Heterogeneous Route for the One-Pot Synthesis of N-Arylamides from Aldoximes and Aryl Halides Using the CuO/Carbon Material

Md. Mominul Islam,[†] Mita Halder,[‡] Anupam Singha Roy,*,[§,||] and Sk. Manirul Islam*,[†]

[†]Department of Chemistry, University of Kalyani, Nadia, Kalyani 741235, West Bengal, India
[‡]Department of Chemistry, University of Calcutta, 92 A. P. C. Ray Road, Kolkata 700009, West Bengal, India
[§]Catalytic Conversion & Processes Division, CSIR−Indian Institute of Petroleum, Dehradun 248005, Uttarakhand, India

S *Supporting Information*

ABSTRACT: Metal oxide nanoparticles (NPs) stabilized by porous carbon materials (PCMs) are very promising for catalysis. In this work, monodispersed small and stable copper oxide (CuO) NPs were prepared with an average size of 10−20 nm without using any capping agent and then these NPs were encapsulated into porous carbon. The chemical and structural properties of the CuO/PCM material were characterized by powder X-ray diffraction, electron microscopy, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, and nitrogen sorption. The obtained CuO/PCM nanocatalytic system has been used for the synthesis of N-arylamides from the reaction of aldoximes and aryl halides. Generally, copper(II) salt was used for the preparation of amides from aldoximes using some ligands and bases, but harsh reaction condition, stoichiometric amount of metal, and lack of recyclability limit their applications in industry. An alternative method is the use of heterogeneous catalysts. More importantly, these heterogeneous catalysts could be easily recycled and reused, showing potential application in organic synthesis.
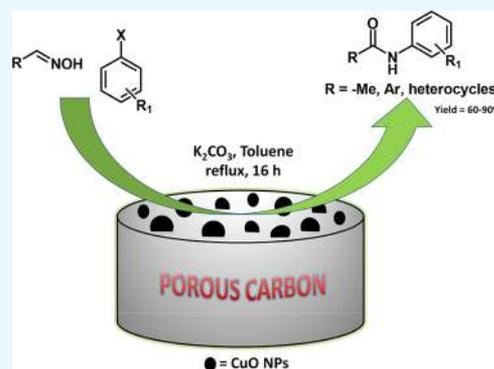
1. INTRODUCTION

Synthesis of N-arylamides has attracted wide attention because of their pharmaceutical, biological, and material importance.[1−9] Practically, N-arylamides are the basic precursor for the synthesis of highly biologically active compounds and drugs.[10−13] Therefore, the synthesis of amide skeleton has become one of the most challenging tasks to the organic chemists. The conventional methods, for the synthesis of amides, involve coupling of activated carboxylic acid derivatives, viz., acid chloride, anhydride, active esters, and so forth with a variety of amines. However, these methods generate futile wastes, and as an upshot, unconsciously serious environmental problems arise.[14] Several alternative graceful methods along with the use of carbonyl compounds (ketones and aldehydes) or carbonyl derivatives (oximes) have been developed for the synthesis of amides.[15] The acid-catalyzed rearrangement of ketoximes, known as Beckmann rearrangement,[16−21] constitutes a straightforward synthetic way to generate N-substituted amides (RCONHR′). Following the same reaction conditions, aldoximes (RCH=NOH) give the corresponding nitriles (RCN),[22] while transition-metal catalysts can be able to convert them into corresponding primary amides.[23−29] Usually, the conversion of aldoximes into primary amides is successfully catalyzed by a number of expensive transition metals such as Pd,[30] Au/Ag,[31] Ir,[32] Ru,[33] and Rh.[34,35] However, less expensive, environment-friendly nature of copper has captured the significant attention. In addition, homogeneous copper catalysts have been used successfully for a variety of organic

reactions.[36−45] Furthermore, the catalyst systems need to be developed further because of the possibility of metal contamination in the final product, lack of recyclability of the metal catalyst, use of additives, and expensive ligand system. Copper oxide (CuO) nanoparticles (NPs) can be applied in catalysis, gas sensing, and photocatalysis.[46−48] The catalytic properties of NPs are related with their size and surface area. Therefore, the development of methodologies for the preparation of small CuO NPs has importance for catalytic applications. Strongly interacting capping agents were required for the synthesis of small CuO NPs.[49−51] High-temperature calcination is required to eliminate these capping agents, so the synthesis of small surface clean CuO NPs still remains a challenge.

However, a large number of copper-catalyzed conversion of aldoximes to primary amides are available in the literature,[27,52−57] but one-pot synthesis of secondary amides from aldoximes is less explored. Rather, a number of procedures[58−60] are reported counting the transformation of ketoximes to N-arylamides. Now, in the case of oximes of unsymmetrical ketones, mixtures of regioisomeric products were formed, which further limited the scope of these reactions. As a result, the development of resourceful, economic, and environment-friendly catalytic system constitutes a motivating area for the

one-pot synthesis of secondary amides from aldoximes. Very recently, Panda and co-workers[61] reported homogeneous copper sulfate-catalyzed synthesis of N-arylamides from aldoximes. To the best of our knowledge, here we report for the first time that the heterogeneous CuO/PCM nanocomposite catalyzed the one-pot synthesis of N-arylamides from aldoximes and aryl halides (Scheme 1). In the present

Scheme 1. Context of the Copper-Catalyzed Amidation of Aryl Halides
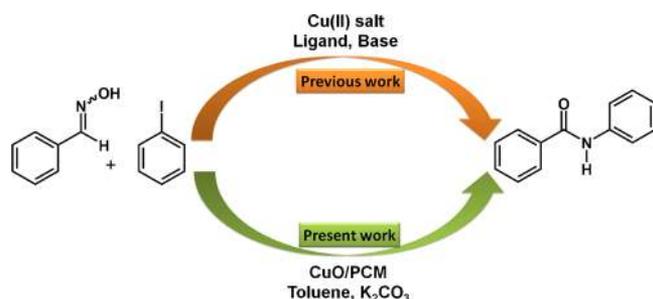
work, we have prepared monodispersed small CuO NPs. To show their relevance in catalysis, we have used these CuO NPs for the synthesis of N-arylamides from aldoximes. After identifying the significant role of CuO in the above reaction, supported CuO NPs on porous carbon were prepared as the heterogeneous catalyst. The CuO/PCM catalyst shows the catalytic activity similar to that of well-defined CuO NPs.

2. RESULTS AND DISCUSSION

The CuO/PCM nanocatalytic system was readily prepared by mixing a porous carbon material (PCM) with the recently prepared suspension of CuO NPs (Scheme 2). The latter CuO NPs were obtained within 1 h from copper acetate, sodium hydroxide, ethanol, and a catalytic amount of acetic acid under refluxing conditions. Our heterogeneous catalyst was prepared by mixing the suspension of CuO dropwise to the solution of glucose, and then the mixture was heated at 120−150 °C for 1 h. Finally, the black product was obtained and heated in an alumina boat inside a tube furnace at 850 °C under N_2 atmosphere. After slow cooling to room temperature, the resulting dried product was obtained (yield = 50−60%). Copper loading was determined by atomic absorption spectroscopy (AAS), and it was about 8.0 wt %.

2.1. Characterization of CuO/PCM. Recently, considerable interests have been focused on metal oxide NPs supported on the PCM as heterogeneous catalysts by virtue of their versatility in chemical compositions and structural

architectures. Figure 1 shows the typical X-ray diffraction (XRD) patterns of the CuO/PCM nanocatalyst. The diffraction
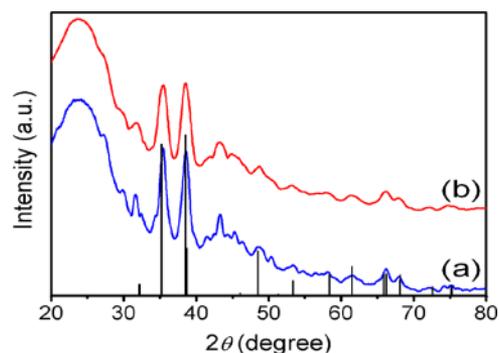

Figure 1. Powder XRD patterns of (a) fresh CuO/PCM catalyst and (b) spent CuO/PCM catalyst (after 10 cycles).

peaks located at about 2θ = 23.6 and 43.2° may be attributed to the presence of amorphous (002) and graphitic (100) carbons.[62] On the other hand, the characteristic peaks at 2θ = 32.44, 35.46, 38.59, 48.69, 53.36, 61.47, 66.18, and 68° observed in both Figure 1a,b are ascribed due to the (110), (002), (111), (202), (020), (113), (311), and (113) facets of the monoclinic crystalline CuO in the CuO/PCM sample.

The distribution of CuO NPs on the carbon support as well as particles sizes was investigated by transmission electron microscopy (TEM) analysis. Figure 2a,b shows the representative images, and the particle size distribution histogram for CuO/PCM was given in the inset. The images reveal homogeneous distribution of the NPs on the carbon support. The histogram shows that CuO NP sizes are in the 10−20 nm range. The average particle size was estimated from the particle distribution histogram, and the obtained value is 14 nm. The selected area electron diffraction (SAED) pattern (Figure 2c) of the CuO/PCM catalyst indicates the crystalline structure of the CuO NPs.

The morphology of the catalyst was studied by scanning electron microscopy (SEM, Figure 3) instrument. Figure 3a shows the typical SEM image of the CuO suspension which showed uniform spherical CuO NPs in the range of ∼20 nm. The SEM image of the CuO/PCM nanocomposite has been shown in Figure 3b, in which CuO NPs are well-dispersed in the range of 10−20 nm. The energy-dispersive analysis of X-ray (EDAX) pattern also showed the presence of C and Cu in the sample (Figure 3c). Elemental mapping, obtained from SEM, indicates the presence of C and Cu and the uniform dispersion of CuO NPs on the surface of the carbon support (Figure 3d,e).

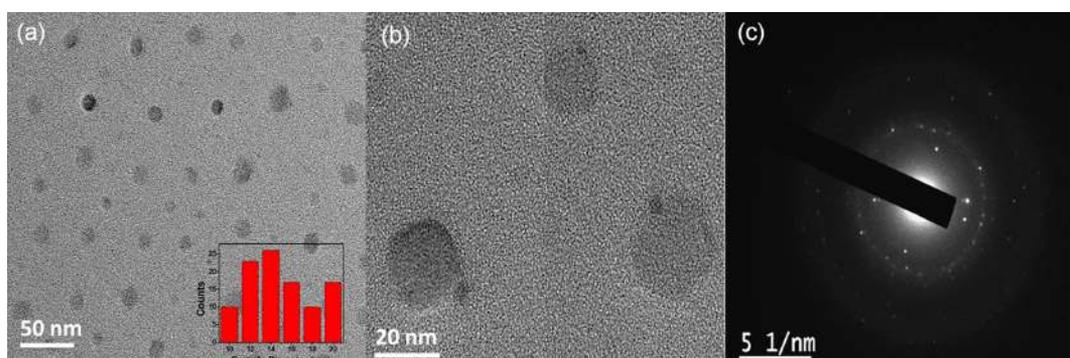**Scheme 2. Synthesis of the CuO/PCM Nanocatalyst**
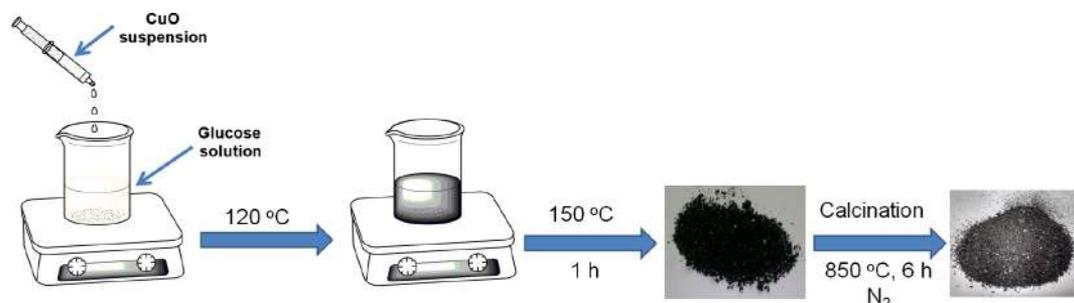
Figure 2. TEM images of the CuO/PCM nanocatalyst (a,b), particle size distribution of CuO/PCM (given in the inset) and SAED pattern of the CuO/PCM nanocatalyst (c).
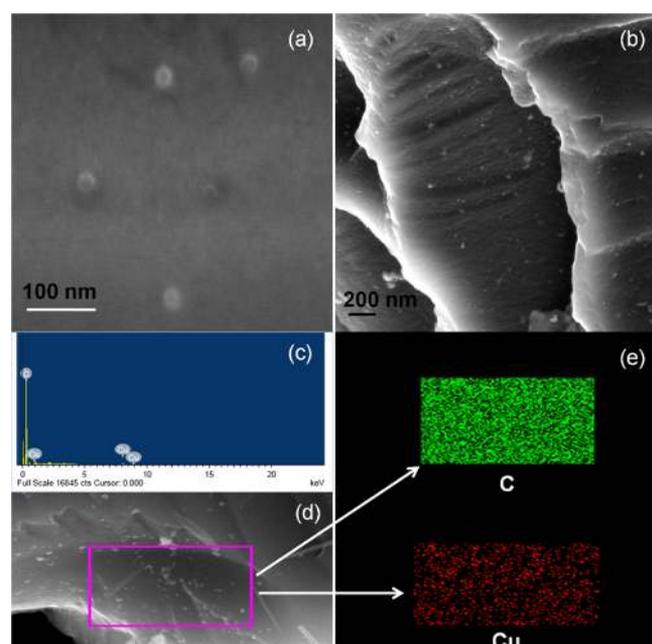

Figure 3. SEM images of suspended CuO NPs (a) and the CuO/PCM nanocomposite (b), EDAX image of the CuO/PCM nanocomposite (c), and elemental mapping of the CuO/PCM nanocomposite (d,e).

Figure 4. Raman spectra of (a) fresh CuO/PCM catalyst and (b) spent CuO/PCM catalyst (after 10 cycles).
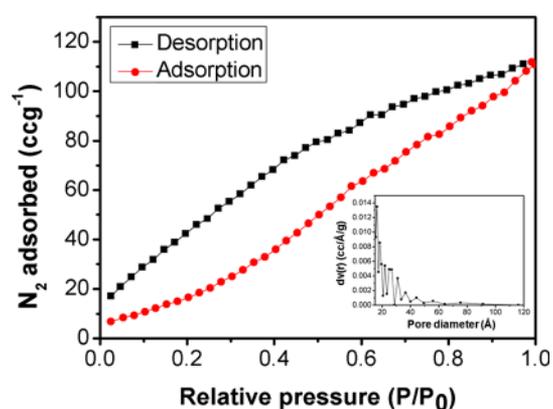
Figure 5. Nitrogen adsorption–desorption isotherms of the catalyst.

Raman spectroscopy is a powerful tool to characterize the carbon material. Figure 4 represents the Raman spectra of fresh and recycled CuO/PCM nanocomposite. The carbon support exhibited two prominent peaks at 1586 cm^{-1} (G band) arising from the sp^2 carbon atoms, whereas the peak at 1345 cm^{-1} indicates the D band. This D band is normally associated with structural defects and amorphous phases. Therefore, the intensity ratio of the D versus G band (i.e., I_D/I_G obtained from Figure 4a) is usually used as a measure for the disorder of the carbon structure and was found to be ~0.87. The CuO/PCM material has I_D/I_G value less than 1 which means this carbon material has less defective structure.

The nitrogen adsorption–desorption isotherms of the CuO/PCM catalyst are shown in Figure 5. The isotherm is a typical type IV isotherm. The Brunauer–Emmett–Teller (BET) surface area of the catalyst was determined to be 84.9 m^2 g^{-1}. The Barrett–Joyner–Halenda (BJH) pore size distribution plot is given in the inset of Figure 5. This material has various pores, and according to the BJH plot calculated from the N$_2$ desorption isotherm, the sample has mesoscale pores ranging from 2 to 5.5 nm.
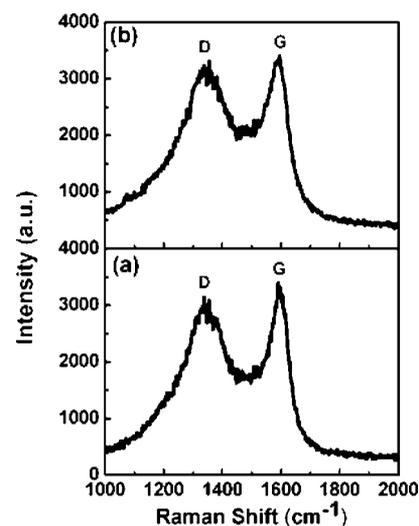
2.2. Catalytic Activity.
We have investigated the catalytic behaviors of CuO, CuO/AC (activated carbon), and CuO/PCM for the synthesis of N-arylamides from aldoximes and aryl halides under a reported reaction condition.[61] To realize our scheme, benzaldoxime (**1a**) and iodobenzene (**2a**) were chosen as model substrates to assess the propensity of arylation of aryl halides. All these catalysts exhibited comparable activity (Table 1). There is a possibility of homogeneous copper salt contamination in the final product, lack of isolation, and

Table 1. Catalytic Behavior of Some Catalysts for the Synthesis of N-Arylamides from Aldoximes and Aryl Halides[61,a]

entry	catalyst	yield (%)
1	CuCl$_2$	52
2	CuO	60
3	CuO/AC	61
4	CuO/PCM	76

[a]Reaction conditions: iodobenzene (100 mg), benzaldoxime (4 equiv), copper catalyst (10 mol %), and K$_2$CO$_3$ (5 equiv) in o-xylene (1 mL) were heated at 130 °C for 12 h.

reusability of the metal salt, which restricts its application in the above reaction. However, we found that the CuO and CuO/AC catalysts partially deactivated after repeated use (Figure 6a). During five recycling tests, the yield of the desired product decreased. The decrease, in the case of CuO, may be due to the agglomeration of the CuO NPs. A significant decrease was observed when we used CuO/AC, and CuO was obtained in the reaction mixture. This suggests the dissolution of CuO/AC in the reaction solution probably because of the low interaction between AC and CuO NPs. We also examined the stability of the CuO/PCM catalyst. Compared to CuO and CuO/AC, CuO/PCM was much more stable during recycling (Figure 6b). No significant decrease in the yield of the amides was observed over repeated use. After five recycles, the yield of amides was sustained at 72%. Therefore, CuO/PCM is a robust catalyst for the synthesis of amides from aldoximes.

Initially, we performed a series of experiments, with a variation of different reaction parameters such as solvent, base, temperature, catalyst loading, and so forth. The results are summarized in Table 2. Among dimethylformamide (DMF), N-methylpyrrolidone (NMP), toluene, CH$_3$CN, p-xylene, and water, used for this experiment, toluene was found to be the best solvent (Table 2, entry 2). Now, we optimize the bases used for this reaction. Among the various bases, K$_2$CO$_3$ gave a higher product yield (Table 2, entry 2). Although NaHCO$_3$ shows almost parallel activity to K$_2$CO$_3$ (Table 2, entry 8), we have chosen K$_2$CO$_3$ as an optimized base for this reaction. As the reaction did not proceed at room temperature (Table 2, entry 9), all the reactions were performed under refluxing conditions. Also, we have studied the activity of the support PCM in this coupling reaction, and no product was found (Table 2, entry 14). The experimental results revealed that the

Table 2. Optimization of Reaction Conditions[a]

entry	solvent	base	yield (%)[b]
1	p-xylene	K$_2$CO$_3$	65
2	toluene	K$_2$CO$_3$	88
3[c]	DMF	K$_2$CO$_3$	52
4[d]	CH$_3$CN	K$_2$CO$_3$	9
5	toluene	Cs$_2$CO$_3$	60
6	toluene	K$_3$PO$_4$	55
7	toluene	KF	10
8	toluene	NaHCO$_3$	82
9[e]	toluene	K$_2$CO$_3$	0
10	NMP	K$_2$CO$_3$	56
11	water	K$_2$CO$_3$	5
12	toluene		0
13[f]	toluene	K$_2$CO$_3$	86
14[g]	toluene	K$_2$CO$_3$	0

[a]Reaction conditions: **1a** (3 mmol), **2a** (1 mmol), catalyst (0.25 mol %), base (4 mmol), 16 h, under air and reflux conditions. [b]Isolated yield. [c]Reaction conducted at 140 °C. [d]Reaction conducted at 70 °C. [e]Reaction conducted at room temperature. [f]Catalyst used 0.5 mol %. [g]PCM as the catalyst.

best optimized reaction condition in terms of yield was obtained using benzaldoxime (3 mmol), iodobenzene (1 mmol), and K$_2$CO$_3$ (4 mmol) in the presence of the CuO/PCM catalyst (6 mg, 0.25 mol %) in toluene under refluxed conditions for 16 h (Table 2, entry 2).

To probe the generality of the reaction conditions, different kinds of aldoximes were coupled with aryl/heteroaryl halides to furnish a library of N-aryl-/-heteroaryl amides. The results are summarized in Table 3. Both electron-donating and electron-withdrawing groups attached to the phenyl ring of aryl iodide were well-tolerated in this procedure giving uniform product yields. p-Nitroiodobenzene reacts with benzaldoxime to furnish 72% product yield (**3d**, Table 3). The reaction of 2-iodopyridine with benzaldoxime is a good example, as it provided N-(pyridine-2-yl)benzamide (**3e**, Table 3) as the main product. This protocol is also successful for the utilization of bromobenzene as the aryl halide partner giving good yield
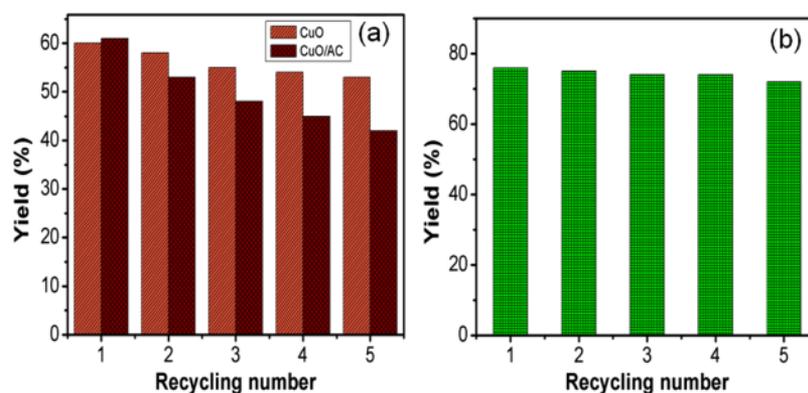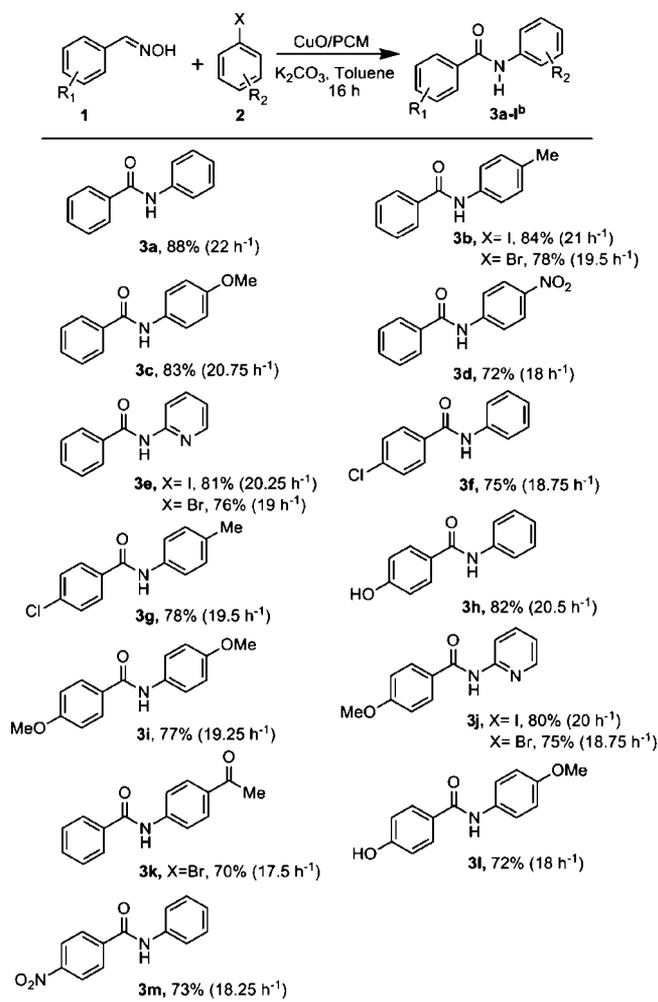

Figure 6. Recycling of (a) CuO and CuO/AC and (b) CuO/PCM catalysts for the synthesis of N-arylamides from benzaldoxime and iodobenzene. Reaction conditions: iodobenzene (100 mg), benzaldoxime (4 equiv), copper catalyst (10 mol %), and K$_2$CO$_3$ (5 equiv) in o-xylene (1 mL) were heated at 130 °C for 12 h.

Table 3. Reaction of Aryl Halides with Aromatic Aldoximes[a]

3a, 88% (22 h⁻¹)

3b, X= I, 84% (21 h⁻¹)
X= Br, 78% (19.5 h⁻¹)

3c, 83% (20.75 h⁻¹)

3d, 72% (18 h⁻¹)

3e, X= I, 81% (20.25 h⁻¹)
X= Br, 76% (19 h⁻¹)

3f, 75% (18.75 h⁻¹)

3g, 78% (19.5 h⁻¹)

3h, 82% (20.5 h⁻¹)

3i, 77% (19.25 h⁻¹)

3j, X= I, 80% (20 h⁻¹)
X= Br, 75% (18.75 h⁻¹)

3k, X=Br, 70% (17.5 h⁻¹)

3l, 72% (18 h⁻¹)

3m, 73% (18.25 h⁻¹)

[a]Reaction conditions: oxime (3.0 mmol), aryl halide (1.0 mmol), K_2CO_3 (4.0 mmol), CuO/PCM catalyst (0.25 mol %), toluene (3 mL), reflux condition, 16 h, under air. [b]Isolated yield. Turnover frequency (TOF) given in parentheses. $\text{TOF} = \frac{\text{mol of product}}{\text{mol of total metal} \times \text{time}}$.

under optimized reaction conditions (**3b**, **3e**, **3j**, **3k**, Table 3). The coupling of 4-chlorobenzaldoxime is highly chemoselective, as the nucleophilic attack occurs only at the N atom, leaving the −Cl group of the aromatic ring unaffected (**3f**, **3g**, Table 3). The nitro-substituted aldoxime also reacts under similar reaction conditions. These results clearly indicate that both electron-donating (−MeO, −Me, −OH) and electron-withdrawing (−Cl, −NO₂) groups attached to the aldoxime part are well-tolerated under the same reaction conditions. 4-Hydroxybenzaldoxime undergoes this reaction to give the corresponding anilide product in excellent yield (**3h**, Table 3). The coupling reaction of 4-bromoacetophenone and benzaldoxime exclusively provided N-(4-acetylphenyl)-benzamide as the final product (**3k**, Table 3).

In the case of aliphatic aldoximes, this protocol reveals equal effectiveness giving the linear N-arylated amides. Acetaldoximes underwent coupling with aryl halides smoothly to produce the corresponding product in superior yield (Table 4).

Next, the scope of our methodology was inspected through the cross-coupling of several heterocyclic aldoximes with aryl halides. The results are summarized in Table 5. Aldoximes containing thiophene and furan moiety react with 2-

Table 4. Reaction of Aryl Halides with Aliphatic Aldoximes[a]

5a, 80% (20 h⁻¹)

5b, 78% (19.5 h⁻¹)

5c, 77% (19.25 h-1)

5d, X= I, 72% (18 h⁻¹)
X= Br, 62% (15.5 h⁻¹)
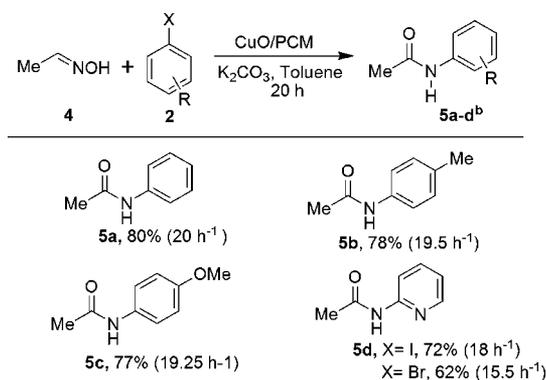
[a]Reaction conditions: oxime (3.5 mmol), aryl halide (1.0 mmol), K_2CO_3 (4.0 mmol), CuO/PCM catalyst (0.2 mol %), toluene (3 mL), reflux condition, 20 h, under air. [b]Isolated yield. TOF given in parentheses.

bromopyridine to form N-heteroarylated amides in good yields (**7b** and **7e**, Table 5).

Table 5. Reaction of Aryl Halides with Heterocyclic Aldoximes[a]

7a, 80% (22.22 h⁻¹)

7b, 78% (21.67 h⁻¹)

7c, 79% (21.95 h⁻¹)

7d, 77% (21.39 h⁻¹)

7e, 74% (20.56 h⁻¹)
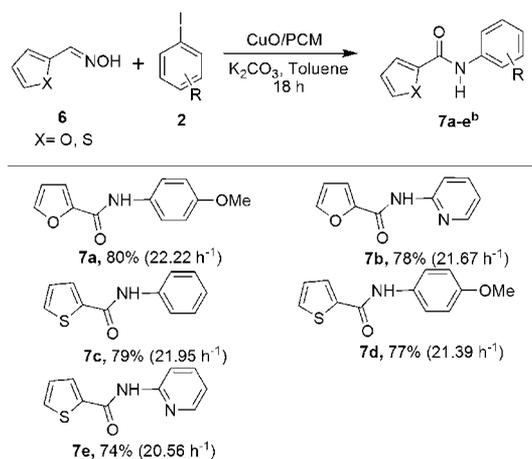
[a]Reaction conditions: oxime (4.0 mmol), aryl halide (1.0 mmol), K_2CO_3 (4.0 mmol), CuO/PCM catalyst (0.2 mol %), toluene (3 mL), reflux condition, 18 h, under air. [b]Isolated yield. TOF given in parentheses.

To realize the mechanism of this CuO/PCM-catalyzed synthesis of N-arylamides from aldoximes, a detailed investigation was carried out. To check whether the reaction proceeds through the radical mechanism, the coupling reaction of benzaldoxime and iodobenzene was performed in the presence of 1 equiv TEMPO, and it was found that the yield of the reaction remained the same. Therefore, the radical mechanism for the reaction is unlikely. Probable reaction mechanism for the one-pot synthesis of amides catalyzed by CuO/PCM under heterogeneous conditions may follow the established mechanism (Scheme 3).[7,11,16,18,63]

To establish the proposed mechanism, we have studied some more reactions using the CuO/PCM catalyst in the coupling of benzaldoxime and iodobenzene (Scheme 4). First, we have performed the coupling reaction under optimized conditions but using dry solvent and molecular sieve (Scheme 4, reaction a). After the reaction, we found the superior yield of the desired

Scheme 3. Plausible Reaction Mechanism
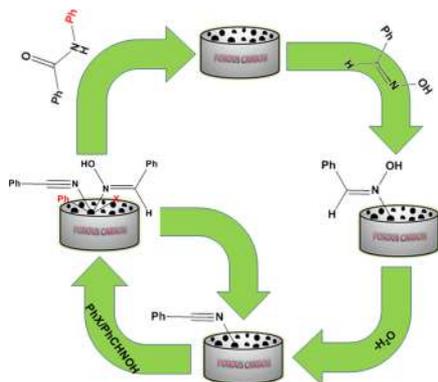
secondary amide. Generally, dehydration and rehydration steps are the proposed mechanism for the conversion of oxime to amide. Here, we have performed the reaction under anhydrous condition, so water may not be acting as a nucleophile for the rehydration step, but still secondary amides were obtained. This indicates that another molecule of oxime acts as a nucleophile and initiates the rehydration step.[64,65] In this pathway, one molecule of nitrile will be produced, which may interact with the metal oxide and form a metal-bound nitrile intermediate to continue the catalytic reaction. When the reaction was carried out between benzamide (1 mmol) (instead of benzaldoxime) and iodobenzene (1 mmol) under air using K_2CO_3 as the base and toluene as the solvent (Scheme 4, reaction b), the secondary amide (N-phenylbenzamide, 95%) was obtained which means primary amide is an intermediate during this coupling reaction. This can be established by another reaction, when we have studied the reaction of benzaldoxime (3 mmol) without using aryl halide under similar reaction conditions (Scheme 4, reaction c). In this case, we have found only benzamide (85%) instead of the secondary amide. Therefore, in conclusion, we can propose that in our case the oxime molecule acts as a nucleophile for the rehydration step and the conversion of aldoxime to secondary amide occurs through the primary amide intermediate.

2.3. Heterogeneity Test. An essential aim of the heterogeneous catalyst is its life span for industrial applications. Heterogeneous nature and the metal leaching of this catalyst

were examined using "hot filtration test"[66] for the synthesis of N-arylamides from benzaldoxime and iodobenzene.

2.3.1. Hot Filtration Test. After 6 h of the reaction, the CuO/PCM material was separated by filtration and 35% yield was observed by gas chromatography (GC) analysis. The filtrate was again refluxed for another 10 h. After 16 h, from the GC analysis we can conclude that there was no considerable conversion taking place in the filtrate after separation of the catalyst (Figure 7). This result confirms that the reaction
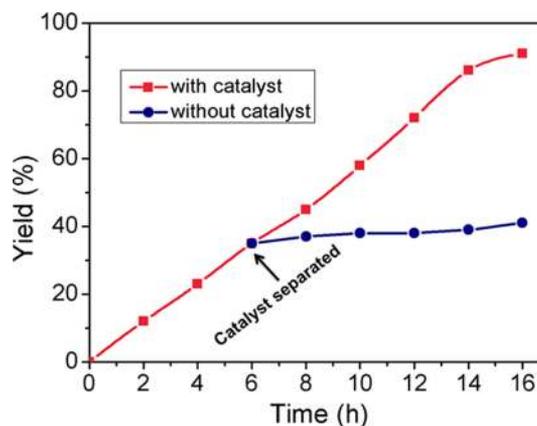

Figure 7. Heterogeneity test of the CuO/PCM catalyst in the synthesis of N-arylamides from benzaldoxime and iodobenzene.

relatively did not progress upon the separation of the catalyst. Further, CuO could not be detected by the AAS measurement of the filtrate or in case if it was detected, it was found below the detection limit (0.003 mg/L). However, the negative result of the hot filtration test should not be considered the actual heterogeneity of the active catalysis species. This is because the insoluble solid support carbon can act as a reservoir as well as a scavenger for the leached CuO. In many conditions, the leached metal can be redeposited on the insoluble solid support during the hot filtration test. Therefore, in this situation, the catalytic pathway would be explained by a "release−capture" mechanism.[67,68]

2.4. Reusability Test. The recyclability of the catalyst is important for the catalysis reaction. The reusability test also

Scheme 4. CuO/PCM-Catalyzed Amide Synthesis Using Different Reaction Parameters under Reflux Conditions
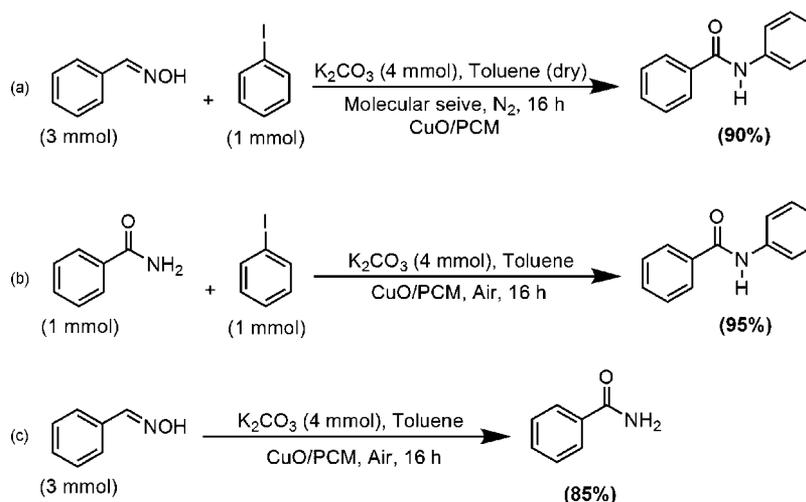
confirms the heterogeneous nature of the catalyst. To examine the reusability of the CuO/PCM material, the catalyst was separated by filtration and washed. The subsequently catalytic runs were repeated with the addition of reactants under optimum reaction conditions, and the nature of the final product as well as yield was recorded. Figure 8 illustrates the
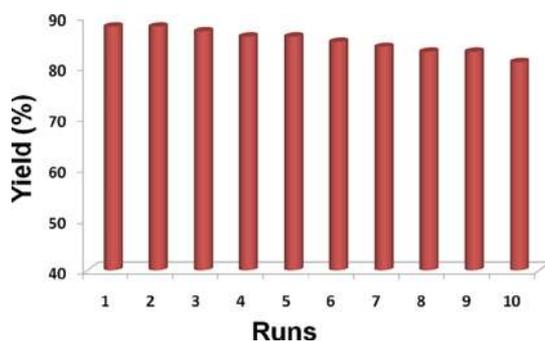

Figure 8. Recycling results of the CuO/PCM nanocatalytic system in N-arylamide synthesis.

recycling ability of the catalyst for the N-arylamide synthesis from benzaldoxime and iodobenzene during 10 cycles. However, the activity of the catalyst decreased slightly from the third run. The TEM image (Supporting Information, Figure S1) of the recycled catalyst after the fifth run showed a small increase in the size of CuO NPs due to agglomeration. This slight loss in the catalytic activity may be due to the increase in size of the CuO NPs. XRD, Raman spectra, and SEM (Supporting Information, Figure S1) of the recycled catalyst were quite similar to that of the fresh catalyst. This indicates the stability and heterogeneous nature of the CuO/PCM catalyst.

3. CONCLUSIONS

In conclusion, we have described a mild and efficient procedure for the synthesis and characterization of the CuO/PCM catalyst. Most importantly, this CuO NP catalyst proved its enormous activity for the synthesis of N-arylamides from several aromatic, aliphatic, and heterocyclic aldoximes. Diversely substituted aldoximes were coupled smoothly to produce moderate-to-good yields. To the best of our knowledge, we are not aware of any report demonstrating the synthesis of N-arylamides from aldoximes using our as-synthesized CuO NP catalyst. In a broader context, this protocol will provide a platform for the design of sustainable C−N cross-coupling reactions for organic synthesis. Efforts to develop the efficacy of our new catalyst systems to other cross-coupling reactions are in progress and will be reported in due course.

4. EXPERIMENTAL SECTION

4.1. Materials. Copper acetate monohydrate (Merck, 99%), acetic acid (Merck, >99%), sodium hydroxide (NaOH) pellets (Alfa Aesar, 98%), and D(+)-glucose (Merck, >99%) were used without further purification. Different aldehydes, aryl halides, and solvents were purchased from Sigma-Aldrich or Merck and used without further purification. Aldoximes were prepared using the literature method reported elsewhere.

4.2. Synthesis of Colloidal CuO NPs. Colloidal CuO NPs were prepared following a reported method.[69] In this method, 0.3 g of copper acetate and 0.2 mL of acetic acid were dissolved in 50 mL of ethanol. The solution was refluxed, followed by the

addition of 0.3 g NaOH. The reaction mixture was continuously refluxed for 1 h. The colloidal solution of CuO was centrifuged at 5500 rpm for 1 h, followed by filtration to yield CuO NP suspension.

4.3. Synthesis of the CuO/PCM Nanocatalyst. The synthesis procedure of the CuO/PCM catalyst is given in Scheme 2. The colloidal CuO NP solution was added dropwise into the glucose solution (2 g in 100 mL H_2O) under vigorous stirring at 120 °C for 1 h. Then the reaction mixture was stirred for another 1 h at temperature 150 °C, followed by cooling to room temperature. The deep black colored product was obtained and ground in mortar. One gram of this black product was then heat-treated inside a tube furnace at 850 °C for 6 h at a rate of 6 °C/min under N_2 atmosphere, followed by slow cooling to room temperature. The yield of the CuO/PCM catalyst was 50−60%.

4.4. Characterizations. Powder XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα source using a radiation wavelength of 1.5418 Å. Diffraction patterns in the 10°−80° region were recorded at a rate of 0.4° (2θ) per min. The field emission SEM (FESEM) images were recorded by Carl Zeiss SUPRA 55VP FESEM. TEM images were recorded on a UHR-FEG TEM system (JEOL, model JEM 2100 F) using a 200 kV electron source. An Acton SpectraPro SP-2500 Raman spectrometer was employed to analyze the nanostructures. N_2 adsorption−desorption isotherms were obtained on a Micromeritics Gemini VII surface area analyzer and reported by the BJH analysis. Each sample was degassed at 300 °C for 3 h. The specific surface area was determined according to the BET method. The products were purified by column chromatography using silica gel (60−120 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 NMR spectrophotometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) using CDCl$_3$ as the solvent. The ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane.

4.5. Synthetic Procedure of N-Arylamides from Aldoximes and Aryl Halides. To a mixture of aldoxime (3 mmol) and aryl halide (1 mmol) in toluene (3.0 mL), the CuO/PCM catalyst (0.25 mol %) and K_2CO_3 (4 mmol) were added, and the mixture was refluxed for 16 h under air. Then, the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was separated, washed with brine and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Finally, the crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (85:15) as the eluent to furnish pure N-arylamides.

4.6. General Procedure for the "Hot Filtration" Test. To a mixture of benzaldoxime (3 mmol) and aryl iodide (1 mmol) in toluene (3.0 mL), the CuO/PCM catalyst (0.25 mol %) and K_2CO_3 (4 mmol) were added, and the mixture was refluxed under air. After 6 h of the reaction time, the catalyst was separated from the reaction mixture under hot condition. The yield of the product was determined by GC. Then, the filtrate was again refluxed for another 10 h, and finally, after 16 h the yield of the desired product was determined by using GC.

In a mixture of benzaldoxime (3 mmol) and aryl iodide (1 mmol) in toluene (3.0 mL), the CuO/PCM catalyst (0.25 mol %), and K_2CO_3 (4 mmol) were added, and the mixture was refluxed under air. To measure the amount of the leached CuO, the catalyst was separated from the reaction mixture under hot condition after 6 h of the reaction time. Then the filtrate was

concentrated under reduced pressure. The HNO_3 solution [5 mL 5% (in aq)] was added to the crude material and stirred. After that, this solution was taken in a 10 mL volumetric flask, and the volume was made up to the mark. Finally, this solution was studied using the AAS measurement to calculate the amount of leached CuO.

4.7. General Procedure for the Recycling Test. After 16 h of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The catalyst was separated, and the organic layer was used for the determination of the yield of the product. The catalyst was washed three times with toluene, ethyl acetate, and water and dried. Finally, the catalyst was reused for the next run under optimized reaction conditions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01028.

> Mechanical experiment, ^1H and ^{13}C NMR spectral data of the compounds, TEM and SEM images and elemental mapping of the recycled CuO/PCM material, and ^1H and ^{13}C NMR spectra of all products (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: a.singha-roy@aston.ac.uk (A.S.R.).
*E-mail: manir65@rediffmail.com (S.M.I.).

ORCID Ⓞ

Anupam Singha Roy: 0000-0003-4052-272X

Present Address

‖Aston University, European Bioenergy Research Institute, Aston Triangle B4 7ET, Birmingham, United Kingdom.

Notes

The authors declare no competing financial interest.

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