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COPPER(II) AND MAGNESIUM(II) CONTAINING HETEROMETALLIC CARBOXYLATE FRAMEWORK: EFFICIENT HETEROGENEOUS CATALYTIC SYSTEM FOR AROMATIC N-ARYLATION

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ABSTRACT

A 2D copper and magnesium-containing heterometallic carboxylate framework have been synthesized hydrothermally and characterized by single-crystal X-ray diffraction analysis and other physicochemical methods. The compound shows excellent catalytic activity in the N-arylation reaction of nitrogen-containing heterocycles with aryl bromides in acetonitrile medium at 80 ºC in the presence of Cs_2CO_3. The compound, which behaves as heterogeneous catalysts, can easily be recovered and reused without significant catalyst deactivation due to either leaching of active species or degradation of the structure. In the framework compound, copper acts as an active center for the catalytic reaction, whereas magnesium promotes the activity of the catalyst.

Keywords: Metal-organic framework, Heterometallic Carboxylate, Heterogeneous Catalysis, N-arylation Reaction.
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INTRODUCTION

N-arylation reaction to form C–N bonds has had great influence in recent times because of their wide applications in the preparation of several biologically and pharmaceutically important compounds.[1,2,3] Copper-assisted classic Ullmann type reaction is one of the familiar synthetic routes for the preparation of such types of compounds under homogeneous conditions and copper is a favored catalyst for environmental and economic reasons.[4,5] Copper is also a very common choice in the field of biochemistry for its bio-activity.[6,7,8,9] Reactivity of the homogeneous catalytic systems is known to be superior over heterogeneous systems. However, for environmental concerns, the heterogeneous catalyst is privileged due to their ease of handling, reusability, recyclability and minimization of unnecessary toxic wastes.[10]

Metal-organic frameworks (MOFs), the polymers in which metal ions or clusters are assembled through organic linkers into extended one-, two- and three-dimensional networks via coordinate bonding, attracted immense attention in heterogeneous catalysis.[11,12,13,14] Coordinatively unsaturated metal centers present in the catalyst or such center generated in situ in reaction conditions act as an active site of the catalysis.[15,16,17] However, examples of N-arylation reactions of nitrogen-containing heterocycles catalyzed by Cu^{II}–MOF (MOF = metal-organic framework) under heterogeneous condition are scanty in the literature.[1,18,19] Still, reports on heterogeneous catalysis over heterometallic MOFs that contain two different metals are only limited.[13] With this in mind, heterometallic framework connecting copper-based one-dimensional network connected to alkaline earth metal to afford two/three-dimensional framework have been explored.[20]

Herein, I wish to report the catalytic efficacy of hydrothermally synthesized 2D MOF, $(\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**1**) (H_2Pdc = pyridine-2,5-dicarboxylic acid), towards N-arylation reaction in a heterogeneous condition where copper(II) acts as an active site for the catalytic reaction and magnesium(II) performs as a promoter.

EXPERIMENTAL

Magnesium nitrate hexahydrate, copper nitrate trihydrate and solvents were purchased from Merck (India) and solvents were distilled and dried before use. Pyridine-2,5-dicarboxylic acid and other chemicals were purchased from Sigma–Aldrich or Merck (India) and were used as received.

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The compound $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**1**) was synthesized through a hydrothermal route.[20] The initial reaction mixture was prepared as follows: pyridine-2,5-dicarboxylic acid (0.167 g, 1 mmol), imidazole (0.136 g, 2 mmol) first added in 10 ml of milli-Q water and the mixture was stirred for 0.5 h, to this mixture Magnesium nitrate hexahydrate (0.128 g, 0.5 mmol) and copper nitrate trihydrate (0.120 g, 0.5 mmol) were added and the final mixture was stirred for 0.25 h. The compound was obtained in a 20 ml capacity Teflon-lined acid digestion bomb at 175 °C for 3 days followed by slow cooling at a rate of 5 °C h^{-1} to room temperature. Crystals suitable for X-ray analyses were obtained in about 52% yield based on Cu.

General Procedure

For the catalytic reaction, at first, aryl halide (1.2 mmol) and Cs_2CO_3 (2 mmol, 0.650 g) were added to compound **1** (0.002 g) in a glass batch reactor. To this solid mixture, nitrogen-containing heterocycle (1.0 mmol) and acetonitrile (2 mL) were added (solid nitrogen-containing heterocycles were added directly with the catalyst) and the reaction mixture was stirred at 80 ºC in an oil bath. After cooling to room temperature, compound **1** was first separated by centrifugation and the solution part was extracted with water and diethyl ether (2 × 15 mL). The organic layers thus collected were combined and washed with brine, dried over Na_2SO_4, and concentrated in a vacuum. The residue was purified by column chromatography on silica gel (mesh 60–120) using an n-hexane/ethyl acetate mixture as the eluent to give the desired product. A hot filtration test was carried out to check the heterogeneous nature of the catalyst. For this, the reaction mixture of pyrazole (1 mmol, 0.068 g), Cs_2CO_3 (2 mmol, 0.65 g), and compound **1** (0.002 g) in acetonitrile (2 mL) with bromobenzene (1.2 mmol, 0.19 g) was stirred at 80 ºC and TLC monitored the progress of the reaction. After 2 h, the compound **1** was separated at reaction temperature by filtration (Whatman 1, pore size 11 mm); further, Cs_2CO_3 (2 mmol, 0.65 g) was added to the solution and it was stirred at that temperature for another 16 h, and the progress of the reaction was examined by TLC analysis.

Detection Method

Elemental analysis was performed by using Perkin-Elmer 240C elemental analyzer. Fourier transformed infrared spectra of KBr pellets were measured on a Perkin–Elmer RX I FT-IR spectrometer. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using CuK_α radiation at the desired temperature. TG-DT analysis was made using a PerkinElmer (SINGAPORE) Pyris Diamond TG/DTA unit. The heating rate was programmed at 5°C min^{-1} with a protecting stream of N_2 flowing at a rate of 150 mL min^{-1}. ^1H NMR spectra were measured on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer. To characterize the bulk of compound **1**, elemental analysis and IR spectroscopic study were undertaken. Anal. Calc. for $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**1**): C, 31.96%; H, 3.45%; N, 5.32%. Found: C, 32.05%; H, 3.42%; N, 5.29%. Selected IR peaks (KBr disk, ν, cm^{-1}): 1688, 1612 [υ_{as} (CO_2^-)], 1395 [υ_s (CO_2^-)], 1357, 1287 [υ_s (C-O)], and 3477 br [υ (O-H)].

X-ray diffraction data of compound **1** were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073Å). Determination of integrated intensities and cell refinement were performed with the SAINT software package using a narrow-frame integration algorithm.[21] An empirical absorption correction (SADABS) was applied.[22] All the structures were solved by direct methods and refined using the full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms with the programs SHELXS97 and SHELXL97.[23] The hydrogen atoms of the compound was refined with isotropic thermal parameters. There were no remarkable peaks in the final difference Fourier maps except the ghost peaks surrounding the metal centers. The crystal data and relevant refinement parameters of the compound were compared with the reported values.[20]

The catalytic reaction product was analyzed by ^1H NMR spectrometry and compared with the literature value. The spectroscopic data (^1H NMR) of these products are consistent with the reported values.

1-Phenyl-1H-pyrazole (Table 2, entry 2a)

^1H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.86 (m, 1H), 7.70 (m, 3H), 7.41-7.30 (m, 3H), 6.40 (m, 1H); Anal. Calcd. for $C_9H_8N_2$: C, 74.98%; H, 5.59%; N, 19.43%. Found: C, 75.1%; H, 5.6%; N, 19.5%.

1-(4-Nitrophenyl)-1H-pyrazole (Table 2, entry 2b)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.34 (d, *J* = 9 Hz, 2H), 8.04 (d, *J* = 2.3 Hz, 1H), 7.89 (d, *J* = 9 Hz, 2H), 7.80 (s, 1H), 6.56 (s, 1H); Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.14%; H, 3.73%; N, 22.21%. Found: C, 57.1%; H, 3.7%; N, 22.2%.

1-(3-Nitrophenyl)-1H-pyrazole (Table 2, entry 2c)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.36 (s, 1H), 8.22 (d, *J* = 8.9 Hz, 2H), 7.91 (m, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.45 (s, 1H); 7.25 (s, 1H); Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.14%; H, 3.73%; N, 22.21%. Found: C, 57.2%; H, 3.7%; N, 22.2%.

1-(2-Nitrophenyl)-1H-pyrazole (Table 2, entry 2d)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.87-7.84 (m, 1H), 7.73-7.65 (m, 3H), 7.59-7.48 (m, 2H), 6.49-6.48 (m, 1H); Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.14%; H, 3.73%; N, 22.21%. Found: C, 57.2%; H, 3.8%; N, 22.3%.

1-(4-Methoxyphenyl)-1H-pyrazole (Table 2, entry 2e)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.83 (s, 1H), 7.69 (s, 1H), 7.60-7.57 (m, 2H), 6.99-6.96 (m, 2H), 6.44 (s, 1H), 3.85 (s, 3H); Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 68.95%; H, 5.79%; N, 16.08%. Found: C, 69.0%; H, 5.8%; N, 16.1%.

1-(4-Nitrophenyl)-1H-imidazole (Table 2, entry 2f)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.38 (d, *J* = 8.9 Hz, 2H), 7.99 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.38 (s, 1H), 7.28 (s, 1H); Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.14%; H, 3.73%; N, 22.21%. Found: C, 57.2%; H, 3.8%; N, 22.2%.

1-(4-Nitrophenyl)-1H-benzimidazole (Table 2, entry 2g)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.46 (d, *J* = 8.8 Hz, 2H), 8.19 (s, 1H), 7.91-7.88 (m, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.62-7.59 (m, 1H), 7.41-7.38 (m, 2H); Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.27%; H, 3.79%; N, 17.56%. Found: C, 65.4%; H, 3.8%; N, 17.6%.

1-(4-Nitrophenyl)-1H-1,2,4-triazole (Table 2, entry 2h)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.72 (s, 1H), 8.43-8.39 (m, 2H), 8.18 (s, 1H), 8.02-7.92 (m, 2H); Anal. Calcd. for $C_8H_6N_4O_2$: C, 50.53%; H, 3.18%; N, 29.46%. Found: C, 50.4%; H, 3.2%; N, 29.4%.

1-(4-Nitrophenyl)-1H-1,2,3-triazole (Table 2, entry 2i)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.40 (d, *J* = 9 Hz, 2H), 8.11 (s, 1H), 7.99 (d, *J* = 9 Hz, 2H), 7.92 (s, 1H); Anal. Calcd. for $C_8H_6N_4O_2$: C, 50.53%; H, 3.18%; N, 29.46%. Found: C, 50.6%; H, 3.2%; N, 29.4%.

N-(Phenyl)aniline (Table 2, entry 2j)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.29-7.24 (m, 4H), 7.12-7.03 (m, 4H), 6.95-6.90 (m, 2H), 5.73 (s, 1H); Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17%; H, 6.55%; N, 8.28%. Found: C, 85.2%; H, 6.6%; N, 8.3%.

RESULTS AND DISCUSSION

Structure of $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (1)

The structure of the compound was reported earlier.[20] Compound **1** features a 2D structure constructed by a ribbon-like 1D chain of hexa-coordinated Cu(II)-centers, CuO_4N_2, which is connected through hexa-coordinated tetra-aqua Mg(II)-centers of MgO_6 unit (Fig.-1a). Each Pyridine-2,5-dicarboxylate ligand coordinated to two Cu-centers and one Mg-center through three carboxylate oxygen atoms and one pyridyl nitrogen atom to give raise to a 2D framework. Topological analysis of the compound reveals that the compound **1** is a 3-nodal 2D net with the Schläfli symbol {4.8^2}2{4^2.8^2.10^2}{8} consisting of

Mg-centers, pdc^{2-} (H_2Pdc = pyridine-2,5-dicarboxylic acid) ligands, and Cu-centers as two, three, and four-coordinated nodes; respectively (Fig.-1b).[24] TGA analysis of compound makes known that the compound is thermally stable up to a 220 ºC after removal of water molecules.

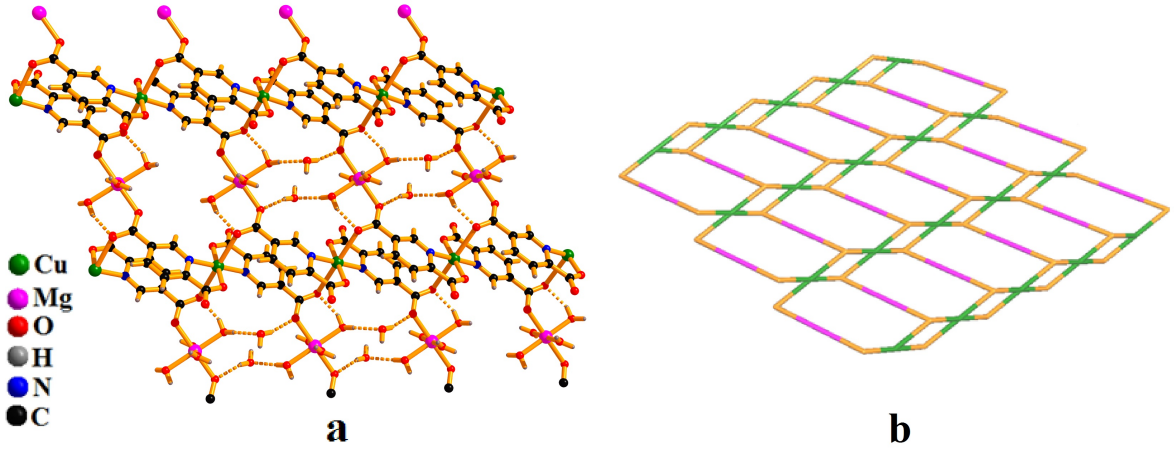


Fig.-1: (a) 2D Structure of Compound 1; (b) Topological View of Compound 1 (Mg-centers (purple), pdc^{2-} (H_2Pdc = pyridine-2,5-dicarboxylic acid) Ligands (yellow), and Cu-centers (green))

Catalytic Studies

The results of the catalytic activity of compound **1** in C–N cross-coupling reactions using pyrazole and phenyl bromide as substrates under various reaction conditions are summarized in Table-1. These optimization studies revealed that solvents, bases and temperature have a remarkable influence on the reactivity of the catalyst in the reaction. Preliminary screening to select the most suitable solvent, several solvents have been employed in C-N coupling reactions. In acetonitrile, the highest yield has been obtained (Table-1, entry 10) amongst all the solvents used (Table-1). In DMF and DMSO medium, a very low yield was obtained as copper leached out from the solid catalyst due to decomposition, which is not desirable from the environmental, economic and catalytic points of view. The optimal condition was found to be the use of Cs_2CO_3 as a base for this catalytic reaction in acetonitrile (Table-1, entry 10) and the catalyst is inactive in the absence of base (Table-1, entry 4). Other inorganic bases, such as K_2CO_3, K_3PO_4, Na_2CO_3, and Na_3PO_4 were also found to be more efficient compared with the soluble organic bases (e. g. Et_3N). Besides, the yield of the products depends on the reaction temperature. Isolated yield was not up to the mark both in high (90°C) and low (70°C) temperatures. While at low temperature, the conversion was lower (Table-1, entry 12), at a high-temperature yield of desired product was still lower due to the formation of undesired non-isolable by-products (Table-1, entry 13). Thus the optimum conditions of the catalytic reaction to achieve the highest yield of the desired product are as follows: Cs_2CO_3 (base), acetonitrile (solvent) and reaction temperature 80 °C. The advantage of this system is that the catalyst is not air or moisture-sensitive; hence, there is no need to carry out the reaction in an inert atmosphere wherein a previous report, it was seen that the yield of the product decreases drastically in the air due to presence of moisture.[1]

To ascertain the role of copper(II) and magnesium(II) centers in compound **1,** we have undertaken a few control experiments. It is well established that copper(II) acts as an efficient catalyst in N-arylation reactions.[1,18,19] To this end we have selected a 1D copper(II) complex $\{[Cu(pdc)(im)_2\}\cdot 2H_2O]\}_n$ (im = imidazole) which catalyzes N-arylation reactions under heterogeneous condition (Table-1, entry 14).[25] The yield, in this case, was lower than that of compound **1** as a catalyst in the same reaction conditions. Notably, the ligand, H_2pdc has no role in the catalytic reaction. One such compound $[Mg(pdc)]_n$ was inactive to catalyze N-arylation reaction (Table-1, entry 15).[26] But, when $Cu(pdc)(im)_2\}\cdot 2H_2O]\}_n$ was used along with $[Mg(pdc)]_n$, the yield increases surprisingly in the same heterogeneous reaction conditions (Table-1, entry 16). However, the yield was not up to the mark compared to compound **1** as a catalyst where both copper and magnesium center is present in the same framework. From the above

results, it may be concluded that the copper center acts as an active site for N-arylation reaction where the magnesium center acts as a promoter.

Under the optimized reaction conditions, the scope and applicability of the C-N cross-coupling reaction using a wide range of substrates were examined (Table-2). Among non-substituted aryl halides, iodobenzene and bromobenzene (Table-1, entries 10 and 17) showed comparable yields. Iodobenzene generally shows greater reactivity than bromobenzene in the cross-coupling reactions. A recent study has proposed that the I^- or I_2 generated from iodobenzene can act as an inhibitor during the catalytic process.[27] The catalyst cannot activate chlorobenzene due to its relative inertness (Table-1, entry 18).

Table-1: Optimization of Reaction Conditions for N–arylation of Pyrazole with Bromobenzene

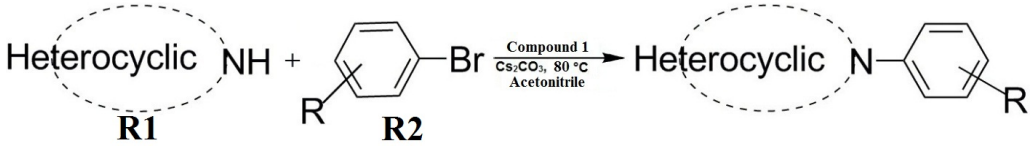
Entry[a]	Catalyst	Base	Solvent	Yield[b] (%)
1	Compound 1	Cs_2CO_3	Toluene	0
2	Compound 1	Cs_2CO_3	Ethanol	40
3	Compound 1	Cs_2CO_3	Acetone	64
4	Compound 1	–	Acetonitrile	0
5	Compound 1	Et_3N	Acetonitrile	18
6	Compound 1	Na_2CO_3	Acetonitrile	36
7	Compound 1	K_2CO_3	Acetonitrile	42
8	Compound 1	$Na_3PO_4{,}12H_2O$	Acetonitrile	48
9	Compound 1	$K_3PO_4{,}3H_2O$	Acetonitrile	56
10	Compound 1	Cs_2CO_3	Acetonitrile	82
11	–	Cs_2CO_3	Acetonitrile	-
12	Compound 1	Cs_2CO_3	Acetonitrile	75
13	Compound 1	Cs_2CO_3	Acetonitrile	72
14	$\{[Cu(pdc)(im)_2\}\cdot 2H_2O]\}_n$	Cs_2CO_3	Acetonitrile	58
15	$[Mg(pdc)]_n$	Cs_2CO_3	Acetonitrile	-
16	$\{[Cu(pdc)(im)_2\}\cdot 2H_2O]\}_n$ and $[Mg(pdc)]_n$ in 1:1 mol ratio and total 0.002 g	Cs_2CO_3	Acetonitrile	74
17[c]	Compound 1	Cs_2CO_3	Acetonitrile	80
18[d]	Compound 1	Cs_2CO_3	Acetonitrile	-

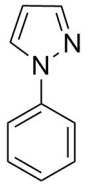
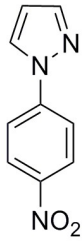
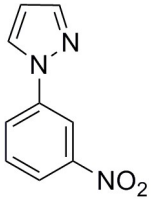
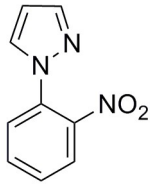
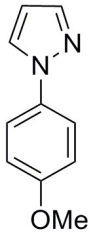
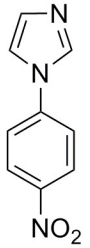
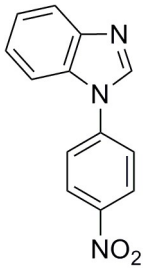
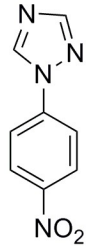
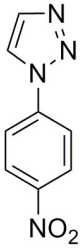
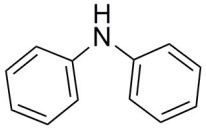
[a]Reaction condition: Bromobenzene (1.2 mmol), pyrazole (1.0 mmol), base (2 mmol), catalyst (0.002 g), solvent (2 mL) at 80 °C for 8 h under N_2 atmosphere (except entry 12 and 13 where the temperature was 70 and 90 °C respectively). [b]Isolated yield. [c]Iodobenzene was used instead of bromobenzene. [d]Chlorobenzene was used instead of bromobenzene.

N-arylation reaction to pyrazole with differently substituted bromobenzene was carried out. Reactions of pyrazole with *p*-NO_2- and *m*-NO_2-functionalized aryl bromide gave excellent yields of desired products, whereas for o-nitrobromobenzene a lower yield was obtained due to steric hindrance (Table-2, entries 2a–2d). Interestingly in the case of *p*-methoxybromobenzene, a moderately good yield was obtained (Table-2, entries 2e) than expected. Though the methoxy group has a very strong positive resonance effect, it may lose its power due to the ability to interact with the metal center. It is reasonable to conclude from Table 2 that electron-withdrawing substituted aryl bromides enhance the reactivity and the electron-releasing group deactivates. The reactivity of other N-containing heterocycles such as imidazole, benzimidazole, 1,2,4-triazole, and 1,2,3-triazole was also examined as N-containing heterocycles to couple with substituted aryl bromide (Table-2, entries 2f–2i). Imidazole pursued the same type of reactivity as

observed for pyrazole. But in the case of benzimidazole, 1,2,4-triazole, and 1,2,3-triazole a moderate yield was obtained. Aromatic amine (aniline) was also activated to yield the desired product with bromobenzene (Table-2, entry 2j). Very few reports were found searching for copper-based MOF for an efficient heterogeneous catalytic system for the N-arylation reaction. N-arylation reaction was studied by a post-synthetically modified Cu-anchored MOF in DMSO medium at 90 °C, which yields the desired product with high selectivity. However, it requires a longer period (20 h) to produce the same amount of yield as reported in this study.[1] In some cases nitro arenes were used to get the desired product in a shorter period (2 h) in DMF medium at 90 °C by using Cu-anchored post-synthetically modified MOF.[28] Zhao et al. used arylboronic acids to plan an alternative pathway for the N-arylation reaction and a moderate to high yield was obtained within 5 h of time in methanol medium by a Cu-MOF catalyzed reaction.[19]

Table-2: N-arylation Reaction of Different N-containing Heterocycles with substituted Aryl Bromide



Product[a]				
 2a, R1= pyrazole, R = H, Yield[b] (wt%) = 82	 2b, R1= pyrazole, R = *p*-NO_2, Yield[b] (wt%) = 90, 88[c]	 2c, R1= pyrazole, R = *m*-NO_2, Yield[b] (wt%) = 85	 2d, R1= pyrazole, R = *o*-NO_2, Yield[b] (wt%) = 76	 2e, R1= pyrazole, R = *p*-OMe, Yield[b] (wt%) = 74
 2f, R1= Imidazole, R = *p*-NO_2, Yield[b] (wt%) = 90, 85[c]	 2g, R1= benzimidazole, R = *p*-NO_2, Yield[b] (wt%) = 67	 2h, R1= 1,2,4-triazole,, R = *p*-NO_2, Yield[b] (wt%) = 78	 2i, R1= 1,2,3-triazole, R = *p*-NO_2, Yield[b] (wt%) = 70	 2j, R1= Aniline, R = H, Yield[b] (wt%) = 76

[a] Reaction condition: Aryl bromide (1.2 mmol), N-containing heterocycles (1.0 mmol), Cs_2CO_3 (2 mmol, 0.65 g) and Compound 1 (2 mg, Cu: 3.8×10^{-4} mol %) in 2 mL Acetonitrile at 80 °C for 8 h. [b]Isolated yield. [c]Fifth cycle.

The catalyst compound **1** was recovered and reused several times by filtration without significant catalytic activity loss. As an amount of 0.002 g of solid catalyst was not enough to recover, reuse, and finally characterize it, the catalyst was collected from different batches of the same catalytic cycle and average values of the data are reported here. The cross-coupling reactions were performed with bromobenzene, pyrazole, and Cs_2CO_3, thus maintaining the optimized reaction conditions. After the first cycle, the catalyst was recovered by centrifugation and then washed thoroughly with diethyl ether. The recovered catalyst was dried under vacuum at 100 ºC. Atomic absorption spectrometric (AAS) analysis of the

recovered catalysts confirmed the copper content of compound **1** remained the same. The catalytic efficiency of the recovered catalyst remained almost the same in every run (Table-2). To check the stability of the recovered catalyst, it was thoroughly characterized by powder XRD spectrometry. Comparison of XRD patterns (Fig.-2), of the virgin and recovered catalyst, convincingly demonstrated structural integrity of the compound retained after reactions.

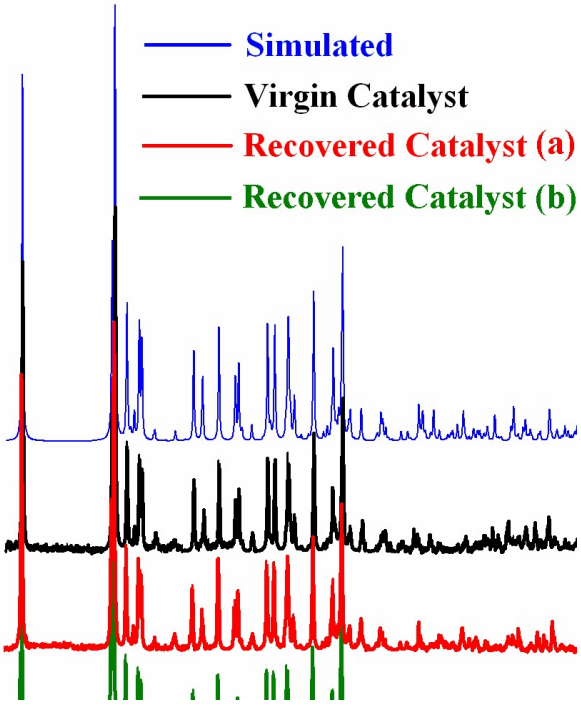


Fig.-2. X-ray Powder Pattern of Virgin Catalyst and Recovered Catalyst ('a' for N-arylation of pyrazole with *p*-NO_2 bromobenzene and 'b' for N-arylation of imidazole with *p*-NO_2 bromobenzene)

To test if copper was leaching out from the solid catalyst during the reaction, a hot filtration test was carried out, and the activity of the supernatant solution was studied. It was observed that after separation of the catalyst from the reaction mixture after 2 h of reaction, coupling reactions do not proceed further. AAS analysis (sensitivity up to 0.001 ppm) of the supernatant solution collected by filtration also confirmed the absence of copper ions in the liquid phase. The above results suggest that Cu was not leached out from the solid catalyst during the reaction.

CONCLUSION

In summary, we have demonstrated that the copper and magnesium-containing carboxylate framework can be used as a highly active catalyst for the C-N cross-coupling reaction of a variety of azoles with differently substituted aryl bromides in a mild heterogeneous condition where copper(II) acts as an active site for the catalytic reaction and magnesium(II) performs as a promoter. The compound is recyclable and stable under reaction conditions, demonstrating practical advantages over homogeneous catalysis.

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