Copper Ferrite (CuFe$_2$O$_4$) Nanoparticles

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Introduction

Ferrite (Fe$_3$O$_4$) nanoparticles (NPs) have been used as a catalyst for many organic transformations because their nano-scale size equates to a large surface area to volume ratio (meaning many accessible active sites). Moreover, iron-based magnetic properties enable easy catalyst recovery by the application of an external magnet. The catalytic scope of iron, however, pales in comparison with copper. Therefore, by substituting copper within the crystal lattice, the catalytic scope is greatly expanded, while the means of easy magnetic recovery are retained. The resulting copper ferrite nanoparticles (CuFe$_2$O$_4$ NPs) contain copper(II) and iron(III) species. Such nanoparticles can be obtained by co-precipitation of copper(II) and iron(III) salts (Scheme 1). They are also commercially available. Herein, the catalytic scope of CuFe$_2$O$_4$ NPs is highlighted and reviewed.

Abstracts

(A) Azide–Alkyne ‘Click’ Reaction
Under homogeneous copper(I) conditions, this reaction can occur at room temperature in water. Under heterogeneous conditions, the reaction requires either 70 °C temperature or the addition of a ligand such as 2,2-bipyridine.

(B) C–C Cross-Coupling
Panda and co-workers demonstrated a synergistic effect between copper and iron within the CuFe$_2$O$_4$ lattice to catalyze the coupling of terminal alkynes with aryl halides. Neither CuO NPs, nor Fe$_3$O$_4$ NPs alone, could catalyze the transformation as effectively.

(C) C–N Cross-Coupling
Panda and co-workers again demonstrated a synergistic effect between copper and iron, this time in the CuFe$_2$O$_4$ NP-catalyzed coupling of N-heterocycles with aryl halides.

(D) C–O Cross-Coupling
The Sun group effectively coupled aryl halides with phenols to generate the corresponding biaryl ethers by catalysis with CuFe$_2$O$_4$ nanoparticles.
(E) C–S Cross-Coupling
The coupling under basic conditions and elevated temperatures of aryl halides with either aromatic thiols or diaryl sulfides afforded the corresponding diaryl sulphide in excellent yields. The catalytic efficiency of various [M]Fe$_2$O$_4$ nanoparticles were compared and M = copper was found to be the most reactive for this transformation.\(^\text{10}\)

(F) C–Se Cross-Coupling
Various diaryl selenides were synthesized by the coupling of aryl halides with diaryl diselenides. The reaction required the use of a base and temperatures of 120°C.\(^\text{11}\)

(G) Sugar Decacylation
Various protected sugars were deacylated with copper ferrite nanoparticles under mild conditions. By altering the solvent and reducing the reaction time, selective deacylation at the anomeric position could be achieved.\(^\text{12}\)

(H) A$^3$ Coupling
The three-component, one-pot coupling of aldehyde, alkyne, and amine was reported. Although A$^3$ coupling has already been achieved for Fe$_3$O$_4$ nanoparticles, substituting copper within the lattice enabled the use of milder conditions.\(^\text{13}\)

(I) Biginelli Condensation
In another demonstration of a three-component one-pot reaction, the Biginelli condensation between an aldehyde, urea or thiourea, and ketones was achieved with CuFe$_2$O$_4$ NPs to afford the corresponding dihydropyrimidinones or dihydropyrimidinethiones.\(^\text{14}\)

(J) Asymmetric Hydrosilylation
With the aid of a chiral BINAP ligand, CuFe$_2$O$_4$ NPs have catalyzed the asymmetric hydrosilylation of prochiral ketones, which afforded the corresponding alcohols upon TBAF workup.\(^\text{15}\)

References
(3) Mahmoodi, N. M. Desalination 2011, 279, 332.