

SYNLETT Spotlight 358

Copper Oxide Nanoparticles

Compiled by Atefeh Shamsian



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

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Introduction

Generally, nanoscale heterogeneous catalysts offer higher surface area and low-coordinated sites, which are responsible for the higher catalytic activity.¹ Particularly, in recent years the application of copper oxide nanoparticles for organic reactions has attracted immense attention.

Indeed, the copper nanoparticle catalyzed reactions provide the advantages of high atom efficiency, simplified isolation of product, and easy recovery and recyclability of the catalyst.²⁻⁴ This catalyst appears as one of the most promising solutions toward efficient reactions under mild and environmentally benign conditions in the context of green chemistry.

Preparation

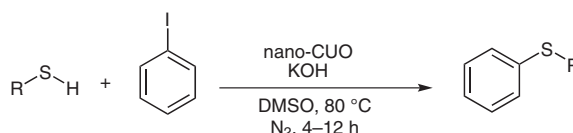
Copper acetate and acetic acid were dissolved in distilled water and the solution was heated to 100 °C before NaOH was added rapidly. After being cooled to room temperature, black powder precipitates were separated by centrifugation, then washed several times with distilled water and ethanol and dried.^{5,6}

The synthesized nanoparticles were characterized by XRD, SEM, TEM, and PL spectrometry.

Abstracts

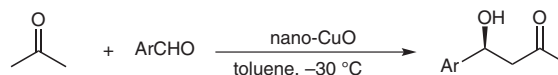
(A) Cross-Coupling of Thiols:

This reaction is the first example of the use of CuO nanoparticles for the catalysis of C–S cross-coupling. The reactions of aryl and alkyl thiols with iodobenzene are effective in the presence of KOH under nitrogen atmosphere.⁷



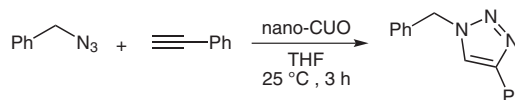
(B) Asymmetric Aldol Reactions:

Kantam and co-workers have reported a new efficient method for the direct asymmetric aldol reactions of aromatic and heteroaromatic aldehydes with acetone to afford chiral β -hydroxy carbonyl compounds in good yields and excellent to moderate enantioselectivities using nanocrystalline copper(II) oxide in the presence of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine.⁸



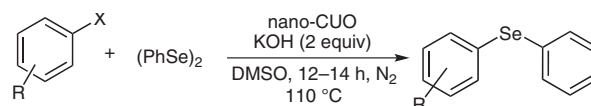
(C) Alkyne–Azide Cycloaddition:

CuO nanoparticles catalyzed the reaction of azide and alkynes as a representative example of click chemistry. In the absence of reductants they show good catalytic activity to form 1,4-disubstituted 1,2,3-triazols even in THF as well as in water.^{9,10}

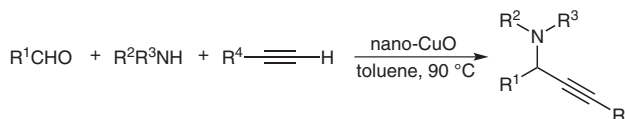


(D) Synthesis of Aryl Selenides:

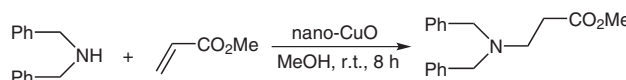
A new, efficient, and ligand-free cross-coupling of aryl halides and diaryl diselenides using a catalytic amount of nanocrystalline CuO as a recyclable catalyst with KOH as base is reported.²

**(E) Synthesis of Propargylamines:**

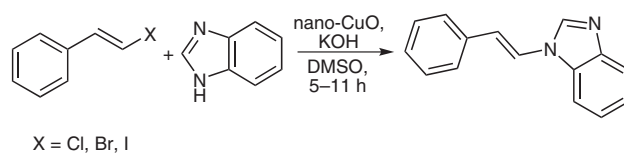
Kantam and co-workers reported an efficient three-component coupling of aldehydes, amines, and alkynes to prepare propargylamines in nearly quantitative yields using nano-crystalline CuO. The reaction does not require any co-catalyst.¹¹

**(F) Aza-Michael Reaction:**

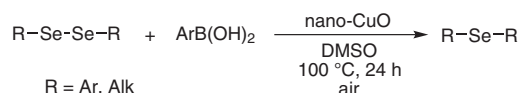
Nanocrystalline copper(II) oxide efficiently catalyzed the conjugate addition of aliphatic amines to α,β -unsaturated compounds to produce β -amino compounds with excellent yields under mild reaction conditions. Similarly, glycine esters are obtained in good yields by insertion of α -diazoacetate into N-H bonds of amines. The catalyst is used in three cycles with minimal loss of activity.¹²

**(G) Vinylation of Imidazoles:**

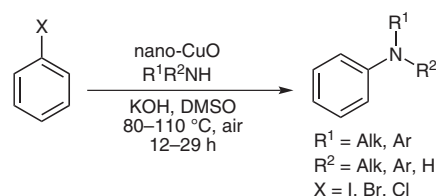
Rama Rao and co-workers reported that recyclable copper oxide nanoparticles catalyzed most efficiently and straightforward the vinylation of imidazoles with vinyl halides under ligand-free conditions. Utilizing this protocol, various imidazoles were cross-coupled with different substituted vinyl halides to obtain the corresponding products in excellent yields while retaining the configuration.¹³

**(H) Cross-Coupling of Diselenides with Aryl Boronic Acids:**

This general cross-coupling was performed with organic diselenides and aryl boronic acids bearing electron-withdrawing and -donating groups affording the corresponding selenides in good to excellent yields. The CuO nanoparticles can be easily recovered and utilized for further catalytic reactions.¹⁴

**(I) C-N Cross Coupling of Amines:**

CuO nanoparticles catalyze the C-N cross-coupling of amines with iodobenzene in excellent yields. The reaction is simple and efficient and operates under air with ligand-free conditions. The catalyst is recyclable without loss of activity.⁴

**References**

- (1) Pacchioni, G. *Surf. Rev. Lett.* **2000**, *7*, 277.
- (2) Reddy, V.; Kumar, A.; Swapna, K.; Rao, K. *Org. Lett.* **2009**, *11*, 951.
- (3) Saha, A.; Saha, D.; Ranu, B. *Org. Biomol. Chem.* **2009**, *7*, 1652.
- (4) Rout, L.; Jammi, S.; Punniyamurthy, T. *Org. Lett.* **2007**, *9*, 3397.
- (5) Zhou, K.; Wang, R.; Xu, B.; Li, Y. *Nanotechnol* **2006**, *17*, 3939.
- (6) Zhu, J.; Li, D.; Chen, H.; Yang, X.; Lu, L.; Wang, X. *Mater. Lett.* **2004**, *58*, 3324.
- (7) Rout, L.; Sen, T.; Punniyamurthy, T. *Angew. Chem. Int. Ed.* **2007**, *46*, 5583.
- (8) Kantam, M.; Ramani, T.; Chakrapani, L.; Kumar, K. *Tetrahedron Lett.* **2008**, *49*, 1498.
- (9) Kim, J.; Park, J.; Kang, H.; Song, H.; Park, K. *Chem. Commun.* **2010**, *46*, 439.
- (10) Song, Y.; Yoo, C.; Hong, J.; Kim, S.; Son, S.; Jang, H. *Bull. Korean Chem. Soc.* **2008**, *29*, 1561.
- (11) Kantam, M.; Laha, S.; Yadav, J.; Bhargava, S. *Tetrahedron Lett.* **2008**, *49*, 3083.
- (12) Kantam, M.; Laha, S.; Yadav, J.; Jha, S. *Tetrahedron Lett.* **2009**, *50*, 4467.
- (13) Reddy, V.; Kumar, A.; Rao, K. *Tetrahedron Lett.* **2010**, *51*, 3181.
- (14) Alves, D.; Santos, C.; Paixão, M.; Soares, L.; Souza, D.; Rodrigues, O.; Braga, A. *Tetrahedron Lett.* **2009**, *50*, 6635.