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Article

Cu₂O/SiC as efficient catalyst for Ullmann coupling of phenols with aryl halides

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ABSTRACT

A Cu₂O/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 H₂ temperature-programmed reduction. All the results indicate that Cu is present on the SiC support primarily as Cu₂O. The SEM and TEM results show that cubic Cu₂O 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 Cu₂O/SiC (5 wt% Cu) as the catalyst, Cs₂CO₃ (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 Cu₂O/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 Cu₂O/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., Cu₂O.

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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 Cu₂O nanocubes of size about 45 nm were highly active and recyclable catalyst for the cross-coupling of aryl halides and phenols. Cu₂O 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 Cu₂O nanoparticles and protect them from oxidation, and graphene-supported Cu₂O 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 Cu₂O by the reduction of a Cu(OH)₂ precipitate using N₂H₄·H₂O, and the obtained Cu₂O/SiC catalyst was used to photocatalytically reduce CO₂ to CH₃OH under visible-light irradiation. In this work, we used SiC as a support to stabilize Cu₂O nanoparticles because a p–n junction can be formed between Cu₂O and SiC. The Cu₂O/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 m²/g has been reported elsewhere [23]. A Cu₂O/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 Cu₂O/SiC catalyst.

For comparison, Cu₂O/Al₂O₃ and Cu₂O/SiO₂ were prepared using the same method as was used for the Cu₂O/SiC catalyst. CuO/SiC was prepared by calcination of Cu₂O/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. H₂ temperature-programmed reduction (H₂-TPR) was performed using an automatic adsorption instrument (TP-5080, Xianquan, China). The Cu loadings of the fresh and recycled Cu₂O/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), Cs₂CO₃ (14 mmol), tetrahydrofuran (THF, 10 mL), and the Cu₂O/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:

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

$$\text{TOF} = \text{Amount of aryl halides (mol)} \times \text{conversion (\%)} \times \\ \text{selectivity (\%)} / (\text{mass of Cu}_2\text{O/SiC (g)} \times \text{Cu}_2\text{O loading (\%)} \times \\ \text{reaction time (h)} / M[\text{Cu}_2\text{O}] \text{ (g/mol)})$$

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 Cu₂O/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 Cu₂O, respectively [25,26], indicating that Cu is present on the SiC support primarily as the Cu₂O phase.

XPS was used to examine the chemical states and surface properties of the Cu₂O/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 Cu₂O [27–29]. This confirms that the

Fig. 1. XRD pattern of $\text{Cu}_2\text{O}/\text{SiC}$ 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 2p XPS spectrum (a) and Cu LMM Auger spectrum (b) of $\text{Cu}_2\text{O}/\text{SiC}$.

Fig. 3. SEM (a, b) and TEM (c, d) images of $\text{Cu}_2\text{O}/\text{SiC}$ catalyst.

These results suggest that the Cu component in the $\text{Cu}_2\text{O}/\text{SiC}$ catalyst is Cu_2O .

Fig. 4 shows the H_2 -TPR results for $\text{Cu}_2\text{O}/\text{SiC}$ and CuO/SiC ; the results for $\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Cu}_2\text{O}/\text{SiO}_2$ 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 $\text{Cu}_2\text{O}/\text{SiC}$ 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 $\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$ 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 $\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$ 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 $\text{Cu}_2\text{O}/\text{SiO}_2$ 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 $\text{Cu}_2\text{O}/\text{SiC}$, CuO/SiC , $\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$, and $\text{Cu}_2\text{O}/\text{SiO}_2$ catalysts.

CuO/SiC, Cu₂O/Al₂O₃, and Cu₂O/SiO₂ shows that the reduction peak of Cu₂O/SiC at around 302 °C can attributed to the reduction of Cu⁺ to Cu⁰, suggesting that Cu is primarily dispersed on SiC as the Cu₂O 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 Cs₂CO₃ and 10 mg of the Cu₂O/SiC catalyst were used (Table 1, entries 10–16). In conclusion, the optimum reaction conditions are as follows: iodobenzene 14 mmol, phenol 14 mmol, Cs₂CO₃ 1.0 equiv., Cu₂O/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 Cu₂O/SiC as the catalyst. The

Table 1

Catalytic performance of Cu₂O/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 Cu₂O/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 equiv. Cs₂CO₃, Cu₂O/SiC 10 mg, THF 10 mL, 150 °C, 3 h, under Ar atmosphere. * Calculated based on the amount of iodobenzene.

Cu₂O/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.

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 Cu₂O/SiC.

$R_1-\text{C}_6\text{H}_4-\text{I} + \text{HS}-\text{C}_6\text{H}_5 \xrightarrow[150\text{ }^\circ\text{C, 3 h}]{\text{Cu}_2\text{O/SiC, Cs}_2\text{CO}_3} R_1-\text{C}_6\text{H}_4-\text{S}-\text{C}_6\text{H}_5$					
Entry	Thiophenol	Aryl halide	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 Cu₂O/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 Cu₂O/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 Cu₂O/SiC in the Ullmann-type C–O cross-coupling reaction probably originates from the p–n junction between SiC and Cu₂O. Cu₂O 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 Cu₂O nanoparticles are dispersed on the β-SiC surface, the electrons in SiC diffuse to Cu₂O and the holes in Cu₂O diffuse to SiC until they reach a balance. A p–n junction is then formed

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

Table 4

Recycling of Cu₂O/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.

[32], which enhances the *O*-arylation activity.

The recyclability of the Cu₂O/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 (Cu₂O). ICP-OES showed that the Cu content of fresh Cu₂O/SiC was 4.81 wt%, and it decreased to 2.53 wt% after use. Weak interactions between Cu₂O nanoparticles and SiC may result in the loss of active components. It is therefore necessary to develop methods for strengthening the forces between Cu₂O and SiC to improve the reusability of the Cu₂O/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 Cu₂O/SiC catalyst via a simple two-step liquid-phase method. The XRD, XPS, SEM, TEM, and H₂-TPR results showed that Cu species were dispersed on the SiC primarily as the Cu₂O 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), Cs₂CO₃ (1 equiv), and THF (10 mL), catalyzed by Cu₂O/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 Cu₂O/SiC catalyst probably originates from the p–n junction between SiC and Cu₂O. The Cu₂O/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

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Cu₂O/SiC as efficient catalyst for Ullmann coupling of phenols with aryl halides

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A Cu₂O/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, 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.

Cu₂O/SiC高效催化卤代芳烃与酚类的Ullmann偶联反应

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摘要: 卤代苯与酚类化合物反应制取二芳基醚是现代有机合成中的一个重要反应。传统的二苯醚合成方法是铜催化卤代苯与酚类化合物的Ullmann型C–O偶联反应, 但是这种方法需要苛刻的反应条件。后来, 人们发现了Pd(0)和Cu(I)基催化剂, 但是前者成本较高, 且需要使用昂贵的配体, 因此其应用受到了限制, 而铜作为一种成本较低的催化剂受到了越来越多的关注。铜催化剂可以分为均相和非均相两大类。均相铜催化剂使用的是铜盐, 并且需要加入配体, 成本较高, 且不易分离和循环利用。非均相铜催化剂研究较多的是CuO, Cu₂O及Cu纳米颗粒, 其中Cu₂O纳米颗粒催化剂对Ullmann型C–O偶联反应具有很高的催化活性, 但是它在潮湿的空气中容易被氧化, 因此需要寻找一种合适的载体防止Cu₂O纳米颗粒被氧化。

SiC具有优良的化学稳定性及导电导热性能, 并且作为载体已经成功应用到很多热催化及光催化反应中。本文以高比

表面积的SiC为载体, 以乙二醇作为溶剂和还原剂, 采用传统的两步液相还原法制备了Cu₂O/SiC催化剂, 并通过X射线衍射、X射线光电子能谱、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和H₂程序升温还原等方法对Cu₂O/SiC催化剂进行了表征. SEM和TEM结果表明, Cu₂O纳米颗粒均匀分散在SiC表面, 同时上述表征结果都表明Cu在SiC上主要以Cu₂O的形式存在.

将制备的Cu₂O/SiC催化剂用于催化卤代芳烃与酚类的Ullmann C–O偶联反应中. 以碘苯和苯酚的Ullmann C–O偶联反应为模型实验, 考察了反应温度、反应时间、溶剂、碱的种类及用量和催化剂用量等条件的影响, 得到了碘苯与苯酚Ullmann C–O偶联反应的最优反应条件为: 卤代芳烃14 mmol, 酚类14 mmol, 1.0当量的Cs₂CO₃, Cu₂O/SiC (5 wt%) 10 mg, 四氢呋喃10 mL, 在Ar气氛下150 °C反应3 h. 在该条件下, 二苯醚收率达到97%, 转化频率(TOF)高达1136 h⁻¹. Cu₂O/SiC催化剂对Ullmann C–O偶联反应具有很好的普适性, 并且对Ullmann C–S偶联反应也表现出很高的活性, TOF高达1186 h⁻¹. 以碘苯和苯酚的Ullmann C–O偶联反应为基准实验, 对催化剂的循环稳定性进行了考察. Cu₂O/SiC催化剂五次循环后二苯醚的收率从97%降低至64%, 这主要是由于活性组分Cu₂O的流失所致.

关键词: 氧化亚铜; 碳化硅; Ullmann偶联; *O*-芳基化; 酚类; 卤代芳烃

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