



Review

Copper nanoparticles as inexpensive and efficient catalyst: A valuable contribution in organic synthesis



Nisha Kant Ojha^a, Grigory V. Zyryanov^{b,c}, Adinath Majee^d, Valery N. Charushin^{b,c}, Oleg N. Chupakhin^{b,c}, Sougata Santra^{b,*}

^a School of Business Studies, Sharda University, Plot No. 32, 34; Knowledge Park-III, Greater Noida 201306, India

^b Department of Organic & Biomolecular Chemistry, Chemical Engineering Institute, Ural Federal University, 19 Mira Str., 620002 Ekaterinburg, Russian Federation

^c I. Ya. Postovskiy Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, 22 S. Kovalevskoy Str., Yekaterinburg 620219, Russian Federation

^d Department of Chemistry, Visva-Bharati (A Central University), Santiniketan 731235, India

ARTICLE INFO

Article history:

Received 14 June 2017

Accepted 5 October 2017

Available online 13 October 2017

Keywords:

Copper nanoparticles
Organic transformations
Cross-coupling
Heterocycle synthesis
Mechanistic explanation

ABSTRACT

Copper nanoparticles have been explored as a new class of heterogeneous catalyst in various chemical transformations. This review surveys the most useful organic transformations which were carried out in the presence of copper nanoparticles as catalyst. Copper nanoparticle catalyzed reactions are advantageous over the conventional metal catalyzed reactions in terms of low catalyst loading, high atom economy, better yields, inexpensive, shorter reaction times and recyclability of the catalyst. From a mechanistic point of view, it has been shown that most of the transformations proceed *via* the formation of organometallic intermediates [C-Cu-X] during the interactions with copper nanoparticles.

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Abbreviations: AFM, atomic force microscopy; BET, Brunauer–Emmett–Teller; BINAP, (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl); CB, carbon black; CDC, cross-dehydrogenative coupling; CN-DSCS, copper nanoparticle-doped silica cuprous sulfate; CNS, central nervous system; COX-2, cyclo-oxygenase-2; Cu/DH, copper nanoparticles supported on diamond nanoparticles; Cu-AIHT, copper aluminum hydrotalcite; CuFeNPs, CuFe₂O₄ nanoparticles; CuNPs, copper nanoparticles; CuNPs/C, copper nanoparticles on activated carbon; DABCO, 1,4-diazabicyclo[2.2.2]octane; DBN, 1,5-diazabicyclo[4.3.0]non-5-ene; DBSA, dodecylbenzenesulfonic acid; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCC, *N,N'*-dicyclohexylcarbodiimide; DCE, 1,2-dichloroethane; DCM, dichloromethane; DLS, dynamic light scattering; DMAc, dimethylacetamide; DMAD, dimethyl acetylenedicarboxylate; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; DNPs, diamond nanoparticles; DTBB, 4,4'-di-*tert*-butylbiphenyl; EDS, energy dispersive spectroscopy; EDX, energy dispersive X-ray; ee, enantiomeric excess; equiv, equivalent; FEG-SEM, field emission gun scanning electron microscopy; FeNPs, iron nanoparticles; FT-IR, Fourier transforms infrared spectroscopy; h, hour; HAP, hydroxyapatite; HIV, human immunodeficiency virus; HRTEM, high-resolution transmission electron microscopy; HT, hydrotalcite; HWE, Horner–Wadsworth–Emmons; ICP, inductively coupled plasma; ICP-AES, inductively coupled plasma atomic emission spectroscopy; ICP-MS, inductively coupled plasma mass spectrometry; MCM-41, Mobil Composition of Matter No. 41; min, minute; mL, milliliter; mmol, millimole; MT₁, melatonin receptor 1; MWCNT, multi-walled carbon nanotube; NC, nanocatalyst; NMP, *N*-methyl-2-pyrrolidone; NMR, nuclear magnetic resonance; NPs, nanoparticles; P₄VPy, poly(4-vinylpyridine); PAMAM-OH, poly(amidoamine) dendrimer with hydroxyl surface groups; PCC, pyridinium chlorochromate; PEG, polyethylene glycol; PMHS, polymethylhydrosiloxane; PMMA, poly(methyl methacrylate); PPAR, peroxisome proliferator-activated receptor; PVA, poly(vinyl alcohol); PVP, poly(*N*-vinyl-2-pyrrolidone); PVPy, poly(4-vinylpyridine); rpm, rotation per minute; SEM, scanning electron microscopy; TBAB, tetra-*n*-butylammonium bromide; TBAF, tetra-*n*-butylammonium fluoride; TBHP, *tert*-butyl hydroperoxide; TEA, triethylamine; TEM, transmission electron microscopy; TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl; TGA, Thermal Gravimetric Analysis; THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine; TNF- α , Tumor Necrosis Factor- α ; TPR, temperature programmed reduction; TS, transition state; UV-DRS, ultraviolet diffuse reflectance spectroscopy; XAFS, X-ray absorption fine-structure spectrum (XAFS); XPS, X-ray photoelectron spectroscopy (XPS); XRD, X-ray diffraction; ZY, zeolite Y.

* Corresponding author.

E-mail addresses: sougatasantra85@gmail.com, ssantra@urfu.ru (S. Santra).

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1. Introduction

The development of more direct catalytic approaches toward the synthesis of chemical products represents one of the key efforts to achieve chemical sustainability [1]. On the other hand, the use of more environmentally-benign catalysts, their recycling, or the simple separation of catalysts from reaction mixtures provide both economic and ecological benefits [2]. Recently metallic nanoparticles have been used comprehensively as alternative catalysts in the organic synthesis due to their high reactivity, sustainability, easy recovery and often the recyclability of the catalyst. Metal nanopar-

ticle catalyzed reactions are advantageous over conventional metal catalyzed reactions in terms of low catalyst loading, inexpensive, high atom economy, better yields, shorter reaction times and recyclability of the catalysts. The high reactivity of nanoparticles is the result of their large surface area (which most certainly affects the reaction rate) and they often exhibit different reactivities from those of the bulk when dispersed down to a nanometer scale [3]. In addition, high dispersivity and high stability during catalytic reactions in most chemical environments make nanoparticles a renowned catalytic system. Due to these features metal nanoparticles, especially copper salts, have been used successfully for C–C,

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