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Cu(II)–metformin immobilized on graphene oxide: an efficient and recyclable catalyst for the Beckmann rearrangement

Ahmed Solaiman Hamed[1] · **Ehab Mohammad Ali**[1]

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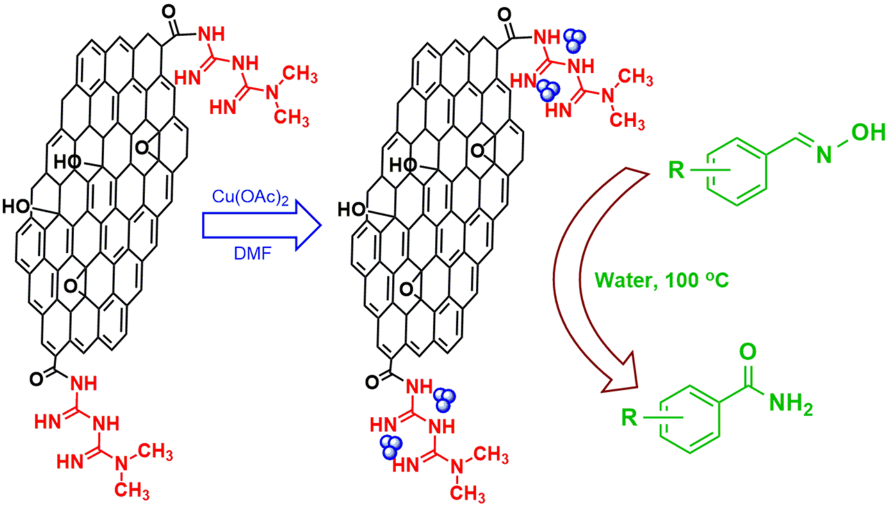
Abstract

In this study, for the first time, the copper(II) nanoparticles (NPs) have been immobilized on metformin-functionalized graphene oxide and then its catalytic applications have been investigated in synthesis of amides from aldoximes (Beckmann rearrangement). The chemical structure of prepared catalyst has been characterized by various analyses like FT-IR, TGA, TEM, SEM, EDX, and ICP. All analyses confirm the successful and stable immobilization of copper NPs on functionalized graphene oxide. This synthesized heterogeneous nanocatalyst showed excellent catalytic activity with high product yields and short reaction times. Also, the suggested catalyst could be recycled ten times without a drastic decrease in its catalytic activity.

Graphic abstract



Keywords Copper · Graphene oxide · Amides · Oximes · Beckmann rearrangement

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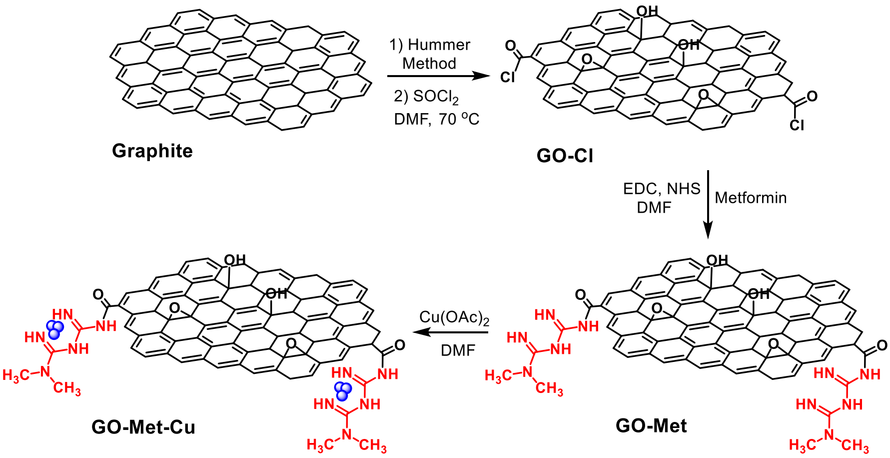
Introduction

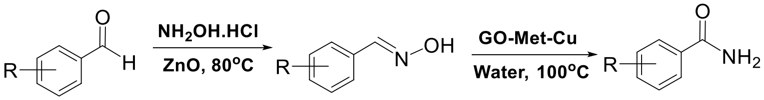
Graphene is an important allotrope of carbon including a single layer of carbon atoms which is interconnected in a hexagonal structure [1–4]. Graphene is one of the strongest materials in conducting electricity and heat and has a transparent structure with one atom thick layer [5–8]. The oxide form of graphene is named graphene oxide (GO), which is prepared by the oxidation of graphite and has many applications [9–11]. Hydroxyl, epoxide, and carboxyl groups are three special functional groups on basal planes and edges of GO. Due to the existence of these functional groups, the immobilization of organic ligands, and consequently, metalation is available [12–15].

The conversion of oximes to corresponding amides has been carried out by various methods, but the most important one is Beckmann rearrangement [16]. This reaction provides an efficient method for the preparation of ε-caprolactam, which is a key intermediate in the manufacture of fibers and resins [17]. The reaction was performed by different methods and conditions [18–23]. Recently, the use of metals is a favorable strategy to achieve primary amide transformations [24]. Asencio et al. [25] studied the application of copper acetate in the synthesis of amides from aldoximes. Their protocol fulfilled the points of green chemistry, including did not apply organic solvents and poison reagents. In 2011, Saidulu et al. [26] supported copper on silica (SBA-15) and investigated its catalytic activity for the rearrangement of benzaldoxime into benzamide. This method was carried out in solvent- and acid-free conditions. Mahajan et al. [27] directly converted ketones to amides via Beckmann rearrangement catalyzed by $FeCl_3{\cdot}6H_2O$ in the presence of $NH_2OH{\cdot}HCl$. Their catalyst was inexpensive, eco-friendly, easy to handle, and stable. Kumari et al. [28] used the complex of chitosan–zink for the synthesis of primary amides. They believed that the catalyst can be separated from the reaction mixture easily and reused several times without considerable loss of its catalytic activity. Despite the applying of these reported methods for the conversion of oximes to amides, the mentioned studies have some disadvantages such as long reaction time, use of microwave power and high temperature, lack of generality, and use non-environmentally friendly conditions. Thus, to succeed in dealing with these disadvantages, the introduction of new methods and metal complex is essential.

Since homogenous systems cannot be recycled and cause contamination of the product [29, 30], this problem can be overcome by the design of heterogeneous systems [31–35]. Thus, in the present study, for the first time, metformin has been covalently immobilized on the surface of GO, and then, copper acetate was coordinated into the amine groups of metformin and the Cu(II) coordinated on metformin linked to graphene oxide (GO–Met–Cu) was prepared (Scheme 1). After full characterization by different analyses, the synthesized nanocatalyst was applied for the conversion of different aldoximes to primary amides in water at 100 °C (Scheme 2).



Scheme 1 Preparation of catalyst (GO–Met–Cu)



1a-l **2a-l** **3a-l**

Scheme 2 Synthesis of primary amides from aromatic aldehydes in presence of GO–Met–Cu

Results and discussion

Synthesis and characterization of the GO–Met–Cu

The nano Cu complex catalyst was prepared according to Scheme 1. In the first step, the metformin ligand was anchored covalently on the surface of synthesized acylated GO by the nucleophilic reaction of amino groups of metformin and carboxyl groups of GO. Then, copper was complexed into the amino ligands of metformin and the catalyst (GO–Met–Cu) was totally prepared. The chemical structure of catalyst was analyzed using different techniques such as FT-IR, SEM, EDX, TEM, ICP, and TGA.

TEM and SEM analyses

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were applied for deep understanding of the morphology, size, and structure of prepared nanocatalyst (Fig. 1). SEM photograph of GO–Met–Cu shows that the GO nanosheets have a uniform surface, including sheet-like structures from one μm to few microns in the lateral dimension (Fig. 1a). TEM image also demonstrates the

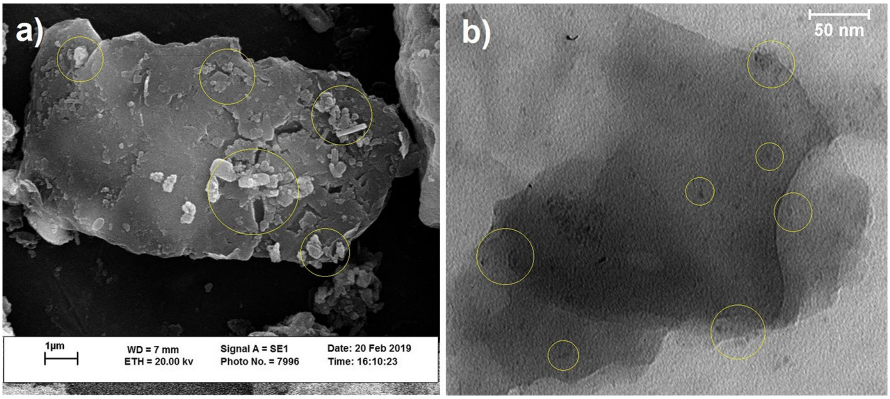


Fig. 1 **a** SEM and **b** TEM images of GO–Met–Cu

same results and shows the sheet-like monolayer structures of GO with relatively transparent view (Fig. 2a). These photographs also confirm the successful linkage of organic and inorganic ligands on GO [36, 37]. Moreover, analysis of energy-dispersive X-ray analysis (EDX) of GO–Met–Cu (Fig. 2) approved the successful carbon nanotubes functionalization. The EDX spectrum clearly shows the presence of carbon, nitrogen, oxygen, chlorine, and copper elements, approving the successful $CuCl_2$ anchoring on the surface of GO–Met [38].

FT-IR analysis

The FT-IR spectrum of all steps of the catalyst preparation including GO, GO with organic ligand (GO–Met), and GO with organic complex and inorganic complex (GO–Met–Cu) are shown in Fig. 3. In the FT-IR spectrum of GO (Fig. 3a), the peaks appeared at 1715 cm^{-1}, 1590 cm^{-1}, 1222 cm^{-1}, and 1040 cm^{-1} are

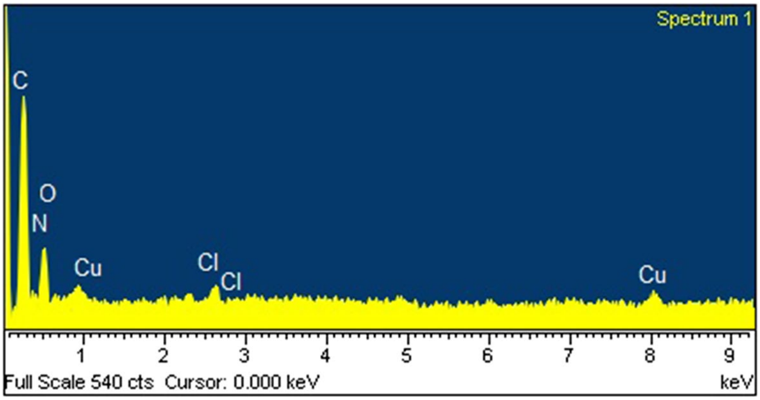


Fig. 2 EDX pattern of GO–Met–Cu

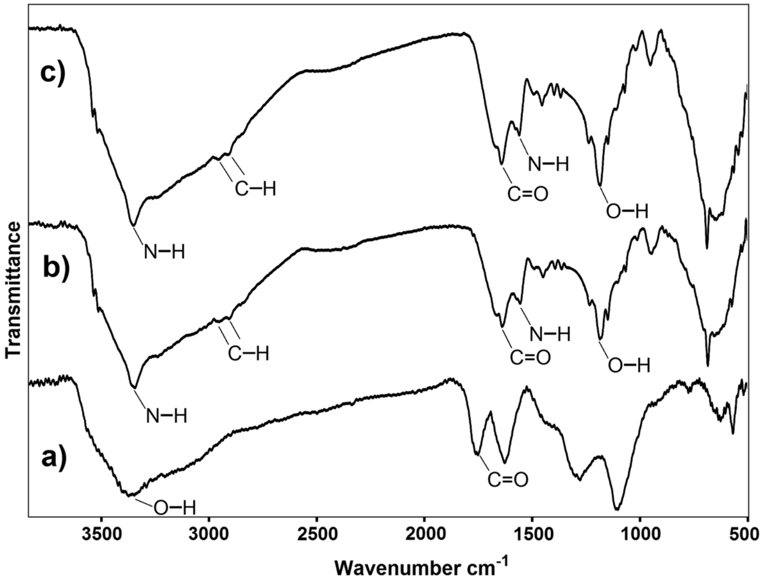


Fig. 3 FT-IR spectra of (a) GO, (b) GO–Met, and (c) GO–Met–Cu

correspond to C=O, C=C, C–O–C, and –OH groups, respectively, and as well as, the broad peak at 3400 cm^{-1} attributed to the O–H stretching bands of hydroxy and carboxylic acid sections [39]. The second spectrum (Fig. 3b) is related to immobilization of the organic ligand (metformin) on the surface of GO. The sharp band appeared at around 3390 cm^{-1} ascribed to the stretching vibrations of amino groups (N–H) of the metformin molecule. Plus, the peak positioned at around 2940 cm^{-1} is assigned to C–H starching of methyl groups on the metformin structure. Moreover, the peaks located at 1635 and 1528 cm^{-1} can be attributed to the stretching vibration of carbonyl (C=O) and amine (N–H) groups of amide structures. Thus, these bands approve that the metformin ligand is successfully immobilized to the surface of the GO sheets through the amidation reaction [36, 37]. In the third spectrum of final catalyst (Fig. 3c), the peaks correspond to C=O and N–H groups shifted to 1628–1522 cm^{-1} because of the coordination of copper to the amine groups of metformin molecule. This evidence confirms the proper coordination of Cu ion to the metformin ligands.

TGA analysis

Thermogravimetric analysis (TGA) is a way of thermal analysis in that the weight of a sample is analyzed over time during the temperature changes. This technique is applied to estimate the functionalization percentage of GO surfaces. As shown in Fig. 4, two main weight losses are observed. The first one about 20% begins at 44 °C and continues to about 530 °C is assigned to the decomposition of oxygenic functional groups (epoxy, hydroxy, and carboxyl) on GO and organic ligands

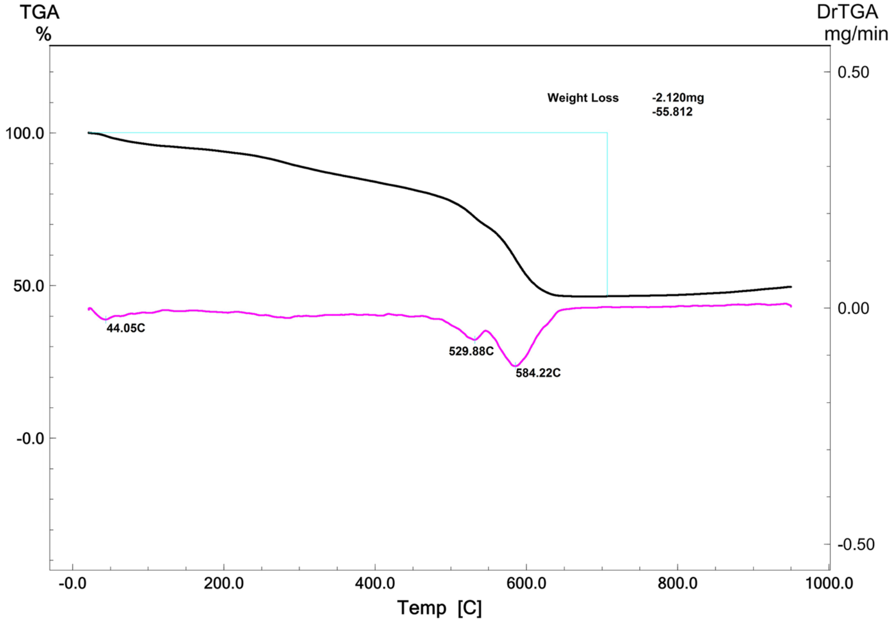


Fig. 4 TGA diagram of GO–Met–Cu

(metformin). Another weight loss (35%) between 530 and 600 °C is attributed to the decomposition of GO nanosheets. According to the obtained results of TGA analysis, ligand grafting has been successfully accomplished.

ICP-OES analysis

One of the best and excellent techniques for estimating metal amount in catalyst structure is inductively coupled plasma (ICP) analysis. Therefore, in order to find the exact amount of the copper content in the prepared catalyst, the ICP technique has been applied. Based on ICP result, the amount of copper ion complexed into the metformin ligand is 4.05%, which is another evidence for the successful grafting of Met–Cu over the surface and the edge of GO nanosheets.

Catalytic application of GO–Met–Cu

The application of the prepared catalyst has been investigated in the synthesis of primary amides via Beckmann rearrangement. In order to find the optimum reaction conditions, the conversion of benzaldoxime to benzamide was selected as a model reaction. The reaction did not proceed in the absence of catalyst in solvent-free conditions even after 5 h (entry 1). Then, different polar and nonpolar solvents in presence of 25 mg of catalyst were examined (entries 2–9). The yield of the reaction was better in polar solvents like methanol, ethanol, and water (entries 7–9), and the best one was water as a green solvent (entry 9). With increasing the temperature to 120 °C, the yield of the reaction was not changed (entry 12), while decreasing the temperature from reflux to room temperature, decreased the yield of the reaction to 32% (entries 13, 14). Moreover, the amount of catalyst has been optimized. The yield of the reaction was decreased to 83% with lower amount of catalyst (15 mg, 0.96 mol%) (entry 15) and using of higher amount of catalyst (30 mg, 1.92 mol%) did not influence on the yield (entry 16). Thus, the optimized reaction conditions were using 25 mg (1.6 mol%) of catalyst at 100 °C in water as a green solvent (entry 11). Moreover, to find the effect of copper, other parts of catalyst (GO, GO–Met, Met), as well as copper acetate on the reaction, the role of them was also investigated in the model reaction under the optimized reaction conditions (entries 17–20). The yield of the reaction in the presence of bare GO and GO linked to metformin (GO–Met) was very low (entries 17, 19), and the reaction was failed in the presence of only metformin as an organic ligand (Met) (entry 18), while the copper acetate can catalyze the reaction with good yield (entry 20) (Table 1).

After finding the optimum reaction conditions (amount of catalyst, temperature, and solvent), the scope of the reaction was examined in a vast range of differently substituted aromatic aldoximes in presence of GO–Met–Cu catalyst (Table 2).

Table 1 Optimization of solvent, temperature, and amount of catalyst for the synthesis of **3a**

Entry	Conditions	Catalyst (mg, mol%)	Temperature (°C)	Time (min)	Yield (%)[a]
1	Solvent free	–	100	300	–
2	Solvent free	GO–Met–Cu (25, 1.6)	100	180	Trace
3	*n*-Hexane	GO–Met–Cu (25, 1.6)	68	180	–
4	$CHCl_3$	GO–Met–Cu (25, 1.6)	61	180	12
5	CH_2Cl_2	GO–Met–Cu (25, 1.6)	40	180	15
6	MeCN	GO–Met–Cu (25, 1.6)	82	180	50
7	MeOH	GO–Met–Cu (25, 1.6)	65	120	63
8	EtOH	GO–Met–Cu (25, 1.6)	78	120	79
9	H_2O	GO–Met–Cu (25, 1.6)	100	120	95
10	H_2O	GO–Met–Cu (25, 1.6)	100	60	95
11	H_2O	GO–Met–Cu (25, 1.6)	100	30	95
12	H_2O	GO–Met–Cu (25, 1.6)	120	30	95
13	H_2O	GO–Met–Cu (25, 1.6)	50	30	60
14	H_2O	GO–Met–Cu (25, 1.6)	rt	30	32
15	H_2O	GO–Met–Cu (15, 0.96)	100	60	83
16	H_2O	GO–Met–Cu (30, 1.92)	100	60	96
17	H_2O	GO (25)	100	60	Trace
18	H_2O	Met (25)	100	60	–
19	H_2O	GO–Met (25)	100	60	Trace
20	H_2O	$Cu(OAC)_2$ (25)	100	60	86

[a] Based on isolated yield

Table 2 Synthesis of primary amides derivatives from aldoximes in presence of GO–Met–Cu

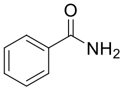
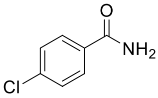
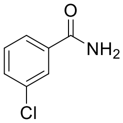
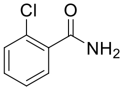
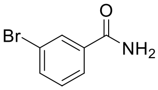
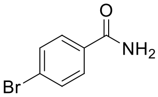
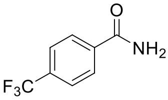
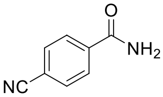
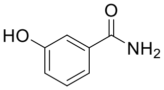
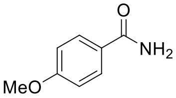
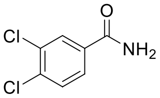
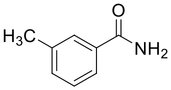
Entry	R	Product[a]	Time (min)	Yields (%)[b]	Mp °C	
					Found	Reported
1	H	 **3a**	30	95	125–127	128–130 [41]
2	4-Cl	 **3b**	45	96	170–172	175–178 [42]
3	3-Cl	 **3c**	55	90	130–131	132–134 [42]
4	2-Cl	 **3d**	60	94	137–139	139–141 [42]
5	3-Br	 **3e**	45	90	156–157	155–157 [43]
6	4-Br	 **3f**	35	95	190–192	191–192 [43]
7	4-CF_3	 **3g**	50	94	182–184	182–184 [42]
8	4-CN	 **3h**	30	96	223–225	222–224 [44]
9	3-OH	 **3i**	55	92	169–171	170–171 [45]

Table 2 (continued)

Entry	R	Product[a]	Time (min)	Yields (%)[b]	Mp °C	
					Found	Reported
10	4-MeO	 **3j**	60	90	166–168	165–167 [42]
11	3,4-$(Cl)_2$	 **3k**	45	93	137–138	138–139 [40]
12	3-CH_3	 **3l**	60	92	95–96	94–95 [43]

[a]Reaction condition: aldoxime (1.0 mmol), GO–Met–Cu (25 mg, 1.6 mol%), and water at 100 °C

[b]Isolated yields

The experimental findings showed that the present catalyst demonstrated high efficiency for both electron-donating and electron-withdrawing substituted aldoximes, although the substrate with electron-withdrawing groups in para position exhibited better yields than electron-donating groups (products **3b**, **3f**, and **3h** in comparison with **3j**). All obtained products were known compounds and were identified by the comparison of their melting points with those synthesized in the previous literature.

Due to the heterogeneity of the catalyst, after completion of the reaction, it can be separated from reaction mixture and reused. Thus, the reusability of the catalyst was analyzed by the model reaction under the optimized reaction conditions. After the completion of the first reaction, the nanoheterogeneous catalyst (GO–Met–Cu) was separated from the reaction mixture by centrifuging (8000 rpm for 15 min), and then, it was washed with two solvents (water and acetone) and dried at 80 °C over night before reusing in the second run. The catalyst can be recycled ten times with only a little reduction in efficiency (Fig. 5).

To find the better understanding of catalyst behavior, the complete mechanism for the synthesis of primary amides derivatives from aromatic aldoximes is suggested according to the literature [40]. Based on Scheme 3, the reaction starts with coordination of copper complex catalyst to aldoxime and production of metal–nitrile intermediate by dehydration of aldoxime. Next, the second aldoxime is attacked to the metal–nitrile intermediate produced in the previous step and finally by removing one nitrile molecule, the final primary amide is formed.

The hot filtration test has also been analyzed on the model reaction under the optimized conditions in order to test catalyst leaching. So, a mixture of GO–Met–Cu (25 mg), benzaldoxime (1.0 mmol) and water (5.0 mL) was

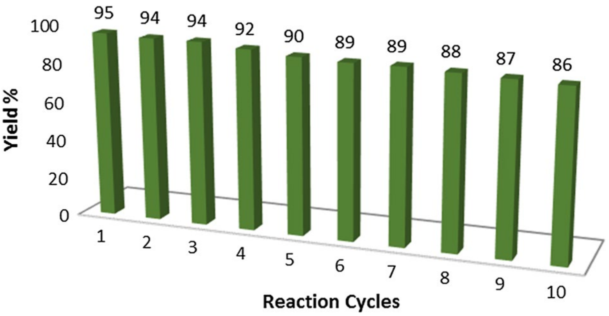
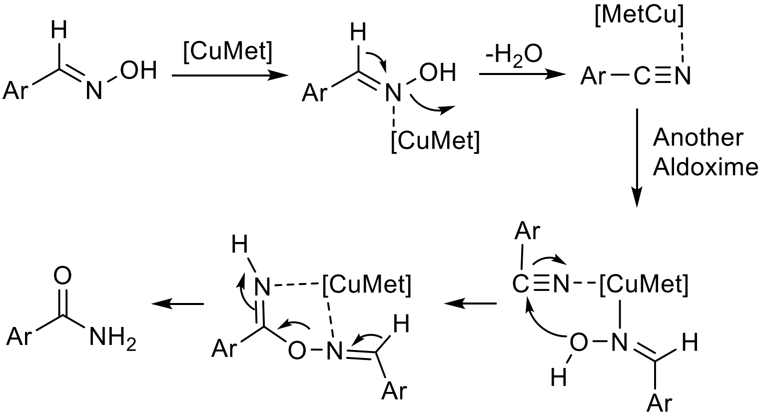


Fig. 5 Reusability of catalyst after ten runs



Scheme 3 A proposed mechanism for conversion of aromatic aldoximes to primary amides in presence of catalyst (GO–Met–Cu)

refluxed for 15 min. After approximately 50% conversion, the catalyst was separated from the reaction mixture and then the reaction was continued for further time (15 min). No product was observed which was monitored by TLC. This result vividly demonstrates that no leaching of copper and copper–metformin took place during the reaction and confirm the stability of catalyst structure.

The merit practical applications of the present study were compared with other heterogeneous systems for the synthesis of benzamide **3a** from benzaldoxime (Table 3). According to Table 3, our prepared catalyst shows excellent catalytic activity in shorter reaction time, higher isolated yields, and milder conditions.

Table 3 The comparison of GO–Met–Cu with other heterogeneous catalysts in synthesis of **3a**

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]	References
1	Au complex (5.0)	Solvent free	100	20	92	[46]
2	$ZnCl_2$ or $Zn(NO_3)_2$ (10)	Heptane	100	18	88	[47]
3	$Pd(OAc)_2$ (5.0)	DMSO	100	15	98	[48]
4	Ru complex (0.5)	H_2O	110	10	97	[49]
5	$Rh(OH)/Al_2O_3$ (4.0)	H_2O	160	7.0	90	[50]
6	$Cu(OAc)_2$ (10)	Dioxane	110	3.0[b]	99	[25]
7	GO–Met–Cu (1.6)	H_2O	100	0.5	95	This work

[a] Based on isolated yield

[b] Day

Experimental

Chemicals and apparatus

Melting points of products were recorded with an Electrothermal type 9100 melting point apparatus. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet Avatar 370 FT-IR Therma spectrometer. Transmission electron microscopy (TEM) was performed with a Leo 912AB (120 kV) microscope (Zeiss, Germany). Scanning electron microscopy (SEM) analysis was done using a MIRA3 TESCAN scanning electron microscope operated at an accelerating voltage of 30 kV. Energy-dispersive X-ray (EDX) analysis was performed using a SAMX instrument. Inductively coupled plasma (ICP) analysis was carried out with a Varian VISTA-PRO, CCD (Australia). Thermogravimetric analysis (TGA) was performed with a Shimadzu thermogravimetric analyzer (TG-50) under air atmosphere at a heating rate of 10 °C min^{-1}.

Preparation of GO–Met

The GO and acylated GO (GO–Cl) have been prepared according to literature [39]. Then, metformin was covalently immobilized on GO nanosheets via condensation reaction of metformin and GO nanosheets [36]. For this purpose, GO (50 mg) was added to a solution of DMF (50 mL) and ultrasonicated for 1 h. After that, the sonicated solution was cooled to 0 °C, and NHS (5 mmol) and EDC (5 mmol) were added. The reaction mixture was stirred for 2 h, and then, metformin (5 mmol) was added to the solution and the temperature was raised to 100 °C and stirred for another 24 h. The prepared GO–Met was collected by centrifuging at 8000 rpm for 20 min and dried in vacuum at 50 °C.

Preparation of GO–Met–Cu

The complex of copper and GO–Met was prepared by adding copper acetate (1.0 g) into the solution of GO–Met (1.0 g) and DMF (80 mL). For the complete metalation, the reaction mixture was refluxed for 6 h. The obtained GO–Met–Cu was collected by centrifuging at 8000 rpm for 20 min. Finally, 20 ml of water was added and the mixture was centrifuged at 8000 rpm for another 20 min and the Cu-coordinated metformin was obtained.

General procedure for the synthesis of aldoximes

Hydroxylamine hydrochloride (0.3 g) was added to a stirred mixture of ZnO (0.15 g) and aldehydes (1.0 mmol) at 80 °C in an oil bath. The progress of the reaction was monitored by TLC. After the complete disappearance of the reactants, the mixture was washed with dichloromethane (3×10 mL) and water (3×30 mL). The organic layer was dried by anhydrous sodium sulfate and evaporated to afford the corresponding aldoximes [40].

General procedure for the synthesis of primary amides derivatives 3a–l

To a mixture of GO–Met–Cu (25 mg) in water (15 mL), aldoximes derivatives (1.0 mmol) was added and stirred at 100 °C for times mentioned in Table 2. After completion of the reaction, as indicated by TLC, the catalyst was separated by centrifuging (8000 rpm for 15 min) and after evaporated the solvent, the products **3a**–**l** were achieved with high purification. All products were characterized by melting points (Table 2).

Conclusions

In summary, for the first time, the heterogeneous copper complex immobilized on GO has been applied as a novel and green catalyst (GO–Met–Cu) for the conversion of aldoximes to primary amides via Beckmann rearrangement. Different techniques (FT-IR, SEM, EDX, TEM, TGA, and ICP) were used to characterize the catalyst structure. All analyses approved that the Cu–metformin was successfully immobilized on the surface of GO as well as the presence of copper in catalyst body. Moreover, our catalyst showed excellent catalytic activity in shorter reaction time, higher isolated yields, and milder reaction conditions in comparison with the previous studies.

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Affiliations

Ahmed Solaiman Hamed[1] · **Ehab Mohammad Ali**[1]

✉ Ahmed Solaiman Hamed
dr.ahmedalmohammedi@uofallujah.edu.iq

[1] College of Applied Sciences, University of Fallujah, Fallujah, Iraq