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Immobilization of copper in organic–inorganic hybrid materials: a highly efficient and reusable catalyst for the Ullmann diaryl etherification

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Abstract—The immobilization of copper in organic–inorganic hybrid materials catalyzing the Ullmann reaction has been described. Phenols reacted with aryl iodides, aryl bromides and aryl chlorides smoothly in the presence of a 3-(2-aminoethylamino)propyl functionalized silica gel immobilized copper catalyst. The protocol involved the use of DMSO as the solvent, and potassium fluoride as the base. The reactions generated the corresponding cross-coupling products in good to excellent yields. Furthermore, the silica-supported copper could be recovered and recycled by a simple filtration of the reaction solution and used for 10 consecutive trials without loss of its reactivity.

The transition-metal-catalyzed aryl carbon–carbon and carbon–heteroatom bond-forming reactions are important fundamental transformations in synthetic chemistry.[1] The formation of diaryl ethers via a C–O cross-coupling reaction represents a powerful and straightforward method in organic synthesis.[2] Diaryl ethers are not only important structures in biological systems, but also common moieties in pharmaceutical research and materials interest.[3] Copper-catalyzed Ullmann-type arylation procedures of phenols with aryl halides are traditional methods to approach these compounds. However, these reactions are carried out at high temperatures and many functional groups cannot be tolerated for a long time. In addition, these reactions often require the use of stoichiometric amounts of copper reagents (copper powder or copper salts), which leads to problems of waste disposal.[4]

To overcome these drawbacks, a palladium-catalyzed coupling reaction between sodium phenoxides and electron-deficient aryl bromides was reported by Mann and Hartwig[5] based on a ligand (dppf). Later, Buchwald described the C–O coupling of aryl halides and phenols by using palladium catalysis in the presence of electron-rich 2-(di-*tert*-butylphosphino)biphenyl as a ligand.[6]

Nevertheless, the use of expensive palladium and non-commercial sophisticated phosphines limits the attractiveness of this method for large-scale or industrial applications. Meanwhile, Buchwald and co-workers also developed an alternative approach to copper(II) triflate catalyzed C–O formation.[7] Due to the relatively high cost of copper triflate and its air sensitivity, it is still desirable to develop more robust and more cost-effective processes for this important reaction. Since then, considerable efforts have been devoted to the discovery of more efficient copper-catalyzed Ullmann O-arylation methods. A number of groups showed that certain additives, such as Chxn–Py–Al, *N*,*N*-dimethylglycine, 2,2,6,6-tetramethylheptane-3,5-dione, 1,10-phenanthroline or neocuproine, and phosphazene P_4–Bu^t, which probably act as copper ligands, enhance reaction rates and allow the couplings to be carried out at milder temperatures, in the presence of reduced amounts of copper and cesium carbonate as the base.[8]

The high costs of transition metal catalysts coupled with the toxic effects associated with many transition metals has led to an increased interest in immobilizing catalysts

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Keywords: Ullmann reaction; Diaryl etherification; Immobilization of copper; Organic–inorganic hybrid materials.

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onto a support. This class of supported reagents can facilitate both the isolation and recycling of the catalyst by filtration thus providing environmentally cleaner processes.[9] Recent examples have immobilized palladium complexes onto amphiphilic polystyrene supports for effecting Suzuki coupling reaction in an aqueous medium as well as a modified aminomethyl polystyrene-supported palladium reagent for use as a catalyst in a range of Sonogashira coupling reactions.[10] The development of organic reagents grafted onto silica gels has attracted increasing attention in recent years because the industry seeks more environmentally friendly chemical manufacturing processes.[11] Recently, we have developed a silica-supported copper(I) catalyzed Sonogashira coupling reaction.[12] To the best of our knowledge, there is no report on the Ullmann diaryl etherification in the presence of supported copper or palladium catalyst.

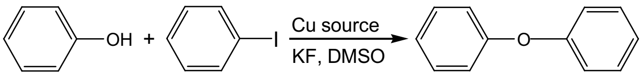
Here, we wish to report the synthesis of 3-(2-aminoethylamino)propyl functionalized silica gel immobilized copper(II) catalyst (Scheme 1), and it was subsequently used as an effective catalyst for the Ullmann cross-coupling reactions of phenols with aryl iodides, aryl bromides and aryl chlorides in the presence of potassium fluoride in DMSO. The reactions generated the corresponding diaryl ethers in good to excellent yields. It is important to note that the silica-supported copper catalyst could be recovered and recycled by a simple filtration of the reaction solution and used for 10 consecutive trials without significant loss of its reactivity.

The synthesis of the organic–inorganic hybrid materials immobilized copper catalyst illustrated in Scheme 1. It was readily prepared through a two-step procedure. The silica gel (100–200 mesh, from Aldrich) was reacted with 3-(2-aminoethylamino)propyltrimethoxysilane in dry toluene at 120 °C for 24 h to afford the 3-(2-aminoethylamino)propyl functionalized silica gel. The organic–inorganic hybrid materials then reacted with copper(II) acetate in ethanol at room temperature for 4 h to generate the silica-supported copper(II) catalyst.

In our initial screening experiments, the Ullmann reaction of iodobenzene and phenol catalyzed by the silica-supported copper catalyst was chosen as model reaction. When we searched for a cross-coupling protocol of iodobenzene and phenol, we observed that iodobenzene could react with phenol in the presence of 5 mol % of silica-supported copper(II) catalyst and 2 equiv of K_2CO_3 in DMF at 130 °C to afford the desired cross-coupling product in 53% yield. Encouraged by this result, we continued our research to improve the yield of product by the optimization of reaction conditions.

In the presence of potassium fluoride, the Ullmann diaryl etherification could be catalyzed by either Cu(I) or Cu(II) in the absence of any palladium. However, no reaction occurred in the absence of any copper and palladium catalyst. As can be seen from Table 1, silica-supported Cu(II) catalysts were superior. Among silica-supported Cu(II) catalysts, which were prepared from different copper(II) sources, silica-supported Cu(II) catalyst from copper(II) acetate was found to be the most effective one (Table 1, entries 1–8). This may be the effect of anion in silica-supported Cu(II) cat-

Table 1. Effect of copper source on the Ullmann diaryl etherification[a]



Entry	Copper source/amount	Yield[b] (%)
1	No	N/A
2	CuI (5 mol %)	25
3	$CuSO_4$ (5 mol %)	34
4	$Cu(OAc)_2$ (5 mol %)	43
5	Silica supported Cu(I)[c] (5 mol %)	41
6	Silica supported Cu(II)[d] (5 mol %)	73
7	Silica supported Cu(II)[e] (5 mol %)	65
8	Silica supported Cu(II)[f] (5 mol %)	92
9	Silica supported Cu(II)[f] (10 mol %)	93
10	Silica supported Cu(II)[f] (15 mol %)	93
11	Silica supported Cu(II)[f] (3 mol %)	74
12	Silica supported Cu(II)[f] (1 mol %)	31

[a] Phenol (1.00 mmol), iodobenzene (1.00 mmol), Cu catalyst (contains 0.05 mmol of Cu), KF (2.00 mmol) in DMSO (4 mL) at 130 °C for 16 h.

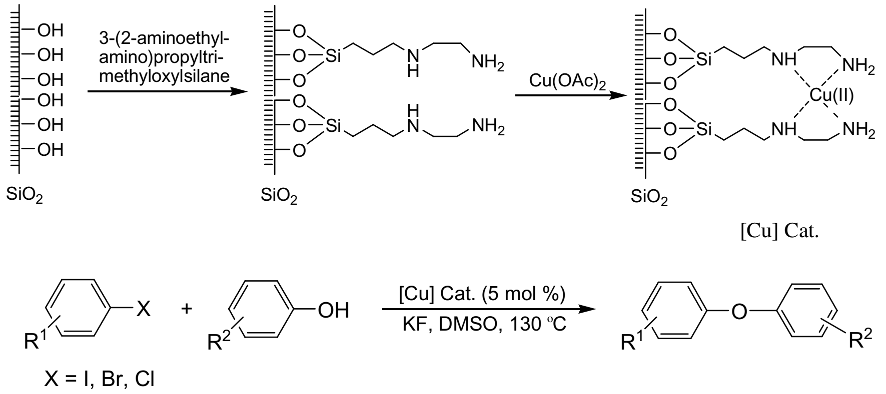
[b] Isolated yields.

[c] Catalyst prepared from CuI.

[d] Catalyst prepared from $CuCl_2$.

[e] Catalyst prepared from $CuSO_4$.

[f] Catalyst prepared from $Cu(OAc)_2$.



Scheme 1.

alysts on its catalytic activity. So, silica-supported Cu(II) from $Cu(OAc)_2$ was used as a catalyst in the following investigation for its high efficiency, easy separation and recycling. In addition, the amount of silica-supported Cu(II) from $Cu(OAc)_2$ was also examined and the optimized loading of Cu(II) on silica was found to be in the range of 5–15 mol % (Table 1, entries 8–12).

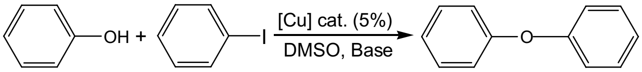
We tested several different bases for the Ullmann coupling reactions catalyzed by the silica-supported copper(II) in DMSO. KF was found to be the most effective. Other bases such as K_2CO_3, Cs_2CO_3, K_3PO_4, KOAc, triethylamine and piperidine were substantially less effective (Table 2, entries 1–7).

We then turned our attention to investigate the effect of solvent on the coupling reaction. When the reactions were conducted in DMF and DMSO, good to excellent yields (72% and 92%, respectively) of products were isolated. No desired cross-coupling product was observed during reactions in EtOH, dioxane, THF, CH_3CN, $HOCH_2CH_2OH$, benzene and toluene (Table 3, entries 1–9).

During the course of our further optimization of the reaction conditions, when using a 5 mol % loading of the silica-supported copper(II), the reactions were generally completed in a matter of hours, but the time, as expected, was inversely proportional to the temperature. A reaction temperature of 130 °C was found to be optimal. Thus, the optimized reaction conditions for this Ullmann reaction are the silica-supported copper (5 mol %), KF (2 equiv) in DMSO at 130 °C for 16 h.

We have investigated the reactions using a variety of aryl iodides, aryl bromides and aryl chlorides, and phenols as the substrates under the reaction conditions and the results are summarized in Table 4. Electron-neutral, electron-rich and electron-poor aryl iodides, as well as electron-poor aryl bromides reacted with phenol very well to generate the corresponding cross-coupling products in excellent yields under the standard reaction conditions (Table 4, entries 1–7). For electron-neutral aryl bromide, moderate yield of the desired product was obtained (Table 4, entry 8). Fortunately, electron-poor aryl chlorides also coupled with phenol to generate the corresponding diaryl ethers in high yields (Table 4, entries 9 and 10). This cross-coupling was also tolerant of *ortho* substitution in aryl halides and led to good yields (Table 4, entries 10 and 15). On the other hand, the substituted phenols with both of electron-withdrawing and electron-donating groups on aromatic rings underwent smoothly with activated aryl bromides and aryl chlorides to produce the desired products in good yields (Table 4, entries 11–17). However, poor yields were obtained for inactivated aryl bromides and aryl chlorides and phenol under the present reaction conditions.

Table 2. Effect of base on the Ullmann diaryl etherification[a]

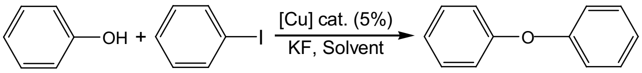


Entry	Base	Yield[b] (%)
1	KF	92
2	K_2CO_3	81
3	Cs_2CO_3	51
4	K_3PO_4	40
5	KOAc	67
6	Triethylamine	53
7	Piperidine	59

[a] Phenol (1.00 mmol), iodobenzene (1.00 mmol), silica-supported Cu catalyst (0.05 mmol of Cu), base (2.00 mmol) in DMSO (4 mL) at 130 °C stirring for 16 h.

[b] Isolated yields.

Table 3. Effect of solvent on the Ullmann diaryl etherification[a]



Entry	Solvent/temperature (°C)	Yield[b] (%)
1	C_2H_5OH/78	N.R.
2	THF/70	N.R.
3	Dioxane/100	N.R.
4	CH_3CN/80	N.R.
5	Toluene/110	N.R.
6	Benzene/80	N.R.
7	$HOCH_2CH_2OH$/120	N.R.
8	DMF/130	72
9	DMSO/130	92

[a] Phenol (1.00 mmol), iodobenzene (1.00 mmol), silica-supported Cu catalyst (0.05 mmol of Cu), KF (2.00 mmol) in solvent (4 mL) at the temperature indicated in Table 3 stirring for 16 h.

[b] Isolated yields.

Table 4. Silica-supported copper catalyzed Ullmann diaryl etherification[a]

Entry	Phenol	Aryl halide	Yield[b] (%)
1	C_6H_5OH	p-$CH_3OC_6H_4I$	90
2	C_6H_5OH	C_6H_5I	92
3	C_6H_5OH	p-$NO_2C_6H_4I$	99
4	C_6H_5OH	p-$NO_2C_6H_4Br$	98
5	C_6H_5OH	m-$NO_2C_6H_4Br$	84
6	C_6H_5OH	p-$CH_3COC_6H_4Br$	82
7	C_6H_5OH	p-CNC_6H_4Br	95
8	C_6H_5OH	C_6H_5Br	73
9	C_6H_5OH	p-$NO_2C_6H_4Cl$	78
10	C_6H_5OH	o-$NO_2C_6H_4Cl$	81
11	p-$CH_3C_6H_4OH$	p-$NO_2C_6H_4Br$	88
12	p-$CH_3C_6H_4OH$	p-CNC_6H_4Br	99
13	p-$CH_3C_6H_4OH$	p-$NO_2C_6H_4Cl$	80
14	p-$CH_3C_6H_4OH$	p-CNC_6H_4Cl	91
15	p-$CH_3C_6H_4OH$	o-$NO_2C_6H_4Cl$	93
16	p-ClC_6H_4OH	p-$NO_2C_6H_4Cl$	78
17	p-ClC_6H_4OH	p-CNC_6H_4Cl	94

[a] Phenol (1.00 mmol), aryl halide (1.00 mmol), silica-supported Cu(II) catalyst (125 mg, contains 0.05 mmol of Cu), KF (2.00 mmol) in DMSO (4 mL) at 130 °C stirring for 16 h.

[b] Isolated yields.

The recyclability of the silica-supported copper was also surveyed. After reaction, the solution was vacuum filtered using a sintered glass funnel and washed with CH_2Cl_2 (5 mL), Et_2O (5 mL), C_2H_5OH (5 mL), and hexane (5 mL), respectively. After being dried, they can be reused directly without further purification. The silica-supported copper can be recovered, recycled and used for 10 consecutive trials without loss of activity (Table 5).

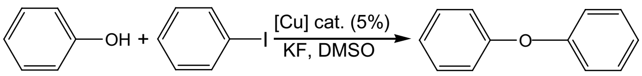
Preparation and characterization of the immobilization of palladium catalyst in organic–inorganic hybrid materials: This catalyst was prepared in the following steps from commercial silica.

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

In a 50 mL round-bottomed flask were introduced successively 20 mL of anhydrous toluene, 3 g of activated silica and 10 mL of 3-(2-aminoethylamino)propyltrimethoxylsilane (AAPTS). The solution was refluxed for 24 h. The solution was filtered and the solid was washed with acetone and dichloromethane, respectively, and dried under reduced pressure at 60 °C. Material (3.38 g) was obtained. FT-IR (KBr, v cm^{-1}): $v_{Si–O} = 1088$; $v_{C–H} = 2941$. Anal. Found: C, 6.56; H, 1.55; N, 2.56, corresponding to 0.914 mmol/g of 2-aminoethylaminopropyl groups based on the nitrogen percentage.

In a small Schlenk tube, 1 g (0.914 mequiv $CH_2CH_2CH_2NHCH_2CH_2NH_2$/g) of the above-functionalized silica was mixed with 0.110 g (0.6 mmol) of $Cu(CH_3CO_2)_2$ in 5 mL of dry ethanol. The mixture was stirred for 4 h under nitrogen atmosphere at room temperature. The solution was filtered and the solid was washed with acetone and methanol, respectively, and the solid was dried under reduced pressure at room temperature for 16 h, leading to a yellow powder (1.05 g). FT-IR (KBr, v cm^{-1}): $v_{Si–O} = 1047$; $v_{C–H} = 2932$. Anal. by ICP (Atomic %): Cu, 2.55.

Table 5. Successive trials by using recoverable Cu(II) catalyst[a]



Trial	Yield[b] (%)
1	92
2	92
3	91
4	92
5	90
6	90
7	91
8	90
9	89
10	88

[a] Phenol (1.00 mmol), iodobenzene (1.00 mmol), silica-supported Cu catalyst (0.05 mmol of Cu), KF (2.00 mmol) in DMSO (4 mL) at 130 °C for 16 h.

[b] Isolated yields.

Typical procedure for the Ullmann diaryl etherification: Under nitrogen atmosphere, an oven-dried round-bottomed flask was charged with the silica-supported copper(II) (125 mg, contains 0.05 mmol of Cu), KF (116 mg, 2.0 mmol), aryl halide (1.0 mmol), phenol (1.0 mmol) and DMSO (4 mL). The reaction mixture was refluxed at 130 °C for 16 h. After cooling to room temperature, the reaction mixture was vacuum filtered using a sintered glass funnel and washed with CH_2Cl_2 (2 × 5 mL). The combined organic materials were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by flash chromatography on silica gel to give the desired cross-coupling product.

The recyclability of the silica-supported copper catalyst: After reaction, the mixture was vacuum filtered using a sintered glass funnel and washed with CH_2Cl_2 (5 mL), Et_2O (5 mL), C_2H_5OH (5 mL), and hexane (5 mL), respectively. After being dried on an oven, they can be reused directly without further purification.

In conclusion, we have developed an efficient and economic catalyst system for the Ullmann diaryl etherification by using the organic–inorganic (silica) hybrid materials-supported copper(II) as the catalyst in DMSO. The cross-coupling reactions of phenols with aryl iodides, aryl bromides and aryl chlorides generate the corresponding coupling products in good to excellent yields at the present reaction conditions. Furthermore, the silica-supported copper(II) can be recovered and recycled by a simple filtration of the reaction solution and used for 10 consecutive trials without decreases in activity.

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