatalyst at 75 °C for 4 h.

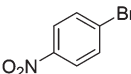

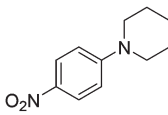
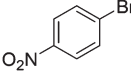

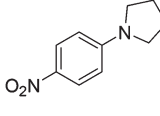
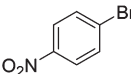
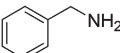
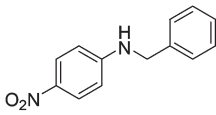
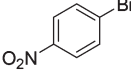

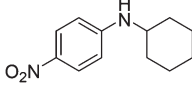
(cellulose) has been utilized for the generation of magnetic carbon. The active catalyst efficaciously catalyzed the oxidation of alcohols, C–N coupling and arylation of aryl halides. Because of the magnetic nature of the catalyst, it can be

Table 2 Fe₃O₄@CPd catalysed arylation of aryl halides^a

Entry	Substrate	Boronic acid	Time	Product	Yield
1			30 min		98%
2			30 min		98%
3			30 min		95%
4			30 min		96%
5			30 min		96%
6			30 min		98%
7			30 min		98%

^a Reaction conditions: 1 mmol aryl halides, 1.2 mmol aryl boronic acids, 2 mmol K₂CO₃, 25 mg of Fe₃O₄@CPd catalyst, 4 mL water, MW 100 watts, 100 °C, 30 min.

Table 3 Fe₃O₄@CPd catalysed amination of aryl halides^a

Entry	Aryl halide	Amines	Time	Product	Yield
1			60 min		98%
2			60 min		97%
3			60 min		89%
4			60 min		98%

^a Reaction conditions: 1 mmol aryl halides, 1.2 mmol amines, 2 mmol K₂CO₃, 25 mg of Fe₃O₄@CPd catalyst, 4 mL DMF, MW 100 watts, 100 °C, 60 min.

separated using an external magnet, which eliminates the requirement of catalyst filtration after completion of the reaction.

Experimental section

Synthesis of the carbon coated magnetic Fe₃O₄@CPd catalyst

FeSO₄·7H₂O (2.78 g) and Fe₂(SO₄)₃ (4.0 g) were dissolved in 150 mL water in a 500 mL beaker. Ammonium hydroxide

(25%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 50 °C. The reaction mixture was cooled down to room temperature and cellulose (10 g) was added to this solution with vigorous stirring which was continued for 6 h under ambient conditions. To this solution, PdCl₂ was added and stirring was continued for another 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 hours.

Catalyst characterization by X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirms the formation of single-phase carbon coated magnetic nanoparticles $\text{Fe}_3\text{O}_4@\text{CPd}$, with spherical morphology and a size range of 20–50 nm. The weight percentage of Pd was found to be 4.81% by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

Oxidation of alcohols using the carbon coated magnetic $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst

10 mmol of alcohol and 100 mg (0.0104 mol% of Pd) $\text{Fe}_3\text{O}_4@\text{CPd}$ catalyst were placed in a 10 mL round bottom flask with a magnetic stirrer bar and H_2O_2 (1.2 equiv.) was then added drop wise to the reaction mixture under constant stirring at room temperature. The reaction was continuously stirred at 75 °C for 4 h. The conversion and selectivity were periodically determined by GC analysis at various time points. After completion of the reaction, stirring was stopped and the catalyst was separated using an external magnet. The crude product obtained was further purified by column chromatography.

Arylation of aryl halides

Aryl boronic acid (1.1 mmol), aryl halide (1.0 mmol), K_2CO_3 (2.0 mmol) and $\text{Fe}_3\text{O}_4@\text{CPd}$ (25 mg) were placed in a crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. Water (4 mL) was added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 100 °C (temperature monitored by a built-in infrared sensor), 100 watts for 30 min. After completion of the reaction, the catalyst was recovered using an external magnet. Products were extracted using ethyl acetate, dried over sodium sulfate, concentrated under reduced pressure and purified using column chromatography.

Amination of aryl halides

Aryl halide (1.0 mmol), amine (1.1 mmol), K_2CO_3 (2.0 mmol) and $\text{Fe}_3\text{O}_4@\text{CPd}$ (25 mg) were placed in a crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. DMF (4 mL) was added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 100 °C (temperature monitored by a built-in infrared sensor), 100 watts for 60 min. After completion of the reaction, the catalyst was easily removed from the reaction mixture using an external magnet. The products were extracted using ethyl acetate, dried over sodium sulfate, concentrated under reduced pressure and purified using column chromatography.

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