

Preparation of alumina supported copper nanoparticles and their application in the synthesis of 1,2,3-triazoles

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Abstract

We report here the synthesis of alumina supported copper nanoparticles from copper(II) acetylacetonate and aluminum isopropoxide precursors using aerogel protocol. The nanoparticles were characterized by XRD, TEM, ²⁷Al MAS NMR, XPS and ICP-AES. Cu–Al₂O₃ nanoparticles are used for the preparation of 1,2,3-triazoles by the reaction of terminal alkynes, sodium azide and alkyl/allyl halides. The nanoparticles are recovered and reused for several cycles with consistent activity.

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1. Introduction

Nanomaterials are of topical interest, because of their intriguing properties different from those of their corresponding bulk materials. Due to their unique properties, they were employed in electronic, optical, catalytic, coating, medical and sensor applications [1]. There are many reports in the literature on the synthesis of transition metal nanoparticles and their application as catalysts [2].

1,2,3-Triazoles have a wide range of applications in the synthesis of pharmaceuticals [3]. Most common method for the preparation of 1,2,3-triazoles is the 1,3-dipolar cycloaddition reactions between substituted alkynes and azide derivatives [4]. Alternatively, triazoles can be prepared by the cycloaddition of azides with electron deficient alkenes, metal acetylides, alkyne Grignard reagents, phosphonium salts, and various substituted alkynes [5]. Organic azides (trimethylsilyl, alkyl, allyl, aryl), metal azides, or hydrazoic acid are commonly used in the cycloaddition reactions with alkynes [6]. Triazoles are also synthesized by using solid supports like polymer or resin bounded azides, alkynes, enamines or β -ketoamides [7]. Wang et al. and Ju and co-workers separately reported the 1,3-dipolar cycloaddi-

tion reactions in water without any catalyst [8]. Sharpless and co-workers [9] prepared triazoles using in situ generated Cu(I) from copper sulphate and sodium ascorbate, stoichiometric amount of copper turnings in water and Cu(I) with stabilizing ligands at room temperature. Copper nanoclusters [10] and Cu(I) salts [11] in the presence of nitrogen bases were also used for the synthesis of 1,2,3-triazoles, whereas in the latter one formation of side products, diacetylenes and bis-triazoles were observed. Orgueira et al. [12] reported the cycloaddition of terminal alkynes and azides by in situ generated Cu(I) from Cu(0) nanosize activated powder in the presence of amine hydrochloride salt. Recently, three component coupling reactions were reported for the preparation of triazoles using catalysts, monometallic palladium [13], bimetallic Pd(0)–Cu(I) [14], microwave assisted Cu(0)–Cu(II) [15] and Cu(II)–sodium ascorbate–L-proline [16]. In microwave assisted synthesis, the reaction time was reduced from 12–48 h to 10–15 min but the temperature was raised to 125 °C during the microwave irradiation.

Copper metal nanoparticles have unusual properties and potential applications. Several groups reported the synthesis of copper and copper oxides by different routes, photochemical, microwave irradiation, thermal decomposition, microemulsion, HRTEM, using supercritical solvents or reducing agents [17]. Deki et al. synthesized copper(I) oxide nanoparticles dispersed in a polymer matrix by thermal relaxation technique [18]. Copper nanoparticles on different supports, SiO₂, Al₂O₃, MgO,

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Y-zeolite are synthesized either in a single step using aerogel method or by dispersing the copper salts and further reduction by hydrogen [19]. They can also be prepared by hot processing, hot pressing or by reactive milling of the homogeneous mixtures of Cu-Al₂O₃ nanoparticles [20].

Herein, we report the synthesis of alumina supported copper nanoparticles (Cu-Al₂O₃ nanoparticles) in a single step by using the modified aerogel method [21] under supercritical conditions using copper(II) acetylacetonate, aluminum isopropoxide, methanol, toluene and deionised water for hydrolysis and their application for one-pot synthesis of 1,2,3-triazoles.

2. Experimental

2.1. Materials

Aluminum isopropoxide, copper(II) acetylacetonate, sodium azide, terminal alkyne and alkyl/allyl halides were purchased from Aldrich or Fluka and used without further purification. ACME silica gel (60–120 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F₂₅₄ plates. Nano-Al₂O₃ was purchased from NanoScale Materials Inc., Manhattan, USA. All the other solvents and chemicals were obtained from commercial sources and purified using standard methods.

2.2. Characterization

X-ray powder diffraction data were collected on a Regaku Miniflex diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 2° min^{-1} in the range of $2\text{--}80^\circ$. Specific surface area is calculated from BET nitrogen isotherms determined at 77 K on a Quantachrome autosorb automated gas sorption instrument. The samples were degassed at 200°C for 3 h before measurements. TEM was performed on a TECNAI 12 FEI TEM instrument. The samples were suspended in dry toluene, treated with ultrasound, and applied to a carbon carrier foil (LaB₆, KO-AP3, $D = 50 \text{ \mu m}$, single tilt holder). Solid state ²⁷Al Magnetic Angle Spin Nuclear Magnetic Resonance (NMR) was measured on a Gemini Varian at 400 MHz spectrometer using Al₂(SO₄)₃ as reference. An IRIS Intrepid II XDL inductively coupled plasma atomic emission spectroscopy (ICP-AES) instrument was used to measure the stoichiometry of the samples.

2.3. Synthesis of Cu-Al₂O₃ nanoparticles by aerogel method

Toluene (300 mL) was added to copper(II) acetylacetonate (13.5 g, 49.9 mmol) in methanol (100 mL) and stirred for 2 h. To the above mixture, aluminum isopropoxide (5.125 g, 25 mmol) was added and stirred for 2 h. To the resultant solution, stoichiometric amount (2.4 mL) of deionized water was added using capillary addition pump over a period of 0.5 h. The mixture was kept under stirring for 18 h at room temperature. The pH of the solution was found to be basic $\sim 7\text{--}8$. The above solution was placed in an autoclave, pressurized to 10 kg/cm^2 and heated to 265°C , kept for 10 min at that temperature, vented to obtain an

aerogel material and further dried at 120°C to remove the traces of solvent to obtain a fine powder of Cu-Al₂O₃ nanoparticles.

2.4. Typical experimental procedure for the synthesis of 1,2,3-triazoles

In a typical procedure, Cu-Al₂O₃ nanoparticles (0.010 g) were added to a mixture of phenylacetylene (0.102 g, 1 mmol), benzyl chloride (0.127 g, 1 mmol) and sodium azide (0.065 g, 1 mmol) in water (2 mL) and the mixture was stirred at room temperature. After completion of the reaction (as monitored by TLC), the catalyst and the solid reaction product were centrifuged and the reaction product was extracted with ethyl acetate. The organic extract was washed with water, dried over sodium sulfate and concentrated to give the crude product. Column chromatography was performed using silica gel (60–120 mesh) with ethyl acetate and *n*-hexane (2:8) as eluent to get pure 1-benzyl-4-phenyl-1*H*-1,2,3-triazole; ¹H NMR (200 MHz, CDCl₃): $\delta = 5.46$ (s, 2H) 7.25–7.39 (m, 8H), 7.67 (s, 1H), 7.77 (d, 2H, $J = 7.3 \text{ Hz}$). All other products gave satisfactory NMR.

3. Results and discussion

3.1. Catalyst characterization

The chemical analysis of the resulting material gave Cu:Al ratio as 1.82:1, which is in close agreement with metal ratios originally charged and further indicates that there is no loss of metal during the venting process. The X-ray diffraction pattern of as synthesized Cu-Al₂O₃ nanoparticles shows the presence of metallic copper and cuprous oxide phases (Fig. 1). The presence of cuprous oxide could be because of the air oxidation of copper during drying at 120°C . XRD peaks for aluminum were not observed, that could be attributed to the amorphous nature. The ²⁷Al MAS NMR of Cu-Al₂O₃ nanoparticles indicate the presence of both octahedral and tetrahedral

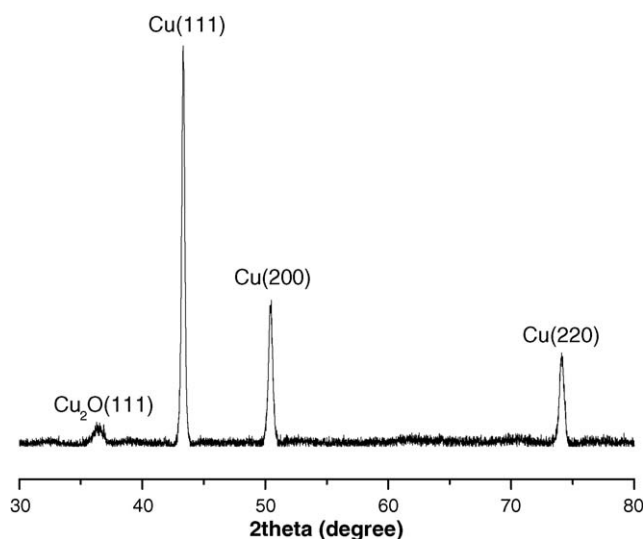


Fig. 1. XRD pattern of as prepared Cu-Al₂O₃ nanoparticles.

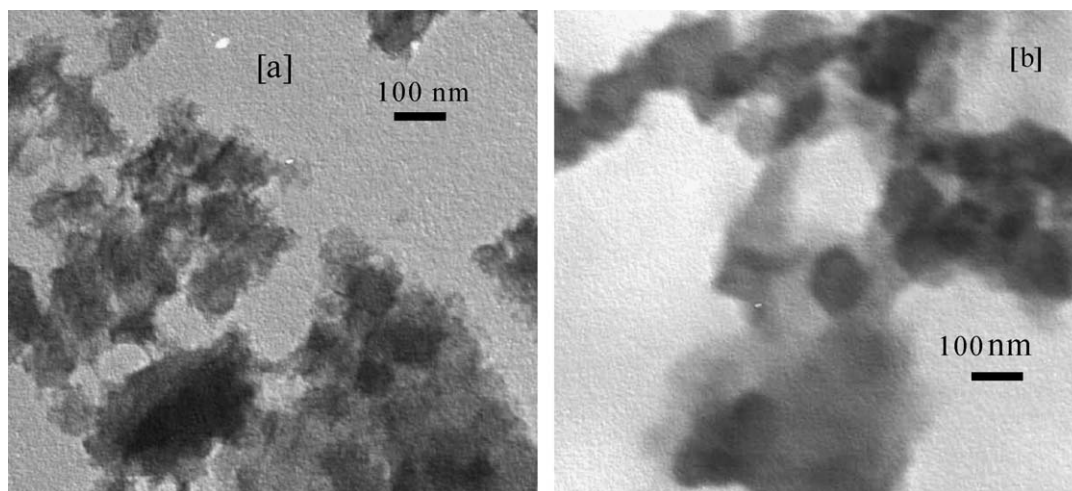


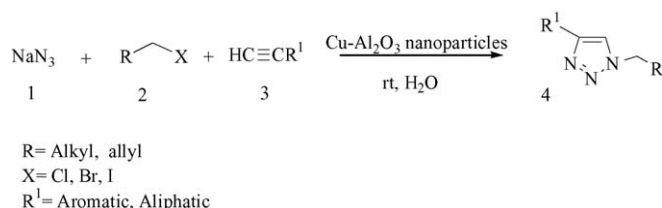
Fig. 2. TEM images of Cu-Al₂O₃ nanoparticles (a) as prepared and (b) used.

aluminum. The presence of tetrahedral aluminum is due to the dehydration of the aluminum hydroxide at the supercritical temperatures [22]. The TEM images reveal uniform distribution of copper on alumina with some agglomeration (Fig. 2a). More agglomeration of the particles was observed in the TEM images of the used catalyst (Fig. 2b). The XPS investigation of Cu-Al₂O₃ nanoparticles at the Cu 2p level shows 2p_{3/2} lines at 934.46 and 932.49 eV respectively, which are closer to binding energies reported for Cu(II), Cu(I) and Cu(0) states [17f]. Unfortunately, it is difficult to distinguish the Cu(0) and Cu(I) by XPS due to the effects of crystal size and surface coverage on the binding energy [23]. The binding energy for Al 2p was observed at 74.43 eV. The BET surface area of the sample was found to be 250 m²/g and an average pore diameter of 64.2 Å.

The catalytic property of Cu-Al₂O₃ nanoparticles was investigated for the 1,3-dipolar cycloaddition reactions between sodium azide, terminal alkyne and alkyl/allyl halides (Scheme 1).

Initially, we have examined the effect of solvent for the reaction between benzyl chloride, phenylacetylene and sodium azide with Cu-Al₂O₃ nanoparticles at room temperature and the results are presented in Table 1. Water is found to be the best solvent for obtaining high yields. The products were quantitatively recovered by simple extraction with ethyl acetate.

For comparison, we did a control reaction and also with the conventionally prepared Cu–Al hydrotalcites [24], no product was observed in 3 h, however increasing the reaction time to 48 h, 50 and 55% (Table 2, entry 1c and d) yields of the desired product were obtained respectively. With nanocrystalline Al₂O₃,



Scheme 1. One-pot synthesis of 1,2,3-triazoles using Cu-Al₂O₃ nanoparticles.

Table 1

Effect of solvent for the synthesis of 1,2,3-triazoles catalyzed by Cu-Al₂O₃ nanoparticles

Entry	Solvent	Time (h)	Isolated yield (%)
1	<i>t</i> -BuOH	3	62
2	<i>t</i> -BuOH:H ₂ O	3	81
3	H ₂ O	3	92

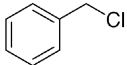
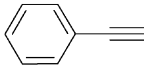
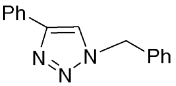
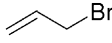
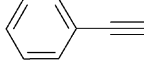
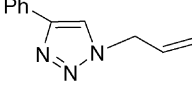
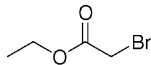
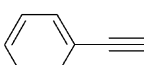
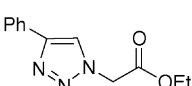
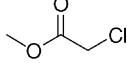
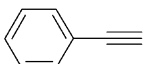
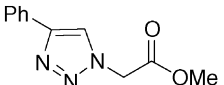
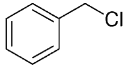
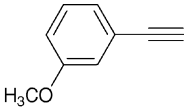
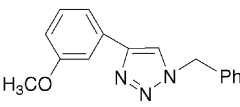
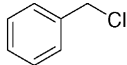
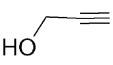
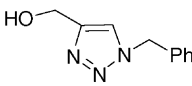
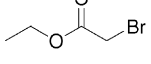
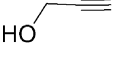
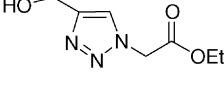
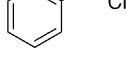
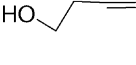
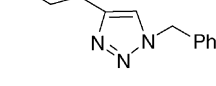
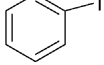
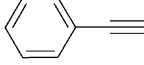
Reaction conditions: terminal alkyne (1 mmol), halide derivative (1 mmol), NaN₃ (1 mmol) Cu-Al₂O₃ nanoparticles (10 mg), at room temperature.

no product was isolated (Table 2, entry 1f). These observations clearly indicate that the present Cu-Al₂O₃ nanoparticles enhance the formation of copper-acetylide and facilitate the cycloaddition process. Further we have tested the catalytic activity of Cu-Al₂O₃ nanoparticles for 1,3-dipolar cycloaddition reactions with variety of substrates under standard conditions and the results are summarized in Table 2. It is clear from Table 2 that the catalyst gave good yields for the reaction between phenylacetylene with different alkyl/allyl halides (Table 2, entries 1–4) and moderate yield with 3-methoxy phenylacetylene (Table 2, entry 5). The reaction of propargyl alcohol with benzyl chloride and ethyl bromoacetate resulted in good yields (Table 2, entry 6 and 7), whereas the homopropargyl alcohol with benzyl chloride resulted in moderate yield (Table 2, entry 8). The reaction between simple iodobenzene and phenylacetylene resulted in no product formation. Fokin and co-workers [25] reported the formation of azides from propargylic, allylic and benzylic halides at room temperature and aryl/vinyl azides at high temperatures (50–60 °C). Similarly, benzylic and allylic azides are prepared in the present protocol using Cu-Al₂O₃ nanoparticles at room temperature, as the substitution is facile with activated halides such as allylic, propargylic and benzylic halides.

4. Recyclability

The heterogeneity of the Cu-Al₂O₃ nanoparticles was evaluated by the following studies. The Cu-Al₂O₃ was removed after the reaction by filtration, fresh aliquots of reactants were added

Table 2
Synthesis of triazoles using Cu-Al₂O₃ nanoparticles

Entry	Halide derivative	Terminal alkyne	Product	Yield (%) ^a
1				92, 50 ^b , 50 ^c , 89 ^d , 0 ^e
2				86
3				85
4				82
5				40
6				5
7				75
8				63
9			No reaction	–

Reaction conditions: terminal alkyne (1 mmol), halide derivative (1 mmol), NaN₃ (1 mmol) Cu-Al₂O₃ nanoparticles (10 mg), and reaction time 3–8 h, at room temperature.

^a Yields of isolated products.

^b Blank reaction, 48 h.

^c Cu/Al hydrotalcite, 48 h.

^d Yield after fourth cycle.

^e Nanocrystalline Al₂O₃, 3 h.

to the filtrate and the reaction was monitored. No product formation was observed. Copper was not detected in the filtrate by ICP-AES.

The reusability of the catalyst was carried out with phenylacetylene, sodium azide and benzyl chloride in fresh water by adopting the following protocol as described in the experimental section. After the completion of reaction, the products were quantitatively recovered by simple extraction with ethyl acetate. The catalyst was allowed to settle and the supernatant solution was pumped out from the reaction flask. The catalyst was washed with ethyl acetate four times (4 × 10 mL), and allowed to settle

and the supernatant ethyl acetate solution was pumped out. Fresh quantities of phenylacetylene, sodium azide and benzyl chloride were introduced. Further the recovered Cu-Al₂O₃ nanoparticles were reused for 3 cycles with consistent activity (Table 1, entry 1e). The copper content was found to be almost same in the fresh and used catalyst after the fourth cycle by ICP-AES. These studies demonstrate that the copper bound to amorphous alumina during the reaction is active and the reaction proceeds on the heterogeneous surface. However, the consistent activity of the catalyst from the recycle experiments clearly reveals that particle agglomeration has less influence on the reactivity (Fig. 2b).

5. Conclusions

In summary, we have described a simple, convenient, and efficient one-pot synthesis of 1,2,3-triazoles regioselectively using Cu-Al₂O₃ nanoparticles. The triazole formation is achieved at room temperature in water. The Cu-Al₂O₃ nanoparticles are reused for several cycles with consistent activity. This procedure can be exploited in the synthesis of various drug intermediates.

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