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Cu(II)-CMC: a mild, efficient and recyclable catalyst for the oxidative alkyne homocoupling reaction

DOI 10.1515/znb-2017-0009
Received January 13, 2017; accepted June 2, 2017

Abstract: Cu(II) heterogenized on sodium carboxymethyl cellulose (Na-CMC) has been thoroughly characterized by different techniques. Cu(II)-CMC has been applied for the first time in the homocoupling reaction of a variety of terminal alkynes. The catalyst furnished good to excellent yields of the desired products and could be reused six times without loss of catalytic activity. The Cu(II)-CMC catalysis protocol is a new efficient route to synthesize 1,3-diynes under mild conditions.

Keywords: Cu(II)-CMC; 1,3-diyne; heterogeneous catalysis; homocoupling reaction; reusable.

1 Introduction

The copper-mediated Glaser-type homocoupling reaction of terminal alkynes is the most promising method for the synthesis of 1,3-diynes. It was first reported by Glaser in 1869 [1]. The 1,3-diynes synthesized by Glaser-type coupling reactions are an important class of building blocks in numerous natural products [2–7], pharmaceutical intermediates and bioactive compounds [2, 8–13] with anti-HIV, antifungal, anticancer activities, etc. Moreover, the application of 1,3-diynes chemistry has been extended to numerous other fields, such as supramolecular switches [14], carbon-rich materials [15], organic conductors [16], and so on.

The homocoupling reaction of terminal alkynes can be performed efficiently through catalysis by a combination of palladium and copper salts [17–19]. However, palladium reagents are very expensive, sensitive to air and require additional ligands in the reaction. In recent years, great efforts have been devoted to the development of copper-mediated homocoupling reactions of terminal alkynes under palladium-free conditions due to their economic advantages and environmental friendliness. The copper-catalytic systems include Cu(I) complexes [20–27], Cu(II) complexes [28–35] and metallic copper [36]. Cu(II) complexes are preferably used as catalytic systems due to the susceptibility of Cu(I) salts to redox processes. They require, however, the utilization of (often foul smelling) nitrogen bases, ligands and/or other additives to protect and stabilize the active Cu(I) catalysts. Most of the reported Cu(II) catalytic systems are homogeneous and have shortcomings in that the separation of catalysts and products and the recycling of the catalysts are difficult. A few Cu(II) complexes heterogenized on inorganic supports have been reported as catalytic systems for the oxidative homocoupling of terminal alkynes, such as CuAl-LDH [33], $Cu(OH)_x/TiO_2$ [37], $Cu(OH)_x$/OMS-2 [38], Cu(II)-clay [39] and Cu(II)-SBA-15 [40]. However, there are certain drawbacks to these Cu(II)-based heterogeneous catalysts, such as the requirement of bases, pure oxygen (1 atm) or long preparation time. Therefore, simpler yet effective and environmentally benign Cu(II)-based heterogeneous catalysts for homocoupling reactions are still desirable.

Sodium carboxymethyl cellulose (Na-CMC) is an important and very useful carboxylate-modified ether derivative from CMC. Its water solubility, non-toxicity, good availability and biodegradation combined with low cost favor its use in diverse applications [41–44], such as drug delivery [45], antibacterial materials [46] and sequestering agents for the removal of heavy metals [47]. Another interesting application is to explore the possibility of using CMC-containing metal complexes directly for organic reactions. As far as we know, there is no report

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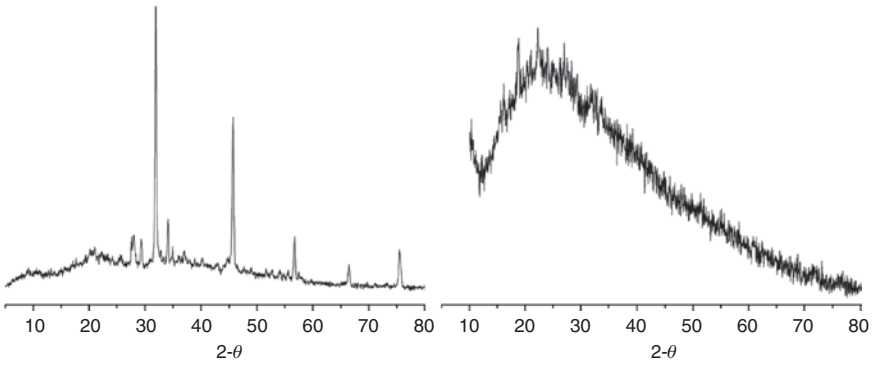


Fig. 1: X-ray diffraction spectra of CMC (left) and Cu(II)-CMC (right).

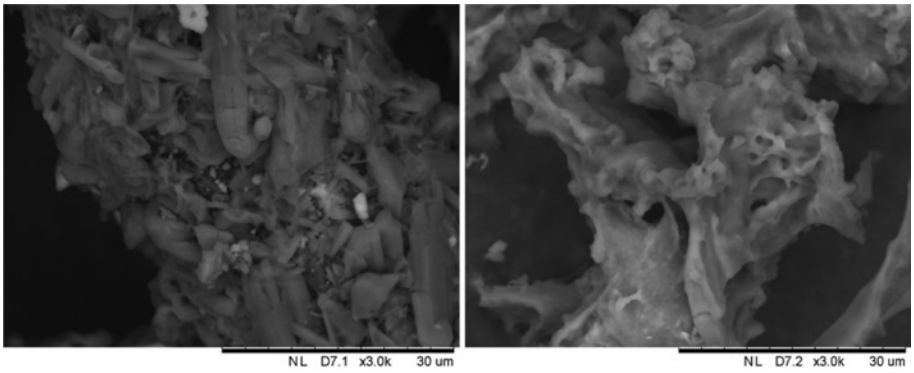


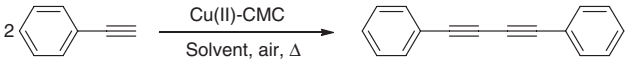
Fig. 2: The representative SEM images for CMC (left) and Cu(II)-CMC (right).

on using copper-containing CMC in the oxidative alkyne homocoupling reaction. Herein, we report an environmentally friendly and highly efficient method for the oxidative alkyne homocoupling under mild conditions with Cu(II)-CMC as a catalyst.

2 Results and discussion

The Cu(II)-CMC was prepared according to a previously reported procedure [48] and characterized by X-ray diffraction (XRD) (Fig. 1), scanning electron microscopy (SEM) (Fig. 2) and inductively coupled plasma mass spectrometry (ICP-MS). The XRD patterns of CMC and the Cu(II)-CMC catalyst are shown in Fig. 1. They show largely crystalline Na-CMC but amorphous Cu(II)-CMC, which is consistent with the SEM images in Fig. 2. The percentage of copper in Cu(II)-CMC was found to be 11.6% as determined by ICP-MS.

First, the reaction conditions of the homocoupling of phenylacetylene were optimized, which was taken as the model reaction (Scheme 1). For the screening of suitable solvents, the reaction conditions were set as follows:



Scheme 1: The model reaction for optimizing reaction conditions.

phenylacetylene (1.0 mmol), catalyst (10 mol%), solvent (2.0 mL), reaction temperature (90°C), reaction time (2 h) and the presence of atmospheric oxygen. The reaction was carried out in DMSO, DMF, toluene, H_2O, 1,4-dioxane and CH_3CN. As is shown in Table 1 (entries 1–6), for the catalysis with Cu(II)-CMC high-polarity solvents exhibited

Table 1: Screening solvent for the homocoupling reaction of phenylacetylene.

Entry	Catalyst	Solvent	Time (h)	Yield (%)[a]
1	Cu(II)-CMC	DMSO	2	91
2	Cu(II)-CMC	DMF	2	60
3	Cu(II)-CMC	Toluene	2	15
4	Cu(II)-CMC	1,4-Dioxane	2	10
5	Cu(II)-CMC	H_2O	2	Trace
6	Cu(II)-CMC	CH_3CN	2	Trace

[a]Isolated yields.

significant advantages over low-polarity solvents, which is consistent with previous reports [30, 35, 40]. Among the tested solvents, the highest yield was obtained in DMSO (91%, Table 1, entry 1). The yield obtained in DMF was moderate 60% (Table 1, entry 2). The yields obtained in toluene and 1,4-dioxane were 15% (Table 1, entry 3) and 10% (Table 1, entry 4), respectively. The lowest yields (Table 1, entries 5 and 6) among the tested solvents were obtained in H_2O and CH_3CN. Therefore, DMSO was selected as the optimum reaction solvent.

Secondly, the reaction temperature was optimized for the model reaction in DMSO. When the reaction temperature was elevated from 90°C to 100°C or 110°C, the yields were almost identical (reaction time 2 h). When decreasing the temperature to 80°C, the yield was reduced to 60% in 7 h. Upon further reducing the reaction temperature, only 27% yield was obtained at 70°C and traces were obtained at 60°C–70°C in 7 h. Hence, 90°C was selected as the optimum reaction temperature. Furthermore, the catalyst loading was also investigated. When the catalyst loading was reduced to 5 mol%, the obtained yield in 4 h was 53%. When the catalyst loading was changed to 15 mol%, the product yield was 91% (2 h) which was the same as that obtained with catalysis by 10 mol% Cu(II)-CMC. Finally, according to the results mentioned above, the optimized reaction conditions for the model reaction were phenylacetylene (1.0 mmol), Cu(II)-CMC (10 mol%) and DMSO (2.0 mL) at 90°C in the presence of air.

The lifetime and reusability of a heterogeneous catalytic system are particularly crucial factors. The recyclability of Cu(II)-CMC was investigated by the following procedures. After the completion of the reaction, Cu(II)-CMC was filtrated and washed with little DMSO. The so obtained Cu(II)-CMC was directly used for the next cycle. The activity of Cu(II)-CMC was constant even after six cycles.

In order to investigate the role of CMC in the oxidative alkyne homocoupling reaction, further experiments were carried out. Reactions were performed using $CuSO_4 \cdot 5H_2O$, Na-CMC and $CuSO_4 \cdot 5H_2O$/Na-CMC as catalysts, respectively, instead of Cu(II)-CMC. It was found that when catalyzed by 10 mol% $CuSO_4 \cdot 5H_2O$, only 50% yield was obtained, much less than with Cu(II)-CMC (91%). In this case the final reaction mixture became homogeneous. The reaction with Na-CMC alone gave no product. Catalysis by $CuSO_4 \cdot 5H_2O$ (10 mol%) in the presence of Na-CMC gave the same yield as with Cu(II)-CMC in 2 h. It is obvious that Na-CMC greatly improves the catalytic efficiency of Cu(II) salts in the alkyne homocoupling reaction.

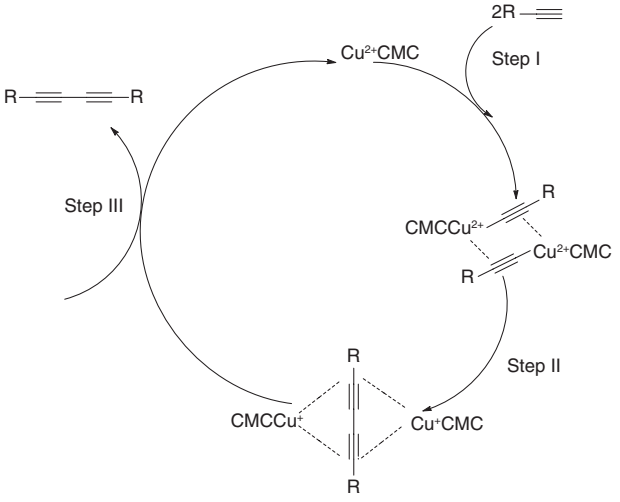
As is reported by Jia and co-workers [35], the yield of the homocoupling reaction of 1-(*n*-propyl)-4-ethynylbenzene with $Cu(OAc)_2 \cdot H_2O$ (10 mol%) as a catalyst is 96%, much higher than with $CuSO_4 \cdot 5H_2O$ (10 mol%; see above). The AcO^- in $Cu(OAc)_2 \cdot H_2O$ acts as the base in the alkyne homocoupling reaction [49]. As there are many carboxylate rests in CMC, in Cu(II)-CMC likewise, they are supposed to act as the base in the alkyne homocoupling reaction.

On the basis of the present results and the literature reports [40], a reaction mechanism is proposed for the oxidative homocoupling of terminal alkynes to 1,3-diyne derivatives with Cu(II)-CMC as a catalyst, which is shown in Scheme 2.

Having the optimized reaction conditions in hand, a variety of terminal alkynes with different functional groups were tested as reagents in order to evaluate the scope of the protocol. As shown in Table 2, the oxidative homocoupling of phenyl acetylenes containing electron-donating (methyl, amino, ethyl, *n*-propyl, *n*-pentyl, -oxymethyl) as well as electron-withdrawing substituents (-F, -Cl) proceeded smoothly to afford the corresponding 1,3-diyne derivatives in 79–95% yield (Table 2, entries 1–8). For aliphatic terminal alkynes the yields of the corresponding 1,3-diynes are slightly lower (Table 2, entries 9–11).

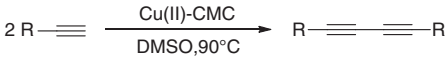
3 Conclusions

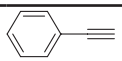
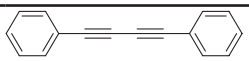
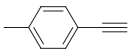
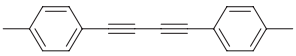
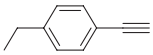
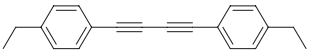
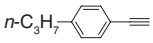
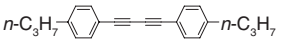
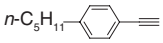
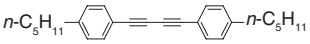
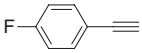
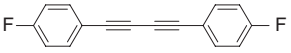
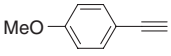
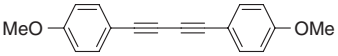
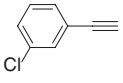
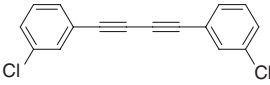
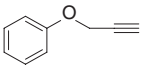
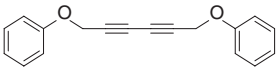
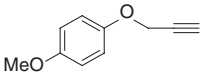
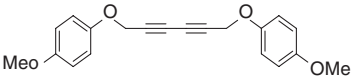
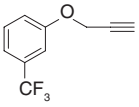
In summary, we have developed an efficient heterogeneous copper(II)-catalyzed protocol for the homocoupling reaction of terminal alkynes in DMSO using Cu(II)-CMC as a reusable catalyst. The protocol is not only suitable for phenyl acetylenes derivatives, but also for aliphatic terminal alkynes.



Scheme 2: Proposed reaction mechanism for the Cu(II)-CMC catalyst.

Table 2: Oxidative homocoupling activity of Cu(II)-CMC on different terminal alkynes.[a]



Entry	Alkyne	Product	Time (h)	Yield (%)[b]
1			2	91
2			2.5	90
3			2	93
4			1.5	95
5			3	83
6			6	89
7			3	79
8			5	91
9			2.5	81
10			4	78
11			6	57

[a]Reaction conditions: terminal alkynes (1.0 mmol), Cu(II)-CMC (10 mol%), DMSO (2.0 mL) and at 90°C in air; [b]isolated yields.

4 Experimental section

4.1 General

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The products were characterized by ^{1}H NMR and ^{13}C NMR (Bruker Avance/400) with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (*J*) in hertz (Hz).

4.2 Catalyst preparation

A copper sulfate solution (10% $CuSO_4 \cdot 5H_2O$ 150 mL) was added dropwise to 300 mL of a 1% Na-CMC solution. The mixture was constantly stirred during the copper sulfate addition. After completion of the addition, the stirring was continued for 5 h at room temperature. The obtained slurry was centrifugated and washed several times with distilled water in order to remove residual Cu(II) ions. Cu(II)-CMC was finally obtained by freeze-drying.

4.3 General procedure for the synthesis of 1,3-diynes

To a stirred solution of the terminal alkynes (1.0 mmol) in DMSO (2.0 mL), Cu(II)-CMC (10 mol%) was added in the open air. The resulting mixture was then warmed to 90°C in air. The process of the reaction was monitored by thin-layer chromatography. After completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate followed by the separation of the catalyst

from the reaction mixture by filtration under reduced pressure. The filtrate was washed with brine solution, dried over anhydrous Na_2SO_4 and the ethyl acetate was removed under reduced pressure. The residue was then purified by column chromatography on silica gel using petroleum ether as eluent to afford the corresponding 1,3-diynes. All of the products are known and were characterized by comparison of their spectral data with those of authentic samples.

4.3.1 1,4-Diphenylbuta-1,3-diyne (1) [40]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, J = 1.2 Hz, J = 1.6 Hz, 4H, Ar-H), 7.40–7.33 (m, 6H, Ar-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.5, 129.3, 128.5, 121.8, 81.6, 73.9.

4.3.2 1,4-Ditolylbuta-1,3-diyne (2) [40]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.0 Hz, 4H, Ar-H), 7.15 (d, J = 8.0 Hz, 4H, Ar-H), 2.37 (s, 6H, CH_3-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 132.4, 129.3, 118.8, 81.6, 73.5, 21.7.

4.3.3 1,4-Bis(4-ethylphenyl)buta-1,3-diyne (3) [40]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.0 Hz, 4H, Ar-H), 7.17 (d, J = 8.0 Hz, 4H, Ar-H), 2.67 (q, J = 8.0 Hz, 4H, CH_2-H), 1.24 (t, J = 8.0 Hz, 6H, CH_3-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 132.5, 128.1, 119.0, 81.6, 73.5, 29.0, 15.3.

4.3.4 1,4-Bis(4-n-propylphenyl)buta-1,3-diyne (4) [35]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.0 Hz, 4H, Ar-H), 7.15 (d, J = 8.0 Hz, 4H, Ar-H), 2.60 (t, J = 8.0 Hz, 4H, CH_2-H), 1.69–1.60 (m, 4H, CH_2-H), 0.94 (t, J = 8.0 Hz, 6H, CH_3-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 132.4, 128.6, 119.0, 81.6, 73.5, 38.1, 24.3, 13.8.

4.3.5 1,4-Bis(4-n-pentylphenyl)buta-1,3-diyne (5) [39]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.0 Hz, 4H, Ar-H), 7.15 (d, J = 8.0 Hz, 4H, Ar-H), 2.61 (t, J = 8.0 Hz, 4H, CH_2-H), 1.63–1.59 (m, 4H, CH_2-H), 1.33–1.31 (m, 8H, CH_2-H), 0.90 (t, J = 6.0 Hz, 6H, CH_3-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 132.4, 128.6, 119.0, 81.6, 73.5, 36.0, 31.5, 30.9, 22.5, 14.0.

4.3.6 1,4-Bis(4-fluorophenyl)buta-1,3-diyne (6) [39]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 4H, Ar-H), 7.04 (t, J = 8.0 Hz, 4H, Ar-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3–161.8 (d, J = 250.0 Hz) 134.6–134.5 (d, J = 10.0 Hz), 117.8, 116.0–115.8 (d, J = 20.0 Hz), 80.4, 73.5.

4.3.7 1,4-Bis(p-methoxyphenyl)buta-1,3-diyne (7) [39]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 12.0 Hz, 4H, Ar-H), 6.85 (d, J = 12.0 Hz, 4H, Ar-H), 3.82 (s, 6H, CH_3-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 134.1, 114.1, 113.9, 81.26, 73.0, 55.4.

4.3.8 1,4-Bis(3-chlorophenyl)buta-1,3-diyne (8) [40]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 2H, Ar-H), 7.43 (d, J = 8.0 Hz, 2H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.30 (t, J = 6.0 Hz, 2H, Ar-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 132.3, 131.1, 130.7, 129.8, 123.3, 80.6, 74.7.

4.3.9 1,6-Diphenoxyhexa-2,4-diyne (9) [50]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, J = 8.0 Hz, 4H, Ar-H), 7.01 (t, J = 8.0 Hz, 2H, Ar-H), 6.96 (d, J = 8.0 Hz, 4H, Ar-H), 4.76 (s, 4H, CH_2-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 129.6, 121.8, 114.9, 74.7, 71.0, 56.2.

4.3.10 1,6-Bis(4-methoxyphenoxy)hexa-2,4-diyne (10) [51]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (d, J = 12.0 Hz, 4H, Ar-H), 6.84 (d, J = 8.0 Hz, 4H, Ar-H), 4.70 (s, 4H, CH_2-H), 3.77 (s, 6H, CH_3-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 151.5, 116.2, 114.7, 74.9, 70.9, 57.1, 55.7.

4.3.11 1,6-Bis(3-(trifluoromethyl)phenoxy)hexa-2,4-diyne (11) [52]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (t, J = 8.0 Hz, 2H, Ar-H), 7.29 (d, J = 8.0 Hz, 2H, Ar-H), 7.19 (s, 2H, Ar-H), 7.14 (d, J = 4.0 Hz, 2H, CH_2-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 132.2, 131.8, 130.1, 125.1, 122.4, 118.6, 118.6, 118.5, 118.1, 112.1, 112.0, 74.1, 71.4, 56.4.

5 Supporting Information

The ^{1}H and ^{13}C NMR spectra of the products and enlarged X-ray diffraction spectra and SEM images of CMC and Cu(II)-CMC are given as Supporting Information available online (DOI: 10.1515/znb-2017-0009).

Acknowledgments: This work was supported financially by Innovative Talents Program of Henan Province (nos. 164100510015 and 174100510025), Foundation of Henan Educational Committee (nos. 15A150054 and 16A350015) and Scientific Research Foundation for Doctors (no. qd16106) of Henan Normal University.

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Supplemental Material: The online version of this article (DOI: 10.1515/znb-2017-0009) offers supplementary material, available to authorized users.