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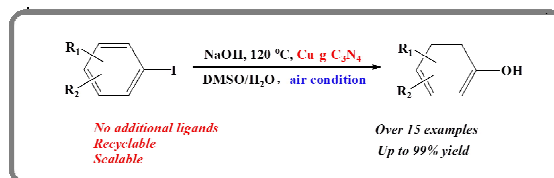
Graphical abstract

Heterogeneous Copper-Catalyzed Hydroxylation of Aryl Iodides under Air Condition

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The ligand-free heterogeneous copper-catalyzed phenols synthesis through the hydroxylation of aryl iodides using cheap bases under air condition was reported.



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In this work, the ligand-free heterogeneous copper Cu-g-C₃N₄ was synthesized and used for the hydroxylation of aryl iodides to synthesize phenols using cheap bases. The catalyst was conveniently prepared, air-tolerant, reusable and scalable, and is very efficient for a wide range of substrates. The synthesis of substituted phenols can be carried out under air condition and has great potential of practical applications.

Serving as the structural constituents of pharmaceuticals, materials, and natural compounds, phenols are very important synthetic intermediates with numerous applications in manufacturing of petrochemical, agrochemical polymers and other chemicals.¹ Effective synthesis methods for phenols are highly required.² Functionalized phenols can be synthesized through different routes, including coupling of hydroxide with aryl halides,³ benzyne protocol,⁴ C-H activation/hydroxylation⁵ and transformation of arene diazonium salts mediated by copper.⁶ Amongst these approaches the most attractive method is the conversion of aryl halides to phenols via the coupling with hydroxide using transition metal salts as the catalysts. Different types of catalysts have been developed, including Pd/ligands homogeneous catalyst systems,³ semi-heterogeneous Pd/polyaniline catalyst,⁷ homogeneous Cu/ligands catalyst systems,⁸⁻¹⁰ and Fe/N,N'-dimethylethylenediamine catalyst.¹¹ Buchwald and co-workers^{3a} did the first work on the hydroxylation in 2006. They realized the preparation of phenols from aryl/heteroaryl bromides and chlorides by applying monodentate phosphine ligands with Pd₂dba₃ as the catalyst under inert atmosphere. Subsequently, some efficient catalytic systems based on palladium/phosphine ligands have been developed by the groups of Willis,^[3b] Kwong,^[3c] Beller,^[3d, 3e] and Stradiotto.^[3f]

Using cheap metals instead of noble metals is always the pursuit of green catalysis. In 2009, the synthesis of phenols by direct cross-coupling of aryl iodides and hydroxide salts with CuI as the catalyst was reported simultaneously using either 1,3-diketone⁸ or 1,10-phenanthroline⁹ ligand in aqueous DMSO system under a nitrogen atmosphere. More recently, several other ligands such as lithium pipercolinate,¹² 8-hydroxyquinoline-N-oxide,¹³ D-glucose,¹⁴ 8-hydroxyquinoline,¹⁵ pyridine-2-aldoxime,¹⁶ 8-hydroxyquinalidine¹⁷ and glycolic acid¹⁸ were developed. These results indicate that the transformation is highly dependent on the use of various special ligands.

Cu-based catalysts have been studied most extensively for this

kind of reactions because they have some unique advantages. However, most reported works were homogeneous, which need special ligands and it is very difficult to recycle the catalysts. A sulfonic acid resin (INDION-770) in combination with copper salts¹⁹ and CuO supported on mesoporous silica²⁰ were reported but expensive CsOH are both required. Tetra-n-butylammonium hydroxide was also employed as the base using CuI-Nanoparticles as catalyst, the reactions were carried out under an inert atmosphere with a long reaction time.²¹ Copper-MOF was also found active in the hydroxylation of aryl iodides, unfortunately, complete decomposition of MOFs occurred after the reaction and the catalyst cannot be recycled.²² Obviously, developing heterogeneous, low cost, highly efficient, and recyclable catalysts for the reactions is highly desirable, but is challenging.

Mesoporous graphitic carbon nitride (mpg-C₃N₄) has recently found wide applications in catalysis due to its special structure and properties.²³ The mpg-C₃N₄ materials show great potential in fabricating supported catalysts.²⁴ In the present work, we synthesized a copper-doped graphitic carbon nitride catalyst (Cu-g-C₃N₄) by using cheap urea and Cu(NO₃)₂ as the precursors through a facile and efficient method. The catalyst was successfully applied in the synthesis of phenols from aryl iodides and hydroxide. Good to excellent yields of phenols could be obtained under air condition with low Cu loading. The catalyst could be reused at least 5 times without decrease in yield. More importantly, the Cu-g-C₃N₄ catalyzed hydroxylation of aryl iodides can be conducted on 10 g scales under experimental condition, thus has great potential of application for synthesizing substituted phenols.

Initially, we selected iodobenzene as the model substrate to optimize the reaction conditions, and the results are summarized in Table 1. In DMSO aqueous solution with a DMSO and water volume ratio of 1:1, a yield of 98.6 % was achieved at 120°C when cesium hydroxide (6.0 eq.) as the nucleophile and Cu-g-C₃N₄ (8 mol%) as catalyst (Table 1, entry 1). When KOH or NaOH was used as the nucleophile, almost quantitative product phenol was formed and no by-product was detected by GC-MS (Table 1, entries 2 and 3). Encouraged by these good results, the effects of concentrations of bases, reaction temperature and reaction solvents on the phenol synthesis were further investigated. It is worth noting that at lower concentrations of the bases or when the temperature was below 120°C, the yield of phenol was low (Table 1, entries 4-12). Solvent composition had

remarkable influence on the yield of the product (Table 1, entries 6, 13-18). Only 14.6 % yield of phenol was formed in pure DMSO (Table 1, entry 13), and no product was detected in pure water (Table 1, entry 18). To further optimize the reaction conditions, the effect of the amount of catalyst Cu-g-C₃N₄ on the reaction was studied. It can be known from Table 1 that reducing the amount of Cu from 8 mol% to 4 mol% did not reduce the yield, and the reaction could finish with excellent yields in 12 h (Table 1, entries 3, 19 and 20). However, when the amount of catalyst Cu-g-C₃N₄ was further decreased to 2 mol%, the yield of phenol was only 50.9 % after 24 h (Table 1, entry 21). The results above indicate that 4 mol% Cu-g-C₃N₄ was the reasonable amount of the catalyst. Excellent result was obtained when the reaction was carried out with 4 mol% Cu-g-C₃N₄ using NaOH as the base in DMSO aqueous solution at 120 °C under air condition (Table 1, entry 20). To verify the crucial role of the catalyst Cu-g-C₃N₄ for the reaction, a control experiment was also conducted in the absence of the catalyst Cu-g-C₃N₄, and the reaction did not occur (Table 1, entry 22). To ascertain the role of the air in the catalytic reaction, we conducted a control experiment under Ar atmosphere. The result is also listed in Table 1. Under Ar atmosphere, the reaction can also be carried out with excellent yield (Table 1, entry 23). The result indicated that the air did not affect the catalytic reaction.

Table 1. Optimization of hydroxylation of iodobenzene catalyzed by Cu-g-C₃N₄ in DMSO aqueous solution^a

Entr y	Base/eq.	Temp /°C	Solvents ^b	Catalyst /mol%	Time/h	Yields ^c / %
1	CsOH/6	120	1.5/1.5	8	12	98.6
2	KOH/6	120	1.5/1.5	8	12	98.7
3	NaOH/6	120	1.5/1.5	8	12	97.1
4	KOH/6	100	1.5/1.5	8	12	8.3
5	KOH/4	120	1.5/1.5	8	12	85.8
6	NaOH/4	120	1.5/1.5	8	12	94.0
7	KOH/3	120	1.0/1.0	8	12	15.2
8	NaOH/3	120	1.0/1.0	8	12	50.1
9	NaOH/3	120	1.5/1.5	8	12	42.8
10	NaOH/4	110	1.5/1.5	8	12	24.4
11	NaOH/4	100	1.5/1.5	8	12	6.5
12	NaOH/4	90	1.5/1.5	8	12	N.D.
13	NaOH/4	120	3.0/0	8	12	14.6
14	NaOH/4	120	2.5/0.5	8	12	20.0
15	NaOH/4	120	2.0/1.0	8	12	58.5
16	NaOH/4	120	1.0/2.0	8	12	42.2
17	NaOH/4	120	0.5/2.5	8	12	18.3
18	NaOH/4	120	0/3.0	8	12	N.D.
19	NaOH/4	120	1.5/1.5	6	12	96.2
20	NaOH/4	120	1.5/1.5	4	12	95.0
21	NaOH/4	120	1.5/1.5	2	12(24) ^d	43.1(50.9) ^d
22	NaOH/4	120	1.5/1.5	0	12	N.D.
23	NaOH/4	120	1.5/1.5	4	12	95.5 ^d

^a All reactions were performed using 1.0 mmol of iodobenzene. ^b DMSO/mL: H₂O/mL. ^c GC yield based on the added iodobenzene, using 1, 4-dioxane as





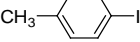
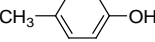
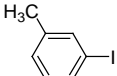
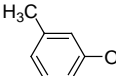
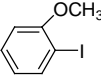
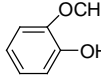
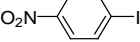
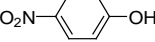
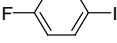
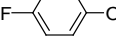
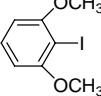
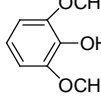
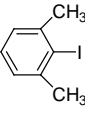
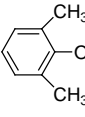
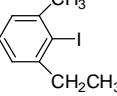
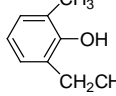
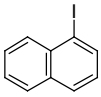
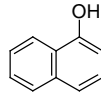
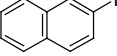
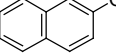
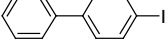
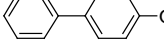








internal standard. ^d Data in parentheses indicate 24 h and its corresponding yield. ^d Under Ar atmosphere.

The catalytic performance of the catalytic system was further investigated using a wide range of aryl iodides as the substrates and NaOH as the base, and the results are listed in Table 2. The cross-coupling reactions of aryl iodides with NaOH proceeded very smoothly at 120 °C under air atmosphere to afford the corresponding coupling products in good to excellent yields. For the substrates with various electron-donating and electron-withdrawing groups such as -Cl, -CH₃, -CH₂CH₂CH₂CH₃, -OCH₃, -Ph, -F, and -NO₂, satisfactory yields of the desired phenols were obtained (Table 2, entries 1-9 and 15). Even the substrates bearing strong donating groups, such as two -OCH₃ groups, the reaction also proceeded efficiently to afford the corresponding coupling product in 85% isolated yields (Table 2, entry 10). The reactions of 2,4-dimethoxy-1-iodobenzene, 2,4-dimethyl-1-iodobenzene, and 3-ethyl-2-iodotoluene with NaOH, which are sterically hindered, provided high yields of the desired coupling products (Table 2, entries 10-12).

Besides, bulky 1-iodonaphthalene and 2-iodonaphthalene also successfully converted into their corresponding phenols in excellent isolated yields (Table 2, entries 13 and 14). The results demonstrated that steric effect did not affect the catalytic reactions significantly. We also carried out the reactions using 1-chloro-4-iodobenzene and 4-fluoroiodobenzene as the reactants, and the -Cl and -F groups were untouched in the reactions (Table 2, entries 1 and 9). To examine the scope for the title reaction, we investigated the reactions using bromobenzene, chlorobenzene and 2-iodine thiophene as the substrates under the optimized reaction conditions. The results are listed in Table 2 (Table 2, entries 16-19). As shown in Table 2, in our catalytic system, aryl bromides and chlorides were inert under the experimental conditions giving no cross-coupling products (Table 2, entries 16 and 17). However, when 2 eq. KI was added, bromobenzene can be converted to the product in moderate yield (Table 2, entry 18). Heteroaryl iodides, such as 2-iodine thiophene, also cannot work (Table 2, entry 19). Thus our catalytic system provides a highly selective coupling reaction of aryl iodides with NaOH under practical air condition, while the -F and -Cl groups are tolerated.

Table 2. Hydroxylation of aryl iodides catalyzed by Cu-g-C₃N₄ in DMSO aqueous solution^a

Entr y	Aryl Halides	Time/h	Products	Yields/% ^b
1		12		83
2		12		83

3		16		78
4		16		84
5		16		89
6		16		83
7		16		80
8		12		89
9		12		82
10		16		85
11		16		89
12		16		80
13		16		79
14		16		82
15		12		93
16		12		0
17		12		0
18 ^c		12		47
19		12		0

^a Reactions were carried out with 1.0 mmol of aryl iodides, 4 mol% of Cu-g-C₃N₄, 4 eq. NaOH, 1.5 mL DMSO and 1.5 mL H₂O at 120°C under air condition. ^b Isolated yields based on the added aryl iodides. ^c 2 eq. KI was added.

The stability and reusability of the catalyst Cu-g-C₃N₄ was investigated using the coupling reaction of iodobenzene with NaOH. The results showed that the catalyst could be reused at least 5 times without decrease in catalytic activity and selectivity (Figure 1). More importantly, we successfully carried out a 10 g scale reaction here. Iodobenzene (10.2 g, 50 mmol), NaOH (8.0 g, 200 mmol, 4 eq.) and Cu-g-C₃N₄ (0.55 g, 2.9 mol%) were stirred in 60 mL of DMSO/H₂O (1:1 in volume) at 120°C under air condition. Complete conversion of iodobenzene was achieved after 20 h and the phenol was confirmed as the sole product by GC with 98.8 % yield, demonstrating the suitability of this protocol in large-scale application.

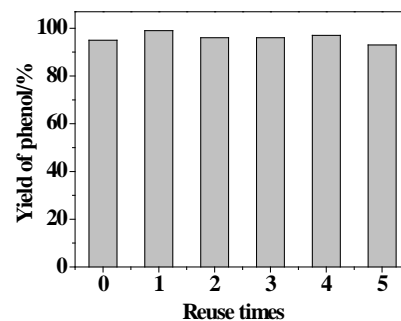


Figure 1. The reusability of the catalyst Cu-g-C₃N₄. Reactions were carried out with 1.0 mmol of iodobenzene, 4 mol% of Cu-g-C₃N₄, 1.5 mL DMSO and 1.5 mL H₂O at 120°C under air condition. Phenol yields were determined by GC.

The catalyst Cu-g-C₃N₄ was characterized systematically (Figures S1-S5). XRD patterns in Figure S1 showed that the catalyst Cu-g-C₃N₄ exhibited the structure of g-C₃N₄.²⁵ No diffraction peaks of copper species were observed in the pattern. The presence of the copper species in Cu-g-C₃N₄ was confirmed by XPS analysis. The high resolution Cu2p XPS spectrum of the sample in Figure S2b showed two main peaks located at about 952.5 eV and 932.3 eV corresponding to Cu2p1/2 and Cu2p3/2, respectively,²⁶ which indicate the existence of Cu⁺ species in the catalyst. The characteristic mode of the triazine units (C₆N₇) at 810 cm⁻¹ ^{24c} is also observed in the FT-IR spectra in Figure S3, indicating the presence of typical structure of g-C₃N₄. Thermogravimetric analysis of the Cu-g-C₃N₄ in Figure S5 illustrated that the catalyst Cu-g-C₃N₄ can bear high temperature up to 600°C.

The reasons for the high activity and recyclability of the catalyst Cu-g-C₃N₄ might partially originate from the special structure and properties of the support. Schnick²⁷ and Arne Thomas²⁸ reported that primary and secondary amines were present at the surface of g-C₃N₄. Here in our catalytic system, the secondary amines at the surface of the catalyst probably act as a ligand of Cu⁺ species to promote the reaction. Besides as the support and stabilizer for the Cu⁺ species, g-C₃N₄ also acted as the reducing agent²⁹ during the catalyst preparation process, leading to formation of Cu⁺ species from Cu(NO₃)₂ precursor. Further exploration about the catalytic mechanism is currently under investigation in our laboratory.

Conclusions

In summary, we have carried out the heterogeneous copper-catalyzed phenols synthesis without additional ligands under air conditions. The cross-coupling reactions of various aryl iodides with NaOH proceeded very smoothly with low Cu amount (4 mol%) at 120°C under air to afford the corresponding coupled products in good to excellent yields. The catalyst Cu-g-C₃N₄ can be reused at least 5 times without decrease in catalytic efficiency. Phenol can be successfully produced with 98.8% yield under the experimental conditions of 10 g scale. The catalyst is easily prepared using cheap raw materials, and is air and moisture-tolerant, stable and recyclable. Thus, the Cu-g-C₃N₄ catalyzed hydroxylation of aryl iodides has great potential of application for synthesizing substituted phenols.

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Notes and references

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²⁵ † Electronic Supplementary Information (ESI) available: [Experimental details, NMR spectra of products, and characterization of the catalyst are available in Supporting Information.]. See DOI: 10.1039/b000000x/

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