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## ARTICLE TYPE

# A highly active and recyclable catalyst for the synthesis of indole and phenyl ether

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A new simple catalytic system consisting of copper-aluminium and hydrotalcite (CuAl-HT) had been developed by a facile one-pot method without harm to the environment. The catalyst was characterized by TEM, XRD and XPS. It could be used as an efficient catalyst for the synthesis of both indole and phenyl ether. As expected, the catalyst afforded high catalytic activity for the selective synthesis of indole via intramolecular dehydrogenative N-heterocyclization of 2-(2-aminophenyl)ethanol. Meanwhile, it also exhibited superior catalytic property for Ullmann-type coupling reaction to synthesis phenyl ether with iodobenzene and phenol. The CuAl-HT catalyst showed higher activity than conventional catalysts based on copper group and could be recycled several times with a stable catalytic activity. This procedure had real economic advantages since one of expensive materials were used.

## Introduction

Benzo-fused N-heterocyclic compounds, particularly indoles, are important precursors for the synthesis of fine chemicals, pharmaceuticals, dyes and agrochemicals.<sup>1</sup> A number of methods for synthesis of indoles have been developed and reviewed.<sup>2</sup> Previously, considerable efforts have focused on the synthesis of indoles by transition-metal-catalyzed N-heterocyclization of non-amino alcohols.<sup>3</sup> However, the synthesis of such substituted N-heterocycles with many traditional approaches suffers from requiring harsh conditions and delivering poor selectivity. Recently, an attractive route for the synthesis of N-heterocycles is to utilize alcohols as substrates as these are readily available and easy to handle.<sup>4</sup> A variety of transition metals catalysts such as ruthenium,<sup>5</sup> iridium<sup>6</sup> and palladium,<sup>7</sup> nickel and copper<sup>8</sup>, have been reported for the intramolecular dehydrogenative N-heterocyclization of 2-(2-aminophenyl)ethanol and derivatives. Although the majority of reported catalytic systems are active for this reaction, they are significantly more expensive, non-recoverable, even long reaction time. From ecological and practical points of view, the development of a reusable and less expensive base-metal catalyst is highly desirable. Given that oxidation of an alcohol to an aldehyde is the key step in this route, the Cu catalyst is an attractive alternative.<sup>9</sup>

On the other hand, aryl carbon-oxygen forming reactions are important transformations in synthetic chemistry.<sup>10</sup> The formation of diaryl ethers via a C-O cross-coupling reaction represents a powerful and straightforward method in organic synthesis.<sup>11</sup> Diaryl ethers are not only important structures in biological systems, but also common moieties in pharmaceutical research and materials interest.<sup>12</sup> Common synthesis of diaryl ethers usually requires the

coupling reaction of phenols with aryl halides in the presence of a catalyst containing a transition metal. It has been reported that Pd-catalyzed methods can function in this role, organic-inorganic hybrid materials<sup>13</sup> also has been used to catalysis Ullmann-type coupling reaction for synthesis phenyl ether, but their high costs and elaborate ligands are drawbacks when compared with copper-mediated reactions.<sup>14</sup>

Herein, we designed and prepared CuAl-HT catalysts with three different contents of copper and aluminum, and their applications for the synthesis of indole and phenyl ether. The catalyst can successfully promote the oxidant-free dehydrogenation of various alcohols under liquid-phase conditions. This feature would increase the scope of this oxidative intramolecular oxidative cyclization and allow us to prepare N-heterocycles using substrate containing alcohol functionality. Meanwhile, the catalysts afforded excellent yields of diaryl ethers in the Ullmann-type coupling reaction to synthesis phenyl ether with iodobenzene and phenol. It is important to note that the CuAl-HT catalyst could be recycled by a simple filtration of the reaction solution and used for 6 consecutive trials without significant loss of its reactivity. What more, this material is easy to achieved, and is no harmless to the environment.

## Experimental

### Materials

Copper(ii) nitrate hydrate, aluminum nitrate nonahydrate, sodium hydroxide, potassiumhydroxide, sodiumcarbonate, potassiumcarbonate, calciumchloride, toluene, dimethylsulfoxide, dioxane, dimethyl formamide, o-xylene, acetonitrile, tetrahydrofuran, sodiumbicarbonate, copperacetate and copper

powder were purchased from Sinopharm Chemical Reagent Co., Ltd. Various reaction reagents, such as 2-(2-aminophenyl)ethanol, sodium isopropyl alcohol, phenol, iodobenzene, p-iodonitrobenzene, p-cresol, p-iodoanisole, p-methoxyphenol, p-chlorophenol and were purchased from Alfa Aesar. All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

### Preparation of CuAl-HT catalysts

CuAl-HT3 (Cu: Al=3:1) is prepared as follows: About 100 mL of deionized water was taken into a 250 mL three neck round bottom flask and stirred at 25 °C with a overhead mechanical stirrer. A mixture of solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (16.46g, 0.0702 moles) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (8.44g, 0.0225 moles) in deionised water were added simultaneously drop-wise from the respective burettes into the round bottomed flask. The pH of the reaction mixture was maintained constantly (8-9) by the continuous addition of the base solution ( $\text{NaOH}/\text{Na}_2\text{CO}_3$ ). The resulting slurry was washed with distilled water thoroughly to give a pH of 7 and separated by filtration. The collected sample ( $\text{Cu}^{2+}\text{Al-HT3}$  (Cu: Al=3:1)) was dried at 70°C for 12 h, and then treated in a 20%  $\text{H}_2/\text{N}_2$  flow ( $100 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$ ) at 300°C (ramping rate,  $5^\circ \text{C min}^{-1}$ ) for 2 h and passivation (0.1%  $\text{O}_2/\text{N}_2$ ,  $40 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$ ) at A Headings are the primary heading type ambient temperature for 4 h. CuAl-HT2 (Cu: Al=2:1) and CuAl-HT3 (Cu: Al=1:1) were prepared using the same procedure.

### Characterization of catalysts

All of the reagents and solvents were commercially available and used without further purification. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-K $\alpha$  radiation as the X-ray source in the  $2\theta$  range of 10-85°. The conversion was estimated by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6,890N/5,973N). Cu-Al content of the catalyst was measured by inductively coupled plasma (ICP) on IRIS Advantage analyzer. The morphology of the catalyst was observed by a Tecnai G2 F30 transmission electron microscopy and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. Inductively coupled plasma (ICP) measurement indicated that it contented 66.58% Cu and 9.84%  $\text{Al}_2\text{O}_3$  in CuAl-HT3, as it contented 59.44% Cu and 12.80%  $\text{Al}_2\text{O}_3$  in CuAl-HT2, 45.20% Cu and 19.86%  $\text{Al}_2\text{O}_3$  in CuAl-HT1.

### Catalytic tests

#### Dehydrogenative reaction

Under nitrogen atmosphere, 10 mL round-bottomed flask was charged with 2-(2-aminophenyl)ethanol (0.5 mmol), KO-t-Bu (0.5mmol),  $\text{CaCl}_2$  (0.25 mmol), o-xylene (4.0 mL) and catalyst (0.1 g). The reaction was performed at 140°C for 12 h and was monitored by GC analysis. For recycling, the recovered catalyst was washed with methanol several times, and then dried under vacuum at 60 °C.

#### Ullmann-type coupling reaction

Under nitrogen atmosphere, 10 mL round-bottomed flask was charged with phenol (1.0mmol), iodobenzene (1.0mmol), KF (2.0 mmol), DMSO (4.0 mL) and catalyst (0.2mmol). The reaction was performed at 135°C for 16 h and was monitored by GC

analysis. For recycling, the recovered catalyst was washed with methanol several times, and then dried under vacuum at 60 °C.

## Results and discussion

### Characterization of catalysts

The phase composition and structure of the catalysts were determined by XRD. Fig. 1 showed the XRD pattern between 10° and 85° of the catalysts. Bragg's reflections at  $2\theta$  value of 43.5°, 50.6°, 74.4° represented (111), (200), (220) planes of fcc crystal structure of metal copper. The sharp and strong peaks revealed that Cu nano-crystals were highly oriented.

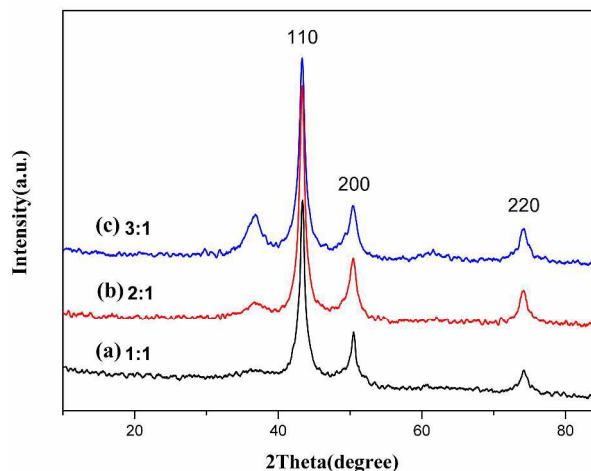


Fig. 1 XRD pattern of the catalysts: (a) CuAl-HT1; (b) CuAl-HT2; (c) CuAl-HT3.

To further probe the morphology of the catalyst, we used TEM measurement to analysis the catalysts. Fig. 2 showed the TEM images of the catalysts, in which well-dispersed copper nanoparticles could be observed clearly. The differences in synthesis conditions and the contents of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  affected the particle size of copper nanoparticles. The TEM images in Fig. 2 showed the copper particle size in the range of 10-30 nm for all of the as-prepared catalysts. This indicated that copper nanoparticles were uniformly distributed in the hydrotalcite, which was advantageous for the catalytic activity.

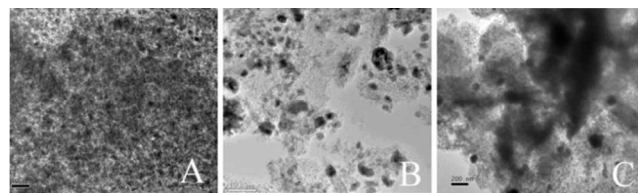
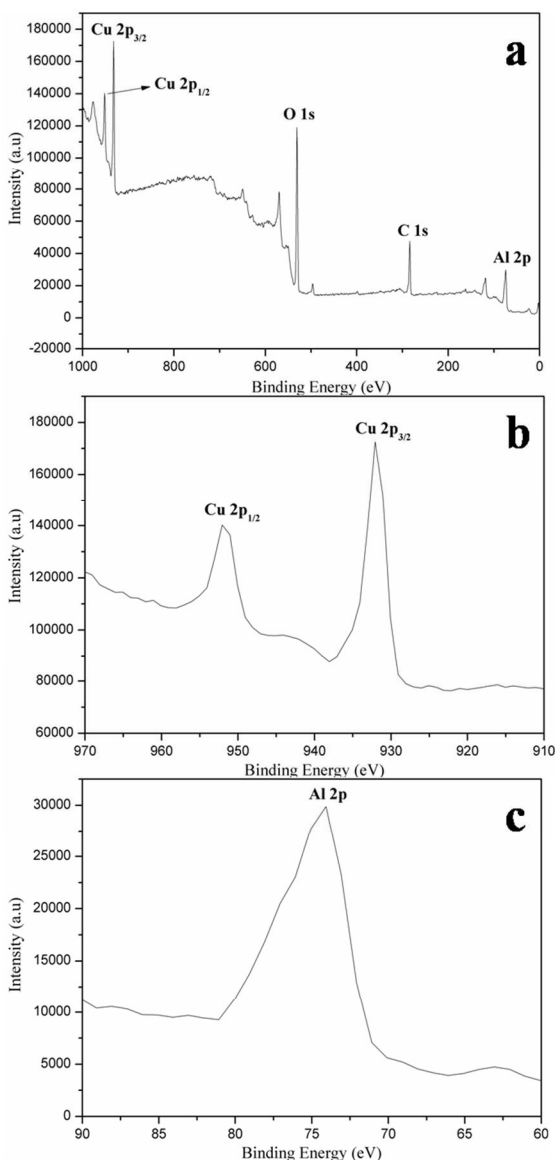


Fig. 2 TEM micrograph of the catalysts: (A) CuAl-HT1; (B) CuAl-HT2; (C) CuAl-HT3.

Fig. 3 presented XPS elemental survey scans of the surface of the CuAl-HT3 catalyst (CuAl-HT1 and CuAl-HT2 are similar to CuAl-HT3). Peaks corresponding to copper, aluminum oxide could be clearly observed. To ascertain the oxidation state of Cu,  $\text{Al}_2\text{O}_3$ , X-ray photoelectron spectroscopy (XPS) studies were carried out. The XPS analysis of the spent Cu(0) and  $\text{Al}_2\text{O}_3$  were shown in the Fig. 3b, c. And, as expected, the spectrum of the Cu

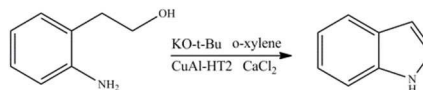
region confirmed the presence of Cu(0) with a peak binding energy of 952.5 eV and 932.7 eV, while Al<sub>2</sub>O<sub>3</sub> with a peak binding energy of 74.4 eV.



**Fig. 3** XPS of the catalysts (a) CuAl-HT3; (b) CuAl-HT3 showing Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> binding energies, and CuAl-HT3 showing Al 2p binding energies

### Catalysts used for indole synthesis

Table 1 presented the influence of solvent on the N-heterocyclization reaction for the synthesis of indole over CuAl-HT2 at different temperature and time. It was observed that the reaction provided a good yield with the use of DMSO and o-xylene as a solvent, employing best results with o-xylene (100 % yield) (Table 1, entries 1-7), which was then employed for further study. According to the experimental data, the yield of indole at 140°C was obviously higher than 100°C (Table 1, entries 7-8).



**Table 1** Effect of solvent, temperature and time reaction<sup>a</sup>.

Entry	solvent	T [°C]/t(h)	Yield [%] <sup>b</sup>
1	MeCN	60/24	39
2	Toluene	100/20	1
3	DMSO	140/12	84
4	Dioxane	140/12	32
5	DMF	140/12	4
6	THF	70/12	trace
7	o-xylene	140/12	100
8	o-xylene	100/12	12

<sup>a</sup> Reaction conditions: 2-(2-aminophenyl)ethanol (0.5 mmol), KO-t-Bu (0.5 mmol), CaCl<sub>2</sub> (0.25 mmol), CuAl-HT2 (0.1 g), under 1 atm of N<sub>2</sub>.

<sup>b</sup> Determined by GC.

The reaction was carried out using 0.5 molar amounts of 2-(2-aminophenyl)ethanol in o-xylene (4 mL) in the presence of CuAl-HT2 as catalyst under different bases. The results were summarized in Table 2. The results of these reactions showed that KO-t-Bu was much more effective and lead to better yields (Table 2, entry 8). Other bases, such as Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>, were also effective (Table 2, entries 4, 6), while KOH, NaOH and K<sub>2</sub>CO<sub>3</sub> were not (Table 2, entries 2, 3, 5). In contrast, the yield of indole was increased by the addition of Lewis acidic additive (CaCl<sub>2</sub>) (Table 2, entries 1, 8). The result indicated that CaCl<sub>2</sub> played a great role on the N-heterocyclization reaction.

**Table 2** Effect of base and additive reaction<sup>a</sup>.

Entry	base	Additive	Yield [%] <sup>b</sup>
1	KO-t-Bu	None	61
2	KOH	CaCl <sub>2</sub>	63
3	NaOH	CaCl <sub>2</sub>	15
4	Na <sub>2</sub> CO <sub>3</sub>	CaCl <sub>2</sub>	99
5	K <sub>2</sub> CO <sub>3</sub>	CaCl <sub>2</sub>	25
6	NaHCO <sub>3</sub>	CaCl <sub>2</sub>	96
7	none	CaCl <sub>2</sub>	96
8	KO-t-Bu	CaCl <sub>2</sub>	100

<sup>a</sup> Reaction conditions: 2-(2-aminophenyl)ethanol (0.5 mmol), KO-t-Bu (0.5 mmol), CaCl<sub>2</sub> (0.25 mmol), o-xylene (4.0 mL) and CuAl-HT2 (0.1 g), 140 °C, 12h, under 1 atm of N<sub>2</sub>.

<sup>b</sup> Determined by GC.

Finally, the catalytic activity for the N-heterocyclization reaction was compared among various catalysts (Table 3). CuAl-HT2 showed the highest catalytic activity and gave the corresponding product in 100% yield under the present conditions (Table 3,

entry10). The reaction was not easily proceeded in the absence of the catalyst, or in the presence of  $\text{Cu}(\text{AcO})_2$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{Cu}$  powder,  $\text{Ni}_{45}\text{Cu}_{10}$ ,  $\text{Cu}/\text{Al}_2\text{O}_3$  and  $\text{Cu}^{2+}\text{Al-HT2}$  (Table 3, entries 1-8). A series of  $\text{Cu-Al}$  catalysts with different  $\text{Cu}/\text{Al}$  mass ratio (Table 3, entries 9, 10, 13) were tested their activity for the reaction. Out of the  $\text{CuAl-HT}$  catalysts with  $\text{CuAl-HT1}$ ,  $\text{CuAl-HT2}$  and  $\text{CuAl-HT3}$ ,  $\text{CuAl-HT2}$  catalyst was found to be the most effective catalyst for the N-heterocyclization reaction. Meanwhile, the catalyst revealed a remarkable activity and was reused up to four consecutive cycles without an appreciable loss of its high catalytic performance (Table 3, entry11). This result might be due to the  $\text{Cu}$  nanoparticles on surface of catalyst were partially oxidized. Furthermore, the reaction was catalyzed by  $\text{CuAl-HT2}$  proceeded even in air to give indole in a yield of 83% (Table 3, entry12).

**Table 3** N-heterocyclization of 2-(2-aminophenyl)ethanol using various catalysts<sup>a</sup>

Entry	Catalyst	Yield [%] <sup>b</sup>
1	none	63
2	$\text{Cu}(\text{AcO})_2$	26
3	$\text{CuCl}_2$	14
4	$\text{CuCl}$	16
5	$\text{Cu}$ powder	69
6	$\text{Ni}_{45}\text{Cu}_{10}$ <sup>16</sup>	66
7	$\text{Cu}/\text{Al}_2\text{O}_3$	67
8	$\text{Cu}^{2+}\text{Al-HT2}$	58
9	$\text{CuAl-HT1}$	98
10	$\text{CuAl-HT2}$	100
11	$\text{CuAl-HT2}$	91 <sup>c</sup>
12	$\text{CuAl-HT2}$	83 <sup>d</sup>
13	$\text{CuAl-HT3}$	97

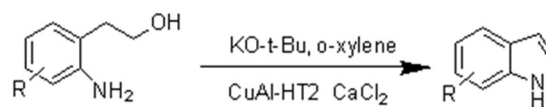
<sup>a</sup> Reaction conditions: 2-(2-aminophenyl)ethanol (0.5 mmol),  $\text{KO-t-Bu}$  (0.5 mmol),  $\text{CaCl}_2$  (0.25 mmol), *o*-xylene (4.0 mL) and catalyst (0.1 g), 140 °C, 12h, under 1 atm of  $\text{N}_2$ .

<sup>b</sup> Determined by GC.

<sup>c</sup> Yield after fifth cycle.

<sup>d</sup> Reaction in air.

We had investigated the reactions using a variety of alcohols as the substrates under the reaction conditions and the results were summarized in Table 4. It could be concluded that all of the electron-neutral, electron-rich and electron-poor alcohols could be reaction very well to generate indoles production excellent yields under the standard reaction conditions.



**Table 4** The substrate extension

Entry	substrates	Yield [%]
1	5-H	100
2	5-Me	99
3	5- $\text{CO}_2\text{Me}$	94
4	5-MeO	99
5	5,6-(MeO)	95
6	6-MeO	94

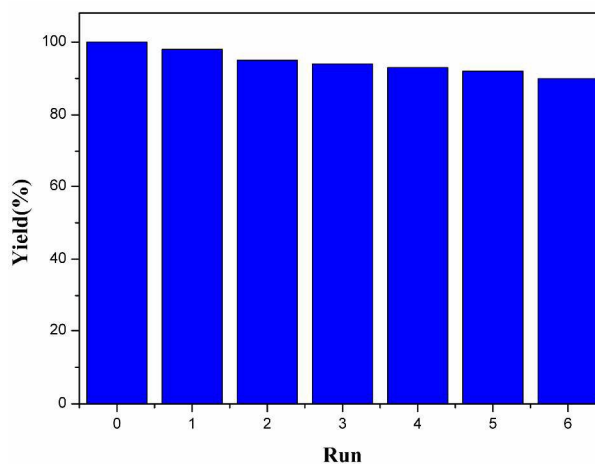
<sup>a</sup> Reaction conditions: alcohols (0.5 mmol),  $\text{KO-t-Bu}$  (0.5 mmol),  $\text{CaCl}_2$  (0.25 mmol), *o*-xylene (4.0 mL) and  $\text{CuAl-HT2}$  (0.1 g), 140 °C, 12h, under 1atm of  $\text{N}_2$ .

<sup>b</sup> Determined by GC.

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The separation and recovery of the catalyst from the reaction system is one of the most important issues, the reusability of  $\text{CuAl-HT2}$  was further investigated. To make the synthetic protocol more economical, recyclability study of the catalyst was examined for the synthesis of indole via dehydrogenative N-heterocyclization (Fig. 4). We observed that the catalyst was highly active under the present reaction conditions and could be effectively reused for six consecutive recycles.

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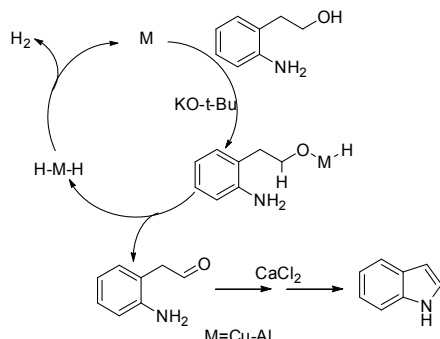


**Fig.4** Catalyst recyclability study.

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From these essential observations and discussions on  $\text{Cu-Al}$  based catalyst, we proposed a catalytic cycle in Scheme 1 for the selective direct synthesis of indole via intramolecular dehydrogenative N-heterocyclization of 2-(2-aminophenyl)ethanol using  $\text{CuAl-HT2}$  catalyst, and named it as “borrowing hydrogen” mechanism.<sup>5, 15</sup> The first step of the reaction would involve the oxidation of an alcohol to the corresponding carbonyl compound and a hydrido  $\text{Cu-Al}$  species. The catalyst with  $\text{KO-t-Bu}$  slightly increased the initial step of the

reaction. Then the carbonyl intermediate would readily cyclize to afford indole via intramolecular nucleophilic attack of amino group to carbonyl carbon followed by dehydration. A Lewis acid ( $\text{CaCl}_2$ ) may promote the formation of indole.<sup>39</sup> Considering the result in Table 2, that  $\text{CaCl}_2$  with higher Lewis acidity played a great role on the N-heterocyclization reaction. From the angle of reaction equilibrium, the removal of water (by anhydrous  $\text{CaCl}_2$ ) clearly helped to drive the reaction towards indole production. Release of hydrogen in the reaction of the hydrido Cu-Al could regenerate the catalytic active Cu-Al species.



Scheme. 1 A possible "borrowing hydrogen" mechanism.

### Catalysts used for phenyl ether synthesis

Table 5 presented the influence of solvent on the Ullmann-type coupling reaction for synthesis phenyl ether over CuAl-HT3 at different temperature and time. It was observed that the reaction provided a good yield with DMSO as solvent, employing best results with DMSO (95 % yield) (Table 5, entries 5-3), which was then employed for further study. According to the experimental data, the yield of phenyl ether at 135°C is obviously higher.

Table 5 Effect of solvent, temperature and time reaction<sup>a</sup>.

Entry	solvent	T [°C]/t(h)	Yield [%] <sup>b</sup>
1	MeCN	70/24	trace
2	Toluene	100/20	trace
3	DMSO	135/16	95
4	Dioxane	90/16	10
5	DMF	130/16	55
6	THF	60/16	trace
7	o-xylene	140/16	trace

<sup>a</sup> Reaction conditions: Phenol (1.00 mmol), iodobenzene (1.00 mmol), CuAl-HT2 (0.02g contains 0.2 mmol of Cu), KF (2.00 mmol) in DMSO (4 mL) at 135°C stirring for 16 h.

<sup>b</sup> Determined by GC.

The reaction was carried out using 1 mole of phenol DMSO (4 mL) in the presence of CuAl-HT3 as catalyst under different bases. The results were summarized in Table 6. The results of these reactions showed that KF was much more effective and lead to better yield (Table 6, entry 1). Other bases, such as  $\text{Na}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$ , were also effective (Table 6, entries 4, 8). The result

indicated that KF played a great role on the Ullmann-type coupling reaction.

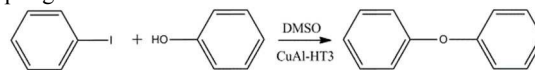


Table 6 Effect of base

Entry	base	Yield [%] <sup>b</sup>
1	KF	95
2	KOH	46
3	NaOH	43
4	$\text{Na}_2\text{CO}_3$	51
5	$\text{K}_2\text{CO}_3$	83
6	$\text{NaHCO}_3$	47
7	none	36
8	$\text{Cs}_2\text{CO}_3$	53

<sup>a</sup>Reaction conditions: Phenol (1.00 mmol), iodobenzene (1.00 mmol), CuAl-HT2 (0.02g, contains 0.2 mmol of Cu), DMSO (4 mL) at 135°C stirring for 16 h.

<sup>b</sup>Determined by GC.

Whereafter, the catalytic activity for the Ullmann-type coupling reaction was compared among various catalysts (Table 7). CuAl-HT3 showed the highest catalytic activity and gave the corresponding product in 94% yield under the present conditions (Table 7, entry11). The reaction was not easily proceeded in the absence of the catalyst, or in the presence of  $\text{Cu}(\text{AcO})_2$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ , Cu powder,  $\text{Ni}_{45}\text{Cu}_{10}$ ,  $\text{Cu}/\text{Al}_2\text{O}_3$  and  $\text{Cu}^{2+}\text{Al-HT3}$  (Table 7, entries 1-8). A series of Cu-Al catalysts with different Cu/Al mass ratio (Table 7, entries 9, 10) were tested their activity for the reaction. Out of the CuAl-HT catalysts with CuAl-HT1, CuAl-HT2 and CuAl-HT3, CuAl-HT3 catalyst was found to be the most effective catalyst for the Ullmann-type coupling reaction.

Table 7 Ullmann-type coupling reaction using various catalysts<sup>a</sup>

Entry	Catalyst	Yield [%] <sup>b</sup>
1	none	10
2	$\text{Cu}(\text{AcO})_2$	38
3	$\text{CuCl}_2$	16
4	$\text{CuCl}$	13
5	Cu powder	60
6	$\text{Ni}_{45}\text{Cu}_{10}$	58
7	$\text{Cu}/\text{Al}_2\text{O}_3$	72
8	$\text{Cu}^{2+}\text{Al-HT3}$	58
9	CuAl-HT1	90
10	CuAl-HT2	91
11	CuAl-HT3	94

<sup>a</sup> Reaction conditions: Phenol (1.00 mmol), iodobenzene (1.00 mmol), KF (2.00 mmol) in DMSO (4 mL) at 130°C stirring for 16 h.

<sup>b</sup> Determined by GC.

We had investigated the reactions using a variety of aryl iodides

and phenols as the substrates under the reaction conditions and the results were summarized in Table 8. It could be concluded that all of the electron-neutral, electron-rich and electron-poor aryl iodides could be reaction with phenol very well to generate the corresponding cross-coupling production excellent yields under the standard reaction conditions.

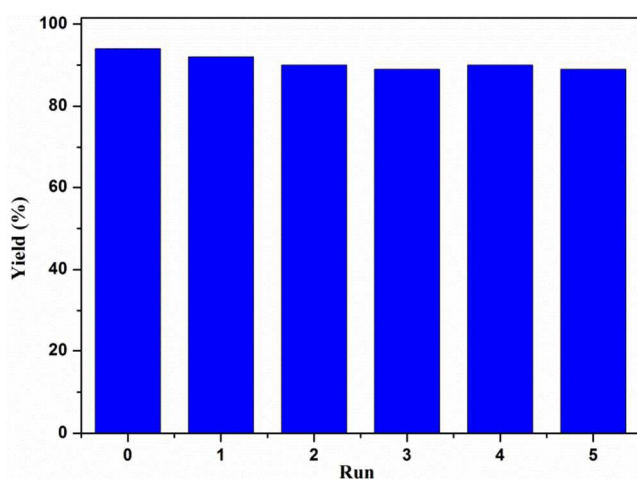
**Table 8** The substrate extension

Entry	Phenol	Aryl iodide	Yield [%] <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> OH	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	88
2	C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> I	94
3	C <sub>6</sub> H <sub>5</sub> OH	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	98
4	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	91
5	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	C <sub>6</sub> H <sub>5</sub> I	90
6	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	98
7	p-ClC <sub>6</sub> H <sub>4</sub> OH	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	92
8	p-ClC <sub>6</sub> H <sub>4</sub> OH	C <sub>6</sub> H <sub>5</sub> I	88
9	p-ClC <sub>6</sub> H <sub>4</sub> OH	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	98

<sup>a</sup> Reaction conditions: Phenol (1.00 mmol), aryl iodide (1.00 mmol), CuAl-HT2 (0.02g, contains 0.2 mmol of Cu), KF (2.00 mmol) in DMSO (4 mL) at 135°C stirring for 16 h.

<sup>b</sup> Determined by GC.

The separation and recovery of the catalyst from the reaction system was one of the most important issues, the reusability of CuAl-HT3 was further investigated. To make the synthetic protocol more economical, recyclability study of the catalyst was examined for the synthesis phenyl ether via Ullmann-type coupling reaction (Fig. 5). We observed that the catalyst was highly active under the present reaction conditions and could be effectively reused for six consecutive recycles.



**Fig.5** Catalyst recyclability study.

## Conclusions

In conclusion, we demonstrated that the CuAl-HT2 catalyst act a

highly efficient, recyclable heterogeneous catalyst for the dehydrogenative N-heterocyclization of 2-(2-aminophenyl)ethanol in the presence of base and a catalytic amount of Lewis acidic. The present catalytic system would provide a new and useful method for the synthesis of various N-Heterocyclic compounds. And also we found an efficient and economic catalyst system for the Ullmann phenyl ether by using the CuAl-HT3 as the catalyst in DMSO. The cross-coupling reactions of phenols with iodobenzene generated the corresponding coupling products with excellent yields at the present reaction conditions. Furthermore, the CuAl-HT can be recovered and recycled by a simple filtration of the reaction solution and used for 6 consecutive trials without decreases in activity.

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## Notes and references

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