

SYNLETT Spotlight 436

Copper Ferrite (CuFe_2O_4) Nanoparticles

Compiled by Reuben Hudson



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

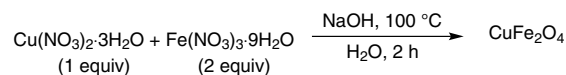
Reuben Hudson was born on the coast of Maine, USA, in 1986. He received his B.A. in chemistry under the advisement of Professor Chris Smart at Vassar College, in Poughkeepsie, NY. Currently, he is working toward his Ph.D. at McGill University, Montreal, Canada, with the groups of Professors Chao-Jun Li and Audrey Moores. His work focuses on the use of easily recoverable heterogeneous catalysts for various organic transformations.

McGill University, Department of Chemistry, 801 Sherbrooke Street West, Montreal, QC, H3A 0B8, Canada
E-mail: reuben.hudson@mail.mcgill.ca

Introduction

Ferrite (Fe_3O_4) nanoparticles (NPs) have been used as a catalyst for many organic transformations¹ because their nano-scale size equates to a large surface area to volume ratio (meaning many accessible active sites).² 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 that of 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_2O_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).³ They are also commercially available. Herein, the catalytic scope of CuFe_2O_4 NPs is highlighted and reviewed.

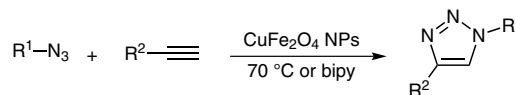


Scheme 1 Synthesis of CuFe_2O_4 NPs by co-precipitation³

Abstracts

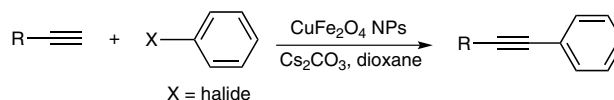
(A) Azide-Alkyne 'Click' Reaction

Under homogeneous copper(I) conditions, this reaction can occur at room temperature in water.⁴ Under heterogeneous conditions, the reaction requires either 70 °C temperature⁵ or the addition of a ligand such as 2,2-bipyridine.⁶



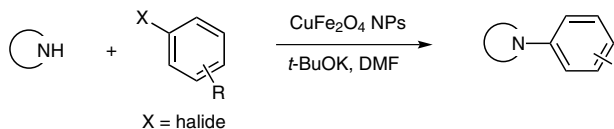
(B) C-C Cross-Coupling

Panda and co-workers⁷ demonstrated a synergistic effect between copper and iron within the CuFe_2O_4 lattice to catalyze the coupling of terminal alkynes with aryl halides. Neither CuO NPs, nor Fe_3O_4 NPs alone, could catalyze the transformation as effectively.



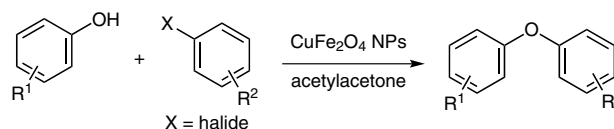
(C) C-N Cross-Coupling

Panda and co-workers⁸ again demonstrated a synergistic effect between copper and iron, this time in the CuFe_2O_4 NP-catalyzed coupling of N-heterocycles with aryl halides.



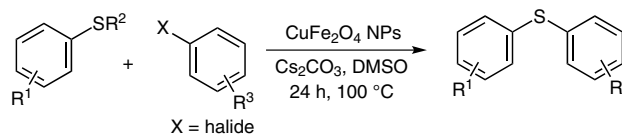
(D) C-O Cross-Coupling

The Sun group⁹ effectively coupled aryl halides with phenols to generate the corresponding biaryl ethers by catalysis with CuFe_2O_4 nanoparticles.



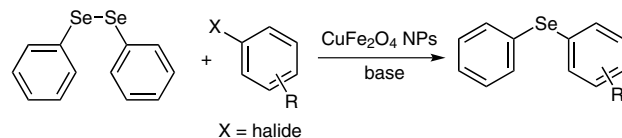
(E) C–S Cross-Coupling

The coupling under basic conditions and elevated temperatures of aryl halides with either aromatic thiols or diaryl sulphides afforded the corresponding diaryl sulphide in excellent yields. The catalytic efficiency of various [M]Fe₂O₄ nanoparticles were compared and M = copper was found to be the most reactive for this transformation.¹⁰



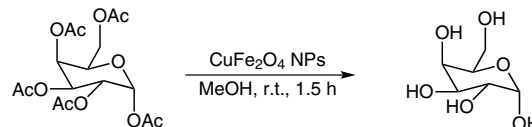
(F) C–Se Cross-Coupling

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.¹¹

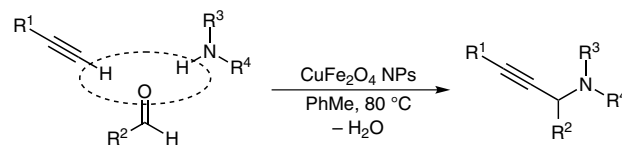


(G) Sugar Deacylation

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.¹²

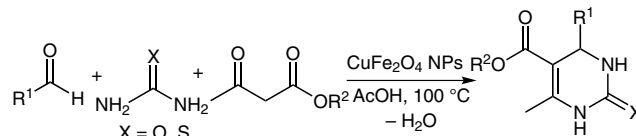
(H) A³ Coupling

The three-component, one-pot coupling of aldehyde, alkyne, and amine was reported. Although A³ coupling has already been achieved for Fe₃O₄ nanoparticles, substituting copper within the lattice enabled the use of milder conditions.¹³



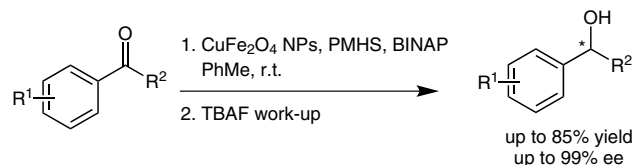
(I) Biginelli Condensation

In another demonstration of a three-component one-pot reaction, the Biginelli condensation between an aldehyde, urea or thiourea, and β-ketoesters was achieved with CuFe₂O₄ NPs to afford the corresponding dihydropyrimidinones or dihydropyrimidinethiones.¹⁴



(J) Asymmetric Hydrosilylation

With the aid of a chiral BINAP ligand, CuFe₂O₄ NPs have catalyzed the asymmetric hydrosilylation of prochiral ketones, which afforded the corresponding alcohols upon TBAF workup.¹⁵



References

- (1) (a) Shi, F.; Tse, M. K.; Pohl, M.-M.; Brückner, A.; Zhang, S.; Beller, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 8866. (b) Rajabi, F.; Karimi, N.; Saidi, M. R.; Primo, A.; Varma, R. S.; Luque, R. *Adv. Synth. Catal.* **2012**, *354*, 1707.
- (2) Zeng, T.; Song, G.; Moores, A.; Li, C. J. *Synlett* **2010**, 2002. (d) Zeng, T. Q.; Chen, W.-W.; Cirtiu, C. M.; Moores, A.; Song, G. H.; Li, C. J. *Green Chem.* **2010**, *12*, 570.
- (3) Sreedhar, B.; Kumar, A. S.; Reddy, P. S. *Tetrahedron Lett.* **2010**, *51*, 1891. (f) Reddy, B. V. S.; Krishna, A. S.; Ganesh, A. V.; Kumar, A. S. *Tetrahedron Lett.* **2011**, *52*, 1359. (g) Firouzabadi, H.; Iranpoor, N.; Gholinejad, M.; Hoseini, J. *Adv. Synth. Catal.* **2011**, *353*, 125.
- (4) Yan, N.; Xiao, C.; Kou, Y. *Coord. Chem. Rev.* **2010**, *254*, 1179.
- (5) Mahmoodi, N. M. *Desalination* **2011**, *279*, 332.
- (6) (a) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057. (b) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596.
- (7) Kumar, B. S. P. A.; Reddy, K. H. V.; Madhav, B.; Ramesh, K.; Nageswar, Y. V. D. *Tetrahedron Lett.* **2012**, *53*, 4595.
- (8) Ishikawa, S.; Hudson, R.; Moores, A.; Li, C.-J. *Heterocycles* **2012**, *86*, 1023.
- (9) Panda, N.; Jena, A. K.; Mohapatra, S. *Chem. Lett.* **2011**, *40*, 956.
- (10) Panda, N.; Jena, A. K.; Mohapatra, S.; Rout, S. R. *Tetrahedron Lett.* **2011**, *51*, 1924.
- (11) Zhang, R.; Liu, J.; Wang, S.; Niu, J.; Xia, C.; Sun, W. *ChemCatChem* **2011**, *3*, 146.
- (12) Swapna, K.; Murthy, S. N.; Jyothi, M. T.; Nageswar, Y. V. D. *Org. Biomol. Chem.* **2011**, *9*, 5989.
- (13) Swapna, K.; Murthy, S. N.; Nageswar, Y. V. D. *Eur. J. Org. Chem.* **2011**, 1940.
- (14) Tasca, J. E.; Ponzinibbio, A.; Diaz, G.; Bravo, R. D.; Lavat, A.; González, M. G. *Top. Catal.* **2010**, 1087.
- (15) Kantam, M. L.; Yadav, J.; Laha, S.; Jha, S. *Synlett* **2009**, 1791.
- (16) Hudson, R.; Silverman, J.; Li, C.-J.; Moores, A. *Proceedings of the 3rd International Conference on Nanotechnology*; Montreal, QC, Canada, **2012**; Paper No. 318.
- (17) Kantam, M. L.; Yadav, Y.; Laha, S.; Srinivas, P.; Sreedhar, B.; Figueras, F. *J. Org. Chem.* **2009**, *74*, 4608.