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Short communication

Cu_2O/nano-$CuFe_2O_4$: A novel and recyclable magnetic catalyst for three-component coupling of carbonyl compounds–alkynes–amines under solvent-free condition

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ABSTRACT

Cu_2O/nano-$CuFe_2O_4$ magnetic composite with different loadings of Cu_2O has been synthesized by feasible and low-cost method. The as-prepared composite was fully characterized by FT-IR, XRD, FEG-SEM, EDS and VSM analyzer. The catalytic activity of magnetic composite for synthesis of propargylamines was evaluated. The catalyst has many obvious advantages and easily separated via an external magnet. It can be reused for five successive runs.

1. Introduction

The catalysts with magnetic nanoparticle-based materials have attracted significant attention in organic transformations, because they posses specific futures including reduce temperature, increase reaction yield, great selectivity, high stability, efficient recovery and good reusability [1]. Among them, the iron oxides are usually applied as simplest magnetically recoverable catalysts, as they are nontoxic, cheap in preparation, amenable to functionalization and easy to handle [2]. They have been extensively used in some organic reactions such as, C–C and C–X couplings [3,4], reduction [5], oxidation [6] and multi-component reactions [7]. While iron oxide NPs could catalyze several reactions, the catalytic scope of magnetic NPs could be expanded by incorporation of a second metal (for example Cu) in the spinal structure of Fe_3O_4. The second metal opens up new catalytic avenues, while the residual iron component continues to provide an effective way in order to do magnetic recovery [8].

Multi-component coupling reactions (MCRs) are a very powerful tool to synthesize various organic compounds from simple starting material via a one-pot methodology. An attractive example of such a process that has been widely studied in recent years is (A^3-coupling) via C–H activation of terminal alkynes [9,10]. The propargylamines that result from A^3 coupling reactions are high valuable building blocks in organic synthesis. They are considered as an important synthetic intermediates for the preparation of various nitrogen-containing biologically active compounds and pharmaceutical important compounds [11,12].

The most conventional methods for the synthesis of propargylamines involve three-component coupling of aldehydes, amines and terminal alkynes in the presence of appropriate catalyst. In recent years, some heterogeneous catalysts are developed for A^3-coupling reactions [13–16]. Although all these methods are effective, these have some drawbacks such as, use of expensive or toxic solvents, tedious work-up procedures, low yields, long reaction times and complex catalyst preparation process. Hence, development of a facile, environmentally friendly and low cost protocol for one-pot synthesis of propargylamine derivatives is an attractive goal for researchers.

We reported herein, synthesis of inexpensive, reusable and magnetically separable Cu_2O/nano-$CuFe_2O_4$ magnetic composite and application of it in synthesis of various propargylamine derivatives under solvent-free reaction conditions (Scheme 1).

2. Experimental

2.1. Preparation of composite

2.1.1. Preparation of nano-$CuFe_2O_4$

The $CuFe_2O_4$ nano-particles were prepared according to literature report [17].

2.1.2. Preparation of $CuFe_2O_4$/Cu_2O composite

Four types of composite with different molar ratios of $CuFe_2O_4$:Cu_2O were synthesized. Nano-$CuFe_2O_4$ (0.036–0.324 g) was dispersed in

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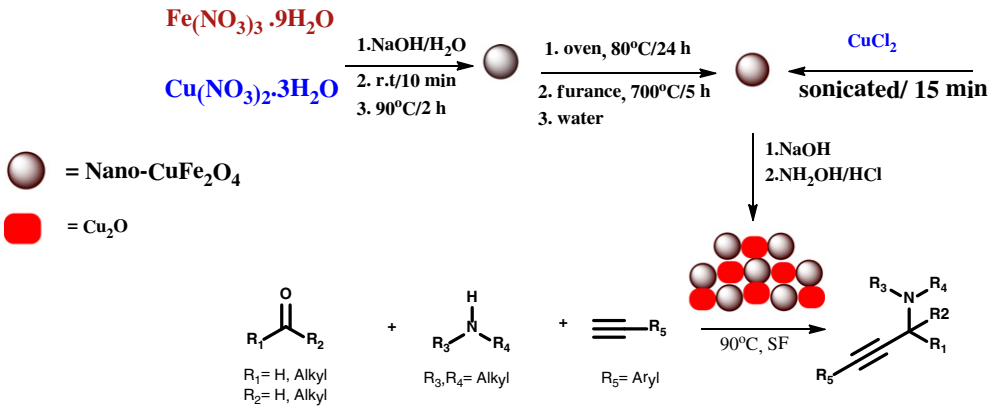

Scheme 1. Synthesis of propargylamines using Cu_2O/nano-$CuFe_2O_4$ magnetic composite.

80 mL of deionized water. 5 mL of (0.1 mol/L) $CuCl_2$ solution was added into the aqueous $CuFe_2O_4$ and sonicated for 15 min. Then, 1.8 mL of (1.0 mol/L) NaOH solution was added drop-by-drop under sonication. The resulting solution turned light blue immediately, indicating the formation of $Cu(OH)_2$ precipitate. Eventually, 12 mL of (0.1 mol/L) $NH_2OH{\cdot}HCl$ was rapidly injected over 5 s into the solution. The solutions were kept in the water bath for 1 h and centrifuged for 3 min. After the top solution was decanted, the precipitate was washed with 6 mL of a 1:1 volume ratio of water and ethanol three times. The Cu_2O/nano-$CuFe_2O_4$ was collected as a brown solid and can be stored in a tight vessel for several months without any change in color or reactivity.

*2.2. General procedure for synthesis of 1-(1,3-diphenylprop-2-ynyl) piperidine (**4a**)*

A mixture of benzaldehyde (0.106 g, 1.0 mmol), piperidine (0.102 g, 1.2 mmol), phenylacetylene (0.153, 1.5 mmol) and Cu_2O/nano-$CuFe_2O_4$ magnetic composite (0.010 g) (the Cu_2O content in the catalyst was 0.002 g or 0.015 mmol, so for 1 mmol of reactant, 0.015 mmol of Cu_2O is needed, which is equal to 0.01 g magnetic composite) were mixed and heated at 90 °C for 1 h under solvent free condition. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with hot ethanol (10 mL). Then, the catalyst was separated by an external magnet from the cooled mixture, washed with acetone, dried in oven and re-used for a consecutive run under the same reaction conditions. The filtrate was concentrated and the resulting residue was purified by short column chromatography on silica gel to afford the desired product in excellent yield (96%).

3. Results and discussion

3.1. Characterization of Cu_2O/nano-$CuFe_2O_4$ composite

The FT-IR spectra of the $CuFe_2O_4$ in the region of 400–4000 cm^{-1} clearly indicated the bands centered at 3400 and 563 cm^{-1}, which justify the OH and metal-O stretching mode, respectively. Compared to $CuFe_2O_4$, the composite had same absorption peaks, with more intensity at metal-O region (see ESI).

The morphology, chemical purity and their stoichiometry of $CuFe_2O_4$ and Cu_2O/nano-$CuFe_2O_4$ composite (optimized amount) were visualized by SEM and EDX analyses (Figs. 1 and 2). It can be observed that the as-prepared nano-$CuFe_2O_4$ particles are uniform and nearly spherical in shape and possess a smooth and clean surface. Fig. 1B shows the SEM image of Cu_2O/nano-$CuFe_2O_4$ composite. Numerous Cu_2O particles can be clearly seen in composite. Compared to the $CuFe_2O_4$, the composite

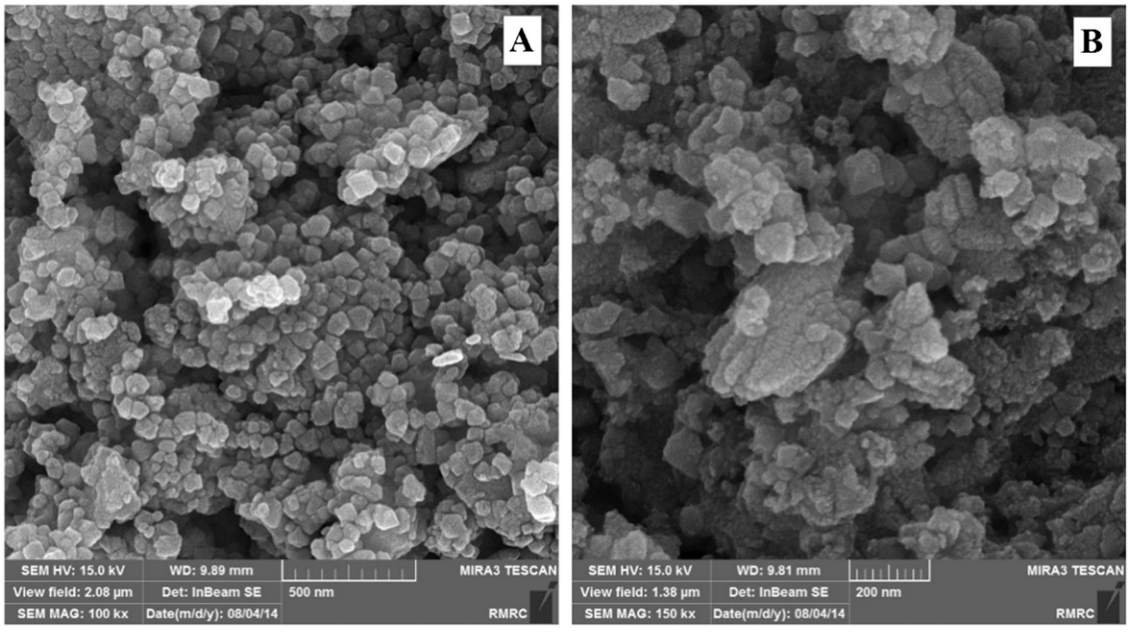

Fig. 1. The SEM image of the (A) nano-$CuFe_2O_4$, (B) Cu_2O/nano-$CuFe_2O_4$ (2:8 mol ratio) magnetic composite.