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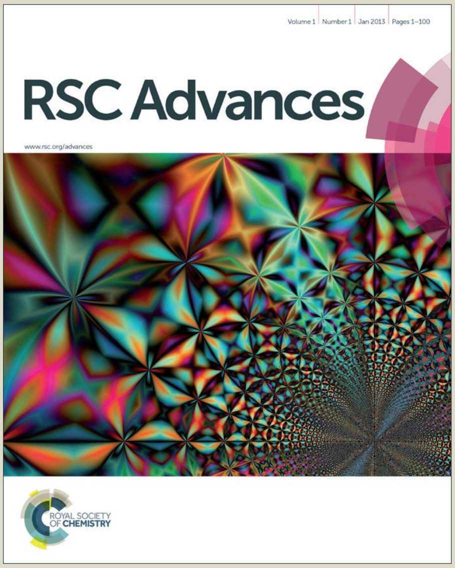

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MCM-41-immobilized 1,10-phenanthroline-copper(I) complex: A highly efficient and recyclable catalyst for the coupling of aryl iodides with aliphatic alcohols

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The heterogeneous C–O coupling reaction between aryl iodides and aliphatic alcohols was achieved in neat alcohol or toluene at 110 ºC in the presence of 10 mol% of MCM-41-immobilized 1,10-phenanthroline-copper(I) complex [MCM-41-1,10-Phen-CuI] with Cs_2CO_3 as base, yielding a variety of aryl alkyl ethers in good to excellent yields. The new heterogeneous copper catalyst can easily be prepared by a simple procedure from commercially available and inexpensive reagents, and recovered by filtration of the reaction solution and recycled for at least 8 times without significant loss of activity.

Introduction

Aryl alkyl ethers are important structures that are often found in many naturally occurring and medicinally relevant compounds[1] and important solvents and synthetic building blocks in organic synthesis.[2] The copper-mediated Ullmann ether synthesis is a classical route for the preparation of these compounds.[3] However, harsh reaction conditions such as high reaction temperatures, the use of strong alkoxide bases, stoichiometric quantities of the copper salts, and the low to moderate yields have

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generally restricted its synthetic applicability. Although palladium-catalyzed C–O bond formation reactions have become effective strategies for their preparation,[4] the drawbacks of the catalyst systems, such as high cost, toxicity, the utilization of environmental unfriendly phosphine ligands, and tedious multistep processes involved in the synthesis of these phosphine ligands often limit their applications in large-scale preparation. In contrast, copper-catalyzed Ullmann coupling between aryl halides and alcohols is an attractive alternative for palladium-catalyzed aryl alkyl ether synthesis due to the relatively low toxicity and cost of the catalyst, as well as a decreased amount of β-H elimination.[5] For these reasons, much effort has been devoted to the development of copper-catalyzed Ullmann C–O coupling reactions for the preparation of aryl alkyl ethers.[6] Although these copper-catalyzed C–O coupling methods are highly efficient for the construction of aryl alkyl ethers, about 10 mol% of copper salts and 20 mol% of ligands are usually utilized to obtain high yields. Moreover, the problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. It is well known that homogeneous catalysis might result in heavy metal contamination of the desired isolated product. These problems are of particular environmental and economic concerns in large-scale syntheses and in industry. To overcome these drawbacks, development of highly efficient heterogeneous catalysts, for example by immobilization of catalytically active species onto an ideal heterogeneous support to generate a molecular heterogeneous catalyst is essential.[7] The heterogenization of C–O coupling catalysts appears to be a logical solution; the use of immobilized catalysts could result

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in easy recovery and recyclability of the copper catalyst, thereby, minimizing copper contamination of the desired isolated products and wastes derived from reaction workup. In spite of some reports on heterogeneous copper-catalyzed C–O coupling between aryl halides and phenols in recent years,[8] to the best of our knowledge, the C–O coupling between aryl halides and aliphatic alcohols catalyzed by heterogeneous copper complexes has not been reported until now.

The discovery of mesoporous MCM-41 materials has provided a new possible candidate for an ideal heterogeneous support for the immobilization of homogeneous catalysts and given an enormous stimulus to research in heterogeneous catalysis.[9] The MCM-41 has high surface area, large and defined pore size, big pore volume and rich silanol groups in the inner channel walls.[10] To date, some functionalized MCM-41-immobilized palladium,[11] rhodium,[12] molybdenum,[13] gold[14] and copper[15] complexes have been prepared and successfully utilized as potentially green and sustainable catalysts in organic synthesis. In continuation of our efforts to develop economical and eco-friendly synthetic pathways for organic transformations,[11d-f,15] herein we wish to report the first preparation of the MCM-41-immobilized 1,10-phenanthroline-CuI complex [MCM-41-1,10-Phen-CuI] and its successful application to C–O coupling reaction between aryl iodides and aliphatic alcohols (Scheme 1). The new heterogeneous copper catalyst exhibits high catalytic activity for the C–O coupling reaction in neat alcohol or toluene with Cs_2CO_3 as base and can easily be recovered by a simple filtration of the reaction solution, and its catalytic efficiency remains unaltered even after recycling eight times.

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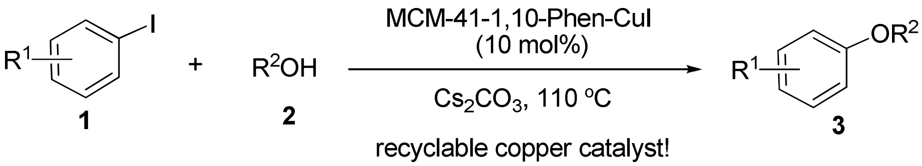
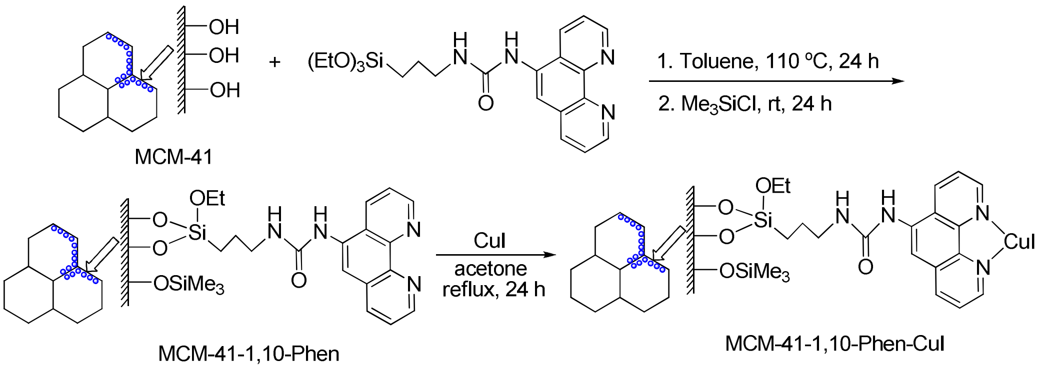


Scheme 1. Heterogeneous Cu-catalyzed C–O coupling between aryl iodides and alcohols.

2. Results and discussion

The new MCM-41-immobilized 1,10-phenanthroline-copper(I) complex [MCM-41-1,10-Phen-CuI] was easily prepared according to the procedure summarized in Scheme 2. Firstly, the mesoporous material MCM-41[16] was treated with 1-(1,10-phenanthrolin-5-yl)-3-(3-(triethoxysilyl)propyl)urea[17] in toluene under reflux for 24 h, followed by the silylation with Me_3SiCl in toluene at room temperature for 24 h to generate the 1,10-phenanthroline-functionalized MCM-41 [MCM-41-1,10-Phen]. The latter was then reacted with CuI in acetone under reflux for 24 h to afford the MCM-41-immobilized 1,10-phenanthroline-copper(I) complex [MCM-41-1,10-Phen -CuI] as a light green powder, the copper content of the catalyst was found to be 0.75 mmol/g according to the ICP-AES measurements.



Scheme 2. Preparation of MCM-41-1,10-Phen-CuI.

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The X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the MCM-41-1,10-Phen-CuI complex are illustrated in Figure 1. Small angle X-ray diffraction of the parent MCM-41 gave three peaks corresponding to hexagonally ordered mesoporous phases. For the MCM-41-1,10-Phen-CuI, the (100) reflection of MCM-41 with decreased intensity was remained after functionalization, while the (110) and (200) reflections became weak and diffuse, which should be attributed to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicate that the structure of the mesoporous material remains unchanged through the grafting procedure and the formation of the catalyst has taken place preferentially inside the pore system of MCM-41. The energy dispersive X-ray spectroscopy (EDS) shows the elements present in the material. EDS analysis of fresh MCM-41-1,10-Phen-CuI complex shows the presence of Si, O, C, N, I, and Cu elements (Figure 2).

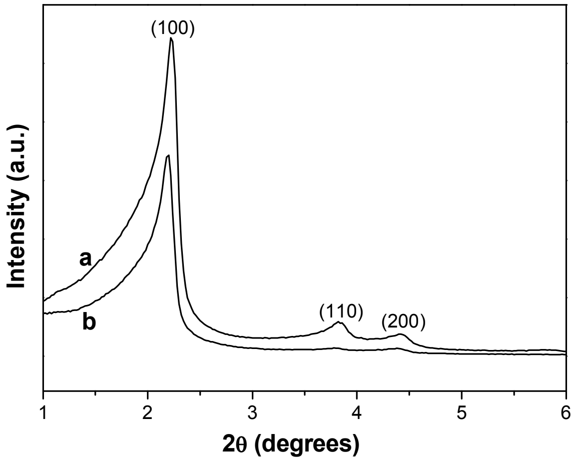

Fig. 1 XRD patterns of MCM-41 (a) and MCM-41-1,10-Phen-CuI (b).

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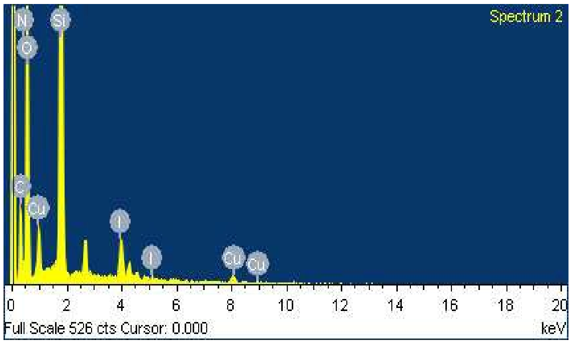

Fig. 2 EDS analysis of MCM-41-1,10-Phen-CuI complex.

In our initial screening experiments, the cross-coupling of 4-methyliodobenzene with butanol was chosen as the model reaction to optimize the reaction conditions, which include base, solvent, and reaction temperature and the results are summarized in Table 1. At first, the solvent effect was examined by using 10 mol% of MCM-41 -1,10-Phen-CuI as catalyst with Cs_2CO_3 as base at 110 ºC (Table 1, entries 1-6). Among the solvents examined, toluene afforded good yield (entry 1), while other solvents such as dioxane, DMSO, DMF and butyronitrile were substantially less effective (entries 2-5). To our delight, when butanol was used as solvent, the reaction proceeded smoothly in neat alcohol to give the desired product **3a** in 92% yield (entry 6). We then turned our attention to investigate the effect of base on the coupling reaction. It is evident that lower yields were obtained when other inorganic bases such as K_2CO_3, Na_2CO_3, and K_3PO_4 were used and organic bases such as piperidine and *n*-Bu_3N were inefficient (entries 7-11). Lowering reaction temperature to 100 ºC resulted in a lower 78% yield (entry 12) and raising reaction temperature to 120 ºC did not improve the yield of the desired product (entry 13). Finally, the amount of the

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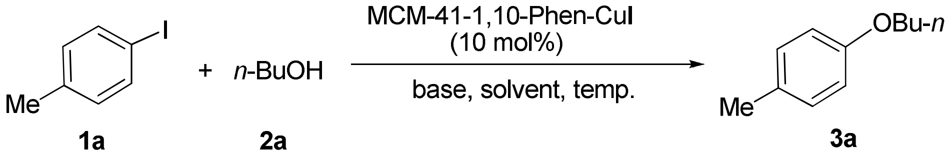
catalyst was also screened and 10 mol% of MCM-41-1,10-Phen-CuI was found to be optimal (entries 6, 14 and 15). To compare with homogeneous copper catalytic system, 10 mol% CuI and 20 mol% 1,10-phenanthroline were used as the catalyst, the desired product **3a** was isolated in 93% yield (entry 16), which indicating that the catalytic activity of the MCM-41-1,10-Phen-CuI complex is comparable to that of the homogeneous analogue. Thus, the optimized reaction conditions for this transformation are the MCM-41-1,10-Phen-CuI (10 mol%) in neat alcohol with Cs_2CO_3 as base at 110 ºC under Ar for 24 h (entry 6).

Table 1 Cross-coupling between 4-methyliodobenzene and butanol in different conditions.[a]



Entry	Base	Solvent	Temp. (ºC)	Yield (%)[b]
1	Cs_2CO_3	toluene	110	84
2	Cs_2CO_3	dioxane	110	33
3	Cs_2CO_3	DMF	110	49
4	Cs_2CO_3	DMSO	110	36
5	Cs_2CO_3	butyronitrile	110	54
6	Cs_2CO_3	*n*-BuOH	110	92
7	K_2CO_3	*n*-BuOH	110	75
8	Na_2CO_3	*n*-BuOH	110	67
9	K_3PO_4	*n*-BuOH	110	46
10	piperidine	*n*-BuOH	110	trace
11	*n*-Bu_3N	*n*-BuOH	110	trace
12	Cs_2CO_3	*n*-BuOH	100	78
13	Cs_2CO_3	*n*-BuOH	120	91

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14[c]	Cs_2CO_3	*n*-BuOH	110	69
15[d]	Cs_2CO_3	*n*-BuOH	110	92
16[e]	Cs_2CO_3	*n*-BuOH	110	93

[a] All reactions were performed using 4-methyliodobenzene (0.5 mmol), *n*-BuOH (1 mmol), base (1 mmol), 10 mol% of MCM-41-1,10-Phen-CuI, solvent (1 mL) under Ar in a sealed tube for 24 h. [b] Isolated yield. [c] 5 mol% of copper catalyst was used. [d] 20 mol% of copper catalyst was used. [e] 10 mol% CuI and 20 mol% 1,10-phenanthroline were used.

With this promising result in hand, we started to examine the scope and limitation of this heterogeneous copper-catalyzed coupling reaction between aryl iodides and aliphatic alcohols under the optimized conditions. Firstly, reactions of aryl iodides with inexpensive primary or secondary alcohols were examined and the results are summarized in Table 2. The butoxylation reactions of a variety of aryl iodides bearing both electron-donating and electron-withdrawing groups with *n*-BuOH (**2a**) proceeded smoothly in neat *n*-BuOH at 110 ºC, leading to the corresponding aryl butyl ethers **3a-3f** in good to excellent yields (78-93%) within 24 h. The results indicated that the electronic effect of substituents on the benzene ring has limited influence on this heterogeneous copper-catalyzed C–O coupling reaction. However, the electron-withdrawing substituent CN seemed to be more sensitive under the optimized coupling conditions, which may be due to the fact that nitriles are also good ligands for copper. When the reaction of 4-iodobenzonitrile was performed in neat *n*-BuOH, a mixture of the corresponding amide and ester as well as other decomposition products was observed even at lower temperature and shorter reaction time. Thus, this reaction was carried out with only 4 equiv of *n*-BuOH in toluene as a solvent for 30 h to afford the desired **3f** in 78% yield. The sterically hindered 2-iodotoluene, 2-nitroiodobenzene

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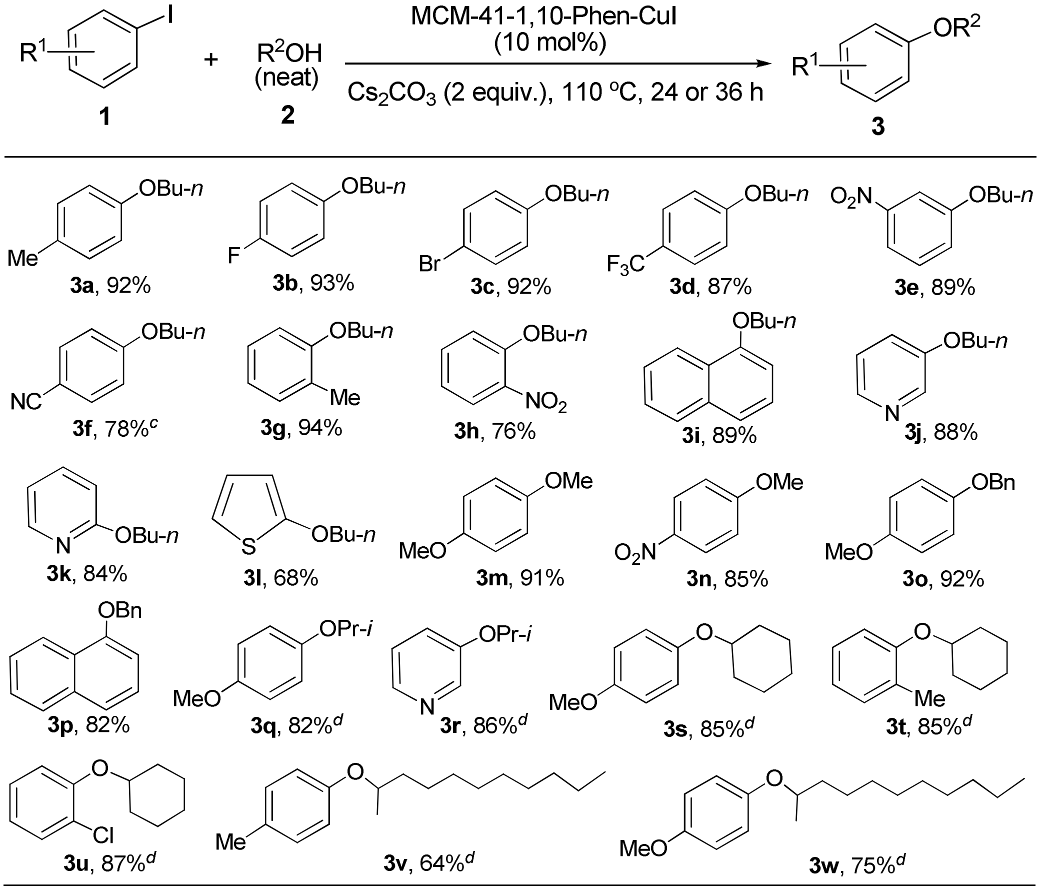
and bulky 1-iodonaphthalene were also coupled with *n*-BuOH effectively to give the corresponding products **3g**, **3h** and **3i** in 94, 76 and 89% yields, respectively. It is noteworthy that heterocyclic substrates such as 2- or 3-iodopyridines and 2-iodothiophene can also be successfully coupled with *n*-BuOH to give the corresponding butyl heteroaryl ethers **3j-3l** in good yields. The C–O coupling reactions of other inexpensive primary alcohols such as methanol and benzyl alcohol with aryl iodides also proceeded smoothly to furnish the corresponding aryl methyl ethers **3m**, **3n** and aryl benzyl ethers **3o**, **3p** in high yields within 24 h. Both strong electron-donating and electron-withdrawing groups on the benzene ring were tolerated well. Encouraged by the above results, we also carried out the reaction of aryl bromides with aliphatic alcohols, unfortunately, aryl bromides were not reactive under the present catalytic system even at elevated temperatures. The similar observation had also been made by Buchwald *et al.* using homogeneous CuI/1,10-phenanthroline system.[6a]

The preparation of aryl alkyl ethers from secondary alcohols and aryl halides represents a more challenging synthetic problem[18] that thus far cannot be generally solved using palladium catalysts due to the presence of β-hydride elimination. Thus, we next examined the possibility of coupling common secondary alcohols that could also serve as solvents under optimized conditions, and the results are listed in Table 2. As shown in Table 2, isopropanol and cyclohexanol could be effectively coupled with aryl or heteroaryl iodides to afford the desired secondary alkyl aryl ethers **3q-3s** in high yields on longer times (36 h). The coupling reactions of sterically hindered 2-iodotoluene and 2-iodochlorobenzene with cyclohexanol also gave the desired products **3t** and **3u** in high yields. Interestingly, 2-undecanol, a long chain secondary alcohol, was also good coupling partner and coupled with aryl iodides smoothly to give the expected long chain secondary alkyl aryl ethers **3v** and **3w** in good yields.

Table 2 Coupling of aryl iodides with primary or secondary alcohols catalyzed by MCM-41-1,10-Phen-CuI[a,b]



3a, 92%
3b, 93%
3c, 92%
3d, 87%
3e, 89%
3f, 78%[c]
3g, 94%
3h, 76%
3i, 89%
3j, 88%
3k, 84%
3l, 68%
3m, 91%
3n, 85%
3o, 92%
3p, 82%
3q, 82%[d]
3r, 86%[d]
3s, 85%[d]
3t, 85%[d]
3u, 87%[d]
3v, 64%[d]
3w, 75%[d]

[a] All reactions were performed using 0.5 mmol of aryl iodide, 1 mL of R^2OH, Cs_2CO_3 (1 mmol), 10 mol% of MCM-41-1,10-Phen-CuI at 110 ºC under Ar in a sealed test tube for 24 or 36 h. [b] Isolated yield. [c] 4 equiv of *n*-BuOH in 1 mL of toluene was used for 30 h. [d] For 36 h.

During our initial screening experiments, we found that toluene was a suitable solvent for the coupling of 4-methyliodobenzene with *n*-BuOH (Table 1, entry 1). For more precious alcohols, it is highly desirable to perform the reaction in a solvent

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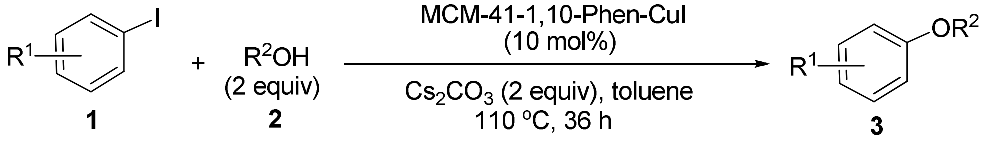
using only a moderate excess of one of the coupling partners. We next carried out the coupling reaction with 0.5 mmol of aryl iodide, 1.0 mmol of alcohol and 1.0 mmol of Cs_2CO_3 in toluene (1 mL) at 110 ºC for 36 h. To demonstrate the scope of this heterogeneous copper-catalyzed method, allylic alcohols, substituted benzyl alcohols, and pyridine-3-methanol were used as substrates and the results are listed in Table 3. Considering the fact that *para*-substituted electron-rich aryl halides are poor substrates for the corresponding palladium-catalyzed transformations, we chose 4-iodoanisole as the aromatic coupling partner for the allylic alcohols. As shown in Table 3, the primary allylic alcohols gave the corresponding allyl aryl ethers **3x** and **3y** in high yields. The electron-rich *p*-, *m*-, or *o*-iodotoluenes were also good substrates for 4-methylbenzyl alcohol and afforded the corresponding aryl 4-methylbenzyl ethers **3z-3b'** in good yields. It is noteworthy that the coupling reactions of sterically hindered 2-methylbenzyl alcohol with the electron-rich 4-iodoanisole or 4-iodotoluene in toluene could proceed smoothly to give the coupling products **3c'** and **3d'** in 94 and 79% yields, respectively. The reaction of pyridine-3-methanol with 4-iodoanisole furnished the desired **3e'** in 65% yield. Interestingly, the coupling reaction between both sterically hindered substrates, 2-chloroiodobenzene and 2-methylbenzyl alcohol in toluene also proceeded effectively to provide the corresponding ether **3f'** in good yield.

Table 3 Heterogeneous copper-catalyzed coupling of aryl iodides with aliphatic alcohols using toluene as solvent.[a,b]



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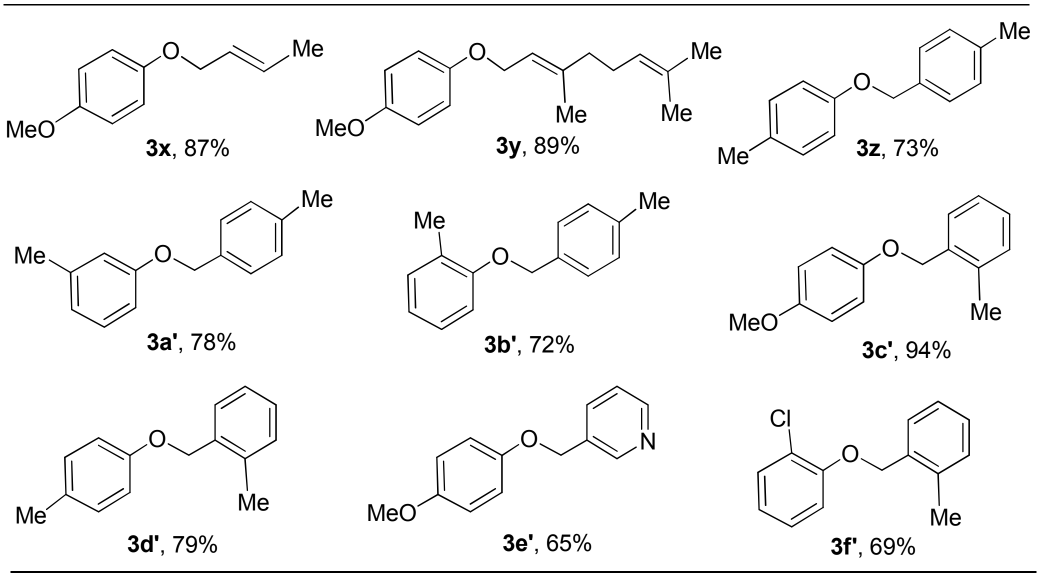

[a] All reactions were performed using 0.5 mmol of aryl iodide, 1 mmol of R^2OH, 1 mmol of Cs_2CO_3, 10 mol% of MCM-41-1,10-Phen-CuI in toluene (1 mL) at 110 ºC under Ar in a sealed test tube for 36 h. [b] Isolated yield.

To determine whether the observed catalysis was due to the heterogeneous catalyst MCM-41-1,10-Phen-CuI or to a leached copper species in solution, the reaction of 4-methyliodobenzene (**1a**) with butanol (**2a**) was carried out until an approximately 50% conversion of **1a** was reached. Then the MCM-41-1,10-Phen-CuI catalyst was removed from the reaction mixture by hot filtration[19] and the filtrate was again stirred in a sealed tube at 110 ºC under Ar atmosphere for 20 h. In this case, no significant increase in conversion was observed, demonstrating that leached copper species from the supported catalyst (if any) are not responsible for the observed catalysis. It was confirmed by ICP-AES analysis that no copper species could be detected in the filtrate (below the detection limit). These results indicated that the catalyst was stable during the reactions and the observed catalysis was intrinsically heterogeneous.

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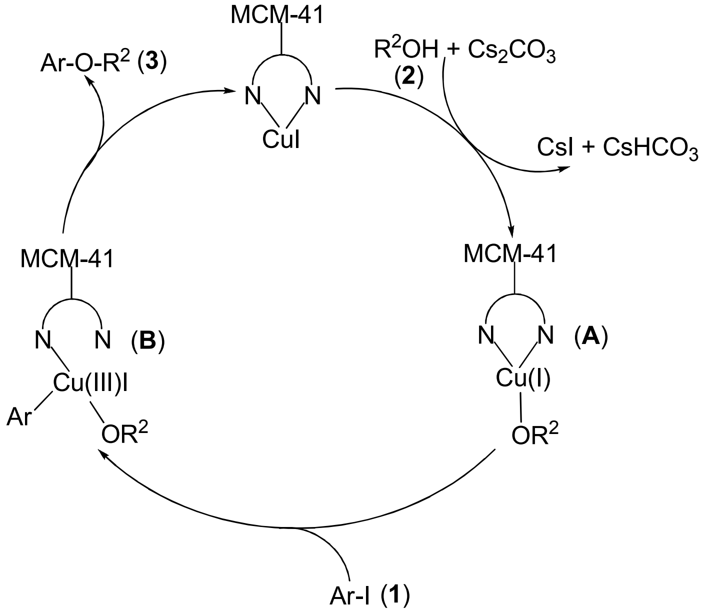

Scheme 3. Plausible mechanism.

Recently, Casitas and Ribas have described the role of organometallic copper(III) complexes in homogeneous catalysis.[20] Although experimental evidences were lacking, organometallic copper(III) species have been invoked in many copper-catalyzed reactions. This heterogeneous copper-catalyzed C–O coupling reaction of aryl iodides with aliphatic alcohols may proceed through oxidative addition followed by a reductive elimination process (Scheme 3). Firstly, the reaction of MCM-41-1,10-Phen-CuI with R^{2}OH **2** in the presence of Cs$_2$CO$_3$ affords an MCM-41-immobilized 1,10-phenanthroline-Cu(I)–OR^2 intermediate **A**. Then oxidative addition of Ar-I **1** to intermediate **A** forms an MCM-41-immobilized 1,10-phenanthroline-ArCu(III)I–OR^2 intermediate **B**. Finally, intermediate **B** undergoes a reductive elimination to give the desired product **3** and regenerate the MCM-41-1,10-Phen-CuI complex.

For the practical application of a heterogeneous transition-metal catalyst system its stability and reusability are important factors. We next examined the recyclability of

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the MCM-41-1,10-Phen-CuI complex by using coupling reaction between 2-methyl-iodobenzene (0.5 mmol) and *n*-BuOH with Cs_2CO_3 (1.0 mmol) as base in *n*-BuOH (1 mL) in the presence of 10 mol% of MCM-41-1,10-Phen-CuI at 110 ºC in a sealed tube under argon atmosphere for 24 h. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water and EtOH. After being air-dried, it can be reused directly without further purification. The recovered copper catalyst was used in the next run, and almost consistent activity was observed for 8 consecutive cycles (Fig. 3). In addition, copper leaching in the supported catalyst was also determined. The copper content of the catalyst was found by ICP analysis to be 0.74 mmol/g after eight consecutive runs, only 1.3% of copper had been lost from the MCM-41 support. The satisfactory reusability of the catalyst should result from the chelating action of bidentate 1,10-phenanthroline ligand on copper and the meso-porous structure of the MCM-41 support. The result is important from industrial and environmental points of view. The high catalytic activity and excellent reusability of MCM-41-1,10-Phen-CuI complex make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

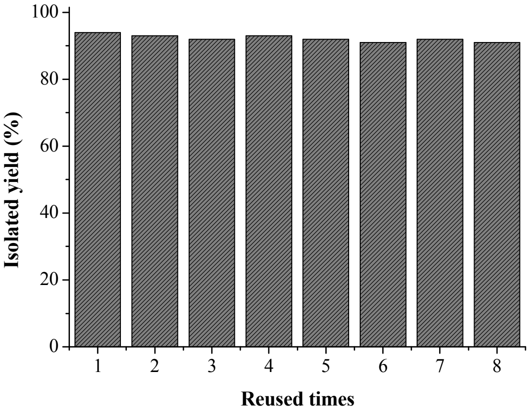

Fig. 3 Recycle of the MCM-41-1,10-Phen-CuI catalyst.

Conclusions

In summary, we have developed a novel, highly efficient and practical method for the synthesis of aryl alkyl ethers through C–O coupling reaction of aryl iodides with aliphatic alcohols by using an MCM-41-immobilized 1,10-phenanthroline-copper(I) complex [MCM-41-1,10-Phen-CuI] as catalyst and Cs_2CO_3 as base in neat alcohol or toluene at 110 ºC under Ar atmosphere. The reactions generated a variety of aryl alkyl ethers in good to excellent yields under mild and green conditions and were applicable to a wide range of aryl iodides and various primary or secondary aliphatic alcohols. The new heterogeneous copper catalyst can be easily prepared by a simple procedure from commercially available and inexpensive reagents and recycled for at least 8 times without significant loss of catalytic activity. The use of recyclable copper catalyst along with mild and environment-friendly reaction conditions will make this methodology a powerful complement to the traditional C–O coupling reactions.

Experimental

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. Mesoporous material MCM-41 was prepared by standard protocol.[16] 1-(1,10-Phenanthrolin-5-yl)-3-(3-(triethoxysilyl)propyl)urea was prepared via the addition of 5-amino-1,10-phenanthroline to 3-(triethoxysilyl)propyl isocyanate

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according to a literature procedure.[17] The products were purified by flash chromatography on silica gel. Mixture of EtOAc and hexane was generally used as eluent. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Copper content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray powder diffraction was obtained on Damax–γA (Rigaku). X-ray energy dispersive spectroscopy (EDS) was performed using a microscope.

Preparation of the 1,10-phenanthroline-functionalized MCM-41 (MCM-41-1,10-Phen)

A solution of 1.47 g of 1-(1,10-phenanthrolin-5-yl)-3-(3-(triethoxysilyl)propyl)urea in 9 mL of dry chloroform was added to a suspension of 1.10 g of the MCM-41 in 90 mL of dry toluene. The mixture was stirred for 24 h at 110 °C under Ar. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The product was then soaked in a solution of 4.2 g of Me_3SiCl in 80 mL of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 120 °C for 5 h to obtain 1.53 g of hybrid material MCM-41-1,10-Phen. The nitrogen content was found to be 3.66 mmol/g by elemental analysis.

Preparation of the MCM-41-1,10-Phen-CuI catalyst

In a small Schlenk tube, 1.2 g of the above-functionalized MCM-41 material (MCM-

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41-1,10-Phen) was mixed with 0.21 g (1.1 mmol) of CuI in 20 mL of dry acetone. The mixture was refluxed for 24 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 1.33 g of a light green copper complex [MCM-41-1,10-Phen-CuI]. The nitrogen and copper contents were found to be 3.41 mmol/g and 0.75 mmol/g, respectively.

General procedure for the heterogeneous copper-catalyzed C–O coupling of aryl iodides with aliphatic alcohols

A test tube equipped with a magnetic stirring bar was charged under Ar with MCM-41-1,10-Phen-CuI (67 mg, 0.05 mmol), Cs_2CO_3 (326 mg, 1.0 mmol), aryl iodide (0.5 mmol), and either (a) the alcohol (1 mL) or (b) the alcohol (1.0 mmol) and toluene (1 mL). The test tube was sealed, and the reaction mixture was stirred at 110 ºC for 24-36 h. The reaction mixture was cooled to room temperature and then diluted with EtOAc (20 mL), and filtered. The MCM-41-1,10-Phen-CuI complex was washed with distilled water (2 × 5 mL) and EtOH (3 × 5 mL), and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel to provide the desired product.

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References

1 (a) J. Buckingham, *Dictionary of Natural Products;* University Press, Cambridge, MA, 1994; (b) A. Tai, T. Sawano and F. Yazama, *Biosci. Biotechnol. Biochem.,* 2011, **75**, 2346-2350; (c) S. B. Singh, K. Herath, J. N. Kahn, P. Mann, G. Abruzzo and M. Motyl, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 3253-3256.

2 (a) N. Yamazaki, I. Washio, Y. Shibasaki and M. Ueda, *Org. Lett.*, 2006, **8**, 2321-2324; (b) H. Jiang, J.-M. Leger and I. Huc, *J. Am. Chem. Soc.*, 2003, **125**, 3448-3449; (c) C. Bolm, J. P. Hildebrand, K. Muniz and N. Hermanns, *Angew. Chem. Int. Ed.*, 2001, **40**, 3284-3308; (d) B. Cao, H. Haengsoon Park and M. M. Joullie, *J. Am. Chem. Soc.*, 2002, **124**, 520-521.

3 (a) F. Ullmann, *Chem. Ber.,* 1904, **37**, 853-857; (b) J. Lindley, *Tetrahedron*, 1984, **40**, 1433-1456.

4 (a) G. Mann and J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, **118**, 13109-13110; (b) C. A. Parrish and S. L. Buchwald, *J. Org. Chem.* 2001, **66,** 2498-2500; (c) D. Prim, J.-M. Campagne, D. Joseph and B. Andrioletti, *Tetrahedron*, 2002, **58**, 2041-2075; (d) P. E. Maligres, J. Li, S. W. Krika, J. D. Schreier and I. T. Raheem, *Angew. Chem. Int. Ed.*, 2012, **51**, 9071-9074; (e) X. Wu, B. P. Fors and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2011, **50**, 9943-9947; (f) S. Gowrisankar, A. G. Sergeev, P. Anbarasan, A. Spannenberg, H. Neumann and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 11592-11598.

5 (a) S. V. Ley and A. W. Thomas, *Angew. Chem. Int. Ed.*, 2003, **42**, 5400-5449; (b) G. Evano, N. Bianchard and M. Toumi, *Chem. Rev.,* 2008, **108**, 3054-3131; (c) F. Monnier and M. Taillefer, *Angew. Chem. Int. Ed.*, 2009, **48**, 6954-6971.

6 (a) M. Wolter, G. Nordmann, G. E. Job and S. L. Buchwald, *Org. Lett.,* 2002, **4**, 973-976; (b) G. F. Manbeck, A. J. Lipman, R. A. Stockland, A. L. Freidl, A. F. Hasier, J. J. Stone and I. A. Guzei, *J. Org. Chem.,* 2005, **70**, 244-250; (c) R. Hosseinzadeh, M. Tajbakhsh, M. Mohadjerani and M. Alikarami, *Synlett*, 2005, 1101-1104; (d) A. Shufir, P. A. Lichtor and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3490-3491; (e) H. Zhang, D. Ma and W. Cao, *Synlett*, 2007, 243-246; (f) R. A. Altmann, A. Shufir, A. Choi, P. A. Lichtor and S. L. Buchwald, *J. Org.*

View Article Online
DOI: 10.1039/C6RA19825B

Chem., 2008, **73**, 284-286; (g) J. Niu, H. Zhou, Z. Li, J. Xu and S. Hu, *J. Org. Chem.,* 2008, **73**, 7814-7817; (h) J. Niu, P. Guo, J. Kang, Z. Li, J. Xu and S. Hu, *J. Org. Chem.,* 2009, **74**, 5075-5078; (i) A. B. Naidu, E. A. Jaseer and G. Sekar, *J. Org. Chem.,* 2009, **74**, 3675-3679; (j) M. Wang, B. Yuan, T. Ma, H. Jiang and Y. Li, *RSC Adv.*, 2012, **2**, 5528-5530; (k) Y. Guo, X.-M. Fan, M. Nie, H.-W. Liu, D.-H. Liao, X.-D. Pan and Y.-F. Ji, *Eur. J. Org. Chem.*, 2015, 4744-4755.

7 (a) Y. Iwasawa, *Tailored Metal Catalysis*, Reidel D. Publishing Company, Dordrecht, Holland, 1986; (b) M. Dusi, T. Mallat and A. Baiker, *Catal. Rev. Sci. Eng.*, 2000, **42**, 213-278; (c) R. M. Rioux, *Model Systems in Catalysis From Single Crystals to Enzyme Mimics*, Springer, 2010.

8 (a) M. Kidwai, N. K. Mishra, V. Bansal, A. Kumar and S. Mozumdar, *Tetrahedron Lett.*, 2007, **48**, 8883-8886; (b) T. Miao and L. Wang, *Tetrahedron Lett.*, 2007, **48**, 95-99; (c) J. Zhang, Z. Zhang, Y. Wang, X. Zheng and Z. Wang, *Eur. J. Org. Chem.*, 2008, 5112-5116; (d) S. Benyahya, F. Monnier, M. Taillefer, M. Wong Chi Man, C. Bied and F. Ouazzani, *Adv. Synth. Catal.*, 2008, **350**, 2205-2208; (e) S. Benyahya, F. Monnier, M. Wong Chi Man, C. Bied, F. Ouazzani and M. Taillefer, *Green Chem.*, 2009, **11**, 1121-1123.

9 (a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710-714; (b) A. Taguchi and F. Schuth, *Micropor. Mesopor. Mater.*, 2005, **77**, 1-45; (c) R. M. Martin-Aranda and J. Cejka, *Top. Catal.*, 2010, **53**, 141-153; (d) A. Corma, *Top. Catal.*, 1997, **4**, 249-260.

10 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834-10843.

11 (a) P. C. Mehnert, D. W. Weaver and J. Y. Ying, *J. Am. Chem. Soc.*, 1998, **120**, 12289-12296; (b) K. Mukhopadhyay, B. R. Sarkar and R. V. Chaudhari, *J. Am. Chem. Soc.*, 2002, **124**, 9692-9693; (c) J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem. Int. Ed.*, 1999, **38**, 56-77; (d) M. Cai, G. Zheng and G. Ding, *Green Chem.*, 2009, **11**, 1687-1693; (e) M. Cai, J. Peng, W. Hao and G. Ding, *Green Chem.*, 2011, **13**, 190-196; (f) W. Hao, H. Liu, L. Yin and M. Cai, *J. Org.*

View Article Online
DOI: 10.1039/C6RA19825B

Chem., 2016, **81**, 4244-4251; (g) F. Havasi, A. Ghorbani-Choghamarani and F. Nikpour, *New J. Chem.*, 2015, **39**, 6504-6512.

12 (a) S.-G. Shyu, S.-W. Cheng and D.-L. Tzou, *Chem. Commun.*, 1999, 2337-2338; (b) Y. Yang and R. M. Rioux, *Chem. Commun.*, 2011, **47**, 6557-6559.

13 (a) C. D. Nunes, A. A. Valente, M. Pillinger, A. C. Fernandes, C. C. Romao, J. Rocha and I. S. Goncalves, *J. Mater. Chem.*, 2002, **12**, 1735-1742; (b) M. Jia, A. Seifert and W. R. Thiel, *Chem. Mater.*, 2003, **15**, 2174-2180.

14 (a) A. Corma, E. Gutierrez-Puebla, M. Iglesias, A. Monge, S. Perez-Ferreras and F. Sanchez, *Adv. Synth. Catal.*, 2006, **348**, 1899-1907; (b) A. Corma, C. Gonzalez-Arellano, M. Iglesias and F. Sanchez, *Angew. Chem. Int. Ed.*, 2007, **46**, 7820-7822; (c) G. Villaverde, A. Corma, M. Iglesias and F. Sanchez, *ACS Catal.*, 2012, **2**, 399-406.

15 (a) R. Xiao, H. Zhao and M. Cai, *Tetrahedron*, 2013, **69**, 5444-545; (b) H. Zhao, W. He, R. Yao and M. Cai, *Adv. Synth. Catal.*, 2014, **356**, 3092-3098; (c) M. Cai, R. Yao, L. Chen and H. Zhao, *J. Mol. Catal. A: Chem.*, 2014, **395**, 349-354; (d) H. Zhao, Y. Jiang, Q. Chen and M. Cai, *New J. Chem.*, 2015, **39**, 2106-2111. (e) H. Zhao, W. He, L. Wei and M. Cai, *Catal. Sci. Technol.*, 2016, **6**, 1488-1495.

16 M. H. Lim and A. Stein, *Chem. Mater.*, 1999, **11**, 3285-3295.

17 M.-J. Li, Z. Chen, V. Wing-Wah Yam and Y. Zu, *ACSNANO*, 2008, **2**, 905-912.

18 (a) M. A. Keegstra, T. H. A. Peters and L. Brandsma, *Tetrahedron*, 1992, **48**, 3633-3652; (b) E. Vedejs, R. W. Chapman, S. C. Fields, S. Lin and M. R. Schrimpf, *J. Org. Chem.*, 1995, **60**, 3020-3027.

19 H. E. B. Lempers and R. A. Sheldon, *J. Catal.*, 1998, **175**, 62-69.

20 A. Casitas and X. Ribas, *Chem. Sci.* 2013, **4**, 2301-2318.

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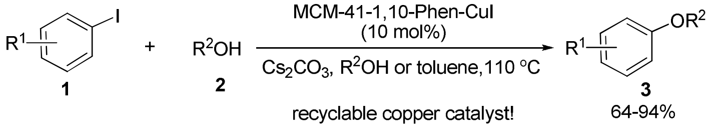
DOI: 10.1039/C6RA19825B

Graphical contents entry

MCM-41-immobilized 1,10-phenanthroline-copper(I) complex: A highly efficient and recyclable catalyst for the coupling of aryl iodides with aliphatic alcohols



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A practical method for the synthesis of aryl alkyl ethers has been developed by a heterogeneous Cu-catalyzed C–O coupling.