ChemPubSoc Europe
DOI: 10.1002/cplu.201500167
CHEMPLUSCHEM
Full Papers

One-Pot Preparation of Propargylamines Catalyzed by Heterogeneous Copper Catalyst Supported on Periodic Mesoporous Organosilica with Ionic Liquid Framework

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Copper supported on periodic mesoporous organosilica (PMO) with alkylimidazolium frameworks is a highly efficient and recoverable catalyst for the preparation of propargylamines through the three-component coupling reaction of aldehydes, alkynes, and amines. The new catalyst is characterized using N_2 adsorption/desorption analysis, transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT-IR), and elemental analysis. The catalyst is easily recovered by a simple filtration process and subsequently reused in the seven reaction cycles without any loss of catalytic activity.

Introduction

Propargylamines are important synthons for the synthesis of different nitrogen-containing pharmaceutical active components and natural products such as β-lactams, peptides, isosteres, and agrochemicals.[1,2] Some propargylamines have even been tested as targets for multifunctional drugs in the treatment of Alzheimer's and Parkinson's diseases.[3]

Traditional methods for the preparation of propargylamines include the reaction of less commercially available propargyl halides with amines[4] or the use of stoichiometric amounts of lithium or magnesium acetylides with imines.[5] However, nowadays one important method to access propargylamines is the transition-metal-catalyzed one-pot reaction of aldehydes, amines, and alkynes. Different complexes and salts of transition metals, such as iron,[6] zinc,[7] Cu/Ru^{II} bimetallic systems,[8] mercury,[9] indium,[10] iridium,[11] gold,[12] silver,[13] nickel,[14] and copper,[15] have been reported for this interesting reaction. However, in comparison with the other transition metals, copper is one of the best potential catalysts for the A^3 coupling reaction because copper catalyst precursors are usually cheap, readily available, and less toxic, and have high reactivity in A^3 coupling reactions.[16]

Despite the high efficiency in some of the reported transition metal catalysts for A^3 coupling reactions, the majority of reported catalytic systems include homogeneous systems, and suffer from the recovery and recycling of the catalyst from the reaction mixture. In particular, because the A^3 coupling reactions have been applied extensively in the synthesis of pharmaceutically active compounds, it seems that the separation of small quantities of toxic metal catalyst from the product can be considered a challenging issue.

Although various types of heterogenized copper catalysts based on SiO_2,[17] Fe_3O_4,[18] MCM-41,[19,20] montmorillonite,[21] zeolites,[22] and mesoporous Cu/Al[23] have been developed for A^3 coupling reactions, the design of new catalytic systems with concomitant mild reaction conditions as well as a low amount of copper catalyst still poses many challenges. Moreover, to the best of our knowledge, the A^3 coupling reaction using a supported copper catalyst based on periodic mesoporous organosilica (PMO) has not been reported.

Periodic mesoporous organosilicas (PMOs) are one of most traditional organic–inorganic hybrid materials and have attracted much research attention because of their mutual advantages of the arrangement of organic and inorganic fragments within the tunable pore wall and ordered mesoporous structure. PMOs with various mesostructures, morphologies, and structures have been developed in the past few years, and have shown unique properties in the field of catalysis.[24]

Recently, we reported gold nanoparticles supported on periodic mesoporous organosilica with an ionic liquid framework (PMO) as an efficient and recyclable catalyst for the three-component coupling reaction of aldehydes, alkynes, and amines.[25] Very recently, we also introduced agarose-supported copper nanoparticles as an efficient catalyst for the three-component click synthesis of 1,2,3-triazoles in water.[26] In continuation of our interest in PMO and heterogeneous copper-catalyzed reactions, herein, we wish to disclose the synthesis and characterization of a copper catalyst supported on PMO and its application as a heterogeneous catalyst in the A^3 coupling reaction of amines, aldehydes, and alkynes under low copper loading and mild reaction conditions.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201500167.

Results and Discussion

The PMO-IL was synthesized through the hydrolysis and polymerization of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride and tetramethylorthosilicate in the presence of Pluronic P123 as a structure-directing agent in acidic medium, according to our last synthetic reports.[25] The catalyst denoted as Cu@PMO-IL was also prepared through the direct reaction between copper chloride ($CuCl_2$) and chloride ions of the imidazolium moieties in the PMO-IL. Then, the resulting materials were characterized by various well-known techniques.

Table 1. Physical and chemical properties of PMO-IL, Cu@PMO-IL, and recovered catalyst.

Material	S_{BET} [$m^2 g^{-1}$][a]	V_t [$cm^3 g^{-1}$][b]	D_{BJH} [cm][c]	% C[d]	% N[d]	Loadingof FG [$mmol g^{-1}$]
PMO-IL	559	1.12	10.6	16.7	3.3	1.16 (IL)
Cu@PMO-IL	470	0.98	10.6	15.0	3.0	1.12 (IL), 0.7 (Cu)
Re-Cu@PMO-IL	427	0.93	10.6	15.4	3.1	1.11 (IL), 0.6 (Cu)

[a] S_{BET} = specific surface area derived from linear part of adsorbed nitrogen in the range 0.05 to 0.3. [b] V_t = total pore volume derived from adsorbed nitrogen from relative pressure ≈ 0.99. [c] D_{BJH} = pore size distributions calculated from the adsorption branch using BJH method. [d] Calculated using elemental analysis (CHN); estimated by TG, elemental analysis, AAS, and ICP techniques.

The N_2 adsorption/desorption isotherms and pore size distributions for both PMO-IL and Cu@PMO-IL are shown in Figure 1. The PMO-IL exhibited a typical type IV isotherm with H1 hysteresis loop, according to the IUPAC classification.[27] A sharp capillary condensation step at the relative pressure 0.8 indicated the formation of highly ordered organofunctionalized mesostructures. Furthermore, the BET calculations showed the successful formation of PMO-IL with a high surface area of 559 $m^2 g^{-1}$, which contained open mesoporous channels with a total pore volume of 1.12 $cm^3 g^{-1}$ (Table 1). Moreover, the pore size distributions calculated from the adsorption branch using the BJH method (Figure 1 B) displayed highly uniform mesopores centered on 10.6 nm. In contrast, the surface area and total pore volume for Cu@PMO-IL were determined to be 470 $m^2 g^{-1}$ and 0.98 $cm^3 g^{-1}$, respectively (Table 1). The remarkable decrease in surface area and pore volume for the catalyst in comparison with the parent PMO-IL could be considered as further evidence for the successful immobilization of active catalyst species into the PMO-IL scaffold. Additionally, the narrowed pore size distributions of the catalyst indicate that its structural order remained intact after modification of the parent PMO-IL with copper precursors (Figure 1 B).

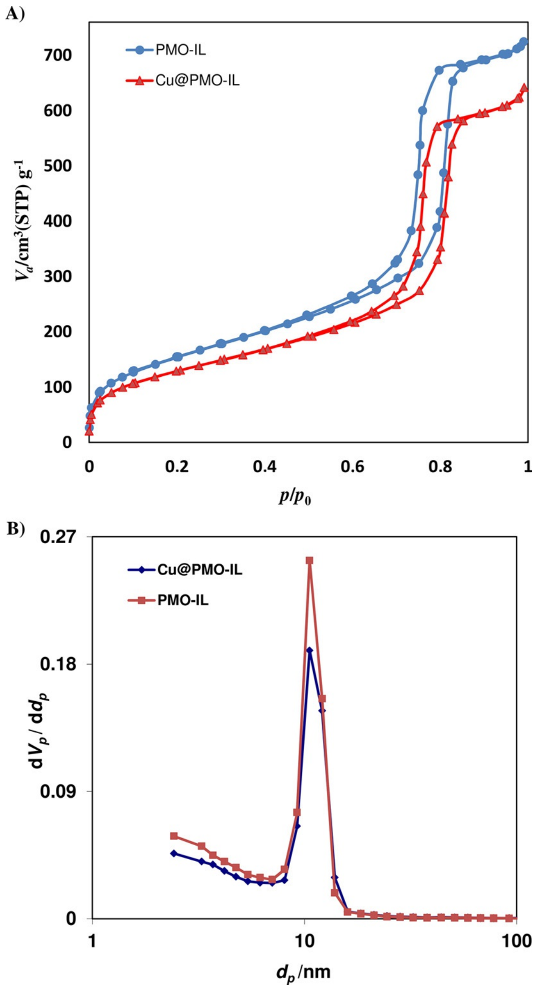


Figure 1. A) N_2 adsorption/desorption isotherms and B) pore size distributions for PMO-IL and Cu@PMO-IL.

The TEM image of PMO-IL demonstrated the formation of a highly ordered two-dimensional hexagonal mesostructure (Figure 2). Furthermore, the TEM image of Cu@PMO-IL provided further confirmation that the ordered mesostructures of the PMO-IL scaffold were well retained during the catalyst preparation process. All the data are also in good agreement with the N_2 sorption analysis (Table 1).

In addition, the presence of Cu was also confirmed by energy dispersive spectroscopy (EDS); the catalyst exhibited three distinct peaks at approximately 1, 8, and 9 keV (Figure 3).

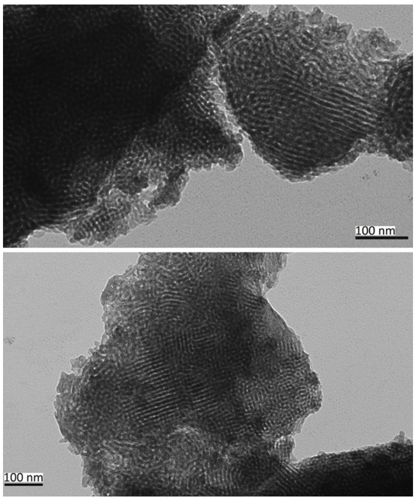


Figure 2. TEM images of PMO-IL (top) and Cu@PMO-IL (bottom).

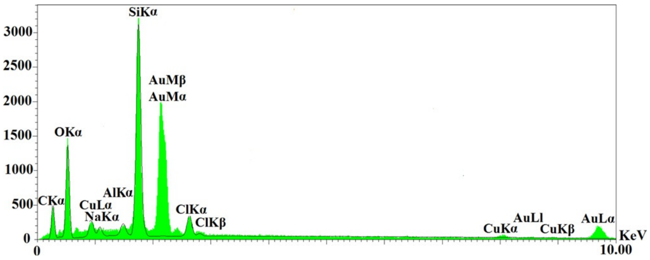


Figure 3. EDX image of Cu@PMO-IL.

The presence of bridged ionic liquids in the framework was confirmed by using the diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) technique. PMO-IL (see Figure A, Supporting Information) and the catalyst (Figure B, Supporting Information) exhibited similar patterns. The peak at 2958 cm^{-1} corresponds to the C–H stretching of propyl functional moieties in the samples.[28] The presence of ionic liquids can be also confirmed by the peak at around 1634 cm^{-1} that relates to the stretching vibration of C=N bonds.[29] Moreover, imidazolium rings can be confirmed in the band at 1560 cm^{-1}, which corresponds to the stretching vibration of C=C bonds.[29] Finally, the stretching vibration of O–H in surface silanol groups appeared at around 3400 cm^{-1}.[30] The aforementioned peaks clearly indicate that the bridged ionic liquids remained intact during the mesostructure formation and surfactant extraction stages.

Thermogravimetric analysis (TGA) of PMO-IL and the catalyst was achieved in the temperature range 20 to 600 °C under air flow (Figures 4 and 5). The TG patterns showed a weight loss of approximately 3–6 % in the range 20 to 100 °C, which could be correlated to the desorption of water and ethanol remaining from the solvent extraction process. The absence of any remarkable weight losses from around 100 to 300 °C also indicated that the used surfactant was carefully washed in the extraction process. Furthermore, the samples displayed major weight losses of 20 % at 300–500 °C, which could be attributed to the loss of bridged ionic liquid precursors from the material networks.

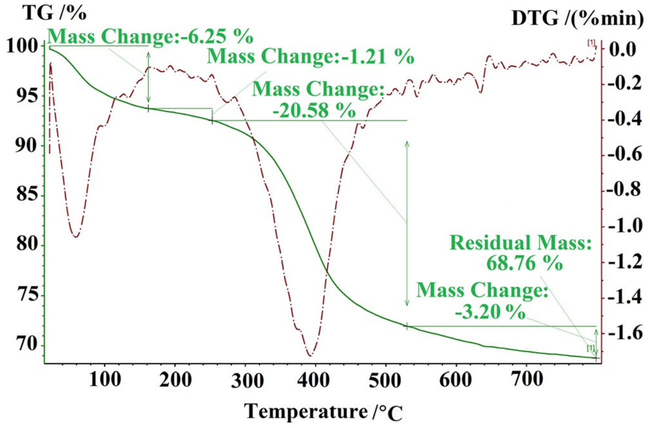


Figure 4. Thermogravimetric analysis of PMO-IL.

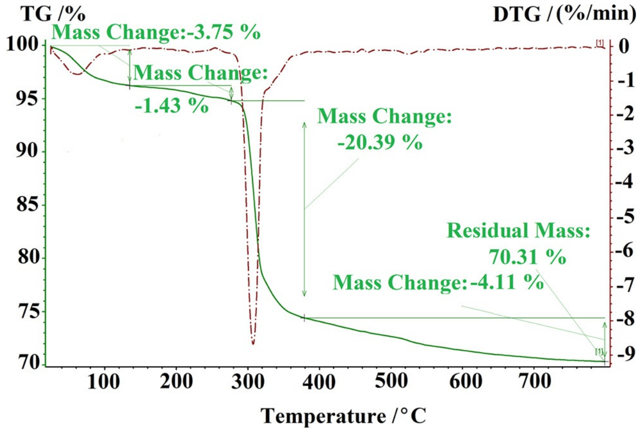


Figure 5. Thermogravimetric analysis of Cu@PMO-IL.

The coordination geometry of the copper ion was studied by diffuse reflectance UV/Vis spectroscopy (DR UV/Vis) (Figure 6). The sample showed an absorption band at 220 nm, which was ascribed to the imidazolium cation. Besides this band, for Cu@PMO-IL, two other peaks were observed at 290 and 400 nm, which were assigned to the $CuCl_4^{2-}$ species.[31] It could be deduced that the copper ion was introduced to the materials through the formation of a $CuCl_4^{2-}$ complex. Hence, the loading of ionic liquid in the materials was calculated to be 1 mmol g^{-1}, which was further confirmed by elemental analysis (Table 1). Finally, the copper content in the Cu@PMO-IL was determined to be 0.7 mmol g^{-1} by using atomic absorption spectroscopy (AAS) and induced coupled plasma (ICP) techniques.

After the initial characterization of Cu@PMO-IL, we investigated the possibility of Cu@PMO-IL as a heterogeneous catalyst in the A^3 coupling of amines, aldehydes, and alkynes. The A^3 coupling of benzaldehyde, piperidine, and phenylacetylene was first selected as a model reaction, and the effect of solvents and reaction temperature were evaluated in this model, and for a best comparison all reactions were performed within 24 h. The study indicated that in the different solvents (toluene, CH_3CN, $CHCl_3$, 1,4-dioxane, DMSO, H_2O, and also solvent-free conditions), the best result was obtained using 0.15 mol %

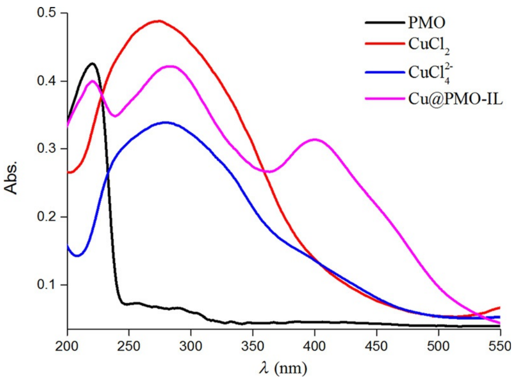
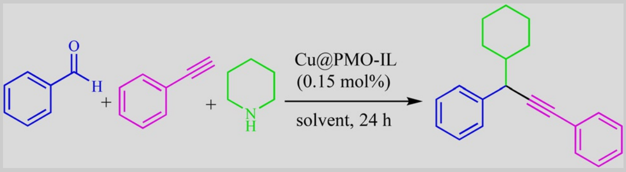


Figure 6. DRS-UV/Vis spectra of PMO (black), $CuCl_2$ (red), $CuCl_4^{2-}$ (blue), and Cu@PMO-IL (violet).

Table 2. Screening of different solvents for the reaction of benzaldehyde, phenylacetylene, and piperidine.[a]



Entry	Solvent	*T* [°C]	Yield [%][b]
1	toluene	60	33
2	toluene	100	63
3	CH_3CN	60	10
4	1,4-dioxane	60	32
5	$CHCl_3$	60	97
6	DMSO	60	trace
7	H_2O	100	trace
8	solvent-free	60	12

[a] Reaction conditions: benzaldehyde (1 mmol), piperidine (1.3 mmol), phenylacetylene (1.2 mmol), Cu@PMO-IL (0.15 mol%), and 2 mL solvent for 24 h. [b] Yield of isolated product. DMSO = dimethyl sulfoxide.

catalyst in $CHCl_3$ at 60 °C (Table 2, entry 5). Interestingly, this finding is in good agreement with our previous report.[25] Encouraged by this promising result, the amount of copper catalyst was optimized. In this regard, it was found that the desired propargylic amine was obtained in 55 and 34% isolated yields in the presence of 0.1 and 0.05 mol% catalyst, respectively; the results showed that 0.15 mol% of catalyst was the most suitable amount for this reaction.

With these optimized conditions, the generality of our catalytic system was also checked in the reaction of phenylacetylene with various aldehydes in the presence of either piperidine or morpholine (Table 3). Remarkably, the A^3 coupling of benzaldehyde, phenylacetylene, and morpholine proceeded to the related product in 96% yield under optimized reaction conditions (Table 3, entry 2). Moreover, the results indicated that various aldehydes containing either electron-releasing or -withdrawing groups such as Me, OMe, *i*Pr OPh, Br, and Cl, can also furnish the related propargylic amines in good to excellent yields (Table 3, entries 3–11). 2-Chloro benzaldehyde, as a relatively sluggish substrate, also afforded the corresponding propargylamines in excellent yields (Table 3, entries 12, 13). Moreover, the presented catalyst showed high activity with regard to aldehydes comprising a heteroaryl moiety. Thus, 2-thiophen carbaldehyde gave the expected propargylamine in 93% yield (Table 3, entry 14). Interestingly, heptanal, as a challenging aliphatic aldehyde, furnished the desired product in excellent yield (Table 3, entry 15). Finally, this reaction was also successful for the coupling of 1-naphthaldehyde with both piperidine and morpholine and phenylacetylene as the carbon nucleophile partner, affording the corresponding propargylic amines in excellent yields (Table 3, entries 16, 17).

We also studied the possibility of recycling the catalyst for the reaction of benzaldehyde with piperidine and phenylacetylene. The results of this study showed that the catalyst is recyclable; seven runs with recycling of the catalyst showed a negligible decrease in catalytic activity (Figure 7).

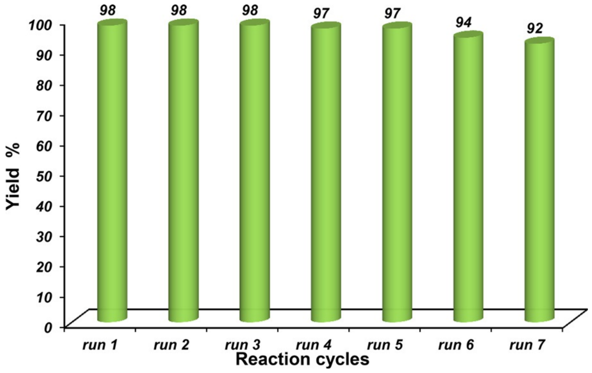
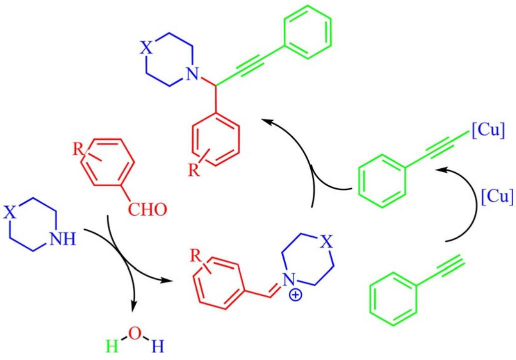


Figure 7. Recyclability of Cu@PMO-IL during A^3 coupling of benzaldehyde, piperidine, and phenylacetylene.

Some analyses were performed to show the recyclability and stability of the catalyst. The N_2 adsorption/desorption analysis indicated that the recovered catalyst showed no change in nanostructure during catalysis progression, and the surface area and pore volume decreased to 427 $m^2 g^{-1}$ and 0.9 $cm^3 g^{-1}$, respectively (Figure C, Supporting Information). Remarkably, the average pore size of the recovered catalyst was essentially retained, which shows the high hydrothermal stability of the catalyst. Also, leaching of copper species after seven runs was determined by ICP analysis to be 2.8%, confirming the stability of the heterogeneous catalyst during the reaction. Moreover, the TG pattern of the recovered catalyst indicated that the catalyst compositions were stable under the reaction conditions used (Figure D, Supporting Information). Also, the DRIFT-IR spectra of the recovered catalyst showed that all of the functional groups were stable and no destruction was observed during the reaction (Figure E, Supporting Information).

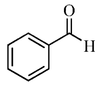
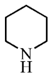
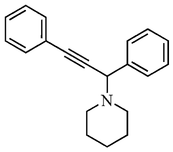
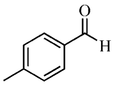
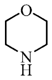
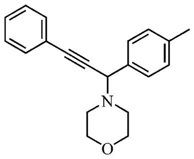
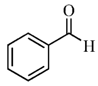
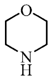
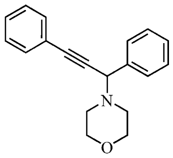
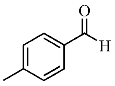
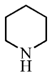
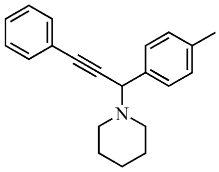
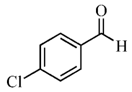
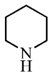
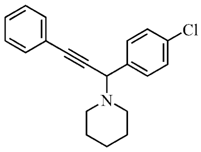
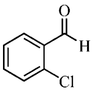
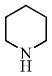
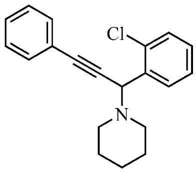
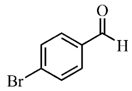
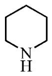
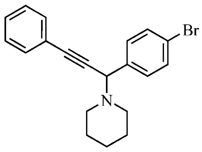
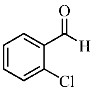
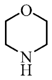
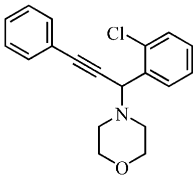
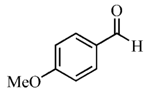
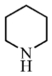
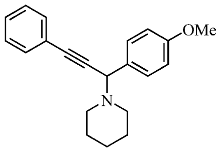
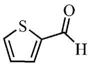
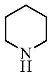
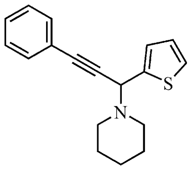
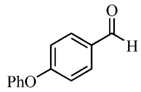
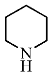
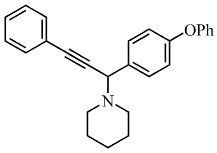
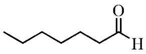
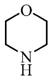
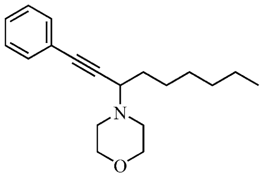
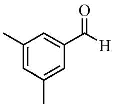
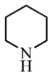
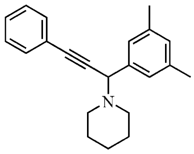
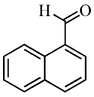
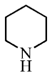
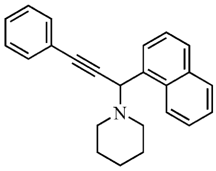
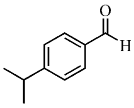
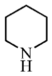
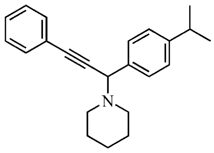
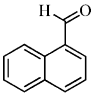
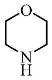
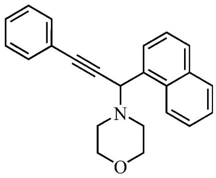
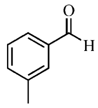
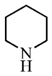
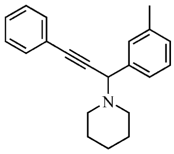
The proposed mechanism for the reaction is the same as the well-known mechanism for the A^3 coupling reaction (Scheme 1). C–H activation of the alkyne by the copper catalyst produces copper acetylide. Then, copper acetylide reacts with the iminium ion produced from the reaction of aldehyde and amine, resulting in the formation of a propargylamine with regeneration of the copper catalyst.[32]

A comparison of the catalytic activity of presented catalyst with some other heterogeneous copper catalysts in the A^3 cou-



Scheme 1. Proposed mechanism for A^3 coupling reaction.

Table 3. Reactions of structurally different aldehydes with amines and phenylacetylene.[a]

Entry	ArCHO	R_2NH	Product	Yield [%][b]	Entry	ArCHO	R_2NH	Product	Yield [%][b]
1				97	10				97
2				96	11				98
3				99	12				98
4				88	13				97
5				94	14				93
6				96	15				94
7				82	16				89
8				87	17				86
9				93					

[a] Reaction conditions: aldehyde (1 mmol), piperidine or morpholine (1.3 mmol), phenylacetylene (1.2 mmol), Cu@PMO-IL (0.15 mol%), and 2 mL $CHCl_3$ for 24 h. [b] Yield of isolated product.

pling of benzaldehyde, morpholine, and phenylacetylene are presented in Table 4. The results indicate that with Cu@PMO-IL as the catalyst, the reaction affords an excellent isolated yield under comparable and mild reaction conditions.

Table 4. Comparison of catalytic activity of Cu@PMO-IL with other heterogeneous copper catalysts in A^3 coupling reaction.

Catalyst	Mol % cat.	T [°C]	Yield [%][b]
Silica-CHDA-Cu[17]	1	80	92[a]
$Cu(OH)x$-Fe_3O_4[18]	0.1	120	99
CuNPs/TiO_2[15j]	0.5	70	91
Cu^0-Mont.[21]	0.05	110	90
GO-$CuCl_2$[15g]	0.6	90	96
CuNPs/MagSilica[15n]	1.1	100	84
SiO_2-NHC-CuI[15]	2	RT	71
MCM-TSCuI[19]	3	80	92
$[Cu(N_2S_2)]Cl$-Y[15h]	3	70	90
Polymer-anchored copper (II) complex[15i]	3	110	82[a]
Cu@PMO-IL	0.15	60	96

[a] With piperidine. [b] Yield of isolated product.

Conclusion

In summary, copper supported on periodic mesoporous organosilica with alkylimidazolium frameworks (Cu@PMO-IL) was found to be an efficient catalyst for A^3 coupling of aldehydes, amines, and phenylacetylene in the presence of a low amount of copper and under mild reaction conditions. The catalyst was characterized by using suitable analyses such as EDS, TEM, TGA, and DRIFT-IR, as well as N_2 adsorption/desorption analysis and elemental analysis. The catalytic system showed high activity for the one-pot coupling of phenylacetylene, piperidine, or morpholine with various aldehydes, including those containing electron-donating (Me, OMe, *i*Pr, and OPh) or -withdrawing groups (Cl and Br), sterically hindered (2-substituted), aliphatic (Heptanal), and heteroatom (thienyl) species under the same reaction conditions. Moreover, the catalyst could be reused at least seven times without significant loss of catalytic activity.

Experimental Section

General

Thin-layer chromatography was performed on silica gel 254 analytical sheets. Column chromatography was performed on silica gel 60 Merck (230–240 mesh) in glass columns (2 or 3 cm diameter) using 15–30 grams of silica gel per gram of crude mixture. The ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, in $CDCl_3$ using TMS as internal standard. Thermogravimetric analysis (TGA) was conducted from room temperature to 800 °C in an oxygen flow with a NETZSCH STA 409 PC/PG instrument. The structures of the prepared materials were observed by transmission electron microscopy (FEI Tecnai 12 BioTWIN), and were verified further by nitrogen adsorption/desorption analysis (BELsorp-max (Japan)). Energy dispersive spectroscopy (EDS) was performed with a Carl Zeiss ΣiGMA instrument. The compounds were analyzed for C, H, and N with an elemental analyzer system (varioEL CHNS). DRS-UV/Vis spectra were obtained with a PerkinElmer Lambda 25 instrument. The copper content in the catalyst was determined by atomic absorption spectrometry (Varian). DRIFT-IR spectra were recorded with a Bruker Vector 22 instrument after mixing the samples with KBr.

Synthesis of ionic liquid precursor

The ionic liquid precursor was prepared with a few modifications to our last synthetic reports.[24b] In a typical method, a suspension of sodium imidazolide in dry THF was prepared from the reaction of dried imidazole (2 g) and NaH 95 % (0.77 g) at a flame-dried two-necked flask containing dry THF (60 mL) under argon. Trimethoxysilane (5.4 mL) was added and the mixture was heated at reflux for 30 h. Then, the reaction mixture was cooled to room temperature and the THF phase removed under reduced pressure until an oily compound was obtained. Subsequently, 3-chloropropyltrimethoxysilane (5.4 mL) and dry toluene (60 mL) were added and the mixture was heated at reflux for 48 h until an insoluble ionic liquid was obtained in the toluene. The toluene phase was removed, and the ionic liquid phase containing NaCl remained. Then, dry CH_2Cl_2 was added for the precipitation of NaCl. The resulting CH_2Cl_2 phase was transferred to another well-dried two-necked flask, and the organic solvent was removed under reduced pressure until the ionic liquid and unreacted starting materials were obtained. Finally, the ionic liquid was washed with dry toluene to remove the starting materials.

Synthesis of PMO-containing ionic liquid, PMO-IL

PMO-IL was synthesized according to our latest methods. In a typical procedure, Pluronic P123 (1.67 g) was dissolved in a mixture of H_2O (10.5 g) and HCl (2 M, 46.14 g). Then, KCl (8.8 g) was added and the system was stirred until a homogenous solution was obtained. A premixture of ionic liquid (0.86 g) and tetramethoxyorthosilicate (2.74 g) in dry methanol was added to the aforementioned solution and stirred at 40 °C for 24 h. The resulting mixture was aged without stirring at 100 °C for 72 h. The obtained PMO with surfactant was filtered, washed with deionized water, and dried at room temperature. The surfactant was extracted from the PMO-IL by a Soxhlet apparatus by using ethanol (100 mL) and c-HCl (3 mL). In a typical extraction, the as-synthesized PMO (1 g) was washed four times with acidic ethanol over 12 h.

Preparation of Cu@PMO-IL

Cu@PMO-IL was prepared through the direct reaction of copper (II) chloride and imidazolium moieties in the PMO-IL.[28] In a typical procedure, PMO-IL (0.5 g, 1.1 mmol g^{-1}) was added to acetonitrile (10 mL) and sonicated for at least 10 min. $CuCl_2$ (0.15 g, 0.88 mmol) as the Cu precursor (already dissolved in 2 mL acetonitrile) was added gradually to the aforementioned suspension, and the mixture was stirred under reflux conditions for 24 h. The resulting system was filtered and washed with acetonitrile (3 × 10 mL) and acetone (2 × 10 mL), respectively. The resulting yellow solid, denoted as Cu@PMO-IL, was dried at 50 °C.

General procedure for A^3 coupling reaction

The catalyst (2 mg, 0.7 mmol g^{-1} Cu) was added to a mixture of aldehyde (1 mmol), phenylacetylene (1.2 mmol), and amine (1.3 mmol) in chloroform (2 mL), and the solution was stirred at 60 °C for 24 h. After completion of the reaction, the solvent was evaporated under reduced pressure. The crude product was obtained by column chromatography (EtOAc, *n*-hexane) to afford propargylamines in good to excellent yields. The known products were confirmed by ^1H NMR and ^{13}C NMR spectroscopy.

Acknowledgements

We are grateful to the Institute for Advanced Studies in Basic Sciences (IASBS) Research Council.

Keywords: copper · heterogeneous catalysis · mesoporous materials · multicomponent reactions · propargylamine

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Manuscript received: April 19, 2015
Revised: June 17, 2015
Final Article published: July 14, 2015