Electronic Supplementary Material (ESI) for Green Chemistry.

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

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Synthesis of carbon coated magnetic Fe_3O_4@CPd catalyst

$FeSO_4 \cdot 7H_2O$ (2.78 g) and $Fe_2(SO_4)_3$ (4.0 g) were dissolved in 150 mL water in a 500 mL beaker. 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 gm) was added to this solution with vigorous stirring which was continued for 6 h at ambient conditions. To this solution, $PdCl_2$ was added and stirring was continued for another 8 h (Scheme 1). Magnetic cellulose supported Pd materials was 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 Fe_3O_4@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 carbon coated magnetic Fe_3O_4@CPd catalyst

10 mmol of alcohol and 100 mg (0.0104 mole% of Pd) **Fe_3O_4@CPd** catalyst were placed in a 10 mL round bottom flask with a magnetic stirrer bar. H_2O_2 (1.2 equiv) was then added drop wise to the reaction mixture under stirring at room temperature. The reaction was continuously stirred at 75◦C for 4 h. Conversion and selectivity was periodically determined by GC analysis. After completion of the reaction, stirring was stopped and the catalyst was separated using 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 Fe_3O_4@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 ^oC (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, dry 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 Fe_3O_4@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 ^oC (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. Product were extracted using ethyl acetate, dry over sodium sulfate, concentrated under reduced pressure and purified using column chromatography.

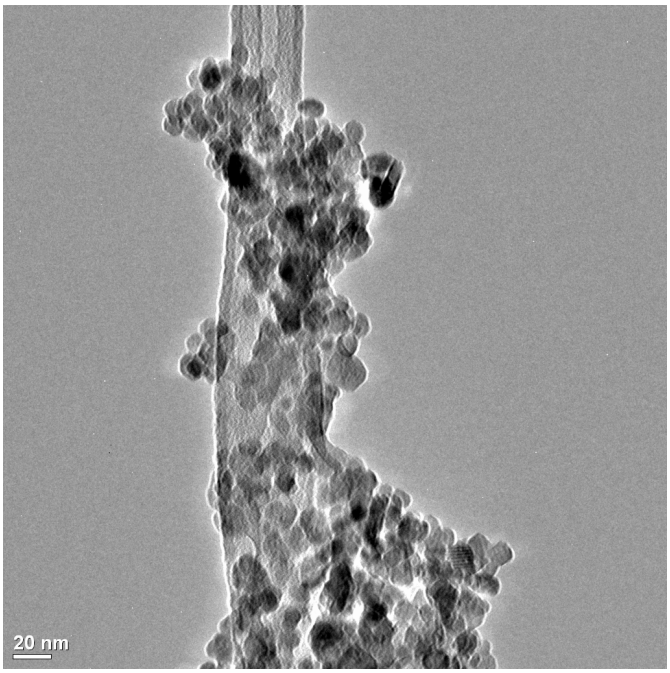


Figure1 TEM image after Fe_3O_4 formation

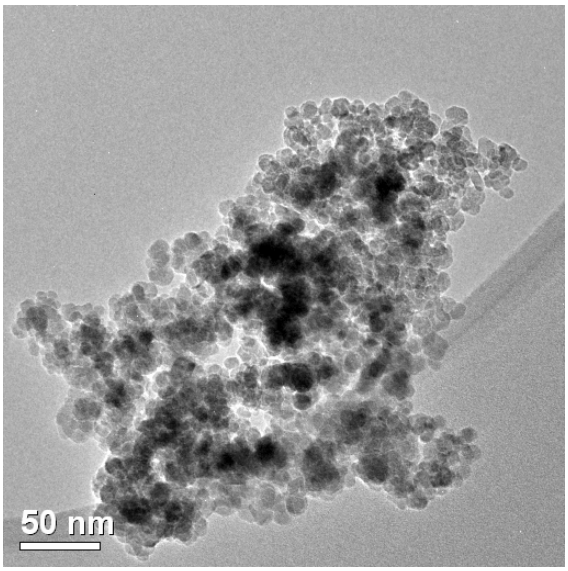


Figure 2 TEM image of Fe_3O_4 immobilized over cellulose

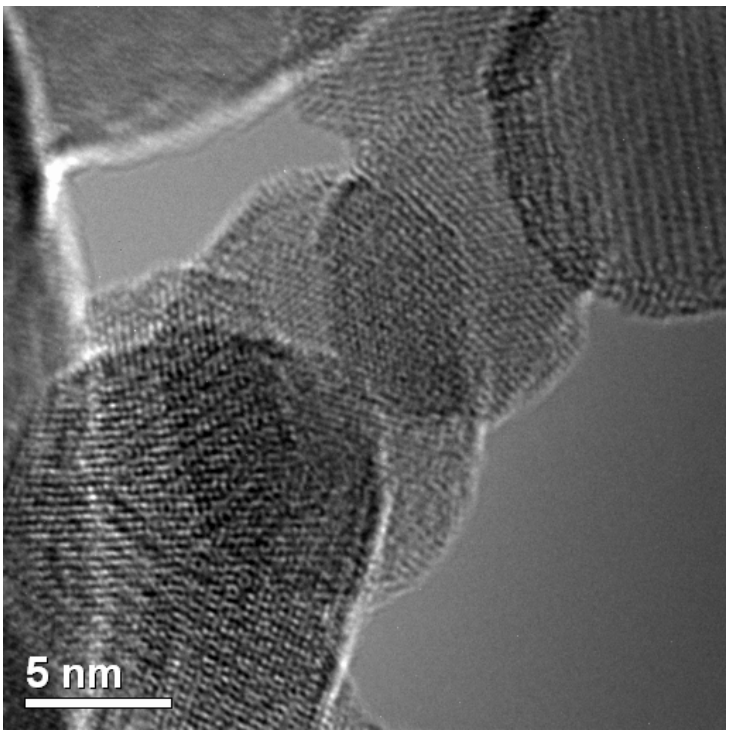


Figure 3 TEM image of the recycled Fe_3O_4@CPd

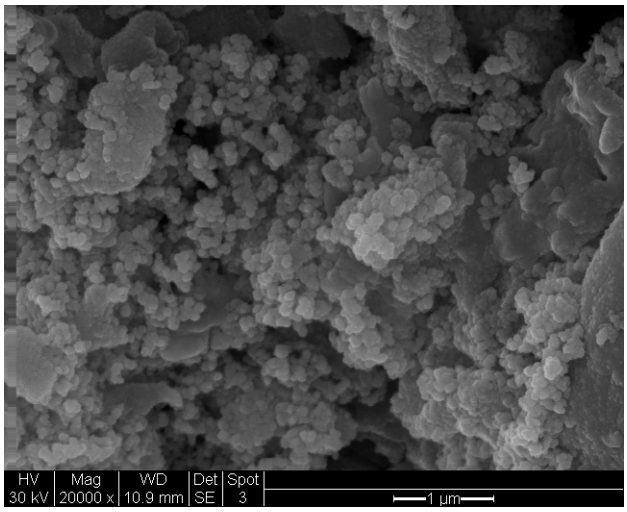
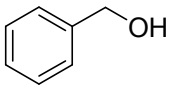
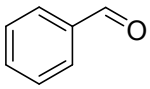
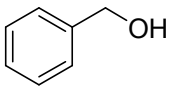
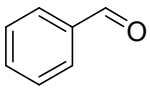
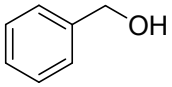
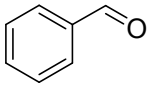


Figure 4 SEM image of the recycled Fe_3O_4@CPd

Table 1 Recyclability of Fe_3O_4@CPd catalyst for oxidation of benzyl alcohol

Entry	Substrate	Product	Yield
1			96%
2			97%
3			96%

a) Reactions were carried out with 10 mmol of benzyl alcohol, H_2O_2(1. 2 equvi) 100 mg (0.0104 mol % of Pd) of Fe_3O_4@CPd nanocatalyst. at 75 ^oC for 4 h.