CuNPs@Al₂O₃-cellulose composite for the ligand-free Suzuki cross-coupling reactions in batch and continuous flow process

Seema Patil [a], Archana Rajmane [a], Sanjay Jadhav [b], Chandrashekhar Rode [b], Arjun Kumbhar [a,*]

[a] Department of Chemistry, Vivekanand College, Kolhapur (Empowered Autonomous), Maharashtra, India
[b] Chemical Engineering and Process Development Division, CSIR—National Chemical Laboratory, Pune 411008, M. S., India

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ABSTRACT

In the present work, we synthesized recyclable CuNPs@Al₂O₃-CELL composite from an inexpensive and commercially available synthetic reagent by a simple method. The catalyst was characterized by various techniques such as TGA (Thermogravimetric analysis), SEM (Scanning electron microscope), TEM (Transmission electron microscopy), XPS (X-ray photoelectron spectroscopy), EDS (Energy dispersive spectroscopy), and AAS (Atomic Absorption Spectroscopy). The composite was applied for the Suzuki coupling reactions in the batch and flow process. The aryl halides were easily coupled with arylboronic acids in 95 % ethanol at 78 °C. We systematically investigated the role of reaction temperature, solvent, and catalyst loading, on the transient and steady-state behavior of the flow reactor through an automated flow chemistry platform. The CuNPs@Al₂O₃-CELL catalytic particles demonstrate minimal deactivation and leaching over a continuous Suzuki coupling reaction at a 20 min nominal residence time at 100 °C. Moreover, the catalyst can be recovered by simple filtration and reused at least five times with a moderate decrease in product yield. The excellent activity and stability of the catalyst have been attributed to the strong chelation of the Cu species with hydroxyl functional groups of the Al₂O₃-CELL composite. The catalytic system was highly efficient in Suzuki coupling of various aryl bromides with different aryl boronic acids, yielding good to excellent product yields (80–96 %) with a TON of 15.914–19.066 and TOF of 2.649–9.533 h^{-1}.

1. Introduction

In recent times, an important part of synthetic chemistry is based on the use of valuable transition metal catalysis [1], particularly copper which is an extensively used cheap metal with huge catalytic demand. Copper plays a significant part in organic synthesis, especially in various coupling reactions like Ullmann, Suzuki, Sonogashira, and Buchwald coupling reactions [2]. Almost all these reactions are catalyzed by traditionally catalysed by Pd catalysts [3–5]. Out of these reactions, the Suzuki coupling reaction is one of the most versatile reactions used for the construction of biaryl units [6–13], which are molecular components in active pharmaceutical ingredients. They are also present in many herbicides, and alkaloids as well as in engineering materials such as conducting polymers, molecular wires, and liquid crystals [14,15]. Recently various advances have been made in these coupling reactions [16–19].

Though these reactions have been carried out using Pd catalysts, the Pd-catalyzed methodologies, have many weaknesses such as being expensive, there is high possibility of contamination of the catalyst at the end of the catalytic cycle, and toxicity of the palladium metal borders its application in bioactive compounds [20,21]. Additionally, these issues create economic and ecological barriers to Pd-catalyzed coupling reactions. Hence from the green chemistry point of view modern synthetic chemistry promotes the use of the less toxic, recyclable, and Pd-free catalytic system, it's a current important challenge in front of synthetic organic chemists [22,23]. To address these challenges, the use of a cheaper heterogeneous metal catalyst instead of Pd is very important [24,25]. Hence recently, more devotion has been rewarded to the copper-based alternative catalysts, as it is less harmful, easily commercially available with reasonable cost, favorable reactivity, and ecological and operational simplicity [26–31]. Heterogeneous and ligand-free catalytic approaches for the carbon-carbon coupling reactions are very important owing to their easy recovery and recyclability. It also reduces the process to be more cost-effective and avoids ligands and metal contamination in the final products [32–35]. In this connection, one of the ways to meet the demands for recyclability, ligand-free, and

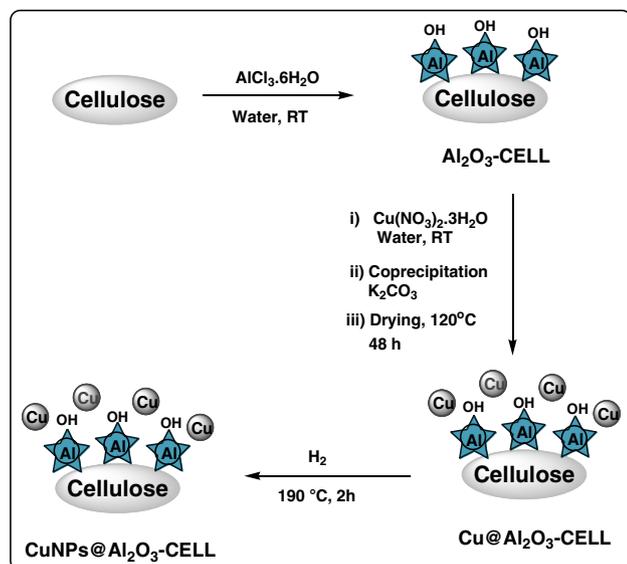**Scheme 1.** Preparation of CuNPs@Al$_2$O$_3$-CELL composite.

environmental concerns is the use of heterogeneous Cu-catalyst for the C-C bond-forming reactions.

To develop new green methodologies for the prevention of environmental issues, bio-polymers are an attractive and promising option as a support for catalysts. These materials also have a high surface area, abundant in various functional groups, which can be used for immobilization and stabilization of various metal catalysts. Over the last few decades, a large number of biopolymers such as cellulose [36], wool [37], alginate [38,39], gelatin [40], agarose [41], and chitosan [42,43] were reported as support for various catalysts [44]. Out of this cellulose has attracted much more attention due to its excellent biocompatibility and adsorption properties.

It is relatively inert to treatment with almost all commonly used solvents. The properties of cellulose may be modified by changing both physical and chemical structures. Hence to make cellulose more reactive, surface-modified have been carried out with metal oxides like Al$_2$O$_3$- cellulose [45] and TiO$_2$-cellulose [46] composite in which the aluminum oxide or titanium oxide can be highly dispersed on the surface of the cellulose with a virtuous degree of adhesion. Another way to enhance process productivity, waste reduction, catalyst reusability, and synthetic efficiency is the use of a fixed bed continuous flow processing technologies which is emerging as one of the alternatives for general reaction processes [47–50].

In continuation of our work associated with the direction of heterogeneous catalysis [51–53], the present work aims to synthesize and characterize the copper incorporated into a hybrid Al$_2$O$_3$-CELL based composite (CuNPs@Al$_2$O$_3$-CELL) which could function as a heterogeneous catalyst for Suzuki coupling reactions in batch as well as fixed bed continuous flow reactor. The CuNPs@Al$_2$O$_3$- CELL catalyst is packed into a stainless-steel fixed bed flow reactor for continuous operation in the Suzuki coupling reaction. We systematically investigate the role of reaction temperature, catalyst loading, cross-linking density, and gel particle size on the transient and steady-state behavior of the flow reactor through an automated flow chemistry platform. This catalyst demonstrated minimal deactivation and leaching over a continuous (12 h) Suzuki coupling reaction at a 20 min nominal residence time at a reaction temperature of 100 °C. The developed modular flow chemistry strategy equipped with the fixed bed flow reactor enables accelerated studies of the fundamental and applied characteristics of CuNPs@Al$_2$O$_3$-CELL catalysts while providing increased safety, higher throughput, and removal of the separation step needed for catalyst recovery compared to homogeneous coupling reactions in batch reactors.

2. Results and discussion

The cellulose-aluminum oxide (Al$_2$O$_3$-CELL) composite, was prepared as described in the literature [54–56]. In a typical reaction, aluminum chloride hexahydrate was dissolved in deionized water. After the addition of cellulose, the mixture was stirred at room temperature. The resulting suspension was filtered and the solid was exposed to
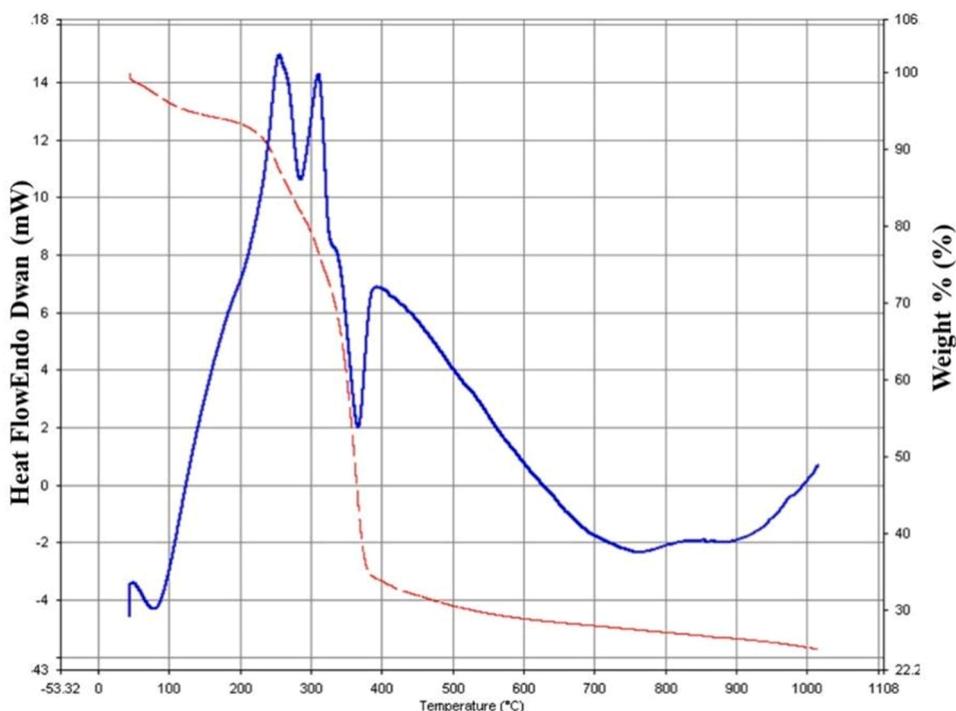

Fig. 1. TGA and DTA spectra of CuNPs@Al$_2$O$_3$-CELL catalyst.
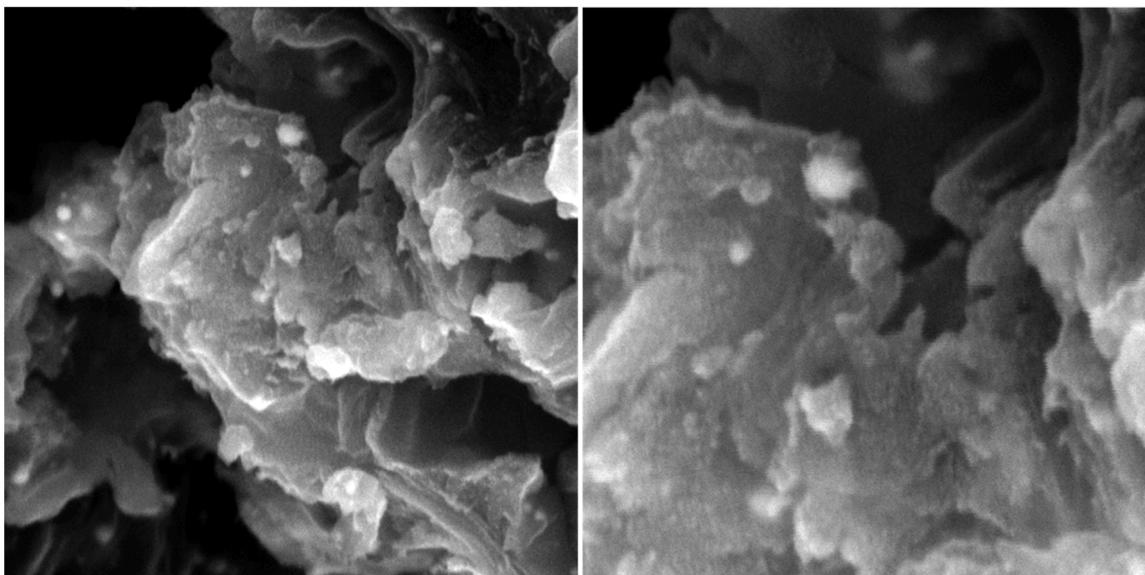
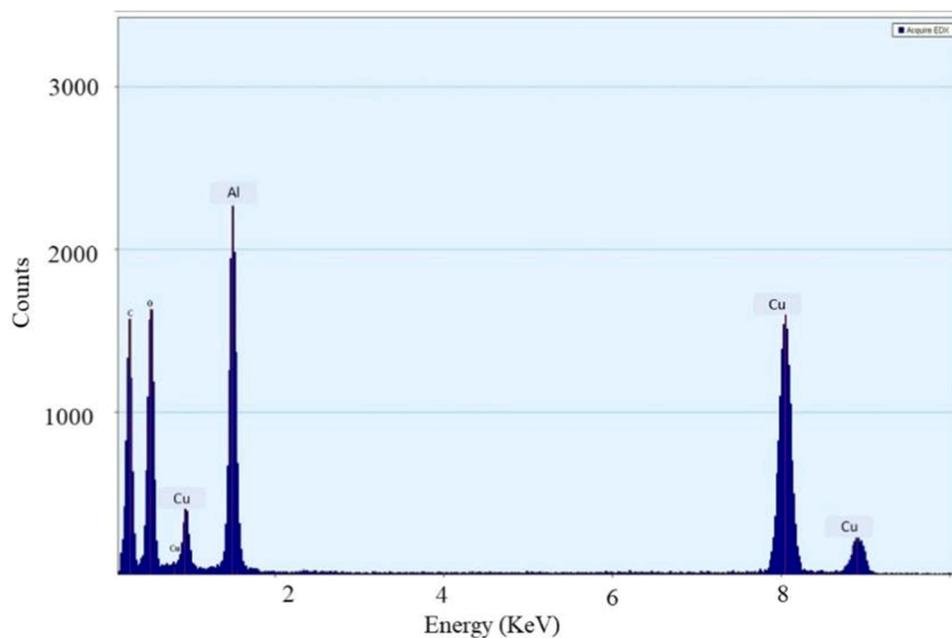**Fig. 2.** SEM analysis of CuNPs@Al$_2$O$_3$-CELL catalyst.

Fig. 3. EDS analysis of CuNPs@Al$_2$O$_3$-CELL catalyst.

ammonia gas, washed thoroughly with deionized water, and dried under vacuum at room temperature and then for 48 h at 120 ℃ (Scheme 1). The resulting Al$_2$O$_3$-CELL composite was mixed with a solution of Cu (NO$_3$)$_2$.3H$_2$O in deionized water and then aqueous solutions of K$_2$CO$_3$. The slurry was aged at 70 ℃ and the solid was exposed to ammonia gas, washed thoroughly with deionized water, and then dried under vacuum at room temperature for 8 h, and then at 120 ℃ for 48 h [57–61]. The resulting Cu@Al$_2$O$_3$-CELL placed in the sample holder was kept in closed furnace and exposed to hydrogen gas (flow rate 1 mL/ min). The furnace was slowly heated to 190 °C and was kept at this temperature for 2 h. At this condition Cu(II) is converted into Cu(0) and formed a black powder-colored CuNPs@Al$_2$O$_3$-CELL composite.

Our next focus was on characterizing the CuNPs@Al$_2$O$_3$-CELL catalyst, to be used in Suzuki coupling reactions. The catalyst underwent analytical characterization by various techniques.

The TGA (Thermo Gravimetric Analysis) curves (Fig. 1) showed that the catalyst is stable up to 290–300 °C. The first weight loss of up to 6–7 % between 25 and 150 °C temperature is due to the evaporation of loosely bonded water. Then the composite begins to lose weight at 225–400 °C due to the oxidative decompositio of cellulose and is evidenced by an exothermic peak in the DTA curve. In conclusion, the catalyst is stable up to 300 °C temperature.

Fig. 2 depicts the SEM analysis (Scanning Electron Microscope) results of CuNPs@Al$_2$O$_3$-CELL. It revealing a fibrous morphology characterized by the presence of small, discrete white Cu particulates dispersed throughout the Al$_2$O$_3$-CELL composite. The catalyst exhibited a fluffy texture and a porous nature. It is noteworthy that open and porous structures are known to enhance mass transfer, thereby contributing to improved catalytic activity. Moreover, the porous support not only increases catalytic activity but also helps prevent the undesirable leaching
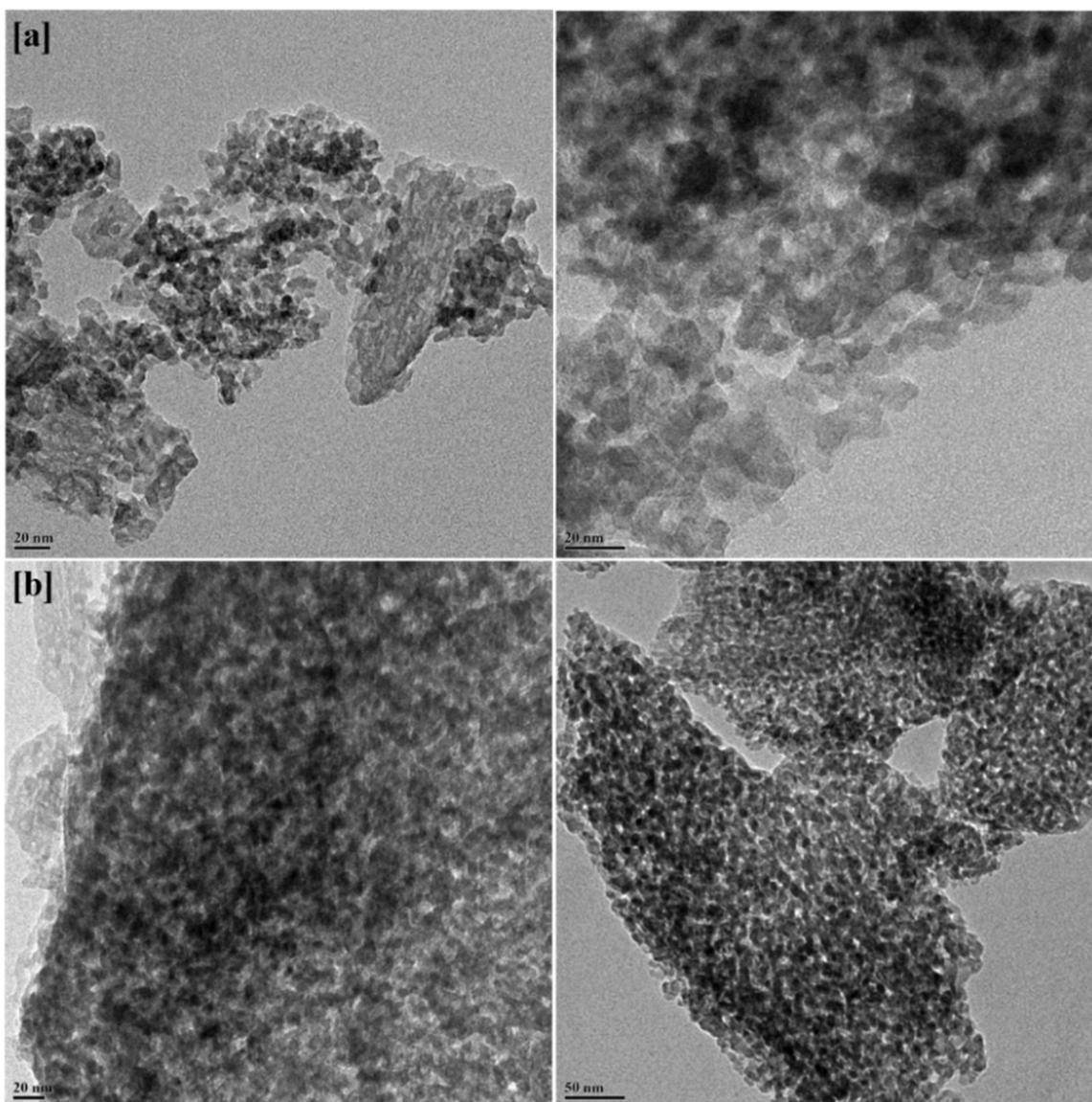
Fig. 4. HR-TEM images of (a) fresh CuNPs@Al$_2$O$_3$-CELL catalyst and (b) reused CuNPs@Al$_2$O$_3$-CELL catalyst after 5th run.

of the metal.

Energy Dispersive Spectroscopy (EDS) analysis was conducted at random surface points of the catalyst to qualitatively assess the elemental composition. The results conclusively confirmed the presence of aluminum (Al) and further revealed the deposition of copper (Cu) on the Al$_2$O$_3$-CELL composite material (Fig. 3).

The CuNPs@Al$_2$O$_3$-CELL catalyst was analyzed using HR-TEM (High-Resolution Transmission Electron Microscopy) as shown in Fig. 4. The analysis revealed that the CuNPs had an average diameter of 40–76 nm (Fig. 4a), which closely matched the values calculated for Cu nanoparticles from XRD data. Additionally, the HR-TEM analysis of the recycled CuNPs@Al$_2$O$_3$-CELL catalyst exhibited evidence of CuNPs agglomeration (Fig. 4b after 5th run), indicative of the retention of copper metal on the surface of the Al$_2$O$_3$-CELL.

In order to assess the chemical oxidation state of copper within the CuNPs@Al$_2$O$_3$-CELL catalyst, an X-ray photoelectron spectroscopy (XPS) experiment was conducted. Analysis of the XPS data, as illustrated in Fig. 5, revealed distinct binding energy peaks at 931.22 eV and 951.34 eV corresponding to the 2P$_{3/2}$ and 2P$_{1/2}$ states, respectively. These findings provide clear evidence that the copper species exist in a zerovalent state [62].

We conducted the synthesis and thorough characterization of the CuNPs@Al$_2$O$_3$-CELL catalyst. Subsequently, we assessed its catalytic performance in Suzuki coupling reactions. To ensure a precise analysis of the catalytic activity, we employed electronically deactivated aryl bromides as substrates, as compared to the more readily coupled aryl iodides. In our initial investigation, we focused on the coupling of 4-bromobenzophenone (1 mmol) with phenylboronic acid (1.1 mmol) utilizing CuNPs@Al$_2$O$_3$-CELL (Scheme 2). This study aimed to evaluate the influence of various factors, including the choice of base, catalyst loading, solvent, and reaction temperature.

An experiment was conducted to analyze the impact of different bases on a model reaction using 95 % ethanol at 78 °C. The study found that inorganic bases (Table 1, entries 1-3 and 7) were more effective compared to organic bases (Table 1, entries 4–7). The results showed that K$_3$PO$_4$ produced the best yield (Table 1, entry 1). Among the organic solvents tested (Table 1, entry 9–16), 95 % ethanol (Table 1, entry 9) was found to be the most suitable for this catalytic system. However, the catalyst's efficiency was lower in water (Table 1, entry 10). The use of 95 % ethanol makes this protocol practical and feasible for large-scale synthesis. Subsequently, we investigated the influence of catalyst loading by conducting the model reaction with varying
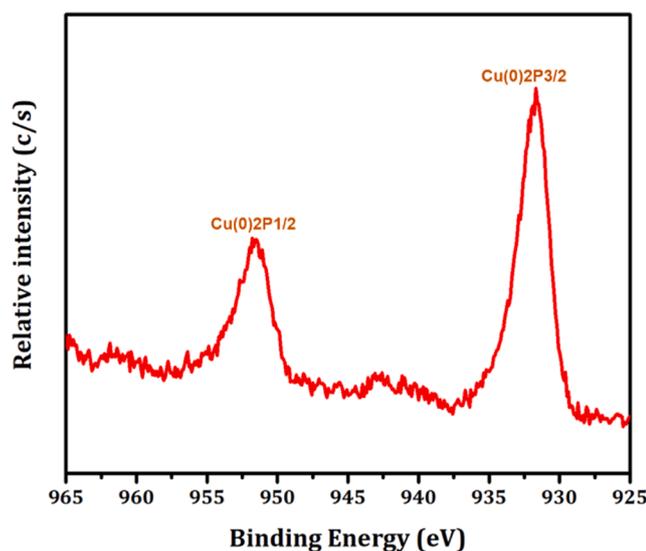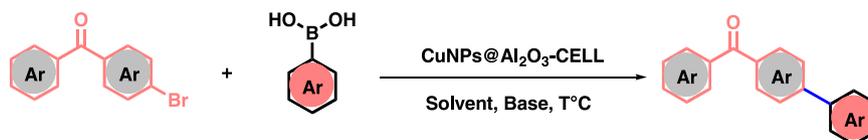
Fig. 5. XPS analysis of CuNPs@Al$_2$O$_3$-CELL catalyst.

quantities of catalyst in the presence of K$_3$PO$_4$ at a temperature of 78 °C. Our observations revealed that increasing the catalyst amount from 5 to 7 mol% did not yield a significant change in the product's yield (Table 1, entries 17 and 18). In contrast, reducing the catalyst quantity from 2 to 4 mol% led to a notable decrease in the product yield, dropping from 94 % to 30 % (Table 1, entries 19–21). Consequently, among the various loadings tested, 5 mol% emerged as the optimal choice, affording the desired product with a 94 % yield in a 95 % ethanol at 78 °C over a 5 h reaction period.

In the course of our optimization investigations, we also explored the impact of temperature (Table 2). Our findings indicated that temperature exerts a substantial influence on both the reaction rate and yield. Elevating the temperature from 40 to 78 °C resulted in a notable enhancement of the reaction yield, escalating from 25 % to 95 % (Table 2, entries 1–5).

To investigate the versatility and applicability of the catalyst, we applied the optimized protocol, which comprised aryl bromide (1 mmol), aryl boronic acid (1.1 mmol), K$_3$PO$_4$ (2 mmol), 5 mol% catalyst, in 95% ethanol and a temperature of 78 °C under air (Table 3). It was notable that aryl bromides yielded products in the range of 80–95 % within reaction times spanning from 2 to 8 h. Furthermore, we successfully synthesized 2-methyl-1,1':4',1''-terphenyl, a fluorescent

Scheme 2. CuNPs@Al$_2$O$_3$-CELL catalyzed Suzuki coupling reaction.

Table 1
Optimization of various reaction parametersfor Suzuki coupling reaction[a].
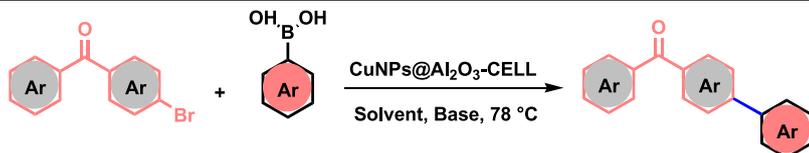
Entry	Reaction Parameters	Catalyst (mol %)	Time (h)	Yield (%)[b]	TON	TOF (h^{-1})
Optimization of Base						
1	K$_3$PO$_4$ (2 mmol)	5.0	05	94	18.737	3.747
2	K$_2$CO$_3$ (2 mmol)	5.0	12	85	16.956	1.413
3	Na$_2$CO$_3$ (2 mmol)	5.0	12	74	14.711	1.225
4	Me$_2$NH (2 mmol)	5.0	12	46	9.136	0.761
5	Pyrrolidine (2 mmol)	5.0	12	30	5.961	0.496
6	Pipyridine (2 mmol)	5.0	12	20	3.948	0.329
7	Et$_3$N (2 mmol)	5.0	12	35	6.968	0.580
8	NaOH (2 mmol)	5.0	12	40	7.974	0.664
Optimization of solvents						
9	95 % EtOH	5.0	05	94	18.737	3.747
10	H$_2$O	5.0	05	30	5.961	1.192
11	CH$_3$CN	5.0	05	70	13.936	2.787
12	DMF	5.0	05	85	16.956	3.391
13	THF	5.0	05	65	12.930	2.586
14	Toluene	5.0	05	75	14.943	2.988
15	DMSO	5.0	05	53	10.529	2.105
16	PEG-400	5.0	05	81	16.104	3.220
Optimization of Catalyst loading						
17	K$_3$PO$_4$ (2 mmol)	5.0	05	94	18.737	3.747
18	K$_3$PO$_4$ (2 mmol)	7.0	05	95	13.549	2.709
19	K$_3$PO$_4$ (2 mmol)	2.0	05	30	14.904	2.980
20	K$_3$PO$_4$ (2 mmol)	3.0	05	45	14.969	2.993
21	K$_3$PO$_4$ (2 mmol)	4.0	05	80	19.937	3.987

[a] Reaction conditions: 4-bromobenzophenone (1 mmol), phenylboronic acid (1.1 mmol), catalyst (1-7 mol %), base (2 mmol), Solvent (5.0 mL), at 78°C in air.
[b] Isolated yields.

Table 2

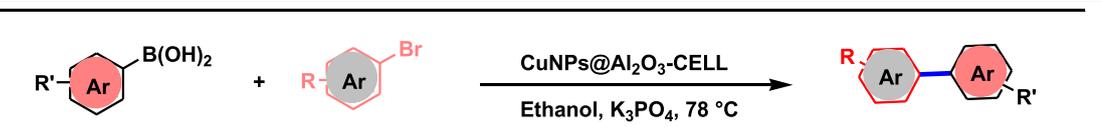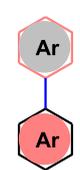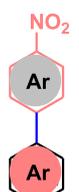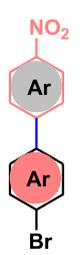Effect of temperature on the Suzuki coupling reaction[a].
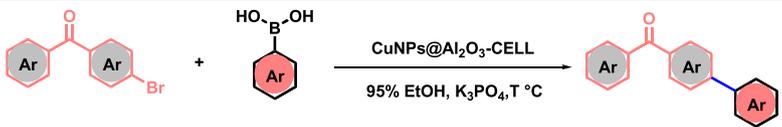
Entry	T °C	Time (h)	Yield[b] (%)	TON	TOF (h^{-1})
1	r.t.	05	25	4.993	0.998
2	40	05	35	6.968	1.393
3	60	05	60	11.923	2.384
4	70	05	80	15.949	3.189
5	78	05	94	18.737	3.747

[a] Reaction conditions: 4-bromobenzophenone (1.0 mmol), phenylboronic acid (1.1 mmol), catalyst (5 mol %), K_3PO_4 (2.0 mmol), 95 % ethanol (5 mL), RT to 78℃.

[b] Isolated yields.

Table 3

The Suzuki coupling reactions of various aryl bromides and phenylboronic acids[a].

1 (96 %, 2 h)
TON = 19.066
TOF = 9.533 (h^{-1})

2 (85 %, 5 h)
TON = 17.000
TOF = 3.400 (h^{-1})

3 (82 %, 6 h)
TON = 16.324
TOF =2.720 (h^{-1})

4 (88 %, 3 h)
TON = 17.478
TOF = 5.826 (h^{-1})

5 (80 %, 5 h)
TON = 15.914
TOF = 3.182 (h^{-1})
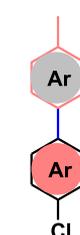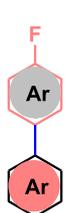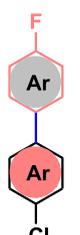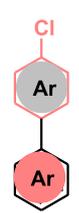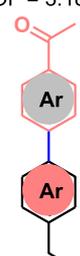
6 (90 %, 6 h)
TON = 17.861
TOF = 2.976 (h^{-1})

7 (91 %, 4 h)
TON = 18.119
TOF = 4.529 (h^{-1})

8 (89 %, 6 h)
TON = 17.711
TOF = 2.951 (h^{-1})

9 (95 %, 4 h)
TON = 18.870
TOF = 4.717 (h^{-1})

10 (90 %, 6 h)
TON = 17.923
TOF = 2.987 (h^{-1})
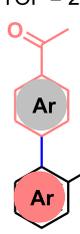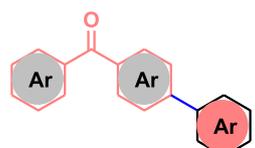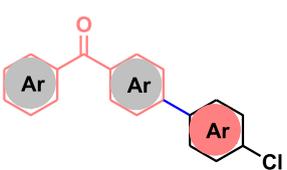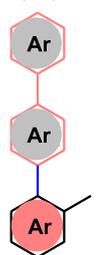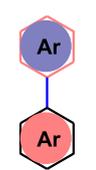
11 (92 %, 6 h)
TON = 18.357
TOF = 3.059 (h^{-1})

12 (94 %, 5 h)
TON = 18.769
TOF = 3.753 (h^{-1})

13 (93 %, 7 h)
TON = 18.548
TOF = 2.649 (h^{-1})

14 (86 %, 8 h)
TON = 17.154
TOF = 2.144 (h^{-1})

15* (42 %, 24 h)
TON = 8.362
TOF = 0.348 (h^{-1})

[a]Reaction conditions: arylbromides (1 mmol), arylboronic acids (1.1 mmol), CuNPs@Al$_2$O$_3$-CELL (5 mol %), K$_3$PO$_4$ (2 mmol), 95 % EtOH (5.0 mL), at 78°C in air.
[b]Isolated yields. [c]Reaction between: 4-chlorobenzene and phenylboronic acid.
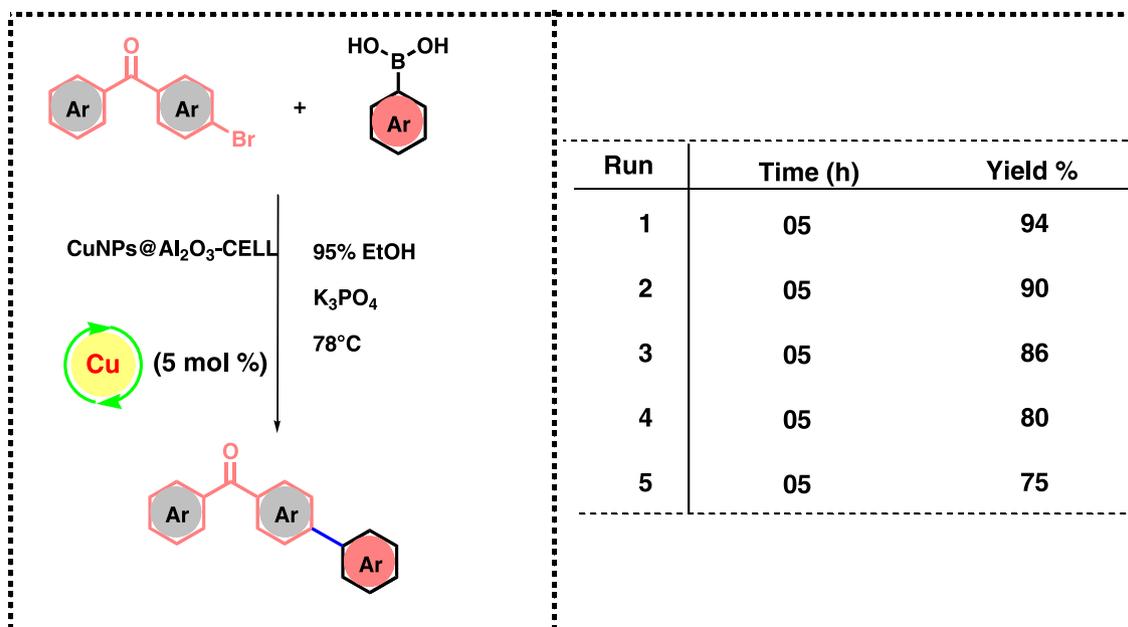
Scheme 3. Recyclability of CuNPs@Al$_2$O$_3$-CELL catalyst in Suzuki coupling reaction.

compound, with an 86 % yield over an 8-hour reaction period by coupling 4-bromo-biphenyl with 2-methyl phenylboronic acid (Table 3, entry 14). A key observation was the catalyst's remarkable selectivity in exclusively producing Suzuki coupling products, without the formation of homocoupling products [63–64]. Encouraged by the excellent results obtained with aryl bromides, we extended our approach to couple 4-chlorobenzene with phenylboronic acid. From a practical standpoint, utilizing readily available and cost-effective aryl chlorides holds great promise for industrial applications [65]. The efficiency of our catalytic protocol, however, was found to be moderate for the reaction involving 4-chlorobenzene and phenylboronic acid, as evidenced by the results presented in Table 3 (entry 15), yielding the analogous product with a 42 % yield within 24 h.

2.1. Heterogeneity of CuNPs@Al$_2$O$_3$-CELL catalyst

To assess the catalyst's heterogeneity, a hot filtration test was conducted, following established methods [66–70]. In this test, after 2.5 h of the model reaction, the catalyst was separated from the reaction mixture by filtration at

78 °C. At this point, the conversion of the reaction had reached 72 %, as determined by Gas Chromatography (GC) analysis of the reaction mixture. Subsequently, the filtrate was stirred for an additional 5 h at 78 °C, and GC analysis revealed that, following the catalyst's removal through filtration, the reaction did not progress any further. These results provide strong evidence that the catalyst in question exhibits true heterogeneity in its nature.

2.2. Recyclability of catalyst

The practical applications of heterogeneous catalysts place significant importance on the catalyst's ability to reuse them. In this study, we examined the recyclability of a catalyst in a model reaction lasting 5 h. Following the reaction, the catalyst was separated via a straightforward filtration process. Subsequently, it was subjected to thorough washing with water, dichloromethane, and acetone before being dried under vacuum. The recovered catalysts were then employed in successive reactions. As detailed in Scheme 3, the catalytic activity exhibited a decline after each catalytic cycle. Remarkably, Atomic Absorption Spectroscopy (AAS) analysis revealed that copper (Cu), an essential
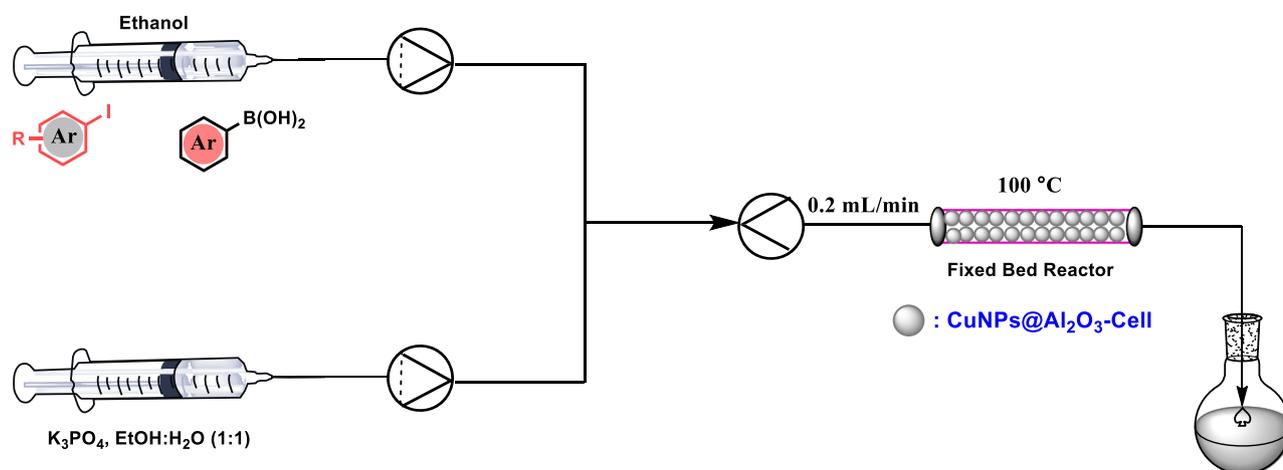
component of the catalyst, remained firmly anchored to the solid support, indicating that leaching of Cu was not the cause of the decreased yield of the desired product. Instead, the decrease in catalytic activity may be attributed to the blockage of active sites on the catalyst's surface.

2.3. Application of CuNPs@Al$_2$O$_3$-CELL catalyst in continuous flow operation

The efficiency of the current method was tested on the Suzuki coupling reaction using fixed bed continuous flow processing technology. Scheme 4 shows a diagram of the fixed bed continuous flow reactor. The reactor contained 5 g of CuNPs@Al$_2$O$_3$-CELL catalyst. A mixture of 0.125 M 4-iodobenzophenone and 0.150 M phenylboronic acid in 95 % ethanol was directed into the fixed bed column packed with the catalyst through a T-piece. The flow rate was optimized at 0.2 mL min^{-1} at 100 °C to facilitate the coupling reaction. The fixed bed continuous flow reactor was operated for 12 h. The conversion rate was ≤96 % within a residence time of 20 min (flow rate 0.2 mL min−1), at 100 °C and atmospheric pressure.

Finally, a scale-up study was performed for continuous operation for 12 h. The percentage yield of the desired product did not decrease up to 8 h of operation with residence times of 5 min. A slight decrease in conversion was observed after 8 h of continuous flow operation (Scheme 3, entry 1–3). Thus, it was found that our flow reaction system applies to the continuous flow synthesis of biaryl molecules which act as pharmaceutical intermediates and is amenable to gram-scale production. A further detailed study is in progress in our laboratory to investigate, whether our optimized flow reaction system applies to the synthesis of a wide variety of substituted molecules that act as pharmaceutically active scaffolds and are amenable to gram-scale production.

The precise mechanistic details governing the CuNPs catalyzed Suzuki coupling reaction remain a subject of uncertainty. However, a plausible mechanism describing the catalytic properties of the CuNPs@Al$_2$O$_3$-CELL catalyst in the model coupling reaction is depicted in Scheme 5. The initial step of the reaction involves the oxidative addition of Cu(0) to 4-bromobenzophenone, leading to the formation of aryl copper bromide species A [71]. Notably, in most instances, this oxidative addition process serves as the rate-determining step in the catalytic cycle. Within this step, Cu undergoes oxidation from Cu(0) to Cu(II).

**Scheme 4.** Suzuki coupling reaction using fixed bed continuous flow reactor.

Additionally, the interaction with a base with phenylboronic acid results in the formation of activated boronic acid derivative B. This intermediate, upon reaction with intermediate A, yields the transmetalation complex C. Ultimately, the reductive elimination of C results in the production of the coupled product 3a.

The present reaction protocol was confirmed with those similar catalysts reported for Suzuki coupling reactions (Table 4). It was observed that the present catalyst is comparable and efficient to reported catalysts. It required comparatively less time.

3. Conclusion

In this current investigation, a cost-effective, efficient, selective, and reusable CuNPs@Al$_2$O$_3$-CELL catalyst was synthesized using readily available synthetic reagents through a straightforward method. The catalyst was found to consist of Cu(0) metal securely anchored on Al$_2$O$_3$-CELL, serving as the active sites for Suzuki coupling reactions in both batch and continuous flow processes. The remarkable activity and stability of this catalyst are attributed to the robust chelation of Cu species with the hydroxyl functional groups present in the Al$_2$O$_3$-CELL hybrid composite. Using a mere 5 mol% of this catalyst, various aryl halides and arylboronic acids could be efficiently coupled in 95 % ethanol at a reaction temperature of 78 °C. Furthermore, a comprehensive exploration of the impact of reaction temperature, choice of solvent, and catalyst loading was conducted, assessing the transient and steady-state behavior of the flow reactor. This investigation was facilitated through an automated flow chemistry platform. Importantly, the CuNPs@Al$_2$O$_3$-CELL catalyst exhibited minimal deactivation and leaching during a continuous 12-hour Suzuki coupling reaction at a high reaction temperature of 100 °C. It was revealed that the catalyst can be recovered by simple filtration and reused at least five times with a moderate decrease in product yield. These advantages make the process highly valuable from the synthetic and environmental points of view.
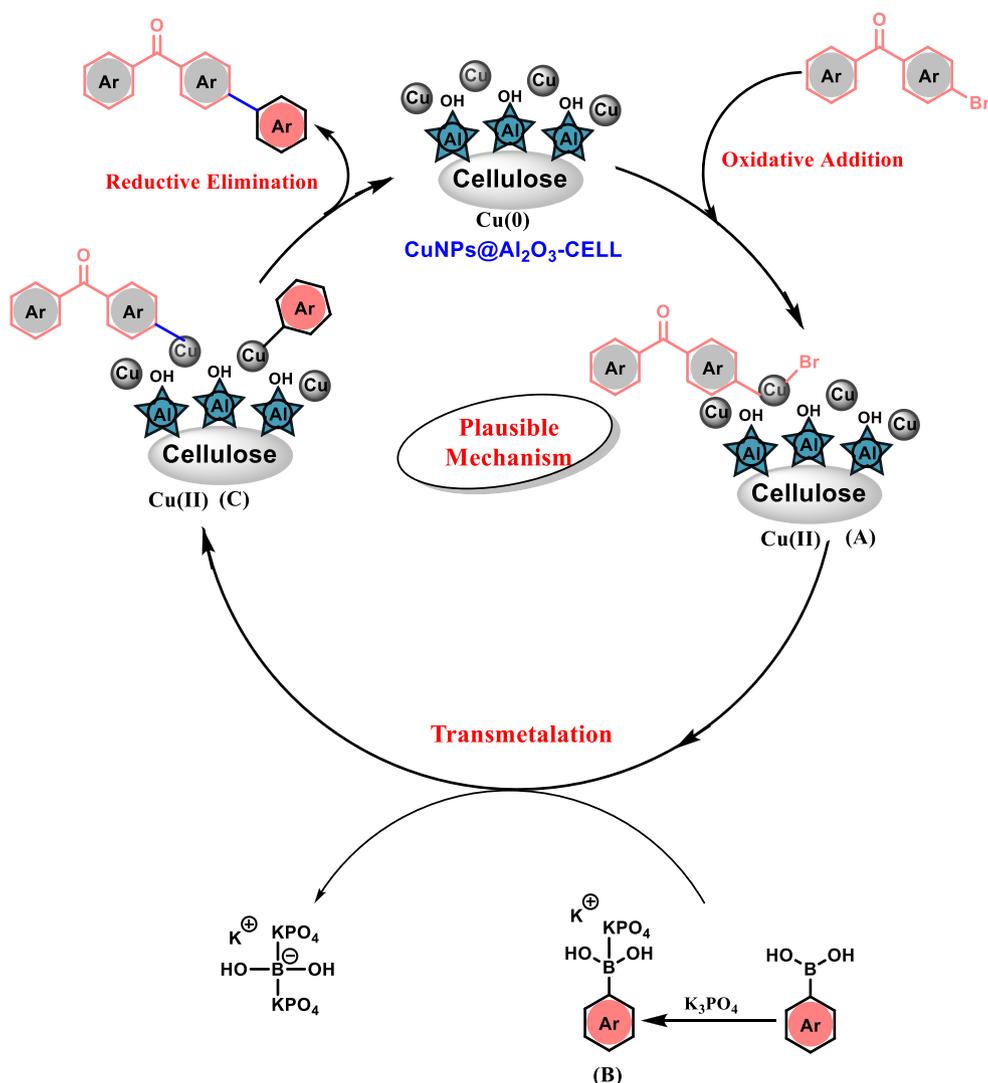
Scheme 5. Plausible mechanism for Miyaura coupling reaction catalyzed by CuNPs@Al₂O₃-CELL.

Table 4
Comparison of the present method with other Cu catalysts

Sr. No.	Catalyst	X	Solvent	T (°C)	Time (min/h)	Yields (%)	Reuse	Ref.
1	Hollow triple-shell CuNiFe₂O₄ nanospheres	Br, I	EtOH/H₂O	80	35-80 min	89-95	9	[71]
2	CuNPs-Arginine-modified Fe₃O₄@carbon magnetic nanoparticles	Br, I	H₂O	RT	1.5-3 h	92-98	6	[72]
3	Cu-Colloid	I	DMF	110	8 h	62	-	[73]
4.	Carbon coated copper nanostructures	I, Br	H₂O	50	2-3.5 h	87-96	-	[74]
5	Copper-Functionalized Silica-Coated Magnetic Nanoparticles	I, Br	Solvent-free	80	25-135 min	90-97	6	[75]
6	Cu(0) Aluminium Hydrotalcite	Cl	DMF	110	4-16 h	40-97	-	[76]
7	Cu-Adenine@boehmite	I, Br, Cl	H₂O	80	60-270 min	86-98	8	[77]
8.	Cu–ninhydrin@GO–Ni MNPs	I, Br, Cl	H₂O	80	50-420 min	89-97	8	[78]
9.	CuNPs@Al₂O₃-CELL (5 mol%)	Br	EtOH	78	2-12 h	80-96	5	**Present work**

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2023.122954.

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