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Preparation and Characterization of an Efficient Nano-Inorganic Composite of $CuO/ZnO/Al_2O_3$ for the Catalytic Amination of Aryl Halides in Aqueous Conditions

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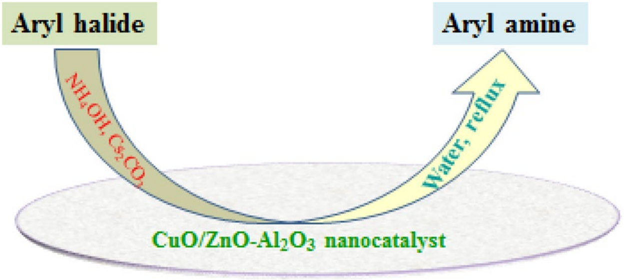
Abstract

In this research, an efficient recyclable nano-inorganic composite of $CuO/ZnO/Al_2O_3$ ($CuO/ZnO/Al_2O_3$ nanocatalyst) is prepared, characterized and used for the amination of aryl halides with aqueous ammonia in water. The catalyst was prepared by co-precipitation method and characterized by various techniques such as the X-ray diffraction, scanning electron microscope, energy dispersive spectroscopy, and brunauer–Emmett–Teller surface area analysis. Various aryl halides reacted with aqueous ammonia and corresponding products were obtained in high yields. $CuO/ZnO/Al_2O_3$ nanocatalyst as an efficient stable catalyst is recyclable up to five consecutive runs by simple filtration.

Graphical Abstract

An efficient recyclable nano-inorganic composite of $CuO/ZnO/Al_2O_3$ ($CuO/ZnO-Al_2O_3$ nanocatalyst) is prepared, characterized and used for the amination of aryl halides with aqueous ammonia in water.



Keywords $CuO/ZnO/Al_2O_3$ nanocatalyst · Amination · Ammonia · Aryl halide

1 Introduction

Synthesis of aryl amines is an active area in organic synthesis because of the occurrence of these moieties in biologically important natural products, pharmaceuticals, and their applications in materials researches [1]. Aryl amines are attractive targets for chemical synthesis because of their utility in fine chemicals, dyes and polymers [2]. The most common approach to prepare aryl amines generally relays on the use of transition-metal catalysts to promote the coupling reaction of aryl halides with ammonia or ammonia derivatives [3].

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Metal-catalyzed reactions are one of the most widely used methodologies for the creating C–N bonds. and they have been used in the C–N coupling of amines and aryl halides. Various catalysts, including Pd, and Cu have been shown to catalyze the amination of aryl halides with ammonia [4–14]. Among these, the copper-catalyzed Ullmann reaction has been proven to be the most convenient synthetic route for installing an N-aryl functionality [6].

Hybrid nanostructures show multi-functionality with synergistic effects between independent domains [15]. From the perspective of heterogeneous catalysis, these mixture nanostructures could provide optimal architectures for bifunctional catalytic systems [16]. In these catalysts, one or two of the components acts as an active surface for the reaction, and the other works as a support to stabilize the whole structure. The inorganic border between the components can either tailor the chemical nature of the active component, or create new species to increase catalytic activities. Therefore, these well-defined hybrid nanostructures are ideal for heterogeneous catalysts [17].

In recent years, Cu-catalysts supported on $ZnO–Al_2O_3$ mixed oxides have gained special interests as industrial catalysts. Specially, $CuO/ZnO/Al_2O_3$ has been paid more attention, and some progresses have been reported [18, 19]. Therefore, for the preparation of $CuO/ZnO/Al_2O_3$ catalyst, various approaches have been reported and different kind of this catalyst was prepared and studied [20–25].

Previously, we have reported the amination of aryl halides in the presence of $CuO–CeO_2$ nanocomposite and poly(4-vinylpyridine)-supported copper iodide nanoparticles catalyst ($P_4VPy–CuI$) [26, 27]. To the best of our knowledge, $CuO/ZnO/Al_2O_3$ nanocatalyst has not used as catalyst in organic synthesis reactions in particular for the amination of aryl halides. Therefore, in continuation of our programs for the study on different nanocatalysts [28–30], we herein, report the preparation, characterization and catalytic activity of an efficient recyclable nano-inorganic composite of $CuO/ZnO/Al_2O_3$ ($CuO/ZnO/Al_2O_3$ nanocatalyst) for the amination of aryl bromides and iodides with aqueous ammonia in water (scheme 1).

$$\underset{X=Br,\ I}{ArX} \xrightarrow[Cs_2CO_3,\ H_2O,\ reflux]{CuO/ZnO/Al_2O_3\ nanocatalyst \atop NH_4OH} ArNH_2$$

Scheme 1 $CuO/ZnO/Al_2O_3$ nanocatalyst catalyzed amination of aryl halides

2 Experimental

All chemical compounds were purchased from Merck chemical companies. Products were characterized by comparison of their spectroscopic data (^1H NMR, IR) and physical properties with those reported in the literature. Yields refer to isolated products.

2.1 Preparation of Catalyst

The $CuO/ZnO/Al_2O_3$ nanocatalyst was prepared via a co-precipitation method, by adding Na_2CO_3 solution (0.5 M) drop-wise into a mixture of $Cu(NO_3)_2·3H_2O$ (0.03 M), $Zn(NO_3)_3·6H_2O$ (0.03 M), and aluminium nitrate (0.03 M), solutions under vigorous stirring. The obtained suspension was aged at $pH = 8.5$ for 15 min at 50 °C, then filtered and washed with warm deionized water (<0.05 µS cm^{-1}). The precipitates were dried 12 h at 100 °C followed by calcination at 300 °C for 3 h to afford the $CuO/ZnO/Al_2O_3$ nanocatalyst.

2.2 Catalyst Characterization

The X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer, Cu–Kα monochromatized radiation source and a nickel filter (Panalytical X'PertPro), in order to investigate the structure and crystallinity of the catalyst. Scherrer equation was used to determine the average crystallite size of the sample. The morphology of the $CuO/ZnO/Al_2O_3$ nanocatalyst was studied by scanning electron microscopy (SEM) method by a JEOL JSM-6500F instrument, equipped with an energy dispersive spectroscopy (EDS) analytical system to study the presence of different components of the catalyst. The brunauer–Emmett–Teller (BET) surface area was tested by N_2 adsorption–desorption method. The analysis was carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The sample was purged with nitrogen gas for 3 h at 300 °C by a VacPrep 061 degas system (Micrometrics).

2.3 General Procedure

A mixture of aryl halide (1 mmol), NH_4OH (2 mmol), Cs_2CO_3 (1 mmol) and $CuO/ZnO/Al_2O_3$ nanocatalyst (0.1 g), in water was stirred at reflux condition. After reaction completion, (monitored by TLC), the mixture reaction was cooled to room temperature and catalyst filtered. Then the residue was evaporated to dryness, the residue was poured into a saturated NaCl solution, extracted with ethyl acetate and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel gave the pure products in high yields.

3 Results and Discussion

3.1 X-ray Diffraction

Figure 1, Shows the XRD pattern of the $CuO/ZnO/Al_2O_3$ nanocatalyst. As reported in literature [31], the diffraction peaks centered at $2\theta = 31.8$, $2\theta = 34.82$, $2\theta = 56.92$, $2\theta = 69.12$ are attributed to the (100), (002), (110) and (200) crystalline planes of ZnO crystals, respectively. The diffraction peaks centered at $2\theta = 36.58$, $2\theta = 47.86$ and $2\theta = 63.32$ may be corresponded to (111), (202) and (113) planes of CuO, respectively [32]. It is valuable to note that the peaks centered at about $2\theta = 36.58$ may be related to α, δ and θ and the peaks centered at about $2\theta = 47.86$ can be attributed to the γ, δ, θ, Al_2O_3 phases, respectively [30]. These explanations can be stated, because the percentages of Al_2O_3 (10%) and CuO (5%) in the target catalyst are nearly close. As presented, the synthesized catalyst is a mixture of three type crystals and overlapping the characteristic peaks may influence the detailed interpretations of the given XRD pattern. Therefore, the XRD data can be a proof to indicate the presence of three crystals in the blended catalyst.

3.2 N_2 Adsorption/Desorption Analysis

As seen from Fig. 2, the isotherms of the support and catalyst display thin hysteresis loops between $p/p^0 = 0.3–0.8$ and $p/p^0 = 0.3–0.85$, respectively. However, according to the IUPAC instructions, these N_2 adsorption/desorption profiles correspond to the approximately non-porous metal oxides' structures and could be categorized as type III [33, 34]. As seen, the hysteresis loop of the support is smaller than the catalyst hysteresis loop. As demonstrated in the Fig. 2a, the amount of adsorbed N_2 gas per gram of catalyst is greater than that of the support in each relative pressure below 0.8. This difference may be due to the high surface area of the $CuO/ZnO/Al_2O_3$ compared to the ZnO support. The specific surface area and porosity of the support and the catalyst were calculated by employing the BET and Barrett-Joyner-Halenda (BJH) methods, respectively. The pore width distribution and structural characteristics of the support and

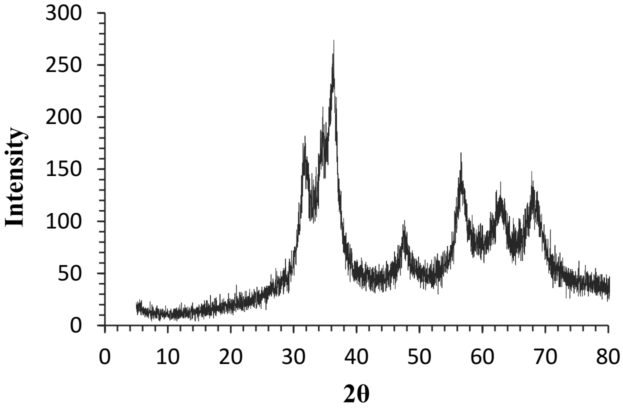


Fig. 1 The XRD pattern of $CuO/ZnO/Al_2O_3$ nanocatalyst

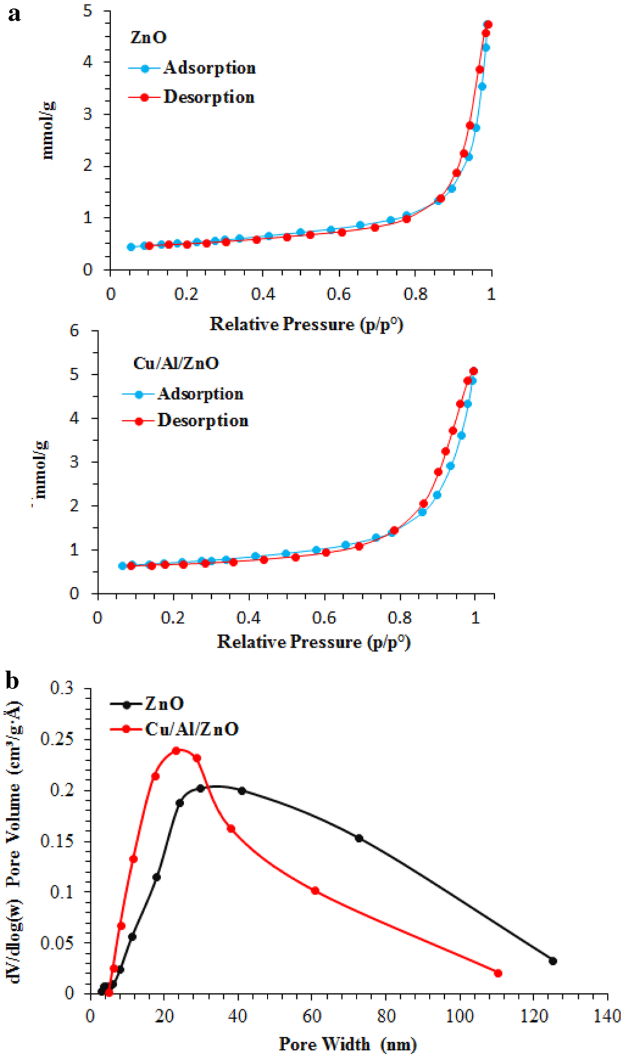


Fig. 2 The N_2 adsorption/desorption and pore width distribution of the ZnO support and catalyst

Table 1 Structural parameters of the support and the nanocatalyst

Catalyst	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Average pore width (nm)
ZnO	39.13	0.164	22.69
$CuO/ZnO/Al_2O_3$	51.11	0.179	17.68

catalyst are presented in Fig. 2b and Table 1, respectively. The Fig. 2b exhibits a wide pore size distribution for both the ZnO support and the $CuO/ZnO/Al_2O_3$ nanocatalyst with a maximum at about 30 and 24 nm, respectively. It is valuable to note that the pores size for both support and catalyst varied between mesoporous to macroporous structures. Thus, this distribution pattern may confirm the non-porous structure of metal oxides which aggregate together [33].The high surface area and total pore volume of the $CuO/ZnO/Al_2O_3$ nanocatalyst are because of the incorporating of the Al_2O_3 phases in target catalyst. It is valuable to note that the total surface area of some Al_2O_3 phases can be varied between 250 and 800 $m^2\ g^{-1}$.

As shown in Table 1, the average pore width of the catalyst is smaller than the support's one. The reason for this may be due to the co-formation of mesoporous Al_2O_3 structure with CuO and ZnO.

3.3 SEM Study

Figure 3 represents the SEM images of the $CuO/ZnO/Al_2O_3$ nanocatalyst with different magnifications. An aggregation of the Al_2O_3 and CuO nanoparticles was observed on the surface of ZnO support. The sizes of these nanoaggregates with different shapes are less than 20 nm. As a quantitative proof, the EDS (Fig. 3c) analysis has been performed, and presented the content of ZnO support greater than 75% by weight. It is valuable to note that the weight percent of Cu and Al in nanocatalyst was lower than that of zinc and therefore was not appeared in EDS spectrum.

3.4 Amination of Aryl Halides

Initially, for the optimization of reaction conditions, the reaction of iodobenzene with aqueous ammonia was chosen as a model and its behavior was studied under a variety of conditions. Influence of several factors such as temperature, CuO loading, catalyst amount and solvent were investigated. Various $CuO/ZnO/Al_2O_3$ amount containing 5, 10 and 15 wt% CuO, were studied. It was found that $5CuO/ZnO/Al_2O_3$ showed the good activity and efficiency (Table 2).

Increase in the CuO loading did not significantly effect on the yield and time of the reaction. Therefore, the reaction was studied in the presence of different amounts of the $5CuO/ZnO/Al_2O_3$ nanocatalyst. Furthermore, it was observed that using 0.1 g of $5CuO/ZnO/Al_2O_3$ nanocatalyst was sufficient for the reaction completion after 3 h. The influence of various solvents on the yield and time of the reaction was also examined and water was preferred as the most efficient solvent. The reaction was evaluated in the presence of different bases. Among the bases were selected, Cs_2CO_3 gave the best result (Table 2). The effect of various amounts of NH_4OH was also studied. It was found that using 2 mmol of NH_4OH in refluxing water was suitable for the reaction completion. Therefore, 2 mmol of NH_4OH, 1 mmol of Cs_2CO_3 and catalyst (0.1 g), in water at reflux conditions was considered to be the most conditions for this reaction. After this, the reaction of various aryl iodides including electron-donating and electron-withdrawing groups, with aqueous ammonia were explored (Table 3). From Table 3, all aryl halides were converted to

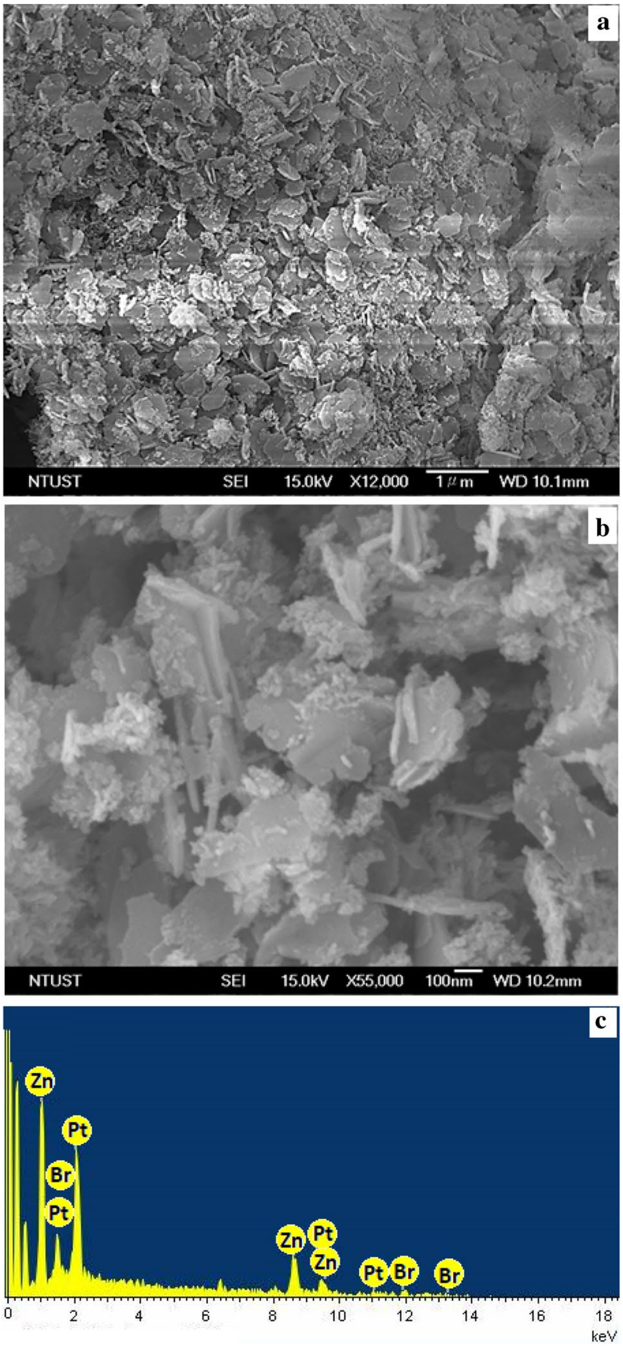


Fig. 3 SEM micrographs (**a, b**) and EDS analysis (**c**) results of $CuO/ZnO/Al_2O_3$ nanocatalyst

Table 2 Optimization of the reaction conditions[a]

Entry	CuO loading (wt%)	Catalyst amount (g)	Condition	Time (h)	Yield (%)[b]
1	5	0.05	EtOH/reflux	12	Trace
2	5	0.1	EtOH/reflux	12	30
3	5	0.05	MeCN/reflux	12	Trace
4	5	0.1	MeCN/reflux	12	50
5	5	0.05	DMF/reflux	12	30
6	5	0.1	DMF/reflux	12	45
7	5	0.05	H_2O/r.t.	24	–
8	10	0.1	H_2O/r.t.	24	–
9	5	0.05	H_2O/reflux	8	50
10	5	0.07	H_2O/reflux	5.5	75
11	5	0.1	H_2O/reflux	3	91
12	10	0.07	H_2O/reflux	5	70
13	10	0.1	H_2O/reflux	3	90
14	15	0.07	H_2O/reflux	3	92
15	15	0.1	H_2O/reflux	3	91

[a] Reaction conditions: iodobenzene (1 mmol), Cs_2CO_3 (1 mmol), NH_4OH (2 mmol), conditions

[b] Isolated pure products

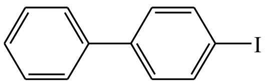
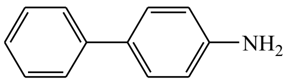
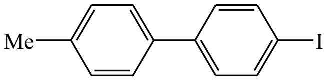
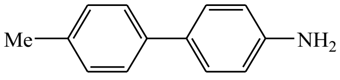
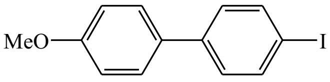
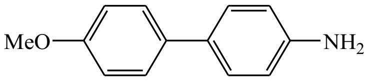
their corresponding amines in high yields. Electron-withdrawing groups such as nitro on aromatic ring increased the yield of reactions, while the electron-releasing groups such as methoxy decreased the yield and increased the time of reactions (Table 3). Moreover, reaction of various aryl bromides with aqueous ammonia were studied. It was found that aryl bromides converted to their corresponding products and suitable results were obtained. However, times of the reactions were increase, and products synthesized in excellent yields.

The activity of the recovered catalyst was also checked under the optimized conditions and reaction of iodobenzene with aqueous ammonia was chosen as a model reaction. After reaction completion, the catalyst was washed with hot acetone, dried and stored for another successive reaction run. This process was repeated for 5 runs and no considerable decrease in yield was observed. The results are revealed in Table 4.

The XRD pattern and SEM image with of the catalyst after five cycle was recorded. As seen from Fig. 4, the intensity of some peaks was reduced but the crystal structure of the catalyst was remained. Comparison of the SEM image of the used catalyst with fresh catalyst shown more agglomeration of the catalyst particles in used catalyst.

The possible mechanism for the amination of aryl halides in the presence of $CuO/ZnO/Al_2O_3$ nanocatalyst is as shown in Scheme 2. Initially, addition of $CuO/ZnO/Al_2O_3$ nanocatalyst to aryl iodide gives the $ZnO/Al_2O_3CuO(Ar)$ (I) that co-ordination of it with the amine followed by deprotonation and CsX elimination provides the desired product.

Table 3 $CuO/ZnO/Al_2O_3$ nanocatalyst catalyzed amination of aryl halides

Entry	Aryl halide	Product	Time (h)	Yield (%)[a]
1	C_6H_5I	$C_6H_5NH_2$	3	91
2	$4\text{-}NO_2C_6H_4I$	$4\text{-}NO_2C_6H_4NH_2$	1	93
3	$4\text{-}ClC_6H_4I$	$4\text{-}ClC_6H_4NH_2$	2.5	92
4	$4\text{-}CF_3C_6H_4I$	$4\text{-}CF_3C_6H_4NH_2$	1	92
5	$4\text{-}OMeC_6H_4I$	$4\text{-}OMeC_6H_4NH_2$	5	88
6	$3,4,5\text{-}(OMe)_3C_6H_2I$	$3,4,5\text{-}(OMe)C_6H_2NH_2$	7	87
7	C_6H_5Br	$C_6H_5NH_2$	4.5	90
8	$4\text{-}MeC_6H_4Br$	$4\text{-}MeC_6H_4NH_2$	6	88
9	$4\text{-}OMeC_6H_4Br$	$4\text{-}OMeC_6H_4NH_2$	7.5	88
10	$4\text{-}NO_2C_6H_4Br$	$4\text{-}NO_2C_6H_4NH_2$	2	92
11			4	89
12			4	88
13			5	88

[a] Isolated pure products. Reaction conditions: aryl halide (1 mmol), NH_4OH (2 mmol), Cs_2CO_3 (1 mmol), catalyst amount (0.1 g), in water at reflux conditions

Table 4 Recyclability study of $CuO/ZnO/Al_2O_3$ nanocatalyst upon the reaction of iodobenzene with aqueous ammonia[a]

Run	1	2	3	4	5
Time (h)	3	3	3	3.5	4.5
Yield (%)[b]	91	91	90	88	87

[a] Reaction conditions: iodobenzene (1 mmol), NH_4OH (2 mmol), Cs_2CO_3 (1 mmol), catalyst amount (0.1 g), in water at reflux conditions

[b] Isolated pure products

4 Conclusion

In summary, we have reported the catalytic activity of an efficient nano inorganic composite of $CuO/ZnO/Al_2O_3$ ($CuO/ZnO/Al_2O_3$ nanocatalyst) as a competent recyclable catalyst for the amination of aryl halides with aqueous ammonia in water. This catalyst easy to handle and can be recovered five runs simply by filtration. Moreover, ease of work-up, heterogeneous reaction conditions, high yields of products, short reaction times, and clean procedure will make this procedure useful.

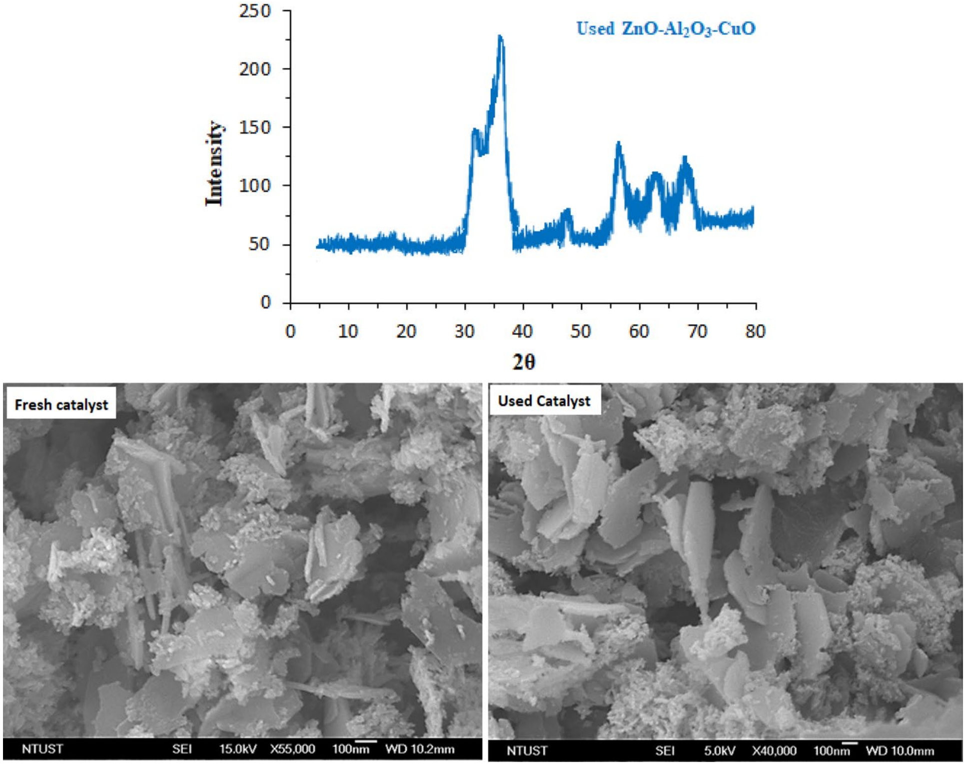
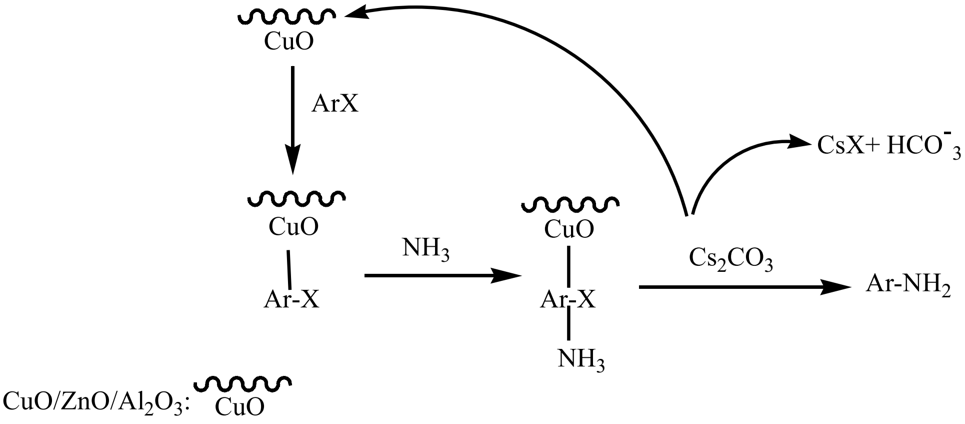


Fig. 4 The XRD pattern and SEM image of the catalyst after the recyclability study



Scheme 2 The probable mechanism for the amination of aryl halides

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