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Article

Recyclable hydrophobic copper (II) phthalocyanine catalyzed *N*-arylation of imidazoles in dimethylsulfoxide

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ABSTRACT

Copper (II) phthalocyanine (CuPc) was used as a catalyst for the *N*-arylation of imidazoles with aryl iodides or bromides. The catalyst showed high activity and could be reused 3 times without any significant loss in activity. The catalyst was characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet-visible spectroscopy.

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1. Introduction

Phthalocyanine transition metal complexes are important industrial pigments and are considered to be potential oxidation catalysts because of their cheap and facile preparation on large scale and in particular their chemical and thermal stability [1–3]. For example, Rezaeifard and coworkers [1] used copper (II) phthalocyanine (CuPc) for the aqueous heterogeneous oxygenation of hydrocarbons. However, few reports exist about other reactions by metal phthalocyanine [3,4]. Shinnu and coworkers [3] reported a novel highly stereoselective multi-component synthesis of *N*-substituted- β -amino ketone derivatives using CuPc as a reusable catalyst. However, the low solubility of metallophthalocyanines is perhaps the most serious limitation in their application as catalysts although it may be overcome by sulfonation and carboxylation at the periphery of the molecule to give water-soluble derivatives [5]. Unfortunately, the separation of water-soluble catalysts from solutions

is also difficult leading to recycling problems.

N-arylated azoles (e.g., arylpyrroles, arylpyrazoles, arylimidazoles, aryltriazoles, arylindoles, arylcarbazoles, etc.) have important applications in the medicinal and material fields [6–8]. The transition-metal-catalyzed cross-coupling of aryl halides with amines, amides, and *N*-heterocyclic nucleophiles has become a powerful strategy for these reactions [9–12]. Some homogeneous and heterogeneous catalysts for the catalytic *N*-arylation coupling reaction have been reported [10,13–15]. However, not much research has been done on the *N*-arylation reaction catalyzed by metal phthalocyanines.

We thus report the first efficient CuPc system for the *N*-arylation of imidazoles with aryl halides. Although homogeneous catalysis under mild reaction conditions is characterized by higher catalytic activity than heterogeneous catalysis, homogeneous catalysts are difficult to separate and recycle. Therefore, the use of homogeneous catalysts in industrial production is limited [16,17]. CuPc is soluble in dimethylsulfoxide

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(DMSO) but not in water. Therefore, in our experiment, DMSO was used as the solvent and was involved in the reaction. CuPc played a homogeneous role in the reaction process because of its excellent solubility in DMSO, which had the remarkable advantage of homogeneous catalysis under mild conditions. Additionally, this material was precipitated by adding water to the reaction system, and isolated by simple centrifugation. Therefore, this reaction has the advantages of both heterogeneous and homogeneous catalysis.

2. Experimental

2.1. Materials and characterization

CuPc was synthesized according to the literature [18]. The structure of the CuPc catalyst is shown in Fig. 1. All reagents were purchased from commercial suppliers and used without further purification. The catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700 FT-IR, USA), X-ray photoelectron spectroscopy (XPS, Kratos XSAM-800, UK) and ultraviolet-visible spectroscopy (UV-Vis, Shimadzu UV-2550, JP).

2.2. General procedure for the *N*-arylation of imidazoles with aryl halides

In a typical experiment, imidazole (1.2 mmol), aryl halide (1.0 mmol), catalyst, and base (2.0 mmol) were added to a hydrothermal reactor (20 mL). The mixture was heated to the desired temperature with stirring. After the completion of the reaction and cooling to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and the obtained product was purified by column chromatography on silica gel using dichloromethane: methanol (100:1, v/v) as the eluent.

2.3. Recycling experiment

The recyclability of the synthesized catalyst was investigated using the coupling reaction between iodobenzene and imidazole. After the completion of each reaction the material was precipitated by adding water to the reaction system and the CuPc composite was removed by centrifuging and washing with 3 mL ethyl acetate. The collected catalyst was dried under vacuum at 70 °C, and reused for a subsequent reaction.

Fig. 1. Structure of the CuPc catalyst.

Fig. 2. Dispersity of CuPc in different solvents. (a) A mixture of DMSO and water ($V_{\text{DMSO}}:V_{\text{H}_2\text{O}} = 1:2$); (b) DMSO.

3 Results and discussion

3.1. Characterization of the catalyst

The effective dispersity of the CuPc catalyst in the solvent seems to be the most important factor that affects its catalytic performance in this reaction. First, the dispersibility of the catalyst was investigated in different solvents, as shown in Fig. 2. The result indicated that the CuPc catalyst was insoluble and hydrophobic in a mixture of DMSO and water ($V_{\text{DMSO}}:V_{\text{H}_2\text{O}} = 1:2$), whereas it was uniformly dispersed in DMSO. Therefore, the reaction could be carried out in a homogeneous system using CuPc as the catalyst. After the completion of each reaction we reused the CuPc catalyst after centrifugation. Therefore, the reaction has the advantages of both heterogeneous and homogeneous catalysis.

Figure 3 shows FT-IR spectrum of the CuPc catalyst. The as-fabricated CuPc sample has several absorption peaks around 724, 901, 1091, 1120, and 1636 cm^{-1} , which can be assigned to the phthalocyanine skeletal and metal-ligand vibrations, respectively [19]. This is consistent with structure of a typical CuPc material.

To further confirm the valence state of the copper complex, an XPS spectrum of the catalyst was obtained and is shown in Fig. 4. The characteristic Cu 2p peak and the satellite peaks are very typical of a stable CuPc layer. The XPS spectrum shows a single Cu 2p_{3/2} peak at 934.8 eV, which can be assigned to Cu²⁺ [20–22]. Therefore, divalent copper was immobilized in the CuPc material without other valence states being present.

Fig. 3. FT-IR spectrum of the CuPc catalyst.

Fig. 4. XPS spectrum of the CuPc catalyst.

3.2. *N*-arylation catalyzed by the CuPc catalyst

A series of experiments were initially conducted using imidazole and iodobenzene as model substrates to evaluate and optimize the most efficient catalytic system (Table 1). Poor conversion was achieved in the reaction in the absence of the catalyst (Table 1, entry 1). In the presence of the catalyst, the yield of product increased significantly. Different bases were then evaluated using the model reaction, and the best result was achieved when using KOH as the alkali (Table 1, entries 2–5). We then investigated the effect of catalyst amount on this reaction (Table 1, entries 5–8). When the amount of CuPc was increased from 5 to 15 mol%, the product yield increased. A nearly equivalent conversion ratio was achieved using 10 and 15 mol% of the catalyst. Therefore, from an economic point of view the 10 mol% catalyst loading is most appropriate. The effect of reaction temperature on the catalytic activity of the CuPc catalyst was also investigated (Table 1, entries 6, 8–10). When the reaction temperature was increased from 90 to 110 °C no significant change in yield was observed. However, a significant decrease in the yield was observed when the temperature was decreased to 80 °C. Therefore, the optimal reaction

Table 1

Screening reaction conditions for the *N*-arylation of imidazole with iodobenzene.

Entry	Base	Temperature (°C)	Time (h)	Catalyst (mol%)	Yield (%)
1	KOH	90	24	—	4.5
2	CsCO ₃	110	24	5	16.8
3	K ₃ PO ₄	110	24	5	24.0
4	NaOH	110	24	5	42.2
5	KOH	110	24	5	75.2
6	KOH	110	24	10	95.5
7	KOH	110	24	15	97.3
8	KOH	100	24	10	93.5
9	KOH	90	24	10	92.6
10	KOH	80	24	10	51.0
11	KOH	90	20	10	75.7
12	KOH	90	16	10	66.9

temperature was determined to be 90 °C. Finally, the reaction time was also found to be an important factor as is shown by a comparison between entries 9, 11, and 12 in Table 1. The most appropriate reaction time was found to be 24 h. Therefore, the optimum conditions were: CuPc catalyst (10 mol%), KOH as base (2.0 mmol), and DMSO as solvent at 90 °C for 24 h.

To determine the scope of the practical use of the CuPc catalyst, *N*-arylations of various substituted aryl halides were carried out under optimal conditions (Table 2). As shown in Table 2, it is clear that the activity of the aryl halides in this reaction

Table 2

CuPc catalyzed *N*-arylation of imidazole with different substituted aryl halides.

Entry	ArX	Product	Isolated yield (%)
1			92.6
2			31.3
3			86.5
4			31.8
5			5.5
6			75.1
7			77.3
8			88.3
9			94.4
10			38.8

Reaction conditions: aryl halides 1.0 mmol, imidazole 1.2 mmol, CuPc 10 mol%, KOH 2.0 mmol, DMSO 2 mL, 90 °C, 24 h.

Table 3CuPc catalyzed *N*-arylation of heterocycles with iodobenzene.

<chem>c1ccccc1I</chem> + Het-NH $\xrightarrow[\text{KOH, DMSO}]{\text{CuPc, 90 } ^\circ\text{C}}$ <chem>c1ccccc1N-Het</chem>			
Entry	Het-NH	Product	Isolated yield (%)
1	<chem>c1ccc2c(c1)c[nH]2</chem>	<chem>c1ccc2c(c1)c(c[nH]2)c3ccccc3</chem>	53.8
2	<chem>c1cc[nH]c1</chem>	<chem>c1ccc2c(c1)c(c[nH]2)c3ccccc3</chem>	92.6
3	<chem>Cc1cc[nH]c1</chem>	<chem>Cc1ccc2c(c1)c(c[nH]2)c3ccccc3</chem>	71.9

Reaction conditions: iodobenzene 1.0 mmol, azoles 1.2 mmol, CuPc 10 mol%, KOH 2.0 mmol, DMSO 2 mL, 90 °C, 24 h.

increase as follows: iodobenzene > bromobenzene > chlorobenzene (Table 2, entries 1, 2, 5). Furthermore, the electron-deficient aryl halides afforded the corresponding *N*-aryl imidazole products in better yields than the electron-rich aryl halides (Table 2, entries 3, 4, 9, 10). Interestingly, steric hindrance had little impact on the outcome of the reaction (Table 2, entries 6–8).

To further evaluate the scope of the catalytic system, the *N*-arylation of iodobenzene was investigated with a variety of nitrogen-containing heterocycles (Table 3). It is clear that benzimidazole and 2-methylimidazole were successfully coupled with iodobenzene to give the corresponding *N*-arylated products in satisfactory yields (Table 3, entries 1 and 3). These results thus show the versatility of the current catalytic system.

3.3. Recycling the catalyst

A series of experiments were also carried out to evaluate the recyclability of the catalyst. The results are listed in Table 4. The catalyst was recovered by centrifugation and reused 3 times without significant loss of activity. The yield was lower in the fourth recycle but we obtained a yield of 90.3% when prolonging the reaction time. To explain the reasons for this decrease in catalyst activity, we characterized fresh and used 5

Table 4CuPc catalyst recycling for the *N*-arylation of imidazole and iodobenzene.

Run	Yield (%)
1	93.1
2	89.3
3	88.7
4	75.3
5*	90.3

Reaction conditions: iodobenzene 2.0 mmol, imidazole 2.4 mmol, CuPc 10 mol%, KOH 4.0 mmol, DMSO 3 mL, 90 °C, 24 h (*30 h).

Fig. 5. UV-Vis spectra of fresh (1) and after 5 runs (2) CuPc in DMSO.

times CuPc catalyst by UV-Vis spectroscopy (Fig. 5).

Generally, the aggregation of CuPc is the main factor that caused catalyst deactivation [23]. As shown in Fig. 5, typical dimer absorption peak was observed at 630 nm, and the broad absorption around 730 nm in the near-infrared region is believed to originate from the Q-band of the benzene ring structure [24]. However, we found that the amount of dimer did not evidently increase before and after the reaction, which indicates that CuPc was stabilized in DMSO. Therefore, the aggregation of CuPc did not lead to low catalytic activity. However, Q-band of the used catalyst moved toward the longer-wavelength side. Therefore, a new species might be generated via an interaction between CuPc and imidazole.

Furthermore, the conditions of this CuPc catalyzed *N*-arylation reaction are mild compared with the systems listed in Table 5. High product yields were achieved at 90 °C in 24 h, which is better than that of the other heterogeneous catalysts. A salen-Cu(II) complex has also shown good catalytic performance during *N*-arylation reactions but this catalyst could not be recycled from the homogeneous system [26]. In our previous research, the Cu⁺-MMT catalyst gave good performance but a high temperature was still required in this system [27]. The catalyst thus has an obvious advantage in terms of its outstanding performance and utilization value.

4. Conclusions

In conclusion, we used hydrophobic divalent CuPc as a catalyst for the *N*-arylation reaction. Good yields were achieved when using CuPc under mild conditions. The CuPc catalyst was

Table 5Comparison of the activity of different heterogeneous catalysts in the *N*-arylation of imidazole with iodobenzene.

Catalyst	Reaction conditions	Isolated yield (%)	Ref.
CuI	10 mol%, 120 °C, DMSO, NaH, 24 h	95	[9]
CuI/PEG	10 mol%, 110 °C, K ₂ CO ₃ , 24 h	91	[10]
Cu ₂ O	10 mol%, 120 °C, KOH, DMSO, 24 h	92	[25]
Salen-Cu(II) complex	10 mol%, 100 °C, DMSO, NaOH, 12 h	98	[26]
Cu ⁺ -MMT	0.2 mol%, 110 °C, DMSO, KOH, 24 h	92	[27]
CuPc	10 mol%, 90 °C, DMSO, KOH, 24 h	93	this study

Graphical Abstract

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The copper (II) phthalocyanine (CuPc) catalyst catalyzed the *N*-arylation of imidazoles with aryl iodides or bromides under mild conditions and was reused 3 times without any significant loss in activity.

used 3 times without significant loss of activity. This catalytic system has the advantages of homogeneous and heterogeneous catalysis, which could be potentially useful in industrial applications. Work is in progress to further broaden the scope of this catalytic system and the results will be reported in due course.

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可循环疏水性铜酞菁催化咪唑的*N*-芳基化反应

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摘要: 研究了二价铜酞菁(CuPc)催化咪唑与芳基碘或溴的*N*-芳基化反应. 结果表明, CuPc表现出高的催化活性, 并且能够重复使用3次活性无明显降低. 采用傅里叶变换红外光谱、X射线光电子能谱和紫外-可见光谱对催化剂样品进行了表征.

关键词: 铜酞菁; *N*-芳基化反应; 芳基卤; 可循环催化剂

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1. 前言

过渡金属酞菁化合物是一种重要的工业染料,具有价格低廉、易制备、化学和热力学稳定等优点,因而有望用作氧化催化剂^[1–3].例如,Rezaeifard等^[1]曾报道了铜酞菁(CuPc)催化碳水化合物水相氧化反应.然而,有关将金属酞菁用于催化其它反应的报道很少^[3,4].Shinu等^[3]将CuPc用作一种可循环的多相催化剂用于 N -取代- β -氨基酮衍生物的多组分立体选择性合成反应.金属酞菁差的水溶性可能限制其实际应用.尽管对酞菁分子进行磺化和羧基化后可以改善其水溶性^[5],但是一些水溶性较好的催化剂却又很难从催化反应体系中分离,以至于不能回收循环使用.

N -芳基唑类化合物(例如芳基吡咯、芳基吡唑、芳基咪唑、芳基三唑、芳基吡啶和芳基呋唑等)在医药和材料领域有着重要应用^[6–8].人们通常使用过渡金属催化芳基卤和胺、酰胺及 N -杂环化合物的反应来合成这类化合物^[9–12].到目前为止,使用均相或多相催化剂用于 N -芳基化偶联反应的报道很多^[10,13–15],但很少采用金属酞菁作为催化剂.

本课题组首次将铜酞菁(CuPc)用于催化咪唑和芳基卤的偶联反应.与多相催化反应相比,均相催化具有温和的反应条件和更高的催化活性,但催化剂的难分离和循环使用限制了其实际应用^[16,17].CuPc催化剂在二甲亚砜(DMSO)中是可溶的,但不溶于水.因此,本文以DMSO为溶剂.反应过程中,CuPc溶解于反应溶液中,起均相催化剂的作用.同时,反应结束后,通过添加水到反应体系中,可以沉淀出固体催化剂.经过离心分离,催化剂可以回收循环利用.

2. 实验部分

2.1. 材料和表征

参照文献[18]合成了CuPc催化剂,其结构如图1所示.本实验中所有的反应试剂购买于国药化学试剂有限公司,使用前均未进一步纯化.通过Nicolet 6700型傅里叶变换红外光谱仪(FT-IR)、Kratos XSAM-800型X射线光电能谱仪(XPS)和Shimadzu UV-2550型紫外-可见分光光度计(UV-Vis)表征了CuPc催化剂.

2.2. 催化咪唑与芳基卤的偶联反应

取1.0 mmol芳基卤,1.2 mmol咪唑,2.0 mmol碱和适量CuPc催化剂加入到20 mL的水热反应釜中,将反应釜

置于设置好温度的油浴反应器中加热搅拌.反应结束后,冷却至室温后打开水热反应釜,加入适量去离子水到混合液中,然后用15 mL乙酸乙酯萃取3次.有机相用无水硫酸钠干燥,过滤,旋转蒸发仪除去溶剂.粗产品通过硅胶柱纯化,用二氯甲烷和甲醇(100:1)作为洗脱剂.

2.3. 循环使用实验

以碘苯与咪唑的偶联为模型反应,研究了催化剂的循环使用性能.每次反应结束后,向体系中加入适量水沉淀出催化剂,然后离心分离获得固体,再用3 mL乙酸乙酯洗涤,70 °C真空干燥,接着用于下次反应.

3. 结果与讨论

3.1. 催化剂的表征

CuPc催化剂在反应溶剂中的分散性是影响催化活性的重要因素.因此,本文首先研究了CuPc催化剂在不同溶剂中的分散性质.如图2所示,CuPc催化剂不溶于DMSO和水的混合溶剂($V_{\text{DMSO}}:V_{\text{H}_2\text{O}} = 1:2$)中,但溶于DMSO中,CuPc催化剂以均相形式参与反应.反应结束后加入水,通过简单的离心即可分离出催化剂,可见该催化剂具有均相催化和多相催化的双重优势.

图3为CuPc催化剂的FT-IR谱.所制备的CuPc催化剂在724, 901, 1091, 1120和1636 cm^{-1} 处具有吸收峰,可分别归属于CuPc催化剂典型的骨架振动和金属配体吸收峰^[19],与纯的CuPc催化剂结构相符.

为了进一步确定CuPc催化剂中铜的价态,利用XPS谱对催化剂进行了表征,结果见图4.可以看出,Cu 2 p 的特征峰和伴峰是很典型的CuPc催化剂中铜的峰型,在934.8 eV处峰归属为+2价铜^[20–22].这表明CuPc催化剂中铜以+2价的形式存在,而没有其他形式的铜.

3.2. CuPc催化 N -芳基化反应

以1.2 mmol咪唑和1.0 mmol碘苯的偶联反应为模型优化了反应条件,结果列于表1.可以看出,在没有催化剂时,该反应基本不能进行(表1,实验1).添加CuPc催化剂以后,反应的产率明显提高.另外,KOH对该反应具有最好的效果(表1,实验2–5).当CuPc催化剂用量从5 mol%增加到10 mol%时,反应产率增加,至15 mol%时,产率变化不大.因此适宜催化剂用量为10 mol%.当反应温度从90 °C增加到110 °C时,反应产率没有明显增加;降至80 °C时,反应活性明显下降(表1,实验6, 8–10).因此,在90 °C反应比较适宜.结果显示,反应24 h后,收率最高.综上,最佳的反应条件应该为:10 mol% CuPc, 2.0

mmol KOH, DMSO为反应溶剂, 在90 °C下反应24 h.

表2为底物扩展实验. 可以看出, 卤代苯活性顺序为碘苯 > 溴苯 > 氯苯(表2, 实验1, 2和5). 此外, 带有吸电子基团的芳基卤活性高于带有供电基团的芳基卤(表2, 实验3, 4, 9和10). 同时, 空间位阻对催化反应的活性影响较小(表2, 实验6–8).

为了进一步考察底物的范围, 表3给出了不同咪唑衍生物的偶联反应结果. 可以看出, 苯并咪唑和2-甲基咪唑也能很好地与碘苯反应生成对应的 N -芳基产物(表3, 实验1和3). 可见, 本文所选的绝大部分底物都具有较好的活性, 仅有少部分底物收率较低甚至不反应.

3.3. 催化剂循环使用性能

表4为CuPc催化剂的循环使用性能. 可以看出, 催化剂至少可以循环使用3次, 活性没有明显下降, 可通过延长反应时间, 进一步提高产率. 为了探明催化剂活性下降的原因, 利用UV-Vis对反应前和循环使用5次后的CuPc催化剂进行了测试.

通常, CuPc的聚集是其失活的主要因素^[23]. 如图5所示, 反应前催化剂在630 nm处吸收峰归属于CuPc中典型的二聚体, 730 nm处吸收峰对应于酞菁中苯环Q带^[24];

反应后催化剂中二聚体的量并没有增加, 表明CuPc在DMSO中是稳定的. 因此, CuPc催化剂活性的下降并不是其聚集所致. 但是, 反应后的CuPc催化剂Q带向长波方向移动, 这可能是由于与反应物咪唑发生了相互作用所致.

此外, 表5比较了不同催化剂对于该反应的活性. 可以看出, CuPc催化体系具有更加温和的反应条件, 在90 °C反应24 h即可获得高的收率, 优于其他多相催化剂. 尽管Salen-Cu复合物催化剂也具有高的收率和比较温和的反应条件, 但催化剂用量较高, 且不能循环使用^[26]. 本课题组曾报道的Cu⁺-MMT体系也表现出优越的性能, 但反应温度较高^[27]. 由此可见, 本文制备的CuPc催化剂具有较高的催化性能, 更有利于实际应用.

4. 结论

首次报道了CuPc催化 N -芳基化反应. 该催化体系具有温和的反应条件和优越的催化性能. 此外, 催化剂可以循环使用3次, 而未见活性明显下降. 该催化体系具有多相催化和均相催化的双重优势, 有望广泛用于工业生产中. 下一步工作将扩大催化剂的使用范围.