Graphene Quantum Dots Modified
with Metformin/Co(II) as Efficient Oxidation Catalyst

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ABSTRACT: *While one of the valuable approaches to obtaining a heterogeneous catalyst is supporting them on a high surface area supports, the strategy mainly suffers from the low number of chelating agents on most of the supports to grip the metal cations catalysts. Therefore, loading multidentate compounds susceptible to binding with metal cations is a potent strategy to improve the catalyst stability on the support. In this report, metformin as a multi-dentate ligand was bonded onto graphene quantum dots as a high aspect ratio compound to afford new support susceptible to chelating Co(II). Deposition of Co(II) on graphene quantum dots modified with metformin gave a new sustainable heterogeneous catalyst that was highly active in the oxidation of alkyl arenes. The reactions were performed in solvent-free conditions at 80 ºC with high conversions up to 96%. The organometallic compound is applicable as a recoverable heterogeneous catalyst with recyclability up to 6 times. The modification of graphene quantum dots with metformin also can gain more attention from medicinal researchers.*

KEYWORDS: *Metformin; Graphene Quantum Dots; Cobalt; Heterogeneous catalyst; Oxidation reaction.*

INTRODUCTION

Catalytic oxidation is one of the fundamental reactions due to its widespread applications in various industries [1-3]. Among them, selective aerobic oxidation using heterogeneous catalysts has been considered the most important transformation regarding their companionship with green chemistry [4,5]. Even though much of the efforts focused on the use of noble metal catalysts in the heterogeneous form [6-11], replacing them with affordable and abundant non-noble metals is interesting for suppressing of high costs of noble metals. Therefore, Co-based catalysts as non-noble-metal ones have been established as efficient tools for the oxidation of a range of species, including CO [12], CH_4 [13], olefins [14], and VOCs [15]. Oxidation of alcohols has been extensively studied with Co catalysts. For instance, single atom Co [16, 17], various Co complexes [18, 19], and Co(II) salts [20] have been used in the oxidation reaction of alcohols.

Metformin (chemically, it is known as *N,N*-dimethylbiguanide) is one of the biguanide derivatives exhibiting good biological and coordinative properties.

Having the biguanide moiety, metformin can chelate metals such as cobalt and makes metals-metformin complexes [21]. Formation of such complexes is valuable in view of the catalysts researchers use such binding to settle of Co(II) on support. Since the main drawback of using Co complexes under a homogeneous system is cobalt leaching, which is one of the biologically toxic pollutants, the application of Co heterogeneous catalysts can solve the problem. The heterogeneous systems have specific advantages such as minimizing metal traces in the final product, easy separation, and efficient recycling [22].

Graphene Quantum Dots (GQDs) are honeycomb lattices of carbon atoms under 100 nm with a maximum of 10 sheets stuck together. Nowadays, GQDs have drawn a lot of attention because of their properties like highly accessible surface area, less cytotoxicity, high chemical stability, and outstanding biocompatibility [23,24]. These fascinating properties led to a great number of applications for these nanomaterials such as theranostic agents, light-emitting diode materials, optical bioimaging probes, and detection probes [23,24]. It is believed that GQDs can attend as a platform for the development of other nanomaterials such as metals and metal oxides to be used as catalysts [25-28]. Thus, GQD is an ideal choice for supporting Co(II) complexes to fabricate a heterogeneous catalyst for the oxidation transformation targets. In continuation of our interest in developing useful catalytic systems for the oxidation of organic compounds [29-34], herein metformin employed as a ligand for anchoring Co(II) to GQD to furnish a heterogeneous catalyst (CoM/GQD) having a high aspect ratio due to the atomic distribution of the catalyst on the support. Easy recovery, sustainability, high surface area, and chemical stability of the new catalyst like most of the heterogeneous catalysts make it attractive for the catalytic agenda [35-37].

EXPERIMENTAL SECTION
Materials and methods

Sigma-Aldrich provided all reagents that they used without further purification. Metformin was purchased from Sigma-Aldrich with $\geq$98% purity and used without further purification. Fourier Transform InfraRed (FT-IR) spectroscopy of Jasco 6300 FTIR instrument in the range of 600–4000 cm^{-1} for FT-IR spectroscopy, Scanning Electron Microscope of TSCAN Company for Energy Dispersive X-ray (EDX) spectroscopy and Philips CM100

BioTWIN transmission electron microscope for Transition Electron Microscopy (TEM) was employed. Co amount of the catalyst was determined by a Flame Atomic Absorption Spectroscopy (FAAS) (Shimadzu 105 model AA-680 atomic absorption spectrometer) with a hollow cathode lamp. The elemental analysis was carried out by an Elementar Analysensysteme GmbH VarioEL. Gas Chromatographic (GC) measurements were performed by Varian 3900 GC.

Preparation of CoM/GQD

The citric acid (10 g) was added to a vessel and heated at 200 °C for 30 min. Then, 30 mL acetone and 30 mL NaOH solution (0.10 M) were poured respectively on the obtained orange oil to give a biphasic system in which the down phase was separated as GQD (5.11 g).

GQD (5.00 g) was added to a balloon containing 10 mL solution of DCC (1.11 g), DMAP (0.28 g), and metformin (1.00 g) in DMSO. The mixture was stirred at 90 °C and after 24 h, 20 mL of acetone was added to the mixture to cause the formation of precipitation. The precipitation was filtered off, washed with acetone, and dried in an oven at 60 °C to give M/GQD as a white solid (4.68 g).

M/GQD (2.00 g) was added to a vessel containing a solution of CoCl$_2$ (0.5 g) in water (10 mL). After 24 h, acetone (20 mL) was added to the mixture to form solids which were separated by a filter paper. The residue was dissolved in 10 mL H$_2$O and sedimentation again was performed with pouring 20 mL acetone. The obtained white solid was dried in the oven at 70 °C.

Determination of Co(II) on CoM/GQD using FAAS

CoM/GQD (0.05 g) was added gradually to a mixture of HCl:HNO$_3$ (3:1) (10 mL) being sonication and the sonication was continued for another 3 h. Next, the unsolved ingredients of the mixture were separated by filtration, and the total volume of the filtrate was increased to 20 mL with distilled water. The diluted solution was analyzed using FAAS against the blank prepared with M/GQD. The Co(II) concentration was obtained using a calibration curve prepared with Co solution standards.

The typical procedure for the oxidation of ethylbenzene

In a typical procedure, CoM/GQD (0.018 mmol or 0.05 g) and ethylbenzene (1 mL) were added to the reaction vessel and the resulting mixture was stirred at 80 °C under O$_2$
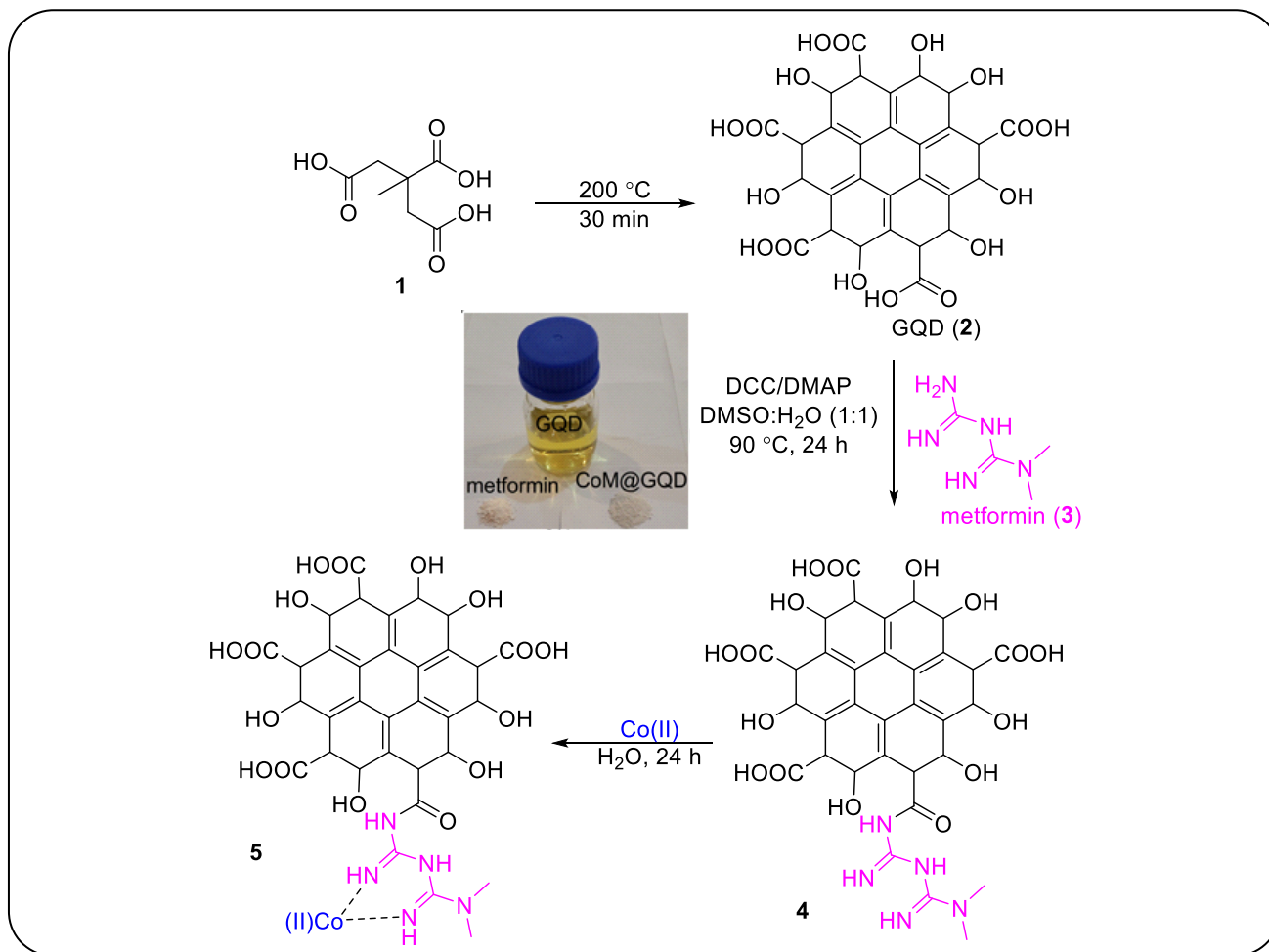
Fig. 1: General protocol for the synthesis of CoM/GQD (5).

The atmosphere is created with a balloon. The initial monitoring of the reaction progress was done by thin-layer chromatography. Upon completion, acetone (2 mL) was added to the reaction vessel to precipitate CoM/GQD which was then separated from the mixture via filtration. The filtrate was analyzed with GC after evaporation of acetone.

RESULTS AND DISCUSSION

Catalyst synthesis

Co(II) has a high tendency to the chelating agents contain amine groups especially those with multiple amines. Metformin has five amines in its structure which makes it attractive for chelating with Co(II) as well as chemically bonding to carboxylic acids of GQD through amidation reaction. Therefore, GQDs were modified with metformin in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC)/*N,N'*-dimethylaminopyridine (DMAP). DCC, as the coupling reagent and DMAP, as a catalyst, activated

carboxylic acid to react with a nucleophile. Finally, Co(II) was anchored to the modified GQD (**4**) for 24 h to give CoM/GQD (**5**) (Fig. 1).

Catalyst characterization

All of the modifications were confirmed with FT-IR spectra. Metformin spectrum showed peaks at 1568, 1625, and 2836/2924 cm^{-1} which are attributed to the vibration modes of N-H bending, C=N, and C-H, respectively. All of these peaks were observed in the FT-IR spectrum of the product, which approves metformin deposition on the support (Fig. 2). Also, GQD showed absorption peaks in accordance with CoM/GQD spectrum such as 1566 cm^{-1} for C=C and 1629 cm^{-1} for C=O, and 3344 cm^{-1} for O-H groups.

EDX was used for the determination of various elements in the CoM/GQD structure. The analysis showed that Co was loaded on the support successfully (Fig. 3). Also, the existence of N in the EDX analysis of CoM/GQD
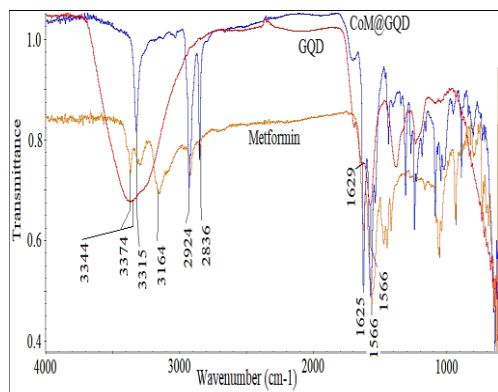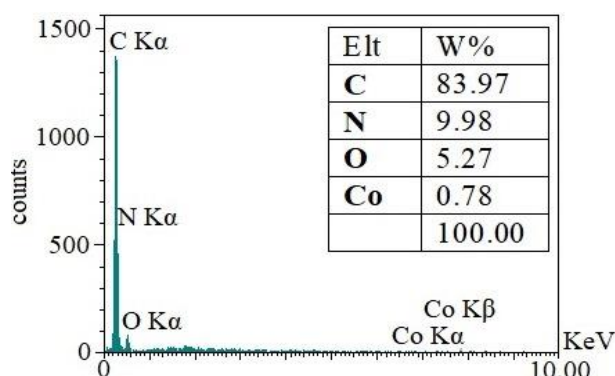
Fig. 2: FT-IR spectra of metformin, GQD, and CoM/GQD.
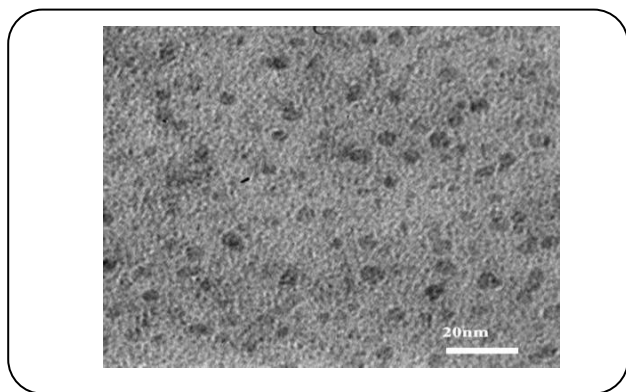

Fig. 3: EDX analysis of CoM/GQD.

Fig. 4: TEM micrograph of CoM/GQD.

indicates that the modification of GQD with metformin was performed efficiently. C and O peaks are attributed to GQDs. This analysis indicates 9.98 w% and 0.78 of the catalyst are N and Co, respectively. The CHNS analysis of CoM/GQD showed C, 81.71%; H, 0.59%; N, 9.12 %. The mole of the N on CoM/GQD was calculated

7.12 mmol per 1 g of the catalyst regarding the atomic weight of N is 14 g/mol. Since each metformin has five N atoms, the mole of metformin is 1.42 mmol per 1 g catalyst. The Co loading on the catalyst was determined to be 0.16 mmol per 1g of the catalyst according to FAAS analysis.

TEM micrograph of CoM/GQD was prepared which evinced the formation of GQD (Fig. 4). GQDs as a zero-dimension material are prepared as nanoparticles with a size smaller than 100 nm. The maximum size distribution of CoM/GQD was obtained between 6-9 nm. The nanoparticle size distribution is controlled by the time in citric acid condensation reaction, in which the long reaction period affords big particles.

Elemental mapping of CoM/GQD was performed using a scanning electron microscope to probe the homogeneity of the catalyst structure (Fig. 5). The survey demonstrates that all of the elements have a uniform distribution on the composite. The most important result of this analysis is the homogeneous dissemination of Co on GQD since Co is the catalyst division of CoM/GQD and it can be acted efficiently when monotonically dispersed on the support.

Oxidation of alkyl arenes

The catalytic activity of CoM/GQD was investigated in the oxidation reaction of alkyl arenes (Table 1). So, the oxidation of 1 mL ethylbenzene was studied under O_2 atmosphere in the presence of 0.10 mmol catalyst (0.05 g) at 80 ℃. The progress of the reaction was monitored by TLC and the GC analysis of the mixture demonstrated acetophenone as the major product with 2% 1-phenyl ethanol as the by-product at the end of the reaction. The conversion and selectivity of this reaction were determined by GC analysis 96% and 98%, respectively. Any decrease in the catalyst amount and temperature caused the reaction yield to decline. In addition, increasing the catalyst amount and temperature from the optimized values did not have any positive effect on the reaction yield or time. The solvent effect was investigated on the reaction and among various solvents screened for the oxidation reaction of ethylbenzene, chloroform gave the highest yield compared to the other solvents. However, solvent-free conditions were the best for the oxidation reaction because of the green chemistry credentials. Also, for the oxidation reaction in acetonitrile, a by-product was observed the GC analysis showed styrene in 29% yield which was afforded through a dehydration reaction.
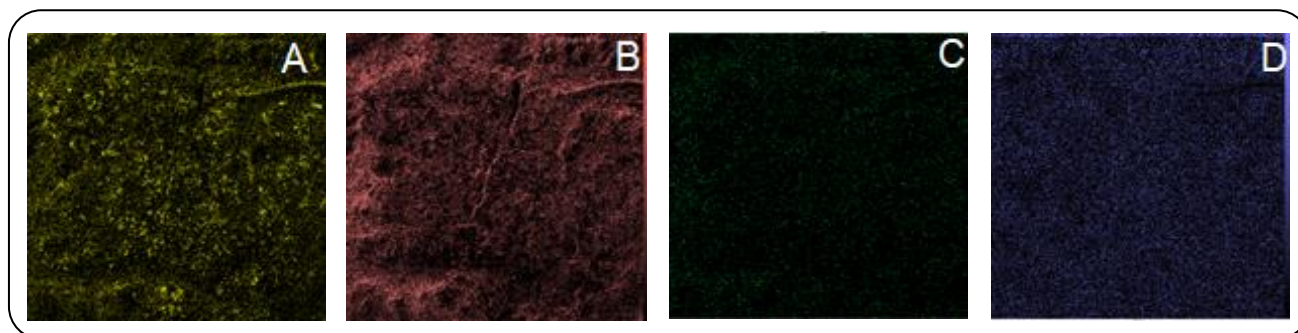
Fig. 5: Elemental mapping of CoM/GQD for atoms carbon (A), oxygen (B), nitrogen (C), and cobalt (D).

Table 1: Optimization of the reaction conditions for the oxidation of ethylbenzene[a]

Entry	Catalyst (mmol)	Temp. ºC	Solvent	Conversion (%)		
				AP	BA	St
1	0.08	80	-	87	2	0
2	0.10	80	-	96	2	0
3	0.12	80	-	96	2	0
4	0.10	70	-	91	2	0
5	0.10	90	-	96	2	0
6	0.10	80	H_2O	56	7	0
7	0.10	reflux	EtOH	41	13	0
8	0.10	reflux	CH_3CN	79	5	29
9	0.10	reflux	$CHCl_3$	94	2	0
10	0.10	80	$PhCH_3$	37	21	0

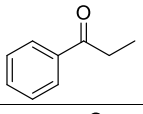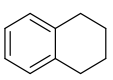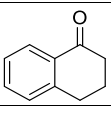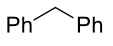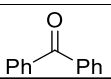[a] *Reaction conditions: ethylbenzene (1 mL), CoM/GQD, O_2 balloon, solvent (5 mL), 24 h.*
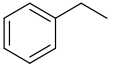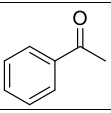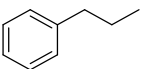
The oxidation reaction was developed using various alkyl arenes such as propylbenzene, 4-ethylphenol, 1,2,3,4-tetrahydronaphtalene, and diphenylmethane (Table 2). Great conversions and excellent selectivities have been obtained for the oxidation reactions.

Potential Co leaching into the mixture of ethylbenzene oxidation reaction was also analyzed with FAAS analysis. For this purpose, the filtrate of the heterogeneous oxidation reaction of ethylbenzene after 1 h was passed from a syringe filter and then dissolved in HNO_3. The Flame Atomic Absorption Spectroscopy (FAAS) analysis of sample evinced that the Co concentration in the reaction mixture was less than the detection limit. This result indicates that virtually no Co leaches from CoM/GQD into the mixture.

The recyclability of CoM/GQD was investigated in the oxidation reaction of ethylbenzene. After carrying out the reaction, the catalyst was separated via filtration as a white solid, washed with acetone (2×5 mL), and reused. Only a minor decrease in the reaction yield was observed after four repetitive cycles for this reaction (Table 3). Also, the 5th and 6th trials were completed in long reaction duration with lower yields. For investigation of the catalyst stability, the amount of Co on the catalyst was determined before use, and after six runs 0.16 mmol per 1 g catalyst was obtained for both of them.

Table 2: Oxidation of various substrates with CoM/GQD[a].

Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1			96	98
2			94	98
3			94	99
4	Ph Ph	Ph Ph	95	100

[a] *Reaction conditions: substrate (1 mL), CoM@GQD (0.10 mmol), O₂ balloon, 80 ºC, 24 h.*

Table 3: Successive trials by using recoverable CoM/GQD for the oxidation of ethylbenzene[a].

Trial	Time (h)	Yield (%)
1	24	96
2	24	96
3	24	96
4	24	95
5	28	93
6	30	91

[a] *Reaction conditions: ethylbenzene (1 mL), CoM/GQD (0.10 mmol), O₂ balloon, 80 ºC.*

In addition, FT-IR spectrum of the recovered catalyst was prepared after separation from the mixture, washing with acetone, and drying in an oven at 70 ºC for 6 h (Fig. 6). The spectrum showed peaks for the catalyst similar to the unused catalyst, which again confirms catalyst stability.

The proposed mechanism for the oxidation reaction of ethylbenzene was described in Fig. 6. Co(II) specie under the reaction with O_2 produces an active peroxide **I** which be able to subsequently receive a hydrogen radical from ethylbenzene (**1**) to afford **1´**. Intermediate **I** transforms **1´** to alcohol **2** through a hydroxyl radical transfer and intermediate **III** obtain during this reaction. It is crucial to consider that existence of GQD with high electron density can help to stabilization of intermediate **III** that seems unstable due to the presence of Co(IV). Intermediate **III** absorbs a hydrogen radical from alcohol **2** to afford intermediates **IV** and **2´**. Intermediate **IV** produces hydroxyl radical which under reaction with intermediate **2´** lead to the formation of product **3**, Co(II)M/GQD, and H_2O.
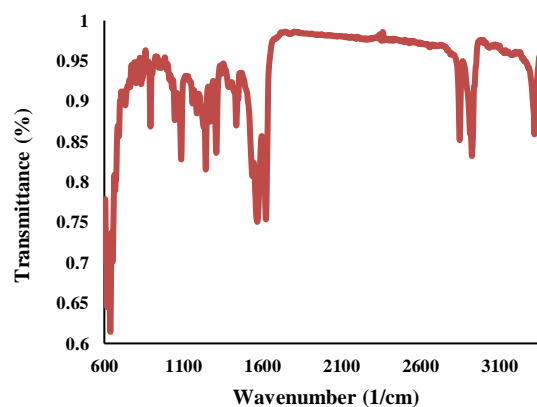

Fig. 6: FT-IR spectrum of recovered CoM/GQD.

A comparison has been done between the results of ethylbenzene oxidation with CoM/GQD and some recent reports using Co/N co-doped carbon [38], Co/N/S co-dopes carbon [39], and hexagonal mesoporous silicas (HMS)/enzyme/Co_3O_4 catalysts [40] (Table 4). While all

Table 4: Comparison of the results for the oxidation of ethylbenzene.

Entry	Catalyst	Solvent	Oxidant	Time (h)	Temp. ℃	Selectivity (%)	Yield (%)
1	Co, N co-doped carbon [38]	H_2O	TBHP	6	80	100	93
2	N and S co-doped Co carbon [39]	-	O_2	5	120	85	48
3	HMS/enzyme/Co_3O_4 [40]	-	O_2	6	120	86.1	55.1
4	CoM/GQD	-	O_2	24	80	98	96
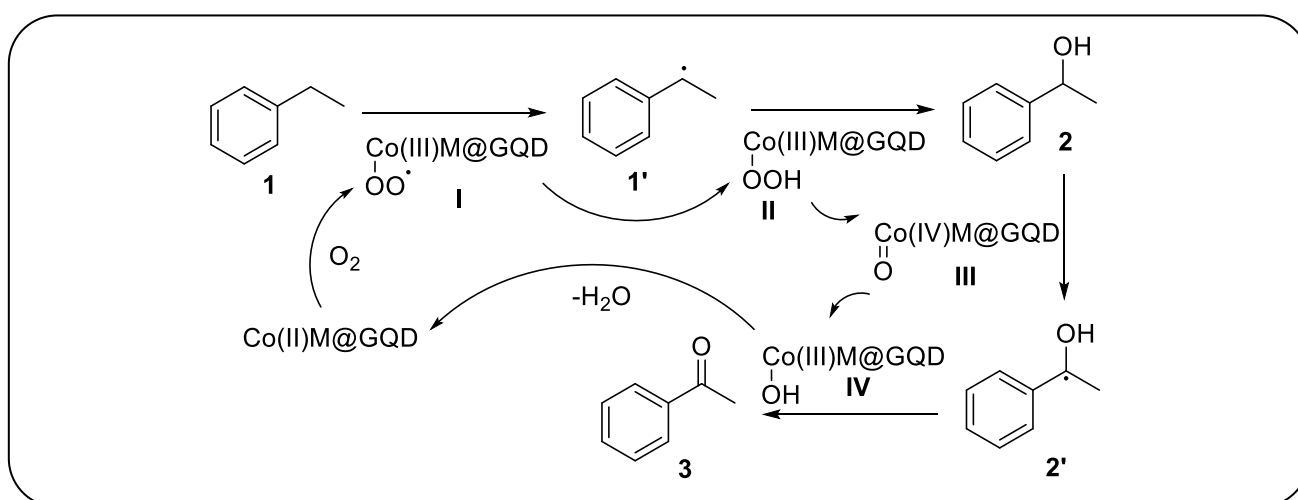
Fig. 6: The proposed mechanism for oxidation of ethylbenzene using CoM/GQD.

the previous reports were carried out in a short duration, oxidation by CoM/GQD has some advantages such as inexpensive oxidant compared to entry 1, lower temperature compared to entries 2 and 3, and high selectivity/conversion compared to all of them.

CONCLUSIONS

In conclusion, metformin as a chelating agent of Co(II) was immobilized on GQD, and then Co(II) was complexed with metformin functionalized GQD. The complex was recognized as an efficient catalyst for the oxidation of some alkyl arenes at 80 ℃ under O_2 atmosphere. The aerobic oxidation reactions afforded corresponding ketones in 94-96% yields with 100% selectivity. The catalyst is recyclable 6 times without any significant reduction in yield, and no catalyst leaching to the reaction mixture was observed, which approves the chemical stability of the new catalyst.

Acknowledgments

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