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Article

Cu_2O/SiC as efficient catalyst for Ullmann coupling of phenols with aryl halides

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ABSTRACT

A Cu_2O/SiC heterogeneous catalyst was prepared via a two-step liquid-phase method using diethylene glycol as both the solvent and the reducing agent. The catalyst was characterized using X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and H_2 temperature-programmed reduction. All the results indicate that Cu is present on the SiC support primarily as Cu_2O. The SEM and TEM results show that cubic Cu_2O nanoparticles are uniformly dispersed on the β-SiC surface. The reaction conditions, namely the temperature, reaction time, and amounts of base and catalyst used, for the Ullmann-type C–O cross-coupling reaction were optimized. A model reaction was performed using iodobenzene (14.0 mmol) and phenol (14.0 mmol) with Cu_2O/SiC (5 wt% Cu) as the catalyst, Cs_2CO_3 (1.0 equiv.) as the base, and tetrahydrofuran as the solvent at 150 °C for 3 h; a yield of 97% was obtained and the turnover frequency (TOF) was 1136 h^{-1}. The Cu_2O/SiC catalyst has a broad substrate scope and can be used in Ullmann-type C–O cross-coupling reactions of aryl halides and phenols bearing a variety of different substituents. The catalyst also showed high activity in the Ullmann-type C–S cross-coupling of thiophenol with iodobenzene and substituted iodobenzenes; a TOF of 1186 h^{-1} was achieved. The recyclability of the Cu_2O/SiC catalyst in the *O*-arylation of phenol with iodobenzene was investigated under the optimum conditions. The yield decreased from 97% to 64% after five cycles. The main reason for the decrease in the catalyst activity is loss of the active component, i.e., Cu_2O.

1. Introduction

The synthesis of diaryl ethers by *O*-arylation of phenols with aryl halides is one of the most significant reactions in modern organic synthesis because diaryl ethers are important structural units in many biologically active compounds, industrial polymers, and natural products. Initially, the Ullmann C–O coupling of phenols with aryl halides was used to synthesize diaryl ethers in the presence of Cu powder [1]. However, this method requires harsh reaction conditions, such as a large excess of the phenol, long reaction times, high temperatures (>200 °C) and stoichiometric amounts of Cu, which restricts its applications [2]. Much research has focused on overcoming these limitations and good progress has been achieved in this area. The development of Pd(0)- and Cu(I)-based catalytic systems enabled major breakthroughs in coupling reactions [3–5]. However,

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Pd-based approaches suffer from drawbacks such as the high cost of Pd and the use of expensive ligands, therefore large-scale industrial applications of this method are limited [3,5]. Cu-based catalysts have been receiving increasing attention as cheap and readily available catalysts for Ullmann-type C–O coupling reactions.

In homogeneous reaction systems, Cu(I)-based catalysts show high activities and selectivities for *O*-arylation in the presence of an organic ligand, but separation of the products and reuse of the catalysts are difficult [6,7]. Heterogeneous Cu-based catalysts for the C–O coupling reaction have therefore attracted attention [8]. Cu nanoparticles and supported Cu nanoparticles have been used as catalysts for *O*-arylation reactions and showed high catalytic activities [9–11]. Nano-CuO and CuO nanoparticles supported on carbon nanotubes modified with iron oxide showed to be highly efficient and reusable catalysts for the C–O cross-coupling of phenols with aryl halides [12,13]. Park et al. [14] reported that Cu_2O nanocubes of size about 45 nm were highly active and recyclable catalyst for the cross-coupling of aryl halides and phenols. Cu_2O nanoparticles show high catalytic activity in C–O cross-coupling reactions, but they are unstable and easily oxidized in moist air. Recent results have indicated that graphene could stabilize Cu_2O nanoparticles and protect them from oxidation, and graphene-supported Cu_2O nanoparticles showed high catalytic activity in C–O cross-coupling reactions [15,16].

Cubic SiC has excellent chemical stability, and thermal and electrical conductivities. It has been used as support in various catalytic and photocatalytic reactions [17–21]. Li et al. [22] modified SiC nanoparticles with Cu_2O by the reduction of a $Cu(OH)_2$ precipitate using $N_2H_4{\cdot}H_2O$, and the obtained Cu_2O/SiC catalyst was used to photocatalytically reduce CO_2 to CH_3OH under visible-light irradiation. In this work, we used SiC as a support to stabilize Cu_2O nanoparticles because a p–n junction can be formed between Cu_2O and SiC. The Cu_2O/SiC catalyst was prepared using a two-step liquid-phase method and showed high activity in the *O*-arylation of phenols by aryl halides, with high yields and turnover frequencies (TOFs).

2. Experimental

2.1. Catalyst preparation

The detailed preparation of β-SiC with a specific surface area of 50 m^2/g has been reported elsewhere [23]. A Cu_2O/SiC catalyst with a Cu loading of 5 wt% was prepared via a two-step liquid-phase route. In the first step, SiC (50 mg) and cupric acetate monohydrate (8.26 mg) were dispersed in absolute ethanol under sonication. The suspension was placed in a heated oven at 60 °C to obtain a mixture of SiC and copper acetate. In the second step, the resulting mixture was dispersed in diethylene glycol (80 mL) and reduced at 180 °C for 2 h to obtain the Cu_2O/SiC catalyst.

For comparison, Cu_2O/Al_2O_3 and Cu_2O/SiO_2 were prepared using the same method as was used for the Cu_2O/SiC catalyst. CuO/SiC was prepared by calcination of Cu_2O/SiC in a muffle furnace at 400 °C for 4 h in air. The Cu loading for each catalyst was 5 wt%.

2.2. Catalyst characterization

The crystalline phases of the catalyst were identified by X-ray diffraction (XRD, Rigaku D-Max/RB X-ray diffractometer) using Cu K_α radiation. The structure and morphology of the catalyst were examined using field-emission scanning electron microscopy (SEM, S-4800, JEM-2100F) and transmission electron microscopy (TEM, JSM-7001F). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 3 MKII de VG spectrometer with a Mg K_α X-ray source. H_2 temperature-programmed reduction (H_2-TPR) was performed using an automatic adsorption instrument (TP-5080, Xianquan, China). The Cu loadings of the fresh and recycled Cu_2O/SiC catalysts were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo iCAP6300, USA).

2.3. Catalytic reaction

The catalytic *O*-arylation reactions were conducted in a sealed stainless-steel reactor. A phenol (14 mmol), aryl halide (14 mmol), Cs_2CO_3 (14 mmol), tetrahydrofuran (THF, 10 mL), and the Cu_2O/SiC catalyst (10 mg) were placed in the reactor. The reaction was performed under Ar at 150 °C for 3 h. After the reaction, the suspension was collected and centrifuged. The supernatant was analyzed using gas chromatography-mass spectrometry (Bruker SCION SQ 456GC-MS, Germany). The yields and TOFs were calculated based on the aryl halide using the following equations:

$$\text{Yield} = \text{Conversion (\%)} \times \text{selectivity (\%)}$$
$$= (1 - n_a/n_b) \times n_{tp}/(n_{tp} + n_{bp}) \times 100\%$$

$$\text{TOF} = \text{Amount of aryl halides (mol)} \times \text{conversion (\%)} \times \text{selectivity (\%)}/(\text{mass of } Cu_2O/\text{SiC (g)} \times Cu_2O \text{ loading (\%)} \times \text{reaction time (h)}/M[Cu_2O] \text{ (g/mol)})$$

where n_a is the moles of aryl halide after reaction, n_b is the moles of aryl halide before reaction, n_{tp} is the moles of target product after reaction, and n_{bp} is the moles of byproduct after reaction.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD pattern of the Cu_2O/SiC catalyst. The diffraction peaks at 35.76°, 41.46°, 60.13°, 71.89°, and 75.72° correspond to β-SiC [18,23]. The peak at 33.6° arises from stacking faults in SiC [24]. The diffraction peaks at 29.58°, 36.51°, 42.30°, 61.43°, and 73.57° can be indexed to the (110), (111), (200), (220), and (311) lattice planes of Cu_2O, respectively [25,26], indicating that Cu is present on the SiC support primarily as the Cu_2O phase.

XPS was used to examine the chemical states and surface properties of the Cu_2O/SiC catalyst. As shown in Fig. 2(a), the peaks for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ observed at around 932.5 and 952.4 eV are attributed to Cu^+. This is in good agreement with the reported values for Cu_2O [27–29]. This confirms that the

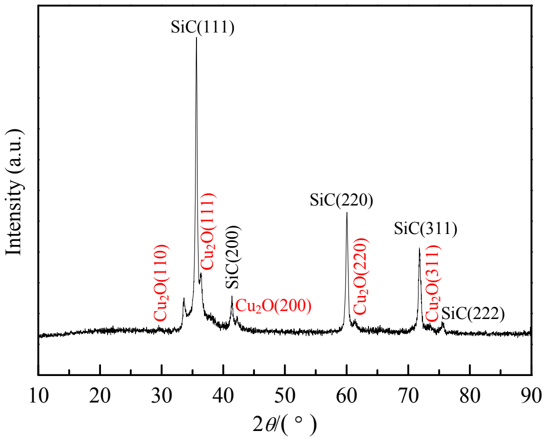


Fig. 1. XRD pattern of Cu_2O/SiC catalyst.

main species dispersed on the SiC support is Cu_2O. Fig. 2(b) shows a Cu LMM Auger peak at 569 eV, which is assigned to Cu_2O [26]. These results show that Cu_2O nanoparticles can be stabilized by using β-SiC as the support.

SEM and TEM were used to examine the morphology and crystal structure of the catalyst. Fig. 3(a) and (b) show that the Cu_2O nanoparticles are well dispersed on the β-SiC surface. Fig. 3(c) clearly shows that the Cu_2O nanoparticles are cubic, and based on statistical analysis, the mean diameter of the Cu_2O nanoparticles is about 61 nm. Fig. 3(d) shows that the Cu_2O nanoparticles have clear lattice fringes, and the interplanar spacing of the nanoparticles is 0.25 nm, corresponding to the (111) plane of Cu_2O [15], which matches the XRD results well.

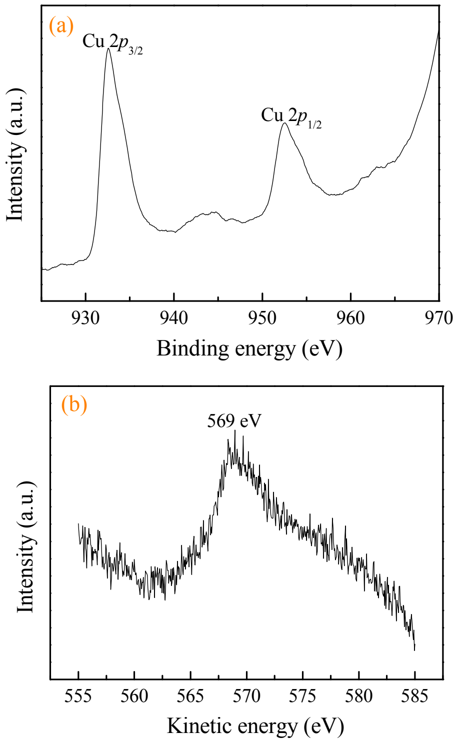


Fig. 2. Cu 2*p* XPS spectrum (a) and Cu LMM Auger spectrum (b) of Cu_2O/SiC.

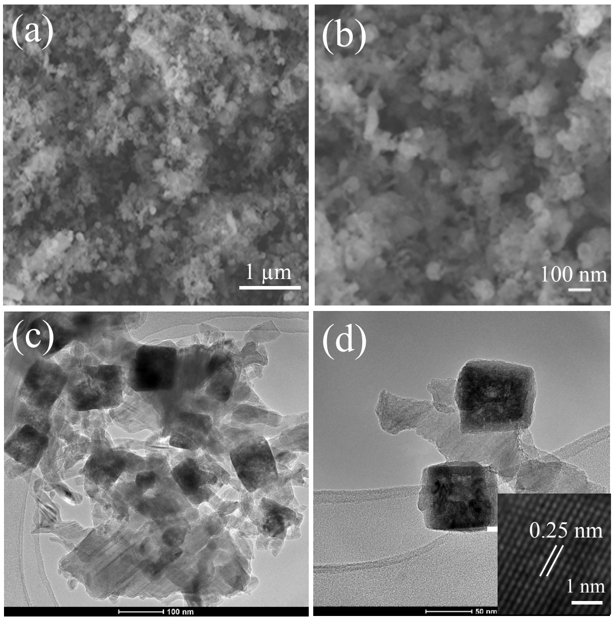


Fig. 3. SEM (a, b) and TEM (c, d) images of Cu_2O/SiC catalyst.

These results suggest that the Cu component in the Cu_2O/SiC catalyst is Cu_2O.

Fig. 4 shows the H_2-TPR results for Cu_2O/SiC and CuO/SiC; the results for Cu_2O/Al_2O_3 and Cu_2O/SiO_2 are also showed for comparison. The CuO/SiC reduction peak appears at around 287 °C, corresponding to the reduction of Cu^{2+} to Cu^0. Only one Cu_2O/SiC reduction peak is observed, at around 302 °C, i.e., at a higher temperature than for CuO/SiC. Two reduction peaks are observed for the Cu_2O/Al_2O_3 catalyst because of partial oxidation of Cu_2O. According to a previous study, CuO is more easily reduced than Cu_2O [30]. Therefore, we can conclude that the reduction peaks for the Cu_2O/Al_2O_3 catalyst at 233 and 287 °C correspond to the reduction of Cu^{2+} to Cu^0 and of Cu^+ to Cu^0, respectively. Similarly, the reduction peaks for Cu_2O/SiO_2 at 236 and 292 °C are associated with the reduction of Cu^{2+} to Cu^0 and of Cu^+ to Cu^0, respectively. A comparison of the peaks for

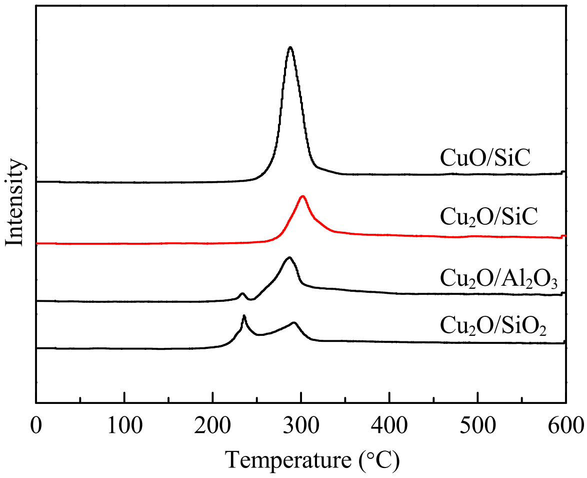


Fig. 4. H_2-TPR profiles of Cu_2O/SiC, CuO/SiC, Cu_2O/Al_2O_3, and Cu_2O/SiO_2 catalysts.

CuO/SiC, Cu_2O/Al_2O_3, and Cu_2O/SiO_2 shows that the reduction peak of Cu_2O/SiC at around 302 °C can attributed to the reduction of Cu^+ to Cu^0, suggesting that Cu is primarily dispersed on SiC as the Cu_2O phase.

3.2. *Effects of reaction conditions*

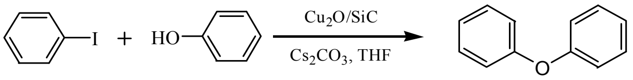
The effects of the reaction conditions, namely temperature, reaction time, amount of base, and amount of catalyst, on the Ullmann-type C–O cross-coupling reaction were investigated; the results are summarized in Table 1. Entries 1–5 show that the yield of diphenyl ether increased with reaction time. When the reaction time was increased from 0.5 to 3 h, the diphenyl ether yield increased from 73% to 97%. However, lengthening the reaction time to 3.5 h did not further increase the yield. We therefore chose 3 h as the reaction time.

The reaction temperature is also an important factor in the Ullmann-type C–O cross-coupling reaction. The yield of diphenyl ether increased from 10% to 97% with increasing reaction temperature from 80 to 150 °C, therefore, subsequent reactions were performed at 150 °C (Table 1, entries 6–9). Increasing the amounts of the base and catalyst also led to the increase in the diphenyl ether yield. The yield of diphenyl ether reached 97% when 1.0 equiv. of Cs_2CO_3 and 10 mg of the Cu_2O/SiC catalyst were used (Table 1, entries 10–16). In conclusion, the optimum reaction conditions are as follows: iodobenzene 14 mmol, phenol 14 mmol, Cs_2CO_3 1.0 equiv., Cu_2O/SiC 10 mg, and THF 10 mL, 150 °C, 3 h, and an Ar atmosphere.

3.3. *Catalytic performance*

Table 2 shows the results for the *O*-arylation of substituted phenols with aryl halides using Cu_2O/SiC as the catalyst. The Cu_2O/SiC catalyst showed high activity in the *O*-arylation of phenol and iodobenzene, with a yield of 97%; the TOF was 1136 h^{-1}, which is much higher than those of most heterogeneous catalysts [13,16] (Table 2, entry 1). The electronic effects of substituent groups on iodobenzene and phenol on the yield of the *O*-arylation reaction were studied.

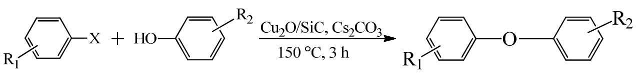
Table 1
Catalytic performance of Cu_2O/SiC in *O*-arylation of phenol and iodobenzene under various reaction conditions.

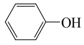
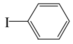
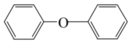
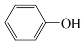
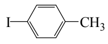
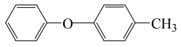
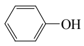
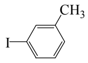
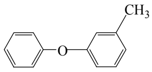
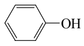
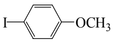
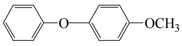
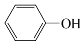
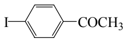
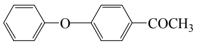
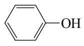
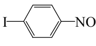
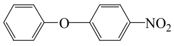
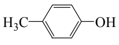
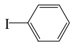
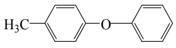
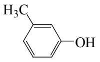
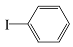
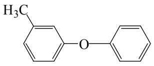
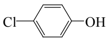
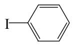
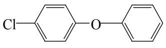
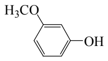
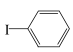
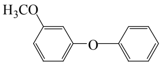
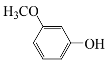
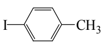
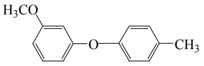
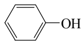
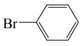
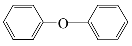
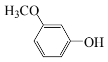
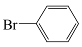
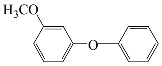
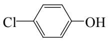
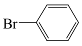
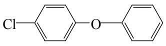
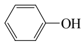
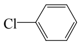
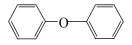
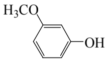
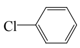
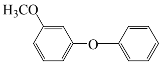
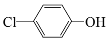
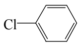
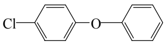


Entry	Time (h)	Temperature (°C)	Amount of base (equiv.)	Amount of catalyst (mg)	Yield (%)
1	0.5	150	1.0	10	73
2	1	150	1.0	10	80
3	2	150	1.0	10	90
4	3	150	1.0	10	97
5	3.5	150	1.0	10	97
6	3	80	1.0	10	10
7	3	100	1.0	10	57
8	3	120	1.0	10	72
9	3	140	1.0	10	82
10	3	150	0.25	10	55
11	3	150	0.5	10	79
12	3	150	0.75	10	89
13	3	150	1.0	0	20
14	3	150	1.0	2	58
15	3	150	1.0	6	82
16	3	150	1.0	12	97

Reaction conditions: aryl halides 14 mmol, phenols 14 mmol, THF 10 mL.

Table 2
Ullmann C–O cross-coupling reactions of aryl halides with phenols catalyzed by Cu_2O/SiC.



Entry	Phenol	Aryl halide	Product	Yield* (%)	TOF (h^{-1})
1				97	1136
2				87	1032
3				83	985
4				89	1056
5				98	1163
6				98	1163
7				95	1127
8				90	1068
9				81	961
10				89	1056
11				90	1068
12				59	700
13				58	688
14				49	581
15				2	24
16				1	12
17				4	48

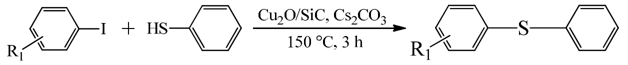
Reaction conditions: aryl halides 14 mmol, phenols 14 mmol, 1.0 equivalent Cs_2CO_3, Cu_2O/SiC 10 mg, THF 10 mL, 150 °C, 3 h, under Ar atomosphere. * Calculated based on the amount of iodobenzene.

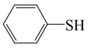
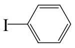
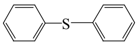
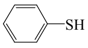
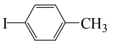
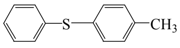
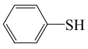
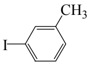
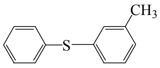
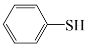
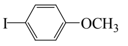
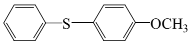
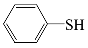
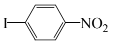
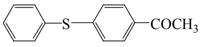
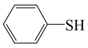
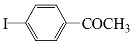
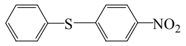
For iodobenzenes with electron-donating substituents such as methyl and methoxy groups the yields were slightly lower (Table 2, entries 2–4). In contrast, the yields were slightly increased by the presence of electron-withdrawing groups such as acetyl and nitro groups on iodobenzene (Table 2, entries 5 and 6). However, for substituted phenols, electron-withdrawing and electron-donating groups both decreased the yields, because of an increase in the number of side reactions, but all the yields were still higher than 80% (Table 2, entries 7–11).

The effects of different aryl halides on the *O*-arylation yield were also investigated. The yields decreased significantly, in the order iodobenzene > bromobenzene > chlorobenzene, be-

Table 3

Ullmann C–S cross-coupling of thiophenol with iodobenzene and substituted iodobenzenes catalyzed by Cu_2O/SiC.



Entry	Thiophenol	Aryl halthide	Product	Yield (%)	TOF (h^{-1})
1				95	1127
2				87	1032
3				97	1151
4				100	1186
5				98	1163
6				89	1056

The reaction conditions were the same as those in Table 2.

cause of the low reactivities of bromobenzene and chlorobenzene (Table 2, entries 12–17).

We also investigated the C–S cross-coupling reactions of thiophenol and iodobenzene and substituted iodobenzenes. The results are shown in Table 3. The product yields were slightly higher because the reactivity of thiophenol is higher than that of phenol in the cross-coupling reaction.

All the above results suggest that Cu_2O/SiC is a highly active heterogeneous catalyst for the *O*-arylation of phenol, substituted phenols, and thiophenol with iodobenzene or substituted iodobenzenes, and the TOF values achieved with the Cu_2O/SiC catalyst for these reactions are much higher than those for most heterogeneous catalysts. The catalyst also shows some catalytic activity in the *O*-arylation of phenol and substituted phenols with bromobenzene and chlorobenzene.

The high activity of Cu_2O/SiC in the Ullmann-type C–O cross-coupling reaction probably originates from the p–n junction between SiC and Cu_2O. Cu_2O is a p-type semiconductor. The β-SiC we used was an n-type semiconductor, based on the positive slope in the Mott-Schottky curve (Fig. 5) [31]. When Cu_2O nanoparticles are dispersed on the β-SiC surface, the electrons in SiC diffuse to Cu_2O and the holes in Cu_2O diffuse to SiC until they reach a balance. A p–n junction is then formed [32], which enhances the *O*-arylation activity.

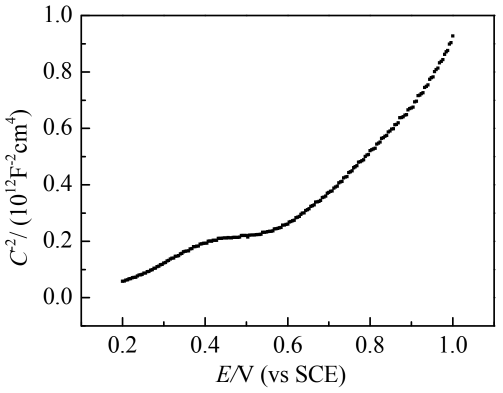


Fig. 5. Mott-Schottky curve of β-SiC in sulfuric acid (0.5 mol/L) solution.

Table 4

Recycling of Cu_2O/SiC catalyst.

Run	1	2	3	4	5
Yield (%)	97	84	75	67	64

Reaction conditions: iodobenzene 14 mmol, phenol 14 mmol, other reaction conditions were the same as those in Table 2.

The recyclability of the Cu_2O/SiC catalyst was investigated by performing the *O*-arylation of phenol with iodobenzene under the optimum conditions. The data in Table 4 show that the yield in the first run was 97%; it decreased to 84% in the second run and to 64% after five runs. The decrease in the activity is caused by loss of the active component (Cu_2O). ICP-OES showed that the Cu content of fresh Cu_2O/SiC was 4.81 wt%, and it decreased to 2.53 wt% after use. Weak interactions between Cu_2O nanoparticles and SiC may result in the loss of active components. It is therefore necessary to develop methods for strengthening the forces between Cu_2O and SiC to improve the reusability of the Cu_2O/SiC catalyst. This could perhaps be achieved by adjusting the thermal treatment conditions or modifying the SiC surface by chemical oxidation with concentrated sulfuric acid or permanganate to increase the number of surface functional groups on SiC.

4. Conclusions

We prepared a Cu_2O/SiC catalyst via a simple two-step liquid-phase method. The XRD, XPS, SEM, TEM, and H_2-TPR results showed that Cu species were dispersed on the SiC primarily as the Cu_2O phase. The effects of the reaction conditions, i.e., temperature, reaction time, amount of base used, and amount of catalyst used, were investigated in the *O*-arylation of iodobenzene with phenol. The optimum conditions were iodobenzene (14 mmol), phenol (14 mmol), Cs_2CO_3 (1 equiv), and THF (10 mL), catalyzed by Cu_2O/SiC (10 mg) at 150 °C for 3 h under Ar. A high yield of diphenyl ether and a TOF of 1136 h^{-1} were achieved under the optimum conditions. The high activity of the Cu_2O/SiC catalyst probably originates from the p–n junction between SiC and Cu_2O. The Cu_2O/SiC catalyst was used with various substrates to obtain a wide range of diaryl ethers. It also showed high activity in the Ullmann C–S coupling reaction, suggesting that this catalyst has general applicability to Ullmann-type cross-coupling reactions.

References

[1] F. Theil, *Angew. Chem. Int. Ed.*, **1999**, 38, 2345–2347.

[2] F. Ullmann, *Ber. Dtsch. Chem. Ges.*, **1904**, 37, 853–854.

[3] M. Palucki, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.*, **1997**, 119, 3395–3396.

[4] J. F. Marcoux, S. Doye, S. L. Buchwald, *J. Am. Chem. Soc.*, **1997**, 119, 10539–10540.

[5] G. Mann, C. Incarvito, A. L. Rheingold, J. F. Hartwig, *J. Am. Chem. Soc.*, **1999**, 121, 3224–3225.

[6] R. Hosseinzadeh, M. Tajbakhsh, M. Mohadjerani, M. Alikarami, *Synlett*, **2005**, 1101–1104.

[7] N. Xia, M. Taillefer, *Chem. Eur. J.*, **2008**, 14, 6037–6039.

Graphical Abstract

Chin. J. Catal., 2017, 38: 658–664 doi: 10.1016/S1872-2067(17)62785-2

Cu_2O/SiC as efficient catalyst for Ullmann coupling of phenols with aryl halides

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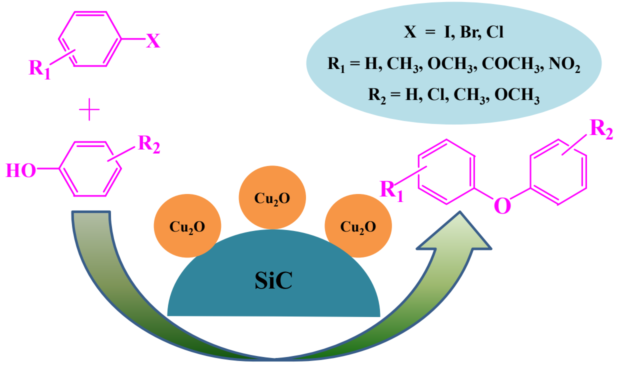
University of Chinese Academy of Sciences;
Dalian University of Technology



A Cu_2O/SiC heterogeneous catalyst was highly active in Ullmann-type C–O cross-coupling reactions of aryl halides and phenols, with a turnover frequency of up to 1136 h^{-1}, and showed general applicability to Ullmann cross-coupling reactions.

[8] F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.*, **2009**, 48, 6954–6971.
[9] M. Kidwai, N. K. Mishra, V. Bansal, A. Kumar, S. Mozumdar, *Tetrahedron Lett.*, **2007**, 48, 8883–8887.
[10] H. Q. Li, C. P. Li, J. Bai, C. L. Zhang, W. Y. Sun, *RSC Adv.*, **2014**, 4, 48362–48367.
[11] P. Puthiaraj, W. S. Ahn, *Catal. Sci. Technol.*, **2016**, 6, 1701–1709.
[12] J. T. Zhang, Z. H. Zhang, Y. Wang, X. Q. Zheng, Z. Y. Wang, *Eur. J. Org. Chem.*, **2008**, 5112–5116.
[13] D. Saberi, M. Sheykhan, K. Niknam, A. Heydari, *Catal. Sci. Technol.*, **2013**, 3, 2025–2031.
[14] J. Y. Kim, J. C. Park, A. Kim, A. Y. Kim, H. J. Lee, H. Song, K. H. Park, *Eur. J. Inorg. Chem.*, **2009**, 4219–4223.
[15] X. Y. Yan, X. L. Tong, Y. F. Zhang, X. D. Han, Y. Y. Wang, G. Q. Jin, Y. Qin, X. Y. Guo, *Chem. Commun.*, **2012**, 48, 1892–1894.
[16] Z. Y. Zhai, X. N. Guo, Z. F. Jiao, G. Q. Jin, X. Y. Guo, *Catal. Sci. Technol.*, **2014**, 4, 4196–4199.
[17] M. J. Ledoux, C. Pham-Huu, *CATTECH*, **2001**, 5, 226–246.
[18] Y. F. Liu, O. Ersen. C. Meny, F. Luck, C. Pham-Huu, *ChemSusChem*, **2014**, 7, 1218–1239.
[19] Z. F. Jiao, Z. Y. Zhai, X. N. Guo, X. Y. Guo, *J. Phys. Chem. C*, **2015**, 119, 3238–3243.
[20] Y. L. Cui, X. N. Guo, Y. Y. Wang, X. Y. Guo, *Chin. J. Catal.*, **2015**, 36, 322–327.
[21] C. H. Hao, X. N. Guo, Y. T. Pan, S. Chen, Z. F. Jiao, H. Yang, X. Y. Guo, *J. Am. Chem. Soc.*, **2016**, 138, 9361–9364.
[22] H. L. Li, Y. G. Lei, Y. Huang, Y. P. Fang, Y. H. Xu, L. Zhu, X. Li, *J. Nat. Gas Chem.*, **2011**, 20, 145–150.
[23] G. Q. Jin, X. Y. Guo, *Microporous Mesoporous Mater.*, **2003**, 60, 207–212.
[24] J. Y. Hao, Y. Y. Wang, X. L. Tong, G. Q. Jin, X. Y. Guo, *Int. J. Hydrogen Energy*, **2012**, 37, 15038–15044.
[25] M. A. Bhosale, B. M. Bhanage, *Adv. Powder Technol.*, **2016**, 27, 238–244.
[26] H. Zhu, M. L. Du, D. L. Yu, Y. Wang, L. N. Wang, M. L. Zou, M. Zhang, Y. Q. Fu, *J. Mater. Chem. A*, **2013**, 1, 919–929.
[27] H. Azimi, S. Kuhri, A. Osvet, G. Matt, L. S. Khanzada, M. Lemmer, N. A. Luechinger, M. I. Larsson, E. Zeira, D. M. Guldi, C. J. Brabec, *J. Am. Chem. Soc.*, **2014**, 136, 7233–7236.
[28] X. W. Liu, F. Y. Wang, F. Zhen, J. R. Huang, *RSC Adv.*, **2012**, 2, 7647–7651.
[29] J. Pal, M. Ganguly, S. Dutta, C. Mondal, Y. Negishi, T. Pal, *CrystEngComm*, **2014**, 16, 883–893.
[30] C. S. Polster, H. Nair, C. D. Baertsch, *J. Catal.*, **2009**, 266, 308–319.
[31] J. D. Hong, X. Y. Xia, Y. S. Wang, R. Xu, *J. Mater. Chem.*, **2012**, 22, 15006–15012.
[32] C. Liu, B. Q. Wang, T. Liu, P. Sun, Y. Gao, F. M. Liu, G. Y. Lu, *Sens. Actuator B*, **2016**, 235, 294–301.

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