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Mesoporous silica-supported copper-catalysts for homocoupling reaction of terminal alkynes at room-temperature[†]

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Amine-functionalized mesoporous silica-supported copper catalysts SBA-15@amine–Cu and SBA-15@Oamine–Cu were prepared and proved to be efficient and reusable for homocoupling of terminal alkynes at room temperature with air as the oxidant. SBA-15@amine–Cu exhibited better recyclability than SBA-15@Oamine–Cu. The differences in the catalytic performances of the catalysts could be ascribed to catalyst structure and the interaction between copper and the supports. The as-prepared catalysts were systematically characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), high resolution-transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and nitrogen physical adsorption. The analysis indicated that the mesoporous structure of the materials was retained during the immobilization process. XPS results suggested that the as-prepared catalysts were not obtained by a simple physical adsorption of CuCl on the supports. It is noted that, for aliphatic alkynes, the catalytic activity of SBA-15@amine–Cu is even higher than that of the homogeneous copper catalytic system and that of some previously reported heterogeneous systems.

Introduction

1,3-Divne derivatives are very important building blocks in the fields of natural products,¹ pharmaceuticals,² optical materials, molecular devices, and organic conductors.³ Thus, many efforts have been paid to the development of efficient and selective methods for the synthesis of diyne derivatives. Homocoupling reaction of terminal alkynes is one of the most effective approaches for the preparation of symmetrical diyne compounds.^{4,5} Although several Pd/Cu(1) co-catalysts have been reported to be efficient for the oxidative homocoupling of various alkynes, these systems have the disadvantage of using expensive palladium catalysts.⁶⁻⁹ The Cu(I)/(I)-catalytic system, due to its easy availability, non-toxicity, ease of handling and low cost, has been widely employed to carry out the homocoupling reaction of terminal alkynes first discovered by Glaser in 1869.10-14 However, most of the reported copper-catalyzed systems are homogeneous,^{11,12} with shortcomings such as complicated

product separation, difficult catalyst recycling and product contamination caused by the residual components of the catalysts. In contrast, the heterogeneous systems with solid catalysts have significant advantages in catalyst/product(s) separation and reuse of catalysts.¹⁵ A few efficient catalytic systems for the heterogeneously copper-catalyzed alkyne homocoupling reactions have been reported, including the use of Cu(OH)_x/TiO₂,¹⁴ copper(0) nanoparticles (CuNPs),¹⁶ CuAl-LDHs,¹⁷ Cu^I-USY,¹⁸ and Cu/PEG.¹⁹ However, these protocols still exhibited some limitations. For example, the catalyst could not be reused,¹⁸ large amounts of catalysts (110 mol% for a copper-containing hydrotalcite system¹⁷ and 10-30 mol% for a copper-containing zeolite system¹⁸) were employed, and high temperature (66-110 °C)^{14,16,18} or high pressure of molecular oxygen (>20 atm)²⁰ had to be used. In addition, copper saltcatalyzed homocoupling reactions of aliphatic alkynes, with weak acidity of the acetylenic proton, are always sluggish.^{12,13,16,21-24} Thus, the development of efficient, reusable copper based heterogeneous catalysts is necessary.

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Due to its well-defined micro-structure that forms the basis of uniform active sites of the catalyst and well-controlled steric effects, mesoporous silica material SBA-15²⁵ has been used as support for palladium/copper catalysts in recent years.^{26–29} However, alkyne homocoupling reactions by the copper catalyst immobilized on

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SBA-15 have never been examined. Meanwhile, nitrogen-containing ligands can form stable complexes with Cu and thus show a broad arena for developing novel silica supported copper catalysts. We have long been interested in developing new catalytic systems for C–C bond formation.^{30–33} Triethylenediamine, an effective, inexpensive commercially available ligand, was previously reported to be immobilized on SBA-15 as an efficient and reusable Pd catalyst for the alkyne homocoupling reactions.³³ To further address the issue of whether expensive Pd and/or ammonium salts are essential for achieving high catalytic activity and yield, we present herein the preparation of two kinds of amine-functionalized SBA-15-copper catalysts and their reusable application on the mild and efficient heterogeneous alkyne homocoupling reactions with air as an environmentally benign oxidant.

Experimental section

Reagents and materials

Mesoporous silica SBA-15 was purchased from Fudan University. CuCl, (3-chloropropyl) trimethoxysilane (97%), but-3-yn-2-ol (98%), and phenylacetylene (98%) were obtained from Alfa Aesar. Triethylenediamine (97%), 4-ethynyltoluene (97%), 4-fluorophenylacetylene (98%), but-3-yn-1-ol (97%), 3,3dimethylbut-1-yne (98%), and hex-1-yne (98%) were obtained from Acros. Ethyl acrylate (98%), sodium hydride (70% in oil), bromine (98%), piperazine (98%) and biphenyl (CP) were obtained from Sinopharm Chemical Reagent Co., Ltd. 4-Methoxyphenylboronic acid (98%), 2-methylbut-3-yn-2-ol (98%), and hex-5-yn-1-ol (98%) were purchased from Lancaster. Bromobenzene (98%, Shanghai Qingpu Chemical Reagent Company) and dec-1-yne (98%, International Laboratory, USA) were used as received without any further pretreatment. Lithium aluminium hydride (98%) was purchased from Tianjin Chemical Reagent Co., Ltd. Toluene and dichloromethane were of analytical grade and dried over CaH2 and distilled before use. All other solvents were of analytical grade and used without further purification.

Characterization

The C and N content analyses were conducted on a Vario EL (Elementar). Copper content was analyzed using an IRIS Advantage ER/S inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Jarrel Ash, Franklin, MA, USA). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB 210 X-ray photoelectron spectrometer, using Monochrome MgKa as the excitation source. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/Max 2400 using CuKa radiation with the following operating parameters: 60 mA, 40 kV, and 2θ scanning from 0.5° to 6° for low-angle XRD. Nitrogen physical adsorption was carried out on a Micrometrics ASAP2010 volumetric adsorption analyzer. The Brunauer-Emmett-Teller (BET) surface area was evaluated from data in the relative pressure range from 0.05 to 0.20. The total pore volume of each sample was estimated from the amount adsorbed at the highest P/P^0 (at 0.99). Pore diameters were determined from the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM2010 (JEM2010, JEOL) microscope operated at 200 kV. The conversion was determined by gas chromatography (GC7890II, Techcomp) analysis equipped with a SE-54 column (30 m \times 0.32 mm \times 0.50 µm film thickness) and a flame ionization detector (FID) using biphenyl as an internal standard. The injection temperature, column temperature and detection temperature were set to 280, 240 and 300 °C, respectively.

General procedure for the preparation of 1,4-diazabicyclo[2.2.2]octan-2-ylmethanol 4 (Scheme 1)

Firstly, to a stirred solution of acrylic acid ethyl ester 1 (500 mmol, 53.2 mL) in 90 mL of carbon tetrachloride, bromine (25.9 mL) was added dropwise at room temperature. After being refluxed for 24 h, the solution was cooled and solvent was removed under reduced pressure to get 2,3-dibromopropionic acid ethyl ester 2 in 94% yield.³⁴ Then, 13.5 mL of 2 in 200 mL of toluene, 8 g of piperazine and 39.2 mL of triethylamine, in 120 mL of toluene, were successively introduced into a 500 mL round-bottomed flask and the mixture was heated to 80 °C with magnetic stirring overnight. The mixture was then cooled and the triethylamine hydrobromide was separated off by filtration. After being rinsed with ethyl acetate, the solvents were evaporated from the filtrate under reduced pressure and the residue was distilled at ambient pressure and the ethyl 1,4-diaza-bicyclo-[2.2.2]octane-2-carboxylate 3 was obtained. Finally, 1.4 g of lithium aluminium hydride in a suspension in 15 mL of THF was introduced into a round-bottomed flask and the suspension was cooled to 0 °C using an ice-cold bath. Then, 4.1 g of 3 in 20 mL of THF was slowly added with magnetic stirring and the mixture was stirred at room temperature overnight. The excess hydride was hydrolysed by the slow addition of 1.4 mL of water, 1.4 mL of 15% aqueous sodium hydroxide solution and then a further 1.4 mL of water. The solid was separated off by filtration. After being rinsed with chloroform, the filtrate was evaporated under reduced pressure. After distillation, the oily 1,4-diaza-bicyclo[2.2.2]octan-2-ylmethanol 4 product was obtained.35

Preparation of SBA-15@amine-Cu catalyst

SBA-15@Cl and SBA-15@amine were prepared according to the previously reported method.^{28,33} Then, SBA-15@amine (1 g) was refluxed with CuCl (51.5 mg) in acetone at 50 °C for 5 h. After filtration, the solid remains were washed three times each with ethyl ether and methanol, sequentially, and then dried under air. Finally, the yellow powder was collected and designated as SBA-15@amine–Cu (Scheme 2).



Scheme 1 Preparation of 1,4-diaza-bicyclo[2.2.2]octan-2-ylmethanol.



Scheme 2 Procedures for the preparation of SBA-15@amine-Cu and SBA-15@Oamine-Cu.

Preparation of SBA-15@Oamine-Cu catalyst

9.95 mmol of sodium hydride in a suspension in 30 mL of THF was introduced into a 50 mL round-bottomed flask and the suspension was cooled to 0 °C using an ice-cold bath under an argon atmosphere, then 7.65 mmol of 1,4-diaza-bicyclo-[2.2.2]octan-2-ylmethanol in 10 mL of THF was slowly introduced into the above flask and the mixture was stirred at room temperature for 2.5 h. The obtained reaction mixture was introduced into another flask in which 2.5 g of SBA-15@Cl and 25 mL of THF already existed. After being refluxed at 65 °C for 24 h, the mixture was cooled to room temperature, and then washed with THF, water, CH_2Cl_2 and methanol respectively. Finally, the cake was dried under vacuum at 60 °C overnight. The obtained solid was designated as SBA-15@Oamine. The preparation approach of SBA-15@Oamine-Cu was similar to that of the SBA-15@amine-Cu catalyst (Scheme 2).

Typical procedure for the homocoupling reactions of terminal alkynes

A mixture of alkyne (0.2 mmol), catalyst (5 mol%), and piperidine (1 mL) was stirred at room temperature under an air atmosphere for the desired time until complete consumption of starting material as judged by TLC and GC analysis, which usually took 4–24 h. After the first reaction cycle, the catalyst was recovered simply by centrifugation and filtration. After being washed with ethyl acetate three times and dried under vacuum, the recovered catalyst was directly used for the next cycle.

Results and discussion

Characterization of the catalyst

The amount of triethylenediamine in SBA-15@amine-Cu and SBA-15@Oamine-Cu evaluated by the nitrogen content is 0.34



Fig. 1 XPS analysis on Cu $2p_{3/2}$ of (a) fresh SBA-15@amine-Cu catalyst; (b) SBA-15@amine-Cu catalyst after the sixth reaction cycle; (c) SBA-15@Oamine-Cu.

and 0.55 mmol g^{-1} , and the amount of Cu determined by ICP-AES is 0.33 and 0.54 mmol g^{-1} , suggesting that Cu species have been successfully loaded onto the functionalized SBA-15. This might be attributed to the easy access of Cu species to anchored limited steric hindrance triethylenediamine, with chelating nitrogen atoms at its ends. Fig. 1 exhibits the XPS analysis of the SBA-15@Oamine-Cu and SBA-15@amine-Cu catalyst before and after the sixth reaction cycle. The binding energy (BE) of Cu 2p_{3/2} was located at 933.7 eV corresponding to Cu(1) for fresh SBA-15@amine-Cu and SBA-15@Oamine-Cu catalysts (Fig. 1a and c). The BE value of Cu 2p_{3/2} of the catalyst (933.7 eV, Fig. 1b) almost remained unchanged after the sixth reaction cycle. In addition, compared with the BE value of Cu 2p_{3/2} of CuCl (932.6 eV, reported by Wagner),³⁶ the relatively large negative BE shift of Cu(1) indicated that the SBA-15@amine-Cu and SBA-15@Oamine-Cu catalysts were not obtained by a simple physical adsorption of CuCl on the amine-functionalized SBA-15. Thus we speculated that triethylenediamine may act as a ligand stabilizing the Cu species with a strong chelate interaction.

To get more accurate details of the structural change in the catalyst preparation, the SBA-15 backbone of each synthetic step was monitored by N_2 sorption. The N_2 sorption isotherms and pore size distributions of modified SBA-15 at the different stages are shown in Fig. 2 and 3 respectively. A summary of surface area, pore volume and pore size is listed in Table 1.

Based on these results, SBA-15 exhibited a type-IV isotherm pattern with an H1 hysteresis loop, which is characteristic of the mesoporous structure. Similar to the parent SBA-15, SBA-15@amine showed a type-IV isotherm with an H1 hysteresis loop, indicating that the mesoporous structure was maintained after modification, while the values of the surface area and pore volume became smaller with introduction of the silane ((3-chloropropyl) trimethoxysilane) and triethylenediamine as expected. The pore size of SBA-15@amine–Cu and SBA-15@Oamine–Cu catalysts decreased after anchoring of Cu, suggesting the presence of the complex inside the channels of SBA-15 in some extent. In addition, the mesoporous structure for



Fig. 2 N_2 sorption isotherms: (a) SBA-15; (b) SBA-15@amine; (c) SBA-15@amine–Cu; (d) SBA-15@amine–Cu after the sixth use; (e) SBA-15@Oamine–Cu.



Fig. 3 Pore size distribution: (a) SBA-15; (b) SBA-15@amine; (c) SBA-15@amine–Cu; (d) SBA-15@Oamine–Cu.

 $\label{eq:solution} \begin{array}{l} \mbox{Table 1} & N_2 \mbox{ sorption results of SBA-15, SBA-15@amine, SBA-15@amine_Cu, SBA-15@amine_Cu after the sixth use and SBA-15@Oamine_Cu \\ \end{array}$

Samples	$S^{a}/m^{2} g^{-1}$	$V^b/\mathrm{cm}^3~\mathrm{g}^{-1}$	Pore size ^c /nm	Decrease in pore size ^{<i>d</i>} /nm
SBA-15	554.7	0.83	6.0	_
SBA-15@amine	392.7	0.60	5.8	0.2
SBA-15@amine-Cu	389.4	0.59	5.7	0.3
SBA-15@amine–Cu after the sixth use	270.0	0.43	5.6	0.4
SBA-15@Oamine-Cu	383.9	0.61	5.9	0.1

^{*a*} BET surface area. ^{*b*} Single point pore volume calculated at a relative pressure P/P^0 of 0.99. ^{*c*} BJH method from the adsorption branch. ^{*d*} The decreased value of pore diameter, compared with the pore size of the parent SBA-15.

the aforementioned catalysts was still well maintained, as evidenced by its type-IV isotherm with an H1 hysteresis loop.

XRD analysis of SBA-15 before and after the modification both show three peaks, a strong peak at 0.8° and two weak peaks at around 1.45° and 1.65° , which were assigned to 100, 110 and 200 reflections. These results indicated the presence of



Fig. 4 Low-angle XRD patterns of (a) SBA-15; (b) SBA-15@amine–Cu; (c) SBA-15@Oamine–Cu; and (d) SBA-15@amine–Cu after the third use.



Fig. 5 HRTEM images of the SBA-15@amine-Cu.

periodic arrangement of channels in a hexagonal geometry (Fig. 4),³⁷ and this is the direct evidence that the mesoporous structure was kept well after introduction of triethylenediamine and Cu. HRTEM images of SBA-15@amine-Cu show clearly the regular meso-structure (Fig. 5). It reveals that the hexagonal symmetry of the pore arrays is still conserved after the immobilization (Fig. 5). This result is consistent with the conclusion given by other techniques shown above.

Homocoupling reaction of terminal alkynes

Phenylacetylene (1a) was chosen as a model substrate for screening the reaction conditions (Table 2). The efficiency of

Table 2 Effects of reaction parameters on the homocoupling reaction of phenylacetylene $(1a)^a$

Entry	Solvent	Base	Oxidant	Time (h)	Yield ^b (%)
1	CH ₃ CN	Triethylenediamine	O_2	24	60
2	CH ₃ CN	Triethylenediamine	Air	24	58
3	CH ₃ CN	K_2CO_3	O_2	24	0
4	CH ₃ CN	Et ₃ N	O_2	24	0
5	CH ₃ CN	NMP	O_2	24	0
6	CH ₃ CN	Piperidine	O_2	24	94
7	Piperidine	_	$\overline{O_2}$	15	82
8	Piperidine	_	Air	15	99
9 ^c	Piperidine	_	Air	15	75
10^d	Piperidine	_	Air	15	78
11^e	Piperidine	_	Air	15	76
12^{f}	Piperidine	_	Air	15	99

^{*a*} Reaction conditions: **1a** (0.2 mmol), base (1 eq.), SBA-15@amine–Cu (1 mol%), and solvent (1 mL) at room temperature. ^{*b*} Determined by GC using biphenyl as internal standard. ^{*c*} The mixture of SBA-15@amine/CuCl as the catalyst. ^{*d*} The mixture of SBA-15-Cl/triethylenediamine/CuCl as the catalyst. ^{*e*} CuCl as the catalyst. ^{*f*} SBA-15@Oamine–Cu as the catalyst.

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the as-prepared SBA-15@amine-Cu catalyst was firstly evaluated in the presence of CH₃CN and triethylenediamine at room temperature. When 1 mol% of SBA-15@amine-Cu was used, either O_2 (1 atm) or air as the oxidant, the corresponding product 2a was obtained in moderate yield (entries 1 and 2). Next, different bases were evaluated in the presence of O₂ (1 atm) (entries 3-5). Piperidine as the base gave a 94% yield of desired product 2a, while no product 2a was found when K₂CO₃, Et₃N or 1-methyl-2-pyrrolidinone (NMP) was used (entry 5 vs. entries 1, 3-5). Interestingly, when piperidine was chosen as both solvent and base, 82% yield of desired product 2a could still be obtained at a relatively shorter reaction time (entry 7 vs. entry 6). It was noteworthy that better efficiency could be observed by using air as the oxidant with piperidine as both solvent and base (entry 8 vs. entry 7). According to the reported possible reaction mechanism of homocoupling, which involves the formation of alkynyl-cuprate(1) and then smooth oxidative dimerization with oxygen to the corresponding 1,3-divne product,²⁴ the reason for the higher activity observed under air with respect to O₂ might be that molecular oxygen from air as the oxidant was more beneficial to the catalytic cycle of the homocoupling than pure O₂. Moreover, with either the mixture of SBA-15@amine and CuCl, or the mixture of SBA-15@Cl, triethylenediamine and CuCl, or CuCl as the catalyst, lower yield of desired product 2a would be obtained (entries 9-11). The results might be attributed to the following reasons: (1) SBA-15 with well-defined micro-structure benefits formation of uniform active sites of the catalyst; (2) triethylenediamine, a spindle-shaped molecule with two nitrogen atoms located at the both tips, was used as a ligand to minimize hindrance for reactants approaching the copper active sites, which facilitates the reaction. Therefore, the copper active species immobilized onto the triethylenediamine ligand functionalized SBA-15 is more favourable for the catalytic cycle of the homocoupling of terminal alkynes. Furthermore, all of the three above mentioned catalysts could not be reused any more. When SBA-15@Oamine-Cu was used as the catalyst, a considerable yield could also be obtained (entry 12).

To evaluate the substrate scope, we examined the protocol by employing various terminal alkynes under the optimized conditions (Table 3). The reactions of aromatic alkynes with both an electron-withdrawing group (-F) and an electrondonating group (-CH₃) provided the corresponding 1,3-divnes in high yields in the presence of 5 mol% SBA-15@amine-Cu for 4 h (entries 2 and 3). No dehalogenation proceeded in the case of halogen-substituted ethynylbenzene derivative 1b, providing an opportunity for further functionalization of the product diyne (entry 2). The reaction of the OH-containing aliphatic alkyne (1d) also proceeded smoothly to give the corresponding diyne (2d) (Table 3, entry 4). It is noteworthy that less reactive aliphatic C6-C10 alkynes^{16,18,21,22} of 3,3-dimethylbut-1-yne (1e), 1-decyne (1f), and 1-hexyne (1g) were successfully converted into the corresponding diynes (2e-g) in high yields (87%-100%, entries 5-7). Furthermore, the present system could be applied to the homocoupling of the halogen-containing linear aliphatic alkyne 5-chloropent-1-yne (1h), selectively affording

Entry	Substrate	Product	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	(2a	4	100 (97) ^c
2	F	F	4	100 (95) ^c
3		-<	4	94 (89) ^c
4		<u>— — — — — — — — — — — — — — — — — — — </u>	18	100 (94) ^c
5		$\rightarrow = = \langle_{2e}$	24	87 (83) ^c
6	<i>n</i> −C ₈ H ₁₇ − = 1f	$n - C_8 H_{17} C_8 H_{17} - n$ 2f	24	100 (90) ^c
7	n-C₄H9 — — 1g	$n - C_4 H_9 C_4 H_9 - n$ 2g	24	91 (88) ^c
8	Cl(CH ₂) ₃ —== 1h	CI(CH ₂) ₃ ———(CH ₂) ₃ C 2h	24	83 (80) ^c

^{*a*} Reaction conditions: **1** (0.2 mmol), SBA-15@amine–Cu (5 mol%) and piperidine (1.0 mL) at room temperature under air. ^{*b*} Determined by GC using biphenyl as internal standard. ^{*c*} Isolated yield.

the corresponding diyne (**2h**) in high yield, which gives an opportunity for further functionalization at the intact chloride group in the diyne product (Table 3, entry 8). Overall, the present SBA-15@amine-Cu-air catalytic system proved to have broad substrate scopes, both aliphatic and aromatic alkynes underwent oxidative homocoupling reactions to give the desired 1,3-diynes in good to excellent yields (83%-100%). And several functional groups, including -OH, -F, -Cl and -CH₃, are all compatible with the reaction conditions.

Recycling of SBA-15@amine-Cu and SBA-15@Oamine-Cu catalysts

Next, we turned our attention to the reusability of the present Cu-supported catalysts. Both the SBA-15@amine–Cu and SBA-15@Oamine–Cu catalysts could be easily separated from the reaction mixture by simple filtration. The recovered catalyst was then reused for the oxidative dimerisation of phenyl acetylene under the same conditions as those of the first run (Table 4). After the third run, the SBA-15@amine–Cu catalyst still exhibited high activity with a slight decrease in the yield, while the yield dropped to 81% for 4 h and good yield was still obtained with longer reaction time (12 h) in the 6th run. Meanwhile, the activity of the SBA-15@Oamine–Cu catalyst was less than that of the SBA-15@amine–Cu catalyst and only 65% yield was obtained for 8 h after the fifth run. As shown in Fig 4d, the XRD of the recovered SBA-15@amine–Cu after the third run

Table 4 Recycling study of the SBA-15@amine-Cu catalyst^a



 a Reaction conditions: **1a** (0.5 mmol), SBA-15@amine–Cu (5 mol%) and piperidine (2.5 mL) at room temperature under air. b Determined by GC using biphenyl as internal standard. c SBA-15@Oamine–Cu (5 mol%) as the catalyst. d 6 h. e 8 h. f 12 h.

still exhibited three well-resolved diffraction peaks which were similar to that of the fresh SBA-15@amine-Cu catalyst, indicating that the well-defined hexagonally ordered structure of the catalyst was not destroyed during the reusability test. In addition, after the third run, the copper content of the SBA-15@amine-Cu catalyst decreased from 0.33 to 0.25 mmol g^{-1} as determined by ICP-AES, indicating that the catalyst used was somewhat unstable, but still active. Moreover, the mesoporous structure of SBA-15@amine-Cu was still maintained after the 6th run, as evidenced by its type-IV isotherm with an H1 hysteresis loop (Fig. 2), which explicated the fact that the SBA-15@amine-Cu catalyst could be reused with stable catalytic activity. In contrast, SBA-15@Oamine-Cu showed worse reusability than the SBA-15@amine-Cu catalyst, and after its fifth use, the homocoupling yield of phenyl acetylene decreased to 65%. The differences in the catalytic performances of the catalysts could be ascribed to catalyst structure and the interaction between copper and the supports. For the SBA-15@Oamine-Cu catalyst, the oxygen atom might also be coordinated with copper, and thus hindered the substrate near the active copper species. In addition, the amounts of copper coordinated with oxygen increased as the balance exchange of Cu with the ligand proceeds, which further made it less effective. Therefore, the activity of the SBA-15@Oamine-Cu catalyst is less effective than that of the SBA-15@amine-Cu catalyst. From the perspective of sustainable development, the SBA-15@amine-Cu which could be reused at least four times would be the best choice.

Furthermore, several new experimental supplements have been done to investigate the efficiency of the catalyst. As shown in Table 5, the catalyst could be recycled from one substrate and then used for homocoupling another, without the contaminating products from the previous reaction(s). After being used for three different substrates (**1a**, **1c**, **1b**), respectively, the catalyst could still be used for the first substrate **1a**, and 86%

Table 5	ble 5 Efficiency of the SBA-15@amine–Cu catalyst ^a				
Run		1	2	3	4
Substrat Yield ^b (9	te %)	1a 100	1c 99	1b 97	1a 86 ^c

^{*a*} Reaction conditions: **1** (0.5 mmol), SBA-15@amine-Cu (5 mol%) and piperidine (2.5 mL) at room temperature under air for 4 h. ^{*b*} Determined by GC using biphenyl as internal standard. ^{*c*} 12 h.

yield of the desired product was obtained with a longer reaction time (12 h). This experimental result further proved that the catalyst could be recycled.

Conclusions

In summary, two air-stable mesoporous silica SBA-15-supported amine-copper catalysts, SBA-15@amine-Cu and SBA-15@Oamine-Cu, have been synthesized and well characterized. SBA-15@amine-Cu, an efficient heterogeneous catalyst, readily available from inexpensive reagents, was successfully applied on dimerization of a variety of alkynes (including aromatic alkynes and demanding aliphatic alkynes) affording corresponding divnes at room temperature, with air as the oxidant. The advantage of the heterogeneous catalysts lied in the ease of separation and recyclability provided by the catalyst support. The SBA-15@amine-Cu catalyst could be reused at least four times with a slight decrease in activity for the homocoupling reaction. It is noted that, for aliphatic alkynes, the catalytic activity of SBA-15@amine-Cu is even higher than that of the homogeneous copper catalytic system and that of the previously reported heterogeneous systems.^{11,12,18} Efforts to extend the applications of this catalyst to other transformations are underway in our laboratory.

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Notes and references

- 1 A. L. K. Shi Shun and R. R. Tykwinski, *Angew. Chem., Int. Ed.*, 2006, **45**, 1034.
- 2 Y. Z. Zhou, H. Y. Ma, H. Chen, L. Qiao, Y. Yao, J. Q. Cao and Y. H. Pei, *Chem. Pharm. Bull.*, 2006, **54**, 1455.
- 3 M. B. Nielsen and F. Diederich, Chem. Rev., 2005, 105, 1837.
- 4 P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 2632.
- 5 H. A. Stefani, A. S. Guarezemini and R. Cella, *Tetrahedron*, 2010, **66**, 7871.
- 6 D. A. Alonso, C. Najera and M. C. Pacheco, *Adv. Synth. Catal.*, 2003, **345**, 1146.
- 7 A. S. Batsanov, J. C. Collings, I. J. S. Fairlamb, J. P. Holland,
 J. A. K. Howard, Z. Y. Lin, T. B. Marder, A. C. Parsons,
 R. M. Ward and J. Zhu, *J. Org. Chem.*, 2005, **70**, 703.
- 8 F. Yang, X. Cui, Y. Li, J. Zhang, G. Ren and Y. Wu, *Tetrahedron*, 2007, **63**, 1963.
- 9 J.-H. Li, Y. Liang and Y. X. Xie, J. Org. Chem., 2005, 70, 4393.
- 10 C. Glaser, Ber. Dtsch. Chem. Ges., 1869, 2, 422.
- 11 K. Yin, C.-J. Li, J. Li and X.-S. Jia, *Appl. Organomet. Chem.*, 2011, 25, 16.
- 12 S. Adimurthy, C. C. Malakar and U. Beifuss, *J. Org. Chem.*, 2009, **74**, 5648.

- 13 D. Wang, J. H. Li, N. Li, T. T. Gao, S. H. Hou and B. H. Chen, Green Chem., 2010, 12, 45.
- 14 K. Yamaguchi, T. Oishi, T. Katayama and N. Mizuno, *Chem.-Eur. J.*, 2009, **15**, 10464.
- 15 R. A. Sheldon and H. van Bekkum, *Fine chemical through heterogeneous catalysis*, Wiley, Weinheim, 2001.
- 16 F. Nador, L. Fortunato, Y. Moglie, C. Vitale and G. Radivoy, *Synthesis*, 2009, 4027.
- 17 B. C. Zhu and X. Z. Jiang, Appl. Organomet. Chem., 2007, 21, 345.
- 18 P. Kuhn, A. Alix, M. Kumarraja, B. Louis, P. Pale and J. Sommer, *Eur. J. Org. Chem.*, 2009, 423.
- 19 X. Lu, Y. Zhang, C. Luo and Y. Wang, Synth. Commun., 2006, 36, 2503.
- 20 S. M. Auer, M. Schneider and A. Baiker, J. Chem. Soc., Chem. Commun., 1995, 2057.
- 21 H. Jiang, J. Tang, A. Wang, G. Deng and S. Yang, *Synthesis*, 2006, 1155.
- 22 J. Li and H. Jiang, Chem. Commun., 1999, 2369.
- 23 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1988, ch. 10.
- 24 F. Bohlmann, H. Schönowsky, E. Inhoffen and G. Grau, *Chem. Ber.*, 1964, **97**, 794.

- 25 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.
- 26 N. C. Mehendale, J. R. A. Sietsma, K. P. De Jong, C. A. Van Walree, R. J. M. K. Gebbink and G. Van Koten, *Adv. Synth. Catal.*, 2007, **349**, 2619.
- 27 J. M. Richardson and C. W. Jones, J. Catal., 2007, 251, 80.
- 28 C. M. Crudden, M. Sateesh and R. Lewis, J. Am. Chem. Soc., 2005, 127, 10045.
- 29 X. J. Feng, M. Yan, T. Zhang, Y. Liu and M. Bao, *Green Chem.*, 2010, **12**, 1758.
- 30 Z. S. Wu, M. Yang, H. L. Li and Y. X. Qi, Synthesis, 2008, 1415.
- 31 H. L. Li, Z. S. Wu, M. Yang and Y. X. Qi, Catal. Lett., 2010, 137, 69.
- 32 H. L. Li, M. Yang, Y. X. Qi and J. J. Xue, *Eur. J. Org. Chem.*, 2011, 2662.
- 33 H. L. Li, M. Yang and Q. S. Pu, *Microporous Mesoporous Mater.*, 2012, 148, 166.
- 34 S. D. Sharma, S. Kanwar and S. Rajpoot, J. Heterocycl. Chem., 2006, 43, 11.
- 35 A. Lochead, S. Jegham, A. Nedelec and A. Solignac, US006057321A, 2000.
- 36 C. D. Wagner, Faraday Discuss. Chem. Soc., 1975, 60, 291.
- 37 P. Han, H. M. Zhang, X. P. Qiu, X. L. Ji and L. X. Gao, J. Mol. Catal. A: Chem., 2008, 295, 57.