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Cu/Cu_2O nanoparticle interface: Rational designing of a heterogeneous catalyst system for selective hydroamination

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One pot highly uniform Cu(0)-Cu(I) oxide nanoparticles (5–10 nm) have been synthesized on nitrogen rich mesoporous carbon nanospheres (Cu-NCN) and efficiently utilized as a heterogeneous catalyst towards hydroamination of aromatic terminal alkynes with aniline derivatives. The catalyst bed provides Cu_2O nanoparticles stabilized by nitrogen functionalities in the carbon nanospheres, which triggers the catalytic system with significantly large Turn over number (TON) and >99% selectivity towards Markovnikov addition product. The structure and morphology of the copper nanoparticles engraved carbon spheres have been studied by performing nitrogen physisorption studies (BET), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) characterization techniques.

1. Introduction

Use of copper-based nanoparticles have attracted substantial attention in various conventional commercial chemical developments owing to their potentiality as viable alternatives to the other expensive noble-metal catalysts such as Au, Ag, Pd, Pt, and also for low cost and high natural abundance of copper. Due to the occurrence of wide range of oxidation states of copper [Cu (0), Cu (I), Cu (II), Cu (III)], copper and copper-oxide nanoparticles exhibit intriguing activity and hence promote several types of reactions including oxidations, reductions, cross coupling, A3 coupling, electrocatalysis and photocatalysis [1]. Besides, high boiling point of copper makes it compatible for high temperature high pressure reactions, gas phase reactions. There are more than a few methods for synthesis of copper and copper oxide nanoparticles such as chemical treatment (micro wave assisted method, ionic liquid assisted method, wet-chemical method, reverse-micelle method) sonochemical methods, electrochemical techniques, photochemical methods, chemical deposition vapour method. However, copper under atmospheric condition prone to oxidize, hence to increase the stability and control growth of copper nanoparticles efforts to develop methods have been explored which includes encapsulation of copper nanoparticles over functionalized support, core-shell Cu nanoparticles or system based on copper oxide nanoparticles which increase the stability of Cu nanoparticles by altering their sensitivity towards water and oxygen [1–3]. In this context, a series of Cu/Cu_2O nanoparticles of size around 5–10 nm have been synthesized on the surface of nitrogen-rich carbon nanospheres (Cu-NCN-1, Cu-NCN-2, and Cu-NCN-3), since carbon nanospheres have gained substantial attention owing to their fine tunable structure, outstanding control over geometry and size of the particle. Beside this, nanospheres provide low viscous properties [4–8]. Such copper nanoparticles engraved carbon nanospheres have been prepared via dual-soft templating method and by altering reducing agent and were proficiently utilized as catalysts in the synthesis of Markovnikov addition product of aromatic terminal alkynes and aniline derivatives. Organo-nitrogen compounds for example enamines, imines, alkylated-amines are widely present in natural products which afford to possess pharmaceutical and biological activities. Besides, they are also present as building blocks in the area of fine chemicals, polymers, agrochemicals, dyes and surfactants [9]. Hence, synthesis of organo-nitrogen compounds developed a considerable interest in pharmaceutical and chemical industries. Such nitrogen-containing compounds can be attained simply by amination of aldehydes or ketones; however, this involves multistep procedures and formation of by-products. An alternative means to achieve such compounds with 100% atom economy is hydroamination, which is direct N—H bond addition across C—C multiple bonds. Though hydroamination is thermodynamically achievable, however, the presence of a considerable kinetic barrier makes the decision for using a catalyst [10]. Over last decade, a numerous catalyst systems in the field of both

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homogeneous and heterogeneous catalysis have been explored [9,11–14]. Although homogeneous systems provide outstanding yields for desired products and TON, however, unlike heterogeneous system it requires tedious methods in the separation of the catalyst, negligible recyclability. Even if, there are limited reports on heterogeneous hydroamination over metal exchanged clay and zeolites however, the TONs were found to be relatively low [15,16]. There are only few reports on heterogeneous hydroamination with AgTPA, Au nanoparticles incorporated MCN with large TON [12,17]. Hence, scheming of a low cost selective heterogeneous catalytic system with large TON appears to be a challenge in amination chemistry. Homogeneous system provide outstanding TON and heterogeneous based catalysts can be reusable. In this situation, designing of controlled nanostructured catalysts appeared as a relevant approach to bridge the gap between homogeneous and heterogeneous catalysis. Functionalized nanoparticles have developed as sustainable alternatives to conventional materials, as robust, high-surface-area heterogeneous catalyst supports, also thereby showing unique activity and high selectivity towards specific reactions. In view of their nano-size, the interaction between the reactants and catalyst rises intensely hence imitating the homogeneous system. Interestingly, it has been found that although Cu (0) is less active for hydroamination, however presence of Cu (I) oxide in the system triggers the reaction with large TON (34×10^5). The nitrogen functionalities present within the carbon nanospheres stabilizes the copper nanoparticles by preventing further oxidation of the Cu (I) oxide nanoparticles and at the same time controls the growth of copper nanoparticles.

2. Experimental section

All solvents and chemicals procured from Sigma-Aldrich Co. and were used without any extra purification. All the reactions were performed under inert atmosphere using Schlenk technique.

2.1. Synthesis of Cu-NCN

Typically, in an aqueous solution of ethanol (ethanol/water ratio = 0.4), 0.125 g of F-127 was added followed by addition of 0.13 g of SDS and 0.25 g cysteine at room temperature under constant stirring. Next, 0.382 mmol of Copper (II) acetate monohydrate was mixed to the solution and after complete dissolution of copper salt 0.25 g 3-aminophenol was added followed by dropwise addition of 0.5 mL 37 wt.% formaldehyde. The mixture was kept under stirring for 24 h and then hydrothermally treated at 100 °C for another 24 h. The obtained Cu nanoparticles encapsulated aminophenol-formaldehyde resin spheres were filtered, washed several times with ethanol, and dried at 100 °C. Finally, Cu nanoparticles encapsulated nitrogen doped carbon nanospheres (Cu-NCN-1) was obtained by carbonizing Cu nanoparticles incorporated resin spheres under flow of nitrogen at 350 °C, kept for 2 h and then dwelling at 700 °C for 4 h, with constant heating rate of 1 °C/min. Cu-NCN-2 and Cu-NCN-3 has been synthesized by similar technique along with addition of hydrazine monohydrate [$Cu/N_2H_4 \cdot H_2O = 1{:}2$ mol ratio] and 0.124 (M) solution of L-Ascorbic acid respectively. For Cu-NCN-3, temperature used for ageing was 80 °C and Copper(II) chloride dihydrate was used as precursor for synthesis of Cu nanoparticles.

2.2. Hydroamination with Cu-NCN

Typically, in a mixture of phenyl acetylene and aniline (1:2 mol ratio), Cu-NCN (3 wt.% w.r.t alkyne, 2.7×10^{-2} mmol of Cu) was added. Subsequently, the mixture was bath-sonicated for 2 mins for effective dispersion of the catalyst and refluxed at 110 °C under inert atmosphere over a period of 24 h. At the end of the reaction, the catalyst was separated and the product was analyzed by Gas Chromatograph (GC, Agilent 7890) connected with an HP5 capillary column (30 m length, 0.28 mmid, 0.5 μm film thickness) and flame ionization detector (FID). Phenylacetylene conversion and selectivity of the product was calculated using calibration curve (obtained by manual injection of authentic standard compounds). The verification of product was performed by injecting authentic standard sample in GC and GC–MS.

2.3. Characterization

SEM images of Cu-NCN were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB6) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analysed by spreading them on carbon tape. TEM images were recorded on a JEM 2100 (JEOL, Japan) microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon formvar coated Ni-grid. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific K-Alpha XPS instrument and binding energies (±0.1 eV) were determined with respect to the C1s peak at 284.5 eV. The porous properties of NCN and Cu nanoparticles incorporated NCN were examined by Nitrogen adsorption–desorption isotherms at 180 °C (Belsorbmax, BEL, Japan) using the BET equation. Pore size distributions were determined using the Barrett–Joyner–Halenda (BJH) cylindrical pore approximation. Percentage of Cu loading in NCN was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using PS 3000 UV (DRE), Leeman Labs Inc. (USA).

3. Results and discussion

3.1. Synthesis and characterization of catalyst

A schematic diagram for synthesis of Cu-NCN has been signified on Fig. 1, where the first step involves the formation of micelles from combination of triblock non-ionic surfactant Pluronic F127 ((EO)106-(PO)70-(EO)106) and an anionic surfactant Sodium dodecyl sulfate, SDS in aqueous-alcoholic solution in presence of acidic amino acid, cysteine. In the next step, Cu ions get adhered over the surface of micelles followed by polymerization of aminophenol and formaldehyde over Cu ions embedded micelles to form micelle-resol complex via sol-gel technique. Thus, Cu ions embedded nano micelles were aggregated by hydrothermal treatment to form corresponding resin spheres. Finally, the Cu nanoparticles embedded nitrogen doped carbon spheres were obtained after carbonizing such Cu embedded resin spheres under nitrogen atmosphere. It has been found that addition of different reducing agent shows effect on the morphology of copper nanoparticles over nitrogen doped carbon nanospheres.

The nitrogen physisorption isotherms of both the Cu-free and Cu-implanted nitrogen-rich carbon nanospheres (Fig. 2) reveals type-IV according to the International Union of Pure and Applied Chemistry (IUPAC), hence indicating the existence of mesopores. The specific surface area, specific pore volume and specific pore diameter have been shown in Table 1, which displays an increase in specific surface area, specific pore diameter and specific pore volume for Cu incorporated nitrogen-rich carbon nanospheres w.r.t nitrogen-rich carbon nanospheres. This occurs due to the implantation of Cu nanoparticles over the surface of nitrogen-rich carbon nanospheres, which enhances the overall specific surface area, pore diameter and pore volume. The specific pore diameter values for both NCN and Cu-NCN being within the range 2.0–50 nm also predict the mesoporous nature of the carbon nanospheres. Cu-NCN-2