

# Heterogenization of cobalt nanoparticles on hollow carbon capsules: Lab-in-capsule for catalytic transfer hydrogenation of carbonyl compounds

Basuvaraj Suresh Kumar<sup>a</sup>, Arlin Jose Amali<sup>a,b,\*</sup>, Kasi Pitchumani<sup>a,b,\*</sup>

<sup>a</sup> Department of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai, 625021, Tamil Nadu, India

<sup>b</sup> Centre for Green Chemistry Processes, School of Chemistry, Madurai Kamaraj University, Madurai-21, Tamil Nadu, India

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## ABSTRACT

Incorporation of cobalt nanoparticles (Co NPs) in porous iron oxide nanospheres (Fe<sub>3</sub>O<sub>4</sub> NSs) templated, glucose derived hollow carbon capsules (HCCs), with an objective to achieve activity and stability simultaneously, facilitates higher catalytic activity of Co NPs in transfer hydrogenation of ketones and aldehydes. A variety of ketones and aldehydes are hydrogenated successfully with excellent yields and high turnover number (TON). This system constitutes one of the most general, heterogeneous, highly stable catalyst, which does not require additives for activation and employs mild reaction conditions. Other significant advantages are low Co content (0.38 mol%) for a catalytic hydrogenation reaction, functional-group tolerance, inexpensive, environmentally benign nature and reusability.

## 1. Introduction

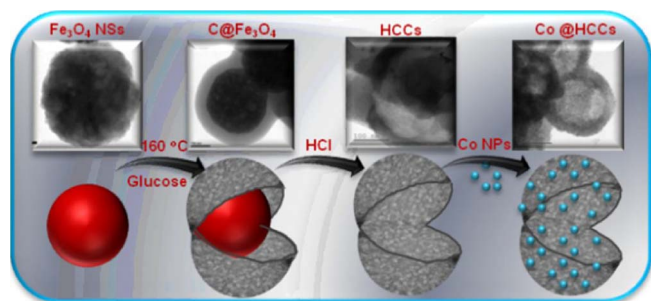
Catalysis is a key technology for achieving environmentally benign processes in chemical, pharmaceutical and materials industries [1,2]. Consequently, in the search towards newer catalysts, greater focus is devoted to metal or metal oxide nanoparticles [3,4], which are amphidextrous combining advantages of both homogeneous and heterogeneous catalysts. In this context, though noble metals are studied extensively [5–9], first row transition metals, which are earth abundant, easily available and inexpensive attract less attention as catalysts. Recently, Fe, Cu, Zn and Co emerged as highly effective, soluble and promising catalysts in various organic reactions [10–13]. Among these base metals, cobalt is the first base metal catalyst made from a non-precious metal properties closely matching those of platinum [14–16] and cobalt catalysts are identified recently as the best candidates for converting biomass to value added products [17], syngas to clean liquid fuels because of lower deactivation rates, low water-gas shift activity and high chain growth probability [18–20].

However, despite their above advantages and utility, for hydrogenation reactions only very few cobalt based catalysts have been reported. For example, Zhang's and Rosler's groups have reported PNP-stabilized homogeneous Co(II) complexes as catalysts for transfer hydrogenation of C=O and C=N bonds [21–23]. Beller and co-workers have developed cobalt-based nanocatalysts by pyrolysis of cobalt(II) acetate phenanthroline complex for hydrogenation process [1,24–26]. However, these heterogeneous Co catalysts require very high pressure

hydrogen and temperature for realizing high catalytic activity. On the other hand, use of hydrogen donor reagents in transfer hydrogenation reactions can avoid the use of autoclaves, high pressure hydrogen, high temperature and thus are highly relevant for industrial applications [27,28]. In a recent study Long et al., have used Co containing metal organic frameworks as the sacrificial template for preparing Co@C-N as heterogeneous catalyst for catalytic transfer hydrogenation using isopropanol as hydrogen transfer agent [29]. However, the synthesis of catalyst requires high temperature. Hence, significant improvements are therefore desirable to realize more sustainable, environmentally friendly, economical, heterogeneous Co catalysts involving use of hydrogen donor reagents for transfer hydrogenation reactions. Herein, we report a “cheap and simple” non-precious metal, *ie.*, Co NPs as heterogeneous catalysts for transfer hydrogenation of carbonyl compounds. The catalyst was prepared by incorporation of Co NPs in porous Fe<sub>3</sub>O<sub>4</sub> NPs templated, glucose derived hollow carbon capsules (HCCs), to achieve efficiency, reusability, high catalytic activity and stability.

HCCs have strong encapsulation ability, controllable permeability, surface functionality, low density and excellent chemical and thermal stabilities. Their tailored structure can find many potential applications in energy storage, *e.g.*, in lithium batteries [30], and also as catalyst supports in heterogeneous catalysis. They provide means to stabilize catalytically active species *via* confinement within their cavity, thereby mitigating deactivation pathways, such as metal sintering or leaching [31]. In addition, the shell subunits shielding the catalytically active species can exert molecular discrimination, based on either chemical

\* Corresponding authors at: Department of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai, 625021, Tamil Nadu, India  
E-mail addresses: [arlinjose.chem@mkuniversity.org](mailto:arlinjose.chem@mkuniversity.org) (A.J. Amali), [pitchumani.chem@mkuniversity.org](mailto:pitchumani.chem@mkuniversity.org) (K. Pitchumani).



Scheme 1. Schematic representation for the synthesis of Co NPs@HCCs.

compatibility or molecular sieving, which pave the way towards selective catalytic transformations. Also, presence of a confined environment may enhance the catalytic activity due to local concentration of substrates [32,33].

## 2. Experimental

### 2.1. Synthesis of cobalt nanoparticles (Co NPs)

Co NPs were synthesized by adding an aqueous solution of  $\text{NaBH}_4$  into an ice cold aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and PVP. In a typical procedure, an aqueous ice-cold solution (8 mL) containing PVP (10.5 mg) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 23.7 mg) was stirred (10 min) under nitrogen atmosphere. Subsequently, an aqueous ice-cold solution (3 mL) containing  $\text{NaBH}_4$  (10 mg) was added dropwise. The reaction was allowed to continue in ice-cold conditions for 3 h to afford Co NPs.

### 2.2. Hydrothermal synthesis of $\text{Fe}_3\text{O}_4$ nanospheres ( $\text{Fe}_3\text{O}_4$ NSs)

Iron (III) chloride hexahydrate (1 mmol, 0.270 gm) and urea (9 mmol, 0.540 gm) were added into ethylene glycol (10 mL) under magnetic stirring. The resultant solution was transferred into a teflon lined stainless steel autoclave, sealed, and heated to 200 °C for 12 h. The

precipitated black products were collected by an external magnet and washed several times with ethanol. Finally, the black colored product was dried in vacuum for 24 h at 60 °C.

### 2.3. Synthesis of carbon@ $\text{Fe}_3\text{O}_4$ nanospheres ( $\text{C}@\text{Fe}_3\text{O}_4$ )

Carbon@ $\text{Fe}_3\text{O}_4$  were synthesized by hydrothermal carbonization of glucose in presence of  $\text{Fe}_3\text{O}_4$ . The synthesized  $\text{Fe}_3\text{O}_4$  solid spheres (100 mg) were dispersed in water (10 mL) containing glucose (1.6 gm) by ultrasonication. The mixture was transferred into a teflon lined stainless steel autoclave, sealed, and heated at 160 °C for 10 h, and then cooled at room temperature. The precipitated black solid was collected from the solution by an external magnet and washed several times with ethanol. Finally, the black coloured product was dried in vacuum for 24 h at 60 °C to afford  $\text{C}@\text{Fe}_3\text{O}_4$ .

### 2.4. Synthesis of hollow carbon capsules (HCCs)

The as synthesized  $\text{C}@\text{Fe}_3\text{O}_4$  nanospheres (1 gm) were dispersed in water (10 mL) to which HCl (40 mL, 3N) solution was added and allowed to stir for 5 h. After completion of the reaction, the reaction mixture was centrifuged (3000 rpm, 15 min), the residue was collected, washed and dried (60 °C, 5 h) to obtain hollow carbon capsules (HCCs).

### 2.5. Incorporation of Co NPs on hollow carbon capsules (Co NPs@HCCs)

Co NPs@HCCs were prepared by deposition method. Typically, HCCs (300 mg) were well dispersed in ethylene glycol (100 mL) under magnetic stirring. To this, a solution containing Co NPs (11 mL) was added dropwise (30 min) under vigorous stirring. The above prepared reaction mixture was stirred for 2 h at 80 °C. After completion of the reaction, the Co NPs incorporated HCCs (Co NPs@HCCs) were separated by centrifugation (3000 rpm, 10 min), washed three times with water and acetone and dried in vacuum to obtain Co NPs@HCCs.

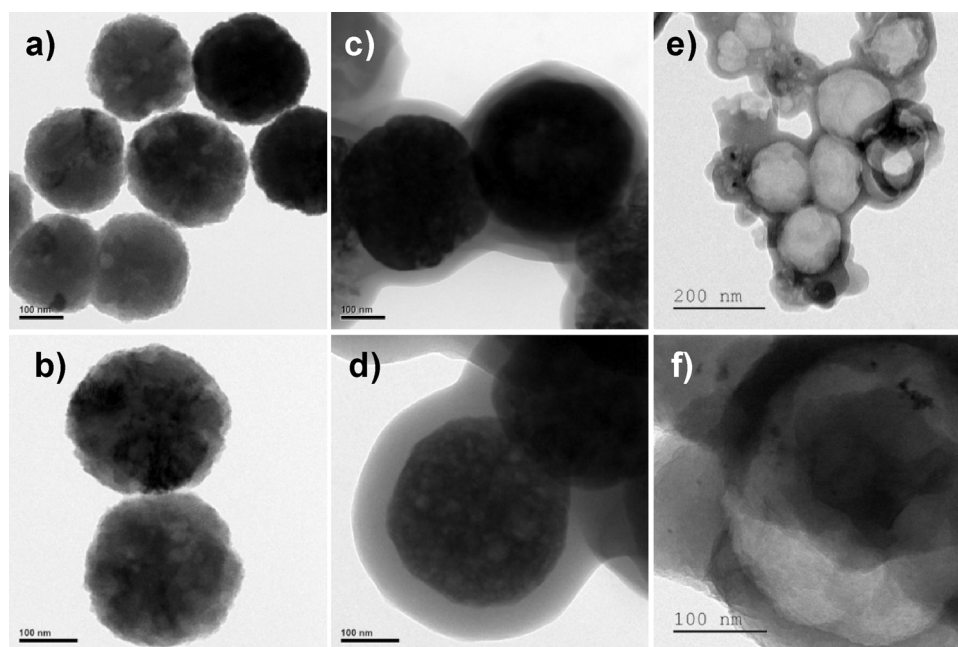


Fig. 1. TEM images of  $\text{Fe}_3\text{O}_4$  NSs (a,b);  $\text{C}@\text{Fe}_3\text{O}_4$  NSs (c,d) and HCCs (e,f).

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