DOI: 10.1002/ejoc.201101206

Green Catalysts Derived from Agricultural and Industrial Waste Products: The Preparation of Phenols from CsOH and Aryl Iodides using CuO on Mesoporous Silica

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Keywords: Supported catalysis / Mesoporous materials / Waste prevention / Sustainable chemistry / Copper / Cross-coupling

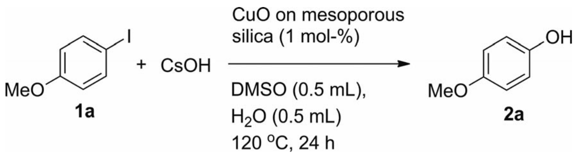
The synthesis of CuO catalysts supported on mesoporous silica derived from rice husks and semiconductor copper from chemical mechanical planarization (Cu-CMP) wastewater is described. These catalysts are active for the coupling reaction of CsOH with aryl iodides. Low catalyst loading (1 mol-%) without the need for ancillary ligands make these very attractive "green" catalysts.

Introduction

Phenolic motifs are important building blocks in organic synthesis and materials chemistry.[1] The traditional methods for preparing these molecules rely on harsh reaction conditions[2] that often prevent functional group tolerance and limit their practical application. Transition-metal-catalyzed coupling reactions of metal hydroxides with aryl halides provides an alternative route to overcome these difficulties.[3–12] Palladium-catalyzed hydroxylation of aryl halides has been reported by Buchwald,[5] Beller,[6] Diaconescu,[7] and Kwong.[8] The use of a combination of copper salts with appropriate ligands has also been reported for the same purpose.[9–12] Ancillary ligands are, however, a necessity in all the above protocols.[5–12] Herein, we report that CuO on mesoporous silica can be used as a catalyst for the coupling of CsOH with aryl iodides under ligand-free conditions.

Recently, we communicated that CuO on mesoporous silica **A** (see Table 1), templated by gelatin, is a very effective catalyst for C–S coupling reactions.[13] Distinct from our previous report, we were determined to find a greener catalytic system that could be used to prepare phenols. In fact, we demonstrate here that these greener catalysts show better catalytic performance than the catalyst that was used previously in the C–S coupling reaction.[13] Rice husks or hulls are a byproduct of human food processing. Owing to the high silica content (around 15 wt.-% in dried rice husk), the rice husks are also a readily available source of silica.[14]

Table 1. Optimization of CuO on mesoporous silica catalyzed coupling of 1-iodo-4-methoxybenzene with CsOH.[a]



Entry	Catalyst (silica source, CuO/silica)	Yield [%][b]
1	**A** (gelatin-silicate, 1:20)	87
2	**B** (gelatin-silicate, 1:5)	76
3	**C** (rice husk, 1:20)	85
4	**D** (rice husk, 1:5)	94
5	CuO	16
6	CuO/SiO_2 (CuO/SiO_2 = 1:5)	23
7	**D** (rice husk, 1:5)	47[c]

[a] Reaction conditions: CuO on mesoporous silica (0.01 mmol, 1 mol-%), 1-iodo-4-methoxybenzene (1.0 mmol), $CsOH\text{-}H_2O$ (3.0 mmol) in DMSO (0.5 mL)/H_2O (0.5 mL). [b] Isolated yield. [c] KOH (3.0 mmol) was used instead of $CsOH\text{-}H_2O$.

Results and Discussion

Mesoporous silicates of high surface area can be obtained from simple hydothermal (100 °C) treatment of an acidic solution (pH 2.0–3.0 and rice husk/acidic solution weight ratio ca. 1:10) and calcination (600 °C) in air (see the Supporting Information, Figure S1 for TEM image and N_2 adsorption–desorption isotherm of the mesoporous silicates). Consequently, the mesoporous silica from rice husks was thought to be a reasonable substitute for the gelatin-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101206.

templated mesoporous silicas (e.g., MCM-41 or SBA-15).[15] Although the CuO supported on silica from rice husks ash and commercial copper salt is known,[16] the direct synthesis of CuO on mesoporous silica from rice husks and copper-containing wastewater has not yet been reported. Here, we report the synthesis of CuO supported on mesoporous silica derived from rice husks and Cu-CMP wastewater from copper chemical mechanical planarization (Cu-CMP) processes through a hydroxide-precipitation and 100 °C-hydrothermal treatment.[17] Finally, the CuO on mesoporous silica catalyst was obtained from high-temperature calcination of the $Cu(OH)_2$-containing mesoporous silica.

The transmission-electron microscopy (TEM) images of CuO on mesoporous silica (Figure 1, a) show a wormhole-like mesostructure; CuO nanoparticles of high electron-density were not observed. At higher magnification, the amorphous structure was observed without any significant CuO lattice infringement. To further demonstrate the even distribution of CuO, TEM EDX-mapping and selected area electron diffraction were used (Figure 1, b–d). Similar distribution profiles of Si, and Cu elements and diffuse ring-diffraction patterns indicate an even distribution of CuO active sites on the mesoporous silica. In accordance with the TEM data, the existence of two broad X-ray diffraction (XRD) peaks at high-angle of 35.8° and 38.2° (i.e., CuO diffraction peaks) reveal that the CuO is well-dispersed onto the surface of the mesoporous silica, where the mesoporous silica from rice husks may prevent the formation of CuO nanoparticles from self-condensation (Figure 1, e). Furthermore, the calcined CuO on mesoporous silica sample presented is uniformly green, rather than black, which is observed for mesoporous silica containing CuO nanoparticles prepared by impregnation methods (Figure 2). When the N_2 adsorption–desorption isotherm was analyzed (Figure 1, f), the BET surface area was found to be about $285\,m^2g^{-1}$; the pore size, calculated by the Barrett–Joyner–Halenda (BJH) method, was centered at 6.5 nm (inset in Figure 1, f). Similar surface area and porosity between mesoporous silica and CuO on mesoporous silica indicate that the CuO is well-dispersed on the pore wall of the mesoporous silica rather than blocking the pores. Accordingly, the CuO active sites are well-dispersed on the mesoporous silica, and highly accessible to the environment, which should give rise to high activity for coupling reactions, with the added feature of recyclability.

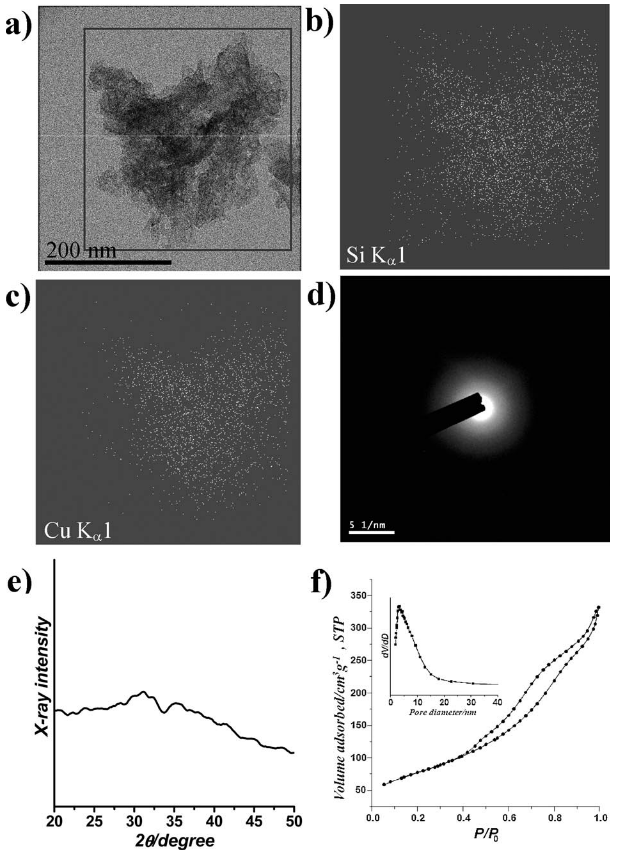


Figure 1. Scanning transmission-electron microscopy images (STEM), in conjunction with EDX elemental mapping of the resulting CuO on mesoporous silica prepared by using Cu-CMP wastewater and rice husks as precursors. (a) TEM image. (b) Si element distribution image. (c) Cu element distribution image. (d) The selected area electron diffraction pattern of the CuO on mesoporous silica sample. (e) High-angle XRD pattern, and (f) N_2 adsorption–desorption isotherm, with (insert) the pore-size distribution of the CuO on mesoporous silica.

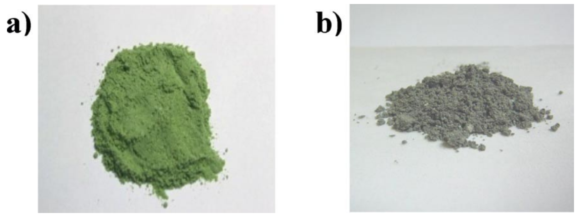
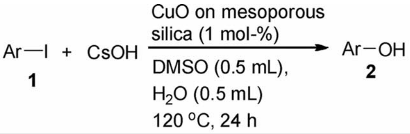
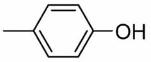
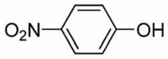
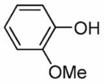
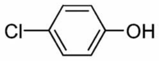
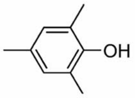
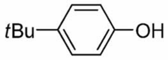
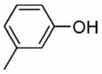
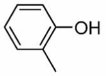
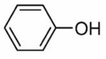
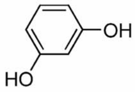
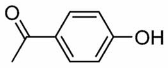
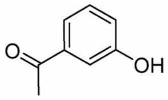
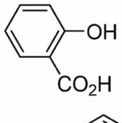
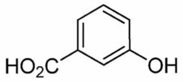
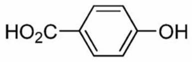
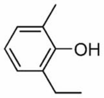


Figure 2. Optical micrographs of the CuO-containing mesoporous silica samples at the same chemical composition (Cu/Si molar ratio ca. 5) synthesized by using different synthetic methods. (a) CuO on mesoporous silica prepared by using rice husks and Cu-CMP wastewater as silica and CuO precursors through the synthetic process developed here. (b) CuO on mesoporous silica obtained from the typical impregnation method.

Initially, 1-iodo-4-methoxybenzene was screened in the coupling with CsOH to determine the optimal reaction conditions; the results are summarized in Table 1. The product was obtained in good to excellent yields by using this catalyst system. Interestingly, catalyst **A** (Cu/silica = 1:20) was not only reactive for C–S coupling reactions;[13] but was also suitable for C–O coupling reactions, affording the target in 87% yield (Table 1, entry 1). It is important to note that catalyst **D** (Cu/silica = 1:5) gave the best result, yielding the product in 94% isolated yield (Table 1, entry 4). The effect of the Cu/silica ratio is not yet clear; when the reaction was carried out using CuO as the catalyst, the product was obtained in only 16% yield (Table 1, entry 5). A control experiment was performed using CuO and SiO_2 as the catalyst, but this resulted in only 23% yield of the product (Table 1, entry 6). These low yields indicate that leached

Table 2. CuO on mesoporous silica catalyzed coupling reaction of aryl iodides with CsOH.[a]



Entry	Product		Yield [%][b]
1		**2b**	89
2		**2c**	94
3		**2d**	77
4		**2e**	85
5		**2f**	55
6		**2g**	67
7		**2h**	72
8		**2i**	83
9		**2j**	94
10		**2k**	88[c]
11		**2l**	83[d]
12		**2m**	68
13		**2n**	77[c]
14		**2o**	88[c]
15		**2p**	93[c]
16		**2q**	72[d]

[a] Reaction conditions unless otherwise stated: CuO on mesoporous silica (0.01 mmol, 1 mol-%), CsOH/H_2O (3.0 mmol) in DMSO (0.5 mL)/H_2O (0.5 mL). [b] Isolated yield. [c] CsOH/H_2O (4.0 mmol) was used. [d] Catalyst (3 mol-%) was used.

species do not have high activities. When KOH was used instead of CsOH, the product was afforded in 47% yield (Table 1, entry 7). Lower yields were observed when 1-iodo-4-methoxybenzene was replaced by bromobenzene (10% GC yield) or chlorobenzene (trace amount) under the same conditions.

Based on the optimized conditions, we examined the scope of this catalytic system. As listed in Table 2, a variety of electron-donating and -withdrawing aryl iodides were studied as CsOH coupling partners, and the corresponding phenols were obtained in good to excellent yields. Functional groups including nitro (Table 2, entry 2), chloro (entry 4), alcohol (entry 10), enolizable ketones (entries 11 and 12), and carboxylic acids (entries 13, 14, and 15) were all tolerated under the conditions employed. The application of more sterically demanding substrates resulted in slightly lower yields (Table 2, entries 3, 5, 13, and 16).

To study the potential recyclability of the catalyst, 4-iodo-4-methoxybenzene was treated with CsOH. As summarized in Table 3, the catalyst could be reused for several runs without significant loss of activity. TEM images (see the Supporting Information, Figure S2) of the CuO on mesoporous silica after the fourth reaction reveal that the pore structure was retained without any significant formation of CuO nanoparticles (from aggregation). By comparing the energy-dispersive spectroscopy (EDS) data of the CuO on mesoporous silica catalysts before and after the fourth run, we found the Cu/Si atomic ratio of the fourth-run sample had decreased from 2.0:10 to 1.6:10. The 20% decrease in the CuO content indicates that the CuO active sites remain highly stabilized on the mesoporous silica during multiple catalytic cycles. The copper species from leaching will form the soluble species such as $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ under strong base conditions,[18] such as those employed here {[CsOH] $\approx$ 3.0 M}. It is therefore understandable that the observed Cu/Si atomic ratio of the fourth-run sample decreased. As mentioned earlier, if the activity mainly came about as a result of leached (homogeneous) components,[2] the CuO and the CuO/SiO_2 should both give good yields of the product, however, only CuO on mesoporous silica was observed to be active, giving the product in 94% isolated yield (Table 1, entry 4). The 20% decrease in the Cu content of the CuO on mesoporous silicate after the fourth reaction cycle indicates that the CuO active sites bond strongly with the mesoporous silica, and this heterogeneous catalyst system shows good activity for the coupling reaction of aryl iodides with CsOH.

Table 3. Reuse of CuO on mesoporous silica **D** for the preparation of **2a**.[a]

Run	1	2	3	4
Yield [%]	94	92	92	88

[a] Reaction conditions: 3.0 mmol scale reaction was performed; after 24 h, the reaction mixture was treated with HCl and diluted with H_2O and EtOAc, the catalyst was recovered by centrifugation then dried in an oven overnight.

Conclusions

We have reported that CuO on mesoporous silica based catalysts can be prepared conveniently from rice husks and wastewater from semiconductor Cu-CMP processing. Furthermore, this system has been shown to be catalytically active for the coupling of CsOH with a variety of aryl iodides. More applications of these novel catalysts in organic synthesis are being developed in our laboratory.

Experimental Section

General Information: All chemicals were purchased from commercial suppliers and used without further purification. Toluene was dried with sodium; dioxane, DME, and DMF were dried with CaH_2 and stored in the presence of activated molecular sieves. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh). NMR spectra were recorded with a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constants (J) are reported in Hertz [Hz]. Standard abbreviations indicating multiplicity are as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br. = broad. Melting points (m.p.) were determined with a Büchi 535 apparatus. GC–MS analyses were performed with a HP 5890 GC connected to a HP 5972 MS. High-resolution mass spectra were carried out with a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

Preparation of Mesoporous Silica from Rice Husks: To directly obtain mesoporous silica from rice husk having a high surface area (ca. 250 $m^2 g^{-1}$) and large porosity, dry rice husks (3.0–5.0 g) were suspended in 50.0 mL of a sulfuric acid solution (pH ≈ 3.0) and then hydrothermally treated at 100 °C for 6 h. Filtration, drying, and calcination at 600 °C in air gave the mesoporous silica with a Brunauer–Emmett–Teller (BET) surface area of approximately 235 $m^2 g^{-1}$ and pore size of approximately 6.0 nm (Figure S1).

Cu^{2+} Removal from Wastewater and the Synthesis of CuO on Mesoporous Silica Catalysts Using Rice Husks: The mesoporous silica can be used directly as an absorbent to remove the Cu^{2+} ions from the waste water from Cu-CMP slurry processing. To remove the Cu^{2+} ions and prepare a well-dispersed CuO-silica catalyst, 1.0 g of mesoporous silica from rice husk was added to 220 mL of 0.015 M Cu^{2+} aqueous solution diluted from the Cu-CMP waste water ($[Cu^{2+}] \approx 0.50$ M). Using the dilute Cu^{2+} solution can prevent the formation of large copper hydroxide aggregation from self-condensation during precipitation. The pH of the gel solution was adjusted to 6.0–7.0 by dropwise addition of 0.15 M NaOH solution, and then the gel solution was hydrothermally treated for 24 h at 100 °C. Filtration, and drying gave the $Cu(OH)_2$-silica. The CuO on mesoporous silica catalyst (Cu/Si ≈ 2:10) was obtained from calcination at 500 °C in air on the $Cu(OH)_2$-silica. Concerning the safety of the reaction effluent, the residual $[Cu^{2+}]$ concentration in the waste solution was measured, and the $[Cu^{2+}]$ concentration was found to be less than 3.0 ppm (this corresponds to the effluent standard for Cu^{2+} ions in Taiwan). Accordingly, this is an environmentally-friendly synthetic strategy for the preparation of the CuO on mesoporous catalyst and this synthetic process is capable of removing toxic Cu^{2+} ions from Cu-CMP waste water. In addition, the Cu^{2+} ion from Cu-CMP waste water was almost completely incorporated into the CuO on silica catalyst.

General Procedure for the Reaction Described in Table 1: A sealable tube equipped with a magnetic stir bar was charged with CsOH/H_2O (504 mg, 3.0 mmol) in a dry-box under a nitrogen atmosphere. The tube was then covered with a rubber septum and removed from the dry-box. Under a nitrogen atmosphere, catalyst (1.0 mol-%), 1-iodo-4-methoxybenzene (234.0 mg, 1.0 mmol), DMSO (0.5 mL), and H_2O (0.5 mL) were added by using a syringe. The septum was then replaced by a Teflon®-coated screw cap and the reaction vessel was heated at 120 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature; HCl (10%, 1.0 mL) was added and the mixture was diluted with EtOAc (20 mL). The resulting solution was filtered through a pad of silica gel then washed with EtOAc (20 mL) and concentrated to give the crude material, which was purified by column chromatography (SiO_2; hexane/EtOAc, 4:1) to give **2a**.

4-Methoxyphenol (2a):[9] Obtained by following the above general procedure using **D** as the catalyst (3.8 mg, 0.01 mmol) and 1-iodo-4-methoxybenzene (234.0 mg, 1.0 mmol). Purification (SiO_2, CH_2Cl_2) provided **2a** as a white solid (116 mg, 94% yield); m.p. 49–51 °C (ref.[9] 55–57 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 5.87 (br. s, 1 H), 6.77 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 114.9, 116.1, 149.5, 153.5 ppm.

General Procedure for the Reaction Described in Table 2: A sealable tube equipped with a magnetic stir bar was charged with CsOH/H_2O (504 mg, 3.0 mmol) in a dry-box under a nitrogen atmosphere. The tube was then covered with a rubber septum and removed from the dry-box. Under a nitrogen atmosphere, catalyst **D** (1.0 mol-%), aryl iodide (1.0 mmol), DMSO (0.5 mL), and H_2O (0.5 mL) were added by using a syringe. The septum was then replaced by a Teflon®-coated screw cap and the reaction vessel was heated at 120 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature; HCl (10%, 1.0 mL) was added and the mixture was diluted with EtOAc (20 mL). The resulting solution was filtered through a pad of silica gel then washed with EtOAc (20 mL) and concentrated to give the crude material, which was purified by column chromatography (SiO_2; hexane/EtOAc or CH_2Cl_2/methanol) to give **2**.

4-Methylphenol (2b):[9] Obtained by following the general procedure for Table 2 using 1-iodo-4-methylbenzene (0.218 mg, 1.0 mmol). The crude mixture was purified by column chromatography (SiO_2; CH_2Cl_2) to give **2b** as a yellow oil (95.9 mg, 89% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 5.29 (br. s, 1 H), 6.73 (d, J = 8.8 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 115.1, 130.0, 130.0, 152.9 ppm.

4-Nitrophenol (2c):[9] Obtained by following the general procedure for Table 2 using 1-iodo-4-nitrobenzene (249.0 mg, 1.0 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 2:1) to give **2c** as a yellow solid (130 mg, 94% yield); m.p. 110–112 °C (ref.[9] 110–115 °C). ^1H NMR (400 MHz, $[D_6]$DMSO): δ = 3.38 (br. s, 1 H), 6.92 (d, J = 8.0 Hz, 2 H), 8.11 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $[D_6]$DMSO): δ = 115.8, 126.1, 139.7, 164.0 ppm.

2-Methoxyphenol (2d):[10] Obtained by following the general procedure for Table 2 using 1-iodo-2-methoxybenzene (0.234 mg, 1.0 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2) to afford **2d** as a colorless oil (95.4 mg, 77% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.83–6.89 (m, 3 H), 6.91–6.94 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 110.7, 114.5, 120.1, 121.3, 145.5, 146.5 ppm.

4-Chlorophenol (2e):[9] Obtained by following the general procedure for Table 2 using 1-chloro-4-iodobenzene (238.5 mg, 1.00 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 4:1) to afford **2e** as a yellow oil (109 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.14 (br. s, 1 H), 6.76 (d, J = 8.0 Hz, 2 H), 7.18 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.6, 125.7, 129.5, 153.8 ppm.

2,4,6-Trimethylphenol (2f):[6a] Obtained by following the general procedure for Table 2 using 2-iodo-1,3,5-trimethylbenzene (246 mg, 1.0 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 4:1) to afford **2f** as a yellow solid (74.9 mg, 55% yield); m.p. 67–69 °C (ref.[6a]: 70–72 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 9 H), 4.10 (br. s, 1 H), 6.78 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.8, 20.3, 122.8, 129.1, 129.3, 149.8 ppm.

4-*tert*-Butylphenol (2g):[19] Obtained by following the general procedure for Table 2 using 1-*tert*-butyl-4-iodobenzene (0.18 mL, 1.0 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2) to afford **2g** as a white solid (100 mg, 67% yield); m.p. 96–98 °C (ref.[19] 96–100 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9 H), 5.75 (br. s, 1 H), 6.77 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.5, 34.0, 114.8, 126.4, 143.6, 152.8 ppm.

3-Methylphenol (2h):[9] Obtained by following the general procedure for Table 2 using 3-iodotoluene (0.128 mL, 1.0 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2) to give **2h** as a yellow oil (77.3 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 5.07 (br. s, 1 H), 6.62–6.65 (m, 2 H), 6.74 (d, J = 7.2 Hz, 1 H), 7.10 (t, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 112.3, 116.0, 121.6, 129.4, 139.8, 155.2 ppm.

2-Methylphenol (2i):[9] Obtained by following the general procedure for Table 2 using 2-iodotoluene (0.10 mL, 1.0 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2) to give **2i** as a yellow oil (89.5 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 4.70 (br. s, 1 H), 6.74 (d, J = 7.6 Hz, 1 H), 6.83 (t, J = 7.6 Hz, 1 H), 7.03–7.12 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.7, 114.9, 120.7, 123.8, 127.0, 131.0, 153.6 ppm.

Phenol (2j):[9] Obtained by following the general procedure for Table 2 using iodobenzene (0.11 mL, 1.00 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2) to give **2j** as a colorless solid (86.3 mg, 92% yield); m.p. 36–38 °C (ref.[9] 40–42 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.74–5.78 (br. s, 1 H), 6.83 (d, J = 7.6 Hz, 2 H), 6.91 (t, J = 7.6 Hz, 1 H), 7.20 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.3, 120.9, 129.7, 155.0 ppm.

1,3-Benzenediol (2k):[20] Obtained by following the general procedure for Table 2 using $CsOH/H_2O$ (672 mg, 4.0 mmol) and 3-iodophenol (220.0 mg, 1.0 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 2:1) to give **2k** as a white solid (96.8 mg, 88% yield); m.p. 104–106 °C (ref.[20] 109–112 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.41 (s, 1 H), 6.15–6.18 (m, 3 H), 6.90 (t, J = 8.0 Hz, 1 H), 9.16 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 102.7, 106.4, 129.9, 158.6 ppm.

4′-Hydroxyacetophenone (2l):[9] Obained by following the general procedure for Table 2 using 4′-iodoacetophenone (246.0 mg, 1.00 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 2:1) to give **2l** as a white solid (112 mg, 83% yield); m.p. 102–103 °C (ref.[9] 109–111 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3 H), 6.97 (d, J = 8.8 Hz, 2 H), 7.92 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 115.6, 129.4, 131.3, 161.6, 198.9 ppm.

3′-Hydroxyacetophenone (2m):[21] Obtained by following the general procedure for Table 2 using 3-iodoacetophenone (246.0 mg, 1.0 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 2:1) to afford **2m** as a pink solid (92.4 mg, 68% yield); m.p. 90–91 °C (ref.[21] 90–95 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3 H), 7.09–7.13 (m, 1 H), 7.34 (t, J = 8.0 Hz, 1 H), 7.50–7.55 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.7, 114.7, 120.8, 121.0, 129.9, 138.4, 155.7, 156.4 ppm.

2-Hydroxybenzoic Acid (2n):[22] Obtained by following the general procedure for Table 2 using $CsOH/H_2O$ (672 mg, 4.0 mmol) and 2-iodobenzoic acid (248 mg, 1.00 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2/MeOH, 9:1) to obtain **2n** as a colorless solid (106 mg, 77% yield); m.p. 149–152 °C (ref.[22] 158–161 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.88–6.95 (m, 2 H), 7.49 (t, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 113.0, 117.2, 119.2, 130.4, 135.7, 161.3, 172.1 ppm.

3-Hydroxybenzoic Acid (2o):[23] Obtained by following the general procedure for Table 2 using $CsOH/H_2O$ (672 mg, 4.0 mmol) and 3-iodobenzoic acid (248.0 mg, 1.0 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2/MeOH = 9:1) to give **2o** as a yellow solid (121 mg, 88% yield); m.p. 193–195 °C (ref.[23] 200–203 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.97–7.00 (m, 1 H), 7.25 (t, J = 8.0 Hz, 1 H), 7.36–7.40 (m, 2 H), 9.85 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 116.1, 120.1, 120.3, 129.8, 132.3, 157.6, 167.6 ppm.

4-Hydroxybenzoic Acid (2p):[10] Obtained by following the general procedure for Table 2 using $CsOH/H_2O$ (672 mg, 4.0 mmol) and 4-iodobenzoic acid (248.0 mg, 1.0 mmol), then purified by column chromatography (SiO_2; CH_2Cl_2/MeOH, 9:1) to obtain **2p** as a yellow solid (128 mg, 93% yield); m.p. 201–203 °C (ref.[10] 213-217 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.83 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H), 11.57 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 115.4, 121.7, 131.9, 161.9, 167.6 ppm.

2-Ethyl-6-methylphenol (2q):[24] Obtained by following the general procedure for Table 2 using 2-ethyl-6-methyl iodobenzene (246.0 mg, 1.00 mmol), then purified by column chromatography (SiO_2; hexane/EtOAc, 9:1) to give **2q** as a yellow oil (97.8 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.6 Hz, 3 H), 2.23 (s, 3 H), 2.61 (q, J = 7.6 Hz, 2 H), 4.37 (br. s, 1 H), 6.78 (t, J = 7.6 Hz, 1 H), 6.98 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 15.8, 23.0, 120.3, 123.0, 126.8, 128.4, 129.2, 151.6 ppm.

Supporting Information (see footnote on the first page of this article): TEM image and N_2/adsorption desorption isotherm of the mesoporous silica and the TEM images of the CuO on mesoporous silica after the fourth reaction cycle.

Acknowledgments

The National Science Council, Taiwan (NSC, 99-2113-M-005-004-MY2 and NSC95-2113-M-006-011-MY3); the National Chung Hsing University and Landmark Project of the National Cheng Kung University are gratefully acknowledged for financial support. We thank Prof. Fung-E. Hong for sharing his GC–MS instruments.

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Received: August 17, 2011