



# A recyclable/reusable hydrotalcite supported copper nano catalyst for 1,4-disubstituted-1,2,3-triazole synthesis via click chemistry approach

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## ARTICLE INFO

### Article history:

Received 1 November 2017

Revised 14 December 2017

Accepted 15 December 2017

Available online 16 December 2017

### Keywords:

Click chemistry

Cycloaddition

Hydrotalcite

Nano particles

Triazole

## ABSTRACT

Using hydrotalcite as solid support, copper nano particles were synthesized and used in azide-alkyne cycloaddition reaction *en route* to the synthesis of 1,4-disubstituted-1,2,3-triazoles. The catalyst is heterogeneous and can be recycled and reused easily. Room temperature reaction condition and the use of ethylene glycol as solvent make it an environment friendly system.

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## Introduction

The syntheses of biologically active compounds are greatly important for the society and the scientists are continuously trying to develop new and efficient methodologies to produce such compounds. Compounds containing 1,2,3-triazole moiety have important biological activities and pharmaceutical properties and are potent agents for treating different diseases and disorders.<sup>1</sup> Triazoles possess inherent properties of high stability, non harmfulness due to which they could be extensively used in the field of drug discovery.<sup>2</sup> Because of such utmost importance of 1,2,3-triazoles, 1,3-dipolar cycloaddition of azides and alkynes to produce triazole had acquired the attraction of the scientific society immensely. The pioneering work which can be considered as the landmark on synthesis of 1,2,3-triazole was reported independently by Sharpless<sup>3</sup> and Meldal<sup>4</sup> in 2002. Earlier, it was Rolf Huisgen who for the first time studied deeply and put forward the thermally induced classical reaction of azide and alkynes to produce 1,4 and 1,5 regioisomers of 1,2,3-triazoles.<sup>5</sup> But this conventional method has the drawback of use of high temperature and production of both the 1,4 and 1,5 regioisomers. Sharpless and Meldal eliminated these drawbacks of Huisgen 1,3-dipolar cycloaddition in their work on azide-alkyne cycloaddition forming regioselectively only

1,4-disubstituted 1,2,3-triazole at room temperature by using copper sulphate as catalyst with sodium ascorbate as reducing agent. This work on 1,3-dipolar cycloaddition can be considered as the milestone of regioselective triazole synthesis which draws attraction of the scientific community towards it and afterwards a handful of works have been done on it. This copper catalysed azide-alkyne cycloaddition is the cream of the crop in “click chemistry”<sup>6</sup> which satisfies almost all the requirements of green chemistry.<sup>2</sup> Various copper forms were applied in the cycloaddition reaction in order to find different convenient routes to form 1,2,3-triazole. Starting from using copper (II) salts in presence of reducing agents to directly copper (I) sources with stabilizing ligands<sup>7,8</sup> and various solid supported copper catalysts to nano copper were reported for the regioselective synthesis of 1,2,3-triazole. Nowadays, heterogeneous catalysis for 1,4-disubstituted-1,2,3-triazole synthesis is of more interest and area of study as from the point of green chemistry view and the advantages of heterogeneous system over homogeneous system are encouraging the scientists to develop new methodologies using various heterogeneous catalysts. Heterogeneous catalysis eliminates the drawbacks of production of bistriazoles and diacetylene as by products in azide-alkyne cycloaddition reactions. It is also noteworthy that heterogeneous catalysis minimizes the amount of metal used in the reaction by immobilisation and recyclability and reusability of the catalyst, besides their properties of easy handling and simple separation, make them more advantageous.<sup>9</sup>

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Keeping in mind the importance of triazoles and advantages of heterogeneous system, in this study we have synthesised triazole derivatives using new solid supported Cu based heterogeneous catalyst. Continuing our previous works<sup>10</sup> on triazole synthesis, here we have developed hydrotalcite supported copper nano particles as heterogeneous catalyst for azide-alkyne cycloaddition reaction. Hydrotalcite is a layered double hydroxide useful as solid support for metals in various reactions.<sup>11,12</sup>

## Materials and method

Reagents and solvents were obtained from commercial suppliers namely Spectrochem, Merck and Sigma Aldrich and used without further purification. All the reactions were carried out in oven-dried glassware under atmospheric conditions. All reported yields are isolated yields.

### Preparation of the catalyst

In order to prepare the catalyst, first we have prepared hydrotalcite with formula  $\text{Ca}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$  according to earlier reported procedure.<sup>13</sup> In brief, the hydrotalcites were synthesised by the co-precipitation method. Two solutions were prepared, solution 1 contained 2 M NaOH and 0.2 M  $\text{Na}_2\text{CO}_3$ , and solution 2 contained  $\text{Ca}^{2+}$  as  $\text{CaCl}_2$  with 0.75 M concentration, together with 0.25 M  $\text{Al}^{3+}$  ( $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ ). Solution 2 was added at a steady rate to solution 1 drop wise, under vigorous stirring. A separating funnel was used to deliver solution 2 to solution 1. The precipitated minerals were washed at ambient temperatures thoroughly with ultra pure water to remove any residual salts and dried in an oven (85 °C) for 8 h.

### Preparation of Cu@HT nanocatalyst

Hydrotalcite was dispersed with  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  (0.5 g) in water (500 mL) at room temperature for 30 min. Hydrazine hydrate (50%, 10 mL) was added drop wise for 30 min and the reaction mixture was stirred at room temperature for 2 h. The obtained solid was centrifuged and washed with distilled water and acetone, to remove un-reacted reagents. The product was dried at 100 °C for 8 h and stored in desiccators. The prepared catalyst was then characterised with different analysis methods (Fig. 1).

### Characterization of the nanocatalyst (Cu NPs@HT)

The prepared catalyst was characterised by TGA, SEM, TEM, XRD and ICP-AES analysis. We can observe the morphology of the as-prepared CuNPs@HT nanocatalyst from the SEM image (Fig. 2 A; JEOL JSM 7100F Scanning Electron Microscope). It can be seen from that the as-prepared nano-catalysts have a plate-like morphology with some hexagonal structure, which is the typical morphology of layered double hydroxides. Fig. 2B, C and D are the TEM (JEOL JEM-2100 electron microscope at a working voltage of 200 kV) images of prepared nanocatalyst taken at various measurement scales where Fig. 2E showed SAED pattern which explores the amorphous nature of catalyst.

The intensity weighted size distribution of prepared nanocatalyst (Fig. 3) also revealing its nano structure. Double distribution leads to different aggregates at two different radii ( $10 \pm 0.5$  nm and  $173 \pm 1.26$  nm). The size distribution (DLS) was measured by using a NaBiTecSpectro-Size300 light-scattering instrument (NaBiTec, Germany) with a source of the He-Ne laser (633 nm, 4 mW) at 298.15 K. The amount of copper immobilised in the solid support HT was confirmed by ICP-OES (Perkin Elmer ICP optima 2000 DV ICP-OES, Inductively Coupled Plasma-Optical Emission Spectroscopy) analysis and it was found that 1.87 wt% copper metal impregnated in the catalyst. The XRD and TGA profiles of Cu NPs@HT are given in supporting information.

### General procedure for the synthesis of 1,4-disubstituted-1H-1,2,3-triazole

To a mixture of azide **1** (1 mmol, 1 equiv.) and acetylene **2** (1.1 mmol, 1.1 equiv.) in ethylene glycol (3 mL), the catalyst (15 mg, 1.87 wt%, 0.4 mol%) was added. The mixture was stirred at room temperature till the completion of the reaction which was confirmed by TLC. After completion of the reaction, it was extracted with EtOAc ( $2 \times 20$  mL), washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give the crude product which was purified through silica gel column chromatography (10–20% EtOAc/hexanes) to get the desired product. The products are characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data.

## Results and discussion

To check the effectiveness of our prepared catalyst, the reaction between benzyl azide and phenyl acetylene was taken as the model reaction. To 1 mmol of the azide, 1.1 mmol of phenyl acetylene was added in presence of 15 mg (0.004 mmol Cu) of the catalyst in ethylene glycol at room temperature. A very good product yield (97%) was obtained after performing the reaction for 1 h (Table 1, entry 2). Lowering the catalyst quantity to 5 mg afforded reasonably good yields (62% yields) of the triazoles (Table 1, entry 3). The reaction of benzyl azide and phenyl acetylene was further carried out with 10 mg and 20 mg of the catalyst affording 73% and 97% yields of the desired triazoles respectively (Table 1, entries 4, 5). Therefore, 15 mg of the catalyst was considered as the optimized amount for AAC reaction. The reaction between benzyl azide and phenyl acetylene was carried out in ethylene glycol without adding catalyst (Table 1, entry 1). No required product was observed in absence of catalyst indicating the necessity of copper for AAC reaction. The reaction between benzyl azide and phenyl acetylene was then carried out with 15 mg of the catalyst at room temperature in different solvents (Table 1, entry 6–13). With ethylene glycol the reaction gave best result of 97% yields (Table 1, entry 2).

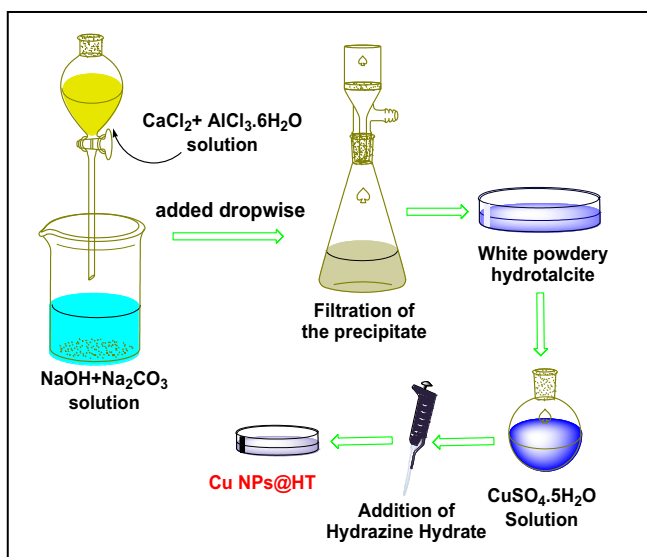


Fig. 1. Sequential preparation of HT supported Cu Nps (Cu NPs@HT) as a catalyst.

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