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A highly efficient three-component coupling of aldehyde, terminal alkyne, and amine via C–H activation catalyzed by reusable immobilized copper in organic–inorganic hybrid materials under solvent-free reaction conditions

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Abstract—Recycling copper(I) immobilized on organic–inorganic hybrid material behaves as a very efficient heterogeneous catalyst in the three-component Mannich coupling reaction of aldehydes, terminal alkynes, and amines via C–H activation to afford the corresponding products in good to excellent yields under solvent-free reaction conditions.

1. Introduction

Propargylamines are versatile intermediates for organic synthesis[1] and important structural elements of natural products and potential drug molecules.[1d,2] Traditionally, these compounds are synthesized by nucleophilic attack of lithium acetylides or Grignard reagents to imines or their derivatives.[3] However, these reagents are stoichiometric and highly moisture sensitive. In addition, the reactions require strictly controlled reaction conditions and sensitive functionalities such as esters are not tolerated. The most attractive synthetic method has been the Mannich one-pot three-component coupling reaction of formaldehyde, secondary amines, and terminal alkynes that was initially restricted to arylacetylene.[4] However, rather harsh conditions, moderate yields, complex workup, and purification procedures have limited its wider application. Since the last decade, there has been a continuing interest in developing transition-metal catalyst to accomplish the Mannich three-component reaction via C–H bond activation.[5] Dax et al. reported the usage of copper as a transition-metal catalyst for a solid-phase Mannich condensation of amines, aldehydes, and alkynes.[6] This polymer-supported three-component Mannich reaction requires one of the reactants immobilized on a resin. Subsequently, a microwave-assisted Mannich three-component coupling reaction in the presence of Cu(I) on Al_2O_3 was reported under solvent-free reaction conditions by Kabalka et al.[7] or in water by Tu et al.[8] Within the past few years, several noble transition-metal salts or their bimetallic systems, such as Au,[9] Ag,[10] Ir,[11] Ru–Cu,[12] Ru–In[13] were used by Li et al., for C–H activation to promote the Mannich three-component coupling reaction under homogeneous conditions. Moreover, some of the reactions were carried out in water,[8,9,10a] ionic liquids,[10b,14] solventless,[7] or supercritical CO_2[15] to meet the need of environmental benign chemistry. Most recently, enantioselective syntheses of propargylamines through one-pot three-component condensation reactions have been developed.[16] However, there are some limitations to the methods mentioned above: (i) the polymer-supported Cu(I)-catalyzed method could not easily generate simple propargylamines that had other functional groups; (ii) the microwave-assisted method under solventless reaction conditions was limited to the aminomethylation of alkynes and excess CuI was used; (iii) Ir(I)-catalyzed method was limited to silylacetylenes; (iv) Cu/Ru-catalyzed method was limited to imines generated from aryl amines and aryl aldehydes; (v) Ag-catalyzed method was limited to aliphatic aldehydes; (vi) an expensive metal catalyst (silver, gold, etc.) was often lost at the end of the reaction when the catalysis was carried out in water or organic solvent.

It should be noted that recently, Mannich three-component reactions have been reported by Choudary et al., using

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Keywords: Mannich three-component coupling; Aldehyde; Terminal alkyne; Propargylamine; Immobilized copper catalyst; Organic–inorganic hybrid materials; Solvent-free.

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hydroxyapatite-supported copper catalyst,[17] and by Kantam et al., using layered double hydroxide-supported gold catalyst,[18] in CH_3CN and THF, respectively. However, the catalyst could be recycled only up to 3–5 times without loss of activity and substrate was limited to aryl alkyne in Kantam's method. Despite the advantages of homogeneous metal catalyst, difficulties in recovering the expensive catalyst from the reaction mixture severely obstruct its wide use in industry. The development of heterogeneous catalyst to replace the homogeneous one for the production of fine chemicals in industrial processes remains an active research area,[19a] because heterogeneous catalyst is easy to separate, potentially reusable, and environment friendly.[19b] Thus, development of highly efficient and reusable heterogeneous catalytic system is desirable for the preparation of propargylamines through the classic Mannich reaction.

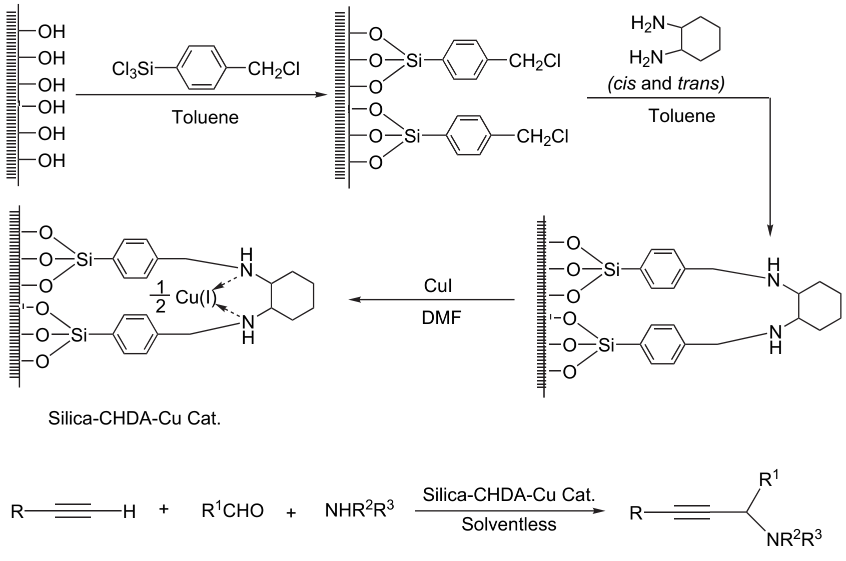
2. Results and discussion

Most Recently, we have developed immobilization of palladium and copper in organic–inorganic hybrid materials and their applications in Sonogashira reaction and Ullmann diaryl etherification.[20] In order to extend the application scope of this kind of catalysts, here we wish to report a highly efficient three-component coupling reaction of aldehydes, terminal alkynes, and amines via C–H activation catalyzed by a reusable immobilized copper in organic–inorganic hybrid materials under solvent-free reaction conditions. In comparison with the above-mentioned methods, this new method showed particular advantages: (i) recyclability of the catalyst up to 15 times without significant loss of catalytic activity; (ii) use of readily available, cheap copper catalyst without Au, Ag, or other additives; (iii) lower catalyst loading (1 mol %); (iv) broad substrate applicability (both aromatic and aliphatic aldehydes, both aromatic and aliphatic terminal alkynes, and both aromatic and aliphatic amines); (v) high yields attained; (vi) solvent-free reaction conditions; and (vii) simple and easy experimental operation. In this paper, we will describe our experimental results.

The silica gel immobilized copper catalyst was prepared according to the four-step procedure summarized in Scheme 1. To a round-bottomed flask, a commercially available silica gel was slurried in a solution of trichloro[4-(chloromethyl)-phenyl]silane in toluene. The suspension was stirred for 20 h at 120 °C under an inert atmosphere, then the silica was isolated and washed subsequently with toluene, dichloromethane, and methanol, and dried at 80 °C for 10 h under reduced pressure. The above benzyl chloride functionalized silica gel was subsequently reacted with 1,2-diaminocyclohexane (cis and trans mixture) in the presence of Na_2CO_3 in toluene at 100 °C for 18 h. After the organics were filtered, the silica was washed with toluene, water, and methanol and dried. The loading of the modified silica was readily quantified via CHN microanalysis and found to be 1.04 mmol g^{-1} of NH. This organic–inorganic hybrid material then reacted with cuprous iodide in DMF at room temperature for 5 h to generate the silica–CHDA–Cu catalyst with 1.589 wt % of Cu.

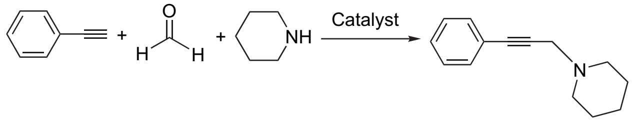
In an effort to develop a better catalytic system, several metals immobilized in organic–inorganic hybrid materials were screened in the Mannich three-component reaction composed of phenylacetylene, piperidine, and *para*-formaldehyde (model reaction) and the results are summarized in Table 1. The Mannich reaction could be catalyzed by either silica-supported Cu(I), Ag(I), or Au(I) in the absence of solvent. But silica-supported Pd(II) failed. Among the supported-catalysts tested, silica–CHDA–CuI was found to be the superior (entries a–j, Table 1). So, silica-supported CuI was used as catalyst in the following investigation for its high efficiency, commercial availability, and lower price.

The solvents also play an important role in the Mannich reaction. Polar solvents, such as DMSO, DMA, and DMF were found to be highly suited for this reaction, while the less polar solvents, such as toluene, afforded the product only in very poor yields. It is interesting to note that under solventless reaction conditions, the reaction also underwent smoothly to generate the corresponding three-component coupling products in excellent yields (entries a–o, Table 1).



Scheme 1.

Table 1. Effect of catalyst and solvent on the Mannich reaction[a]



Entry	Catalyst	Solvent	Yield[b] (%)
a	Silica–CHDA–CuI	Solvent-free	95
b	Silica–CHDA–CuBr	Solvent-free	93
c	Silica–CHDA–CuCl	Solvent-free	89
d	Silica–CHDA–AgI	Solvent-free	87
e	Silica–CHDA–AgBr	Solvent-free	88
f	Silica–CHDA–$AgNO_3$	Solvent-free	81
g	Silica–CHDA–AgOTf	Solvent-free	91
h	Silica–CHDA–AuI	Solvent-free	85
i	Silica–CHDA–AuCl	Solvent-free	88
j	Silica–CHDA–$Pd(OAc)_2$	Solvent-free	0
k	Silica–CHDA–CuI	DMSO	88
l	Silica–CHDA–CuI	DMF	85
m	Silica–CHDA–CuI	CH_3CN	91
n	Silica–CHDA–CuI	Toluene	12

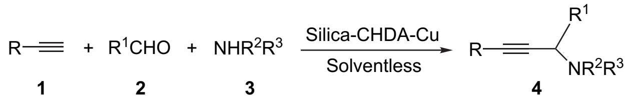
[a] Phenylacetylene (1.00 mmol), piperidine (1.00 mmol), and *para*-formaldehyde (1.00 mmol), silica-supported metal catalyst (containing 0.01 mmol of metal) in the solvent indicated in Table 1 with stirring at 80 °C for 12 h.

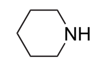
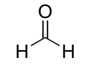
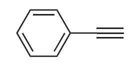
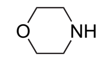
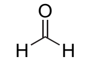
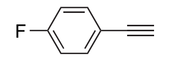
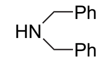
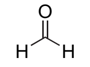
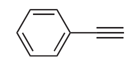
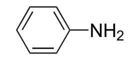
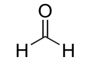
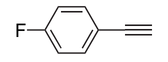
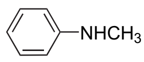
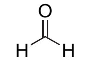
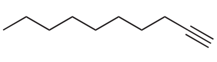
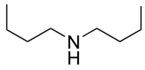
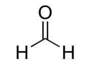
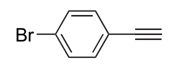
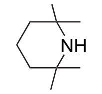
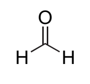
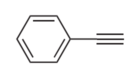
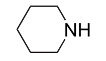
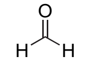
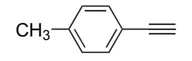
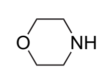
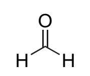
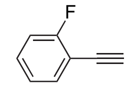
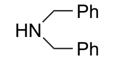
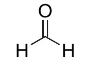
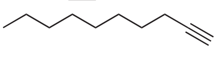
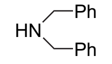
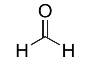
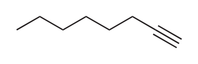
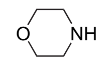
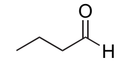
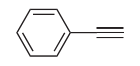
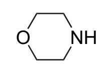
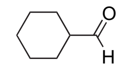
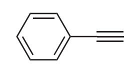
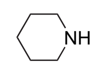
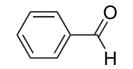
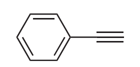
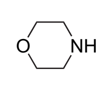
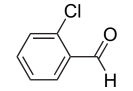
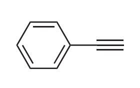
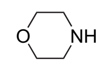
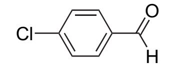
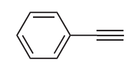
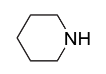
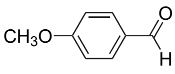
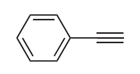
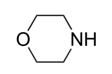
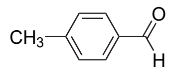
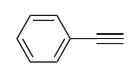
[b] Isolated yields.

During the course of our further optimization of the reaction conditions, when using 1 mol % loading of the silica-supported copper, the reactions were generally completed in a matter of hours, but the time in the absence of solvent, as expected, was inversely proportional to the temperature. A reaction temperature of 80 °C was found to be optimal. Thus, the optimized reaction conditions for the Mannich reaction are the silica–CHDA–Cu (1 mol %) under solvent-free conditions at 80 °C for 12 h.

To examine the scope of this three-component coupling reaction, we extended our studies to different combinations of aldehydes, amines, and alkynes. As depicted in Table 2, both aromatic and aliphatic aldehydes, including those bearing functional groups such as alkyl, alkoxy, and chloro substitutions were able to undergo the corresponding three-component coupling reaction. Aryl aldehyde with electron-withdrawing group (entry p, Table 2) reacted smoothly; however, electron-rich groups bound to the benzene ring such as 4-methoxybenzaldehyde and 4-methylbenzaldehyde reduced the reactivity (entries q and r, Table 2). The reaction of aryl aldehydes was also tolerant of *ortho* substitution and led to the good yield of product (entry o, Table 2). The decreased yields for aliphatic aldehydes might be caused by the trimerization of aliphatic aldehydes. Different amines also have an effect on the reaction: besides the fact that dialkylamines reacted smoothly in these conditions, anilines also formed the corresponding products also in good yields (entries d and e, Table 2). Aromatic alkynes with different substituents, such as alkyl, fluoro, bromo, and chloro groups, also underwent the corresponding three-component coupling reaction smoothly and generated the products in high yields under the present reaction conditions (entries b, d, f, h, and i, Table 2).

Table 2. Silica-supported copper-catalyzed Mannich reaction[a]



Entry	Amine	Aldehyde	Alkyne	Yield[b] (%)
a				95
b				85
c				99
d				82[c]
e				85[c]
f				84
g				90
h				93
i				95
j				92
k				90
l				91
m				82
n				92
o				90
p				96
q				83
r				90

[a] Aldehyde (1.00 mmol), alkyne (1.00 mmol), amine (1.00 mmol), and silica–CHDA–Cu catalyst (40 mg, contains 0.01 mmol of Cu) under solvent-free at 80 °C for 12 h.

[b] Isolated yields.

[c] Silica–CHDA–Cu catalyst (80 mg, contains 0.02 mmol of Cu) was used.

In order to enhance the efficiency of the solid-state Mannich condensation catalyst and reduce waste, the possibility of recycling the catalyst was investigated. Figure 1 showed a summary of the results. It could be seen that the catalyst remained active through at least 15 cycles. After the product

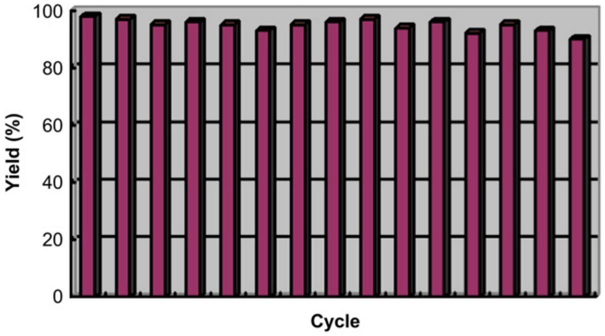


Figure 1. Yields obtained with recycled silica–CHDA–Cu catalyst.

was removed from the silica-supported catalyst using an organic solvent, the catalyst was reused directly for the next trial without further treatment.

3. Conclusion

In conclusion, a highly efficient silica-supported copper-catalyzed three-component coupling reaction of aldehydes, alkynes, and amines via C–H activation has been developed under solventless reaction conditions. The process was simple and generated a diverse range of propargylamines in excellent yields. The reaction was applicable to both aromatic and aliphatic aldehydes, alkynes, and amines. The catalyst could be readily recovered and reused, thus making this procedure more environmentally acceptable whilst no catalyst leaching was observed.

4. Experimental

4.1. General

Starting materials and solvents were purchased from common commercial sources and were used without additional purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard at ambient temperature on a Bruker 250 or 300 FT spectrometer operating at 250 MHz or 300 MHz for ^1H and 62.5 MHz or 75 MHz for ^{13}C, respectively. All spectra were calibrated at δ 7.26 or δ 0.00 ppm for ^1H and δ 77.03 for ^{13}C. GC/MS data were obtained by using a Hewlett–Packard 6890 series GC equipped with a 5973 mass selective detector. IR spectra were obtained by using a Nicolet NEXUS 470 spectrophotometer. Reactions were performed in oven-dried glassware under nitrogen using standard inert atmosphere techniques. Flash column chromatography was performed on silica gel, SiO_2.

4.2. Preparation and characterization of the immobilization of copper catalyst in organic–inorganic hybrid materials

This catalyst was prepared in the following steps from commercial silica.

Activation of silica: 10 g of silica (100–200 mesh, Aldrich) was introduced in a round-bottom flask equipped with a reflux condenser, 80 mL of concentrated H_2SO_4 and 15 mL of HNO_3 were added and the mixture was heated in oil bath at 140 °C for 24 h. The solution was filtered and the white powder was washed with distilled water until neutral pH was attained. The solid was again washed with acetone, methanol, and dichloromethane, and dried under vacuum at 150 °C for 48 h.

In a 50 mL round-bottom flask were introduced successively 20 mL of anhydrous toluene, 2.5 g of activated silica, and 1.0 g of trichloro[4-(chloromethyl)phenyl]silane. The solution was refluxed for 20 h at 120 °C under an inert atmosphere. The solution was filtered and the solid was washed subsequently with toluene, dichloromethane, and methanol, and dried under reduced pressure at 80 °C for 10 h. The material of 2.91 g was obtained. FTIR (KBr, ν cm^{-1}): ν_{Si-O}=1092; ν_{C-H}=3024. Anal. Found: C, 9.31; H, 1.21, corresponding to 1.12 mmol g^{-1} of benzyl chloride groups based on C percentage.

To a 25 mL round-bottomed flask, 2.0 g of the above benzyl chloride functionalized silica gel, 0.3 g of Na_2CO_3, 0.14 g of 1,2-diaminocyclohexane (cis and trans mixture), 10 mL of toluene were added. The mixture was heated at 100 °C for 18 h. After cooling, the organics were filtered; the solid was washed thoroughly with toluene, water, and methanol, and dried under vacuum at 60 °C overnight. Solid of 2.02 g was obtained. The loading of the modified silica was readily quantified via CHN microanalysis and found to be 1.04 mmol g^{-1} of NH based on N percentage. (Anal. Found: C, 12.49; H, 1.69; N, 1.49.)

To a 25 mL round-bottomed flask, 40 mg of CuI and 10 mL of DMF were added. The suspension was stirred at room temperature under an inert atmosphere for 1 h, and then 1 g of the above functionalized silica gel was added. The mixture was stirred at room temperature for 5 h, then the organics were filtered, the solid was washed thoroughly with DMF and methanol, and dried under vacuum at 60 °C overnight. Green powder of 1.02 g (silica–CHDA–Cu catalyst) was obtained. Anal. by ICP (atomic %): Cu, 1.589.

4.3. The recyclability of the silica-supported copper

After carrying out the reaction, the mixture was vacuum filtered using a sintered glass funnel and washed with CH_2Cl_2 (5 mL), Et_2O (5 mL), C_2H_5OH (5 mL), and hexane (5 mL). After dried on oven, they can be reused directly without further purification.

4.4. General Mannich procedure

Amine (1.00 mmol) and terminal alkyne (1.00 mmol) were added to a mixture of silica–CHDA–Cu(I) catalyst (40 mg, contains 0.01 mmol of Cu) and aldehyde (1.00 mmol) contained in a clean, dry, 10 mL round-bottomed flask under nitrogen atmosphere. The mixture was stirred at 80 °C for 12 h on oil bath. After the reaction was completed and cooled to the room temperature, ethyl acetate (2×5 mL) was added and the slurry was stirred at room temperature to ensure removal of the product from the surface of catalyst. The mixture was vacuum filtered using a sintered glass funnel and the product was purified by flash chromatography on silica gel to yield the desired propargylamines.

Propargylamines **4a–c**, **4e–n**, **4p**, and **4r** have been previously reported.[7c,21]

4.4.1. *N*-[3-(4-Fluorophenyl)prop-2-ynyl]-*N*-phenylamine 4d. Light orange oil. IR (film) 3410, 2229 (C≡C), 1603 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.96 (s, 1H), 4.18 (s, 2H), 6.77 (d, J=9.5 Hz, 2H), 6.80–6.87 (m, 1H), 6.98–7.05 (m, 2H), 7.26–7.31 (m, 2H), 7.39–7.45 (m, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 34.7, 82.4, 86.3, 86.4, 113.8, 115.6, 115.9, 118.8, 119.2, 119.2, 129.5, 133.8, 133.9, 147.3, 161.0, 164.4. MS *m/z* (%) 226 (M$^+$+1, 17), 225 (M$^+$, 100). Anal. Calcd for $C_{15}H_{12}FN$: C, 79.98; H, 5.37; N, 6.22. Found: C, 79.82; H, 5.45; N, 6.39.

4.4.2. *N*-[1-(2-Chlorophenyl)-3-phenyl-2-propynyl]morpholine 4o. Yellow oil. IR (film) 2986, 2205 (C≡C), 1608 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.63–2.69 (m, 4H), 3.67–3.73 (m, 4H), 5.15 (s, 1H), 7.24–7.29 (m, 5H), 7.38–7.43 (m, 1H), 7.48–7.53 (m, 2H), 7.72–7.78 (m, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 49.7, 58.9, 67.1, 84.6, 88.2, 122.8, 126.3, 128.1, 129.1, 129.8, 130.4, 131.7, 134.5, 135.5. MS *m/z* (%) 311 (M$^+$, 14), 225 (100). Anal. Calcd for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49. Found: C, 73.36; H, 5.69; N, 4.55.

4.4.3. *N*-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]-piperidine 4q. Oil. IR (film) 2998, 2188 (C≡C), 1610, 1511 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.41–1.52 (m, 2H), 1.55–1.73 (m, 4H), 2.50–2.65 (m, 4H), 3.83 (s, 3H), 4.79 (s, 1H), 6.90–6.99 (m, 2H), 7.31–7.39 (m, 3H), 7.52–7.64 (m, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 24.8, 26.5, 50.9, 55.5, 62.0, 86.7, 87.9, 113.6, 123.6, 128.3, 128.6, 129.9, 130.9, 132.0, 159.2; MS *m/z* (%) 305 (M$^+$, 13), 221 (100). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.74; H, 7.76; N, 4.47.

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