



# Copper-based magnetic catalysts for alkyne oxidative homocoupling reactions



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## ABSTRACT

We successfully prepared copper-based magnetic catalysts combining copper oxide and magnetite nanoparticles. These systems are active and selective in the oxidative homocoupling reaction of phenylacetylene in the absence of an external base. These systems are particularly interesting since the addition of an external base induces copper leaching by production of soluble molecular copper-base complexes. Some of these systems were also supported on oxidized few layer graphene to investigate a potential role of this support. We discover that this supported system is three times more active than the other ones. We propose that the role of graphene support is to improve catalyst dispersion, but also to provide a favorable micro-environment around the active phase via a pre-adsorption of the substrate on the support, which affords a substrate rich micro-environment around the active particles. Recycling experiments show that the graphene-supported systems cannot be recycled, while the other ones can. This result could be explained by a competitive pre-adsorption between the substrate and the product of the reaction on the surface of the support.

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## 1. Introduction

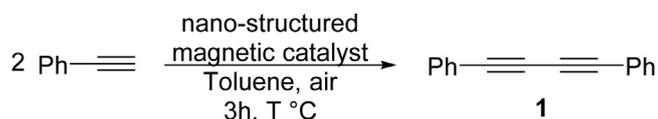
1,3-Diynes derivatives constitute an important class of compounds present in natural products [1], molecular complexes [2] and polymers [3]. In addition, they are utilized as starting materials in the synthesis of substituted heterocyclic compounds [4–7]. A practical approach to the synthesis 1,3-diynes is thus desirable, and transition metal catalyzed oxidative cross-coupling of alkynes has emerged as a potential candidate [8]. More particularly, symmetrical 1,3-diynes are generally synthesized via oxidative homocoupling reactions with copper salts. Originally developed with stoichiometric amounts of copper(II) [9], these reactions were rendered catalytic by the addition of a base and dioxygen [10–12]. Milder reaction conditions in air have also been disclosed with palladium(II) and copper(I) salts as a co-catalysts [13–15]. However, recent efforts to develop efficient processes more respectful of the environment have led to the study of base-free copper catalytic systems [16,17], as well as solvent-free systems [18,19]. Nonetheless, these catalytic systems still suffer from usual shortcomings of homogeneous catalysis, such as catalyst/products

separations and recyclability of the catalyst. Even though numerous catalysts for alkyne homocoupling reaction have been reported, heterogeneous processes remain under-developed. Few heterogeneous oxidative homocoupling of alkynes have been reported [20] and most require the use of an external base [20–23], the combination of an external base and dioxygen [24], or catalytic amount of base and air [25]. More recently, efficient base free catalytic systems have been disclosed, still requiring however a dioxygen atmosphere [26–28]. These systems are particularly interesting since the addition of an external base induces copper leaching by production of soluble molecular copper-base complexes, which have been reported to be the active catalytic species [29]. Such catalytic systems can be further improved by seeking even simpler systems, which do not necessitate any additives and use air as an oxidant. Only two recent reports describe the utilization of a copper-based heterogeneous catalyst (Cu-TiO<sub>2</sub> [30], and Cu/MnO<sub>x</sub> [31]) for the oxidative homocoupling reaction of alkynes without any additives.

As no oxidative homocoupling of terminal alkynes proceeds with only bulk copper oxide such as CuO, Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> [26], we envisioned utilizing a nano-structured catalytic system [32,33]. To address the sustainability and the cost of the entire catalytic processes, we chose to take advantage of magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) as an interesting alternative to solve the recovery and recycling issues deriving from the small size of these nanocatalysts [34,35]. Herein we report the synthesis of magnetic Cu-based

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**Scheme 1.** Oxidative homocoupling of phenylacetylene with nano-structured magnetic catalysts.

nanoparticles and their utilization in the oxidative homocoupling reaction of phenylacetylene (Scheme 1).

## 2. Experimental section

Commercially available compounds were purchased and used without further purification unless otherwise stated. The suppliers of the chemicals are listed in Table S1. NMR experiments were carried out with a Bruker Advance 300 MHz spectrometer, using deuterated chloroform as solvent. Compound **1** was synthesized according to the reported procedure [36], and fully characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy and GC–MS.

### 2.1. Catalyst characterization

Morphology and structure investigations were performed by TEM on a JEM 1011 microscope with an accelerating voltage of 100 kV. The particles size distributions were obtained from measurements of at least 250 particles. The BET surface area were determined by nitrogen adsorption, using a single point Thermo-Quest Surface Area Analyzer Qsurf S1. XPS measurements were performed on a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al K $\alpha$  source (1486 eV 9 run at 14 kV and 15 mA). The samples were analyzed as powders mounted on a double-sided adhesive tape. FT-IR spectra were recorded with an IR Perkin Elmer Spectrum One Spectrophotometer, using an Attenuated Total Reflectance (ATR). Micro Raman spectroscopy was performed on a Raman Invia Renishaw spectrometer equipped with CCD detector and Leica microscopy using a  $\times 50$  objective lens. The X-Ray-diffraction (XRD) patterns were obtained with a Thermo ARL X'TRA powder diffractometer, operating in the Bragg-Brentano geometry and equipped with a Cu-anode X-Ray source (K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ), using a Peltier Si(Li) cooled solid state detector. TGA analysis were performed with a SETARAM 92-16.18 Thermobalance from room temperature to 1000 °C with a rate of 10 °C/min. The analyses were carried out in air. Magnetic measurements were carried out with a Quantum Design MPMS 5XL SQUID, which uses Superconducting Quantum Interference Device (SQUID) Magnetometer to monitor changes in magnetic flux. Data can be collected between H=0 to  $\pm 50$  kOe and T= 1.7 K to 400 K. The analyses were conducted at room temperature. The metal content was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a Spectro-Genesis instrument.

### 2.2. Material synthesis

The microwave synthesis were performed with a CEM Discover S-class system. The instrument consists of a single mode cavity with continuous power generation and control of power supply. It is capable of supplying power in 1 W increments from 0 to 300 W. The system is equipped with a vertically focused IR temperature sensor.

#### 2.2.1. Fe<sub>3</sub>O<sub>4</sub>

In a typical experiment the desired amount of Fe(OAc)<sub>2</sub> (1 g, 5.8 mmol) was dissolved in deaerated EtOH 96 wt% (44 mL). The solution was then thermally treated at 120 °C for 15 min at 250 W by

mono-mode microwave (80 mL vessel). The product was then magnetically recovered using a neodymium magnet and washed three times with EtOH 96 wt% (total volume of 210 mL). The solid phase was recovered using a neodymium magnet, dried under vacuum for 10 h and stored under inert atmosphere.

#### 2.2.2. CuO<sub>x</sub>[ac]/Fe<sub>3</sub>O<sub>4</sub>

In a typical experiment, the desired amount of Fe(OAc)<sub>2</sub> (1 g, 5.8 mmol) and Cu(OAc)<sub>2</sub> (63 mg, 0.35 mmol) were dissolved in deaerated EtOH 96 wt% (44 mL). This solution was thermally treated at 120 °C for 15 min at 250 W by mono-mode microwave (80 mL glass vessel). The product was then filtered and washed three times with EtOH 96 wt% (total volume of 210 mL). The solid phase was magnetically recovered using a neodymium magnet, dried under vacuum for 10 h and stored under inert atmosphere.

#### 2.2.3. CuO<sub>x</sub>[ca]/Fe<sub>3</sub>O<sub>4</sub>

In a typical experiment, the desired amount of Fe(OAc)<sub>2</sub> (1 g, 5.8 mmol) and Cu<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>·2NHET<sub>2</sub> (130 mg, 0.2 mmol) were dissolved in deaerated EtOH 96 wt% (44 mL). This solution was thermally treated at 120 °C for 15 min at 250 W by mono-mode microwave (80 mL glass vessel). The product was then filtered and washed three times with EtOH 96 wt% (overall amount 210 mL). The solid phase was magnetically recovered using a neodymium magnet, dried under vacuum for 10 h and stored under inert atmosphere.

#### 2.2.4. CuO<sub>x</sub>[ca]@Fe<sub>3</sub>O<sub>4</sub>

In a typical experiment, the desired amount of Fe(OAc)<sub>2</sub> (1 g, 5.8 mmol) was dissolved in deaerated EtOH 96 wt% (44 mL). This solution was thermally treated at 120 °C for 15 min at 250 W by mono-mode microwave (80 mL glass vessel). Cu<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>·2NHET<sub>2</sub> (130 mg, 0.2 mmol) was then added to this dispersion and treated again by microwave with the same reaction parameters. The product was then filtered and washed three times with EtOH 96 wt% (total volume of 210 mL). The solid phase was recovered using a neodymium magnet, dried under vacuum for 10 h and stored under inert atmosphere.

#### 2.2.5. Few layer graphene oxidation

Few layer graphene (8 g) was purified by suspending it in concentrated HCl (150 mL) and stirring at room temperature for 10 h. The suspension was filtered and the solid was washed with distilled water (9  $\times$  40 mL) until a neutral supernatant was obtained. The solid was then dried in an oven at 105 °C for 40 h. The graphene functionalization was achieved by suspending the purified graphene in concentrated HNO<sub>3</sub> (150 mL) and heated to reflux at 140 °C for 3 h. The suspension was then cooled and filtered. The solid was washed with distilled water (9  $\times$  40 mL) until a neutral supernatant was obtained. Lastly, it was dried in oven at 105 °C for 60 h.

#### 2.2.6. CuO<sub>x</sub>[ca]/G

Oxidized graphene (G) (1 g) and Cu<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>·2NHET<sub>2</sub> (370 mg, 0.5 mmol) were dissolved in deaerated isopropanol (44 mL) and sonicated for 2 min. This dispersion was then thermally treated at 180 °C for 12 min at 250 W by a mono-mode microwave (80 mL glass vessel). The product was then filtered, washed four times with isopropanol (total volume of 280 mL). Every time, the particles were recovered by centrifugation (3000 rpm for 5 min). Lastly, the particles were dried under vacuum for 10 h and stored under inert atmosphere.

#### 2.2.7. Fe<sub>3</sub>O<sub>4</sub>/G

Oxidized graphene (1 g) and Fe(OAc)<sub>2</sub> (700 mg, 4 mmol) were suspended in deaerated isopropanol (44 mL) and sonicated for

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