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FULL PAPER

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Application of GO/COF as a novel, efficient and recoverable catalyst in the Knoevenagel reaction

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Abstract
Hybrid composite based on graphene oxide (GO) and covalent organic framework (COF) [GO/COF] was developed via a simple solvothermal method, at which GO was applied as a platform to load COF based on melamine and terephthaldehyde. The synthesized hybrid nanocomposite was characterized by FT-IR, XRD, EDX and SEM techniques. Morphological analyses carried out by SEM confirm the successful growth of COF over GO. Then, the resultant composite was employed as an amazing and cost-effective catalyst in the condensation of several aldehydes with malononitrile and produced the corresponding coupling products in high yields (up to 84%) at room temperature under solvent-free conditions with an amount of catalyst, 15 mg in a very short reaction time of 10 min. The catalyst could be reused without a noteworthy drop in catalytic activity at least eight times. The use of GO/COF catalyst outcomes under mild reaction conditions in very short reaction time, exceptional catalytic activity, high recyclability and an easy work-up process for the Knoevenagel condensation.

KEYWORDS
covalent organic framework, graphene oxide-based nanocomposite, hybrid material, Knoevenagel reaction

1 | INTRODUCTION

Heterogeneous catalysis is a key process in the manufacture of a wide range of chemicals and is at the heart of green chemical processes.[1] The features of the heterogeneous catalytic systems including easy product separation, efficient recyclability of catalysts and minimization of chemical waste, can overcome the limitations of their homogeneous catalysis counterpart.[2] Composites have proven to be popular heterogeneous supports for the immobilization of homogeneous catalysts.[3]

Recently, nanotechnology with wide diversity of nanomaterials create a new revolution in science and especially chemical fields.[4,5] The combination of the functional components to attain nanocomposite materials has gained growing attention, as such nanocomposites permit graceful amalgamation of chemical and physical properties, synergistic effects and multiple functions of individual components.[6–8] The carbon-based composite materials are striking for various applications because their outstanding chemical, mechanical, thermal and electric properties.[9,10] The composite materials based on graphene and its derivatives possess unique properties such as chemical stability, low toxicity, biocompatibility, and flexibility for surface functionalization.[11,12] Hence, the surface of these composites can be grafted with an extensive variety of functional groups, making further reactions and modification.[13] Among the various kinds of nanocomposites, Graphene oxide (GO) ones have received interesting attention due to their unique properties.[14]

GO, as an oxidized derivative of graphene and a single-layered material has attracted noteworthy interest as one of the most interesting and potential materials due to its extremely large surface area, low cost, and excellent mechanical and thermal properties.[15] In particular, its good hydrophilic properties owing to the presence of oxygen-containing hydrophilic groups, including hydroxyl, carbonyl, and carboxyl groups, not only makes GO readily dispersible in water to produce stable colloidal suspension, but also facilitates the preparation of GO-based composites in solution. Furthermore, GO sheets show remarkable improvements in chemical and physical properties when incorporated in composite materials with potential applications in many areas, such as solar cell, resonators, electronic devices, and supercapacitors.[16,17]

Covalent organic frameworks (COFs), an emerging class of crystalline porous materials fabricated from purely organic building blocks linked by reversible covalent bonds have attracted much attention due to their highly ordered structure and accessible distinct pores.[18,19] The fascinating features of tunable pore size, perpetual porosity, large surface area, low density, and plentiful functional groups on the channel walls render COFs great potential in an extensive variety of applications, including gas separation,[20] gas storage,[21] chemical sensors,[22] optoelectronics,[23] drug delivery[21] and catalysis.[24] However, COFs are generally irregular in morphology and it is hard to control their growth rationally.[25] Consequently, shapeless bulk materials are produced. Moreover, the light density makes COF materials difficult to precipitate from the matrix. These unexpected disadvantages bring troublesomeness and impediment in their further application. Hence, their composites with other materials is of substantial significance in promoting extensive applications of COFs.[26–28] Incorporation of the merits of COFs and GO to construct a novel class of composites with both enhanced functionality and large surface area is of great significance and interest.[29] In particular, the GO sheets can offer a center for COF growth.

The Knoevenagel condensation of aldehydes with compounds containing activated methylene groups is one of the most useful and widely employed methods for carbon–carbon bond formation with numerous applications in the synthesis of fine chemicals as well as heterocyclic compounds of biological significance.[30] Conventionally, this reaction is catalyzed by weak bases like primary, secondary, and tertiary amines under homogeneous conditions, which could require high amount of catalyst with the attendant difficulties in recovery and recycling of catalyst. Various solid-supported catalysts have been applied to this reaction.[31–33] However, to the best of our knowledge, the Knoevenagel condensation catalyzed by GO/COF hybrid was not previously mentioned in the literature. In this work, we wish to report the utilization of GO/COF hybrid material as an efficient heterogeneous catalyst for the Knoevenagel reaction. High activity was observed and the GO/COF catalyst was easily isolated from the reaction mixture by simple filtration and reused without significant degradation in activity.

2 | EXPERIMENTAL

2.1 | Materials

The reagents and chemicals including graphite powder, potassium permanganate, hydrogen peroxide (30%), sulfuric acid (95–97%), hydrochloric acid (37%), 3-aminopropyltriethoxy silane (APTES, KH550, $H_2N(CH_2)_3Si(OCH_2CH_3)_3$), melamine, terephthaldehyde, dimethyl sulfoxide (DMSO), chloroform, ethanol, benzaldehyde, malononitrile, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 2-chlorobenzaldehyde, 4-methoxybenzaldehyde, 4-methylbenzaldehyde, 2-hydroxybenzaldehyde were purchased from Merck Company (Darmstadt, Germany) and used without further purification.

2.2 | Apparatus

Fourier transform infrared (FT-IR) spectra of the samples were recorded with a Jasco-680 spectrometer (Japan) in the range of 4000–400 cm^{-1} using KBr pellet. The X-ray diffraction (XRD) patterns of the samples were recorded in the reflection mode using a Bruker, D8 Advance diffractometer. The surface morphology of the resulting materials was investigated using field emission-scanning electron microscopy (FE-SEM; EM10C-ZEISS, 80 KV, Zeiss Co., Germany, Oberkocken). The ultrasonic bath (Tecno-GAZ SPA Ultrasonic system, Italy, Parma) was used at a frequency of 60 Hz and power of 130 W.

2.3 | Fabrication of GO

GO was synthesized according to modified hummer's technique.[34] Typically, 2.0 g of graphite powder, 1.0 g of sodium nitrate and 6 g of potassium permanganate were added to 60 ml of sulfuric acid (98%) and stirred in an ice bath for 90 min. Then, the reaction mixture was placed in a 40 °C water bath and stirred for 2 hr, followed by adding 150 ml of deionized water. Consequently, the temperature was elevated to 98 °C and stirred for 30 min. After the temperature reduced to 60 °C, 10 ml of H_2O_2 (30%) was added and stirred for another 2 hr. The resulting product was filtered and washed with hydrochloric acid (5%) and deionized water until the pH of the washing water becomes neutral, and afterward dried at 60 °C for 12 hr.

2.4 | Preparation of GO-NH_2

GO was placed in a 110 °C oven for 12 hr to remove the adsorbed water. GO was modified with APTES ($H_2N(CH_2)_3Si(OCH_2CH_3)_3$) as follows: 20 mg of GO was dispersed in 20 ml of ethanol for 15 min using an ultrasonic bath. Then APTES (1 wt%) was added and refluxed at 75 °C for 12 hr. The obtained product was washed with ethanol to remove additional APTES and dried at 60 °C for 10 hr.

2.5 | Preparation of GO/COF

0.20 g of GO-NH_2, 0.5 g (3.96 mmol) of melamine, 0.5 g (3.73 mmol) of terephthaldehyde and 25 ml of DMSO were mixed and transferred to a 150 ml Teflon-lined autoclave, sealed and heated in an oven at 180 °C for 12 hr. After cooling, the resulting solid was collected by filtration, washed by ethanol several times, and dried overnight at room temperature. Schematic illustration of the all steps for the synthesis of GO/COF hybrid material is shown in Figure 1.

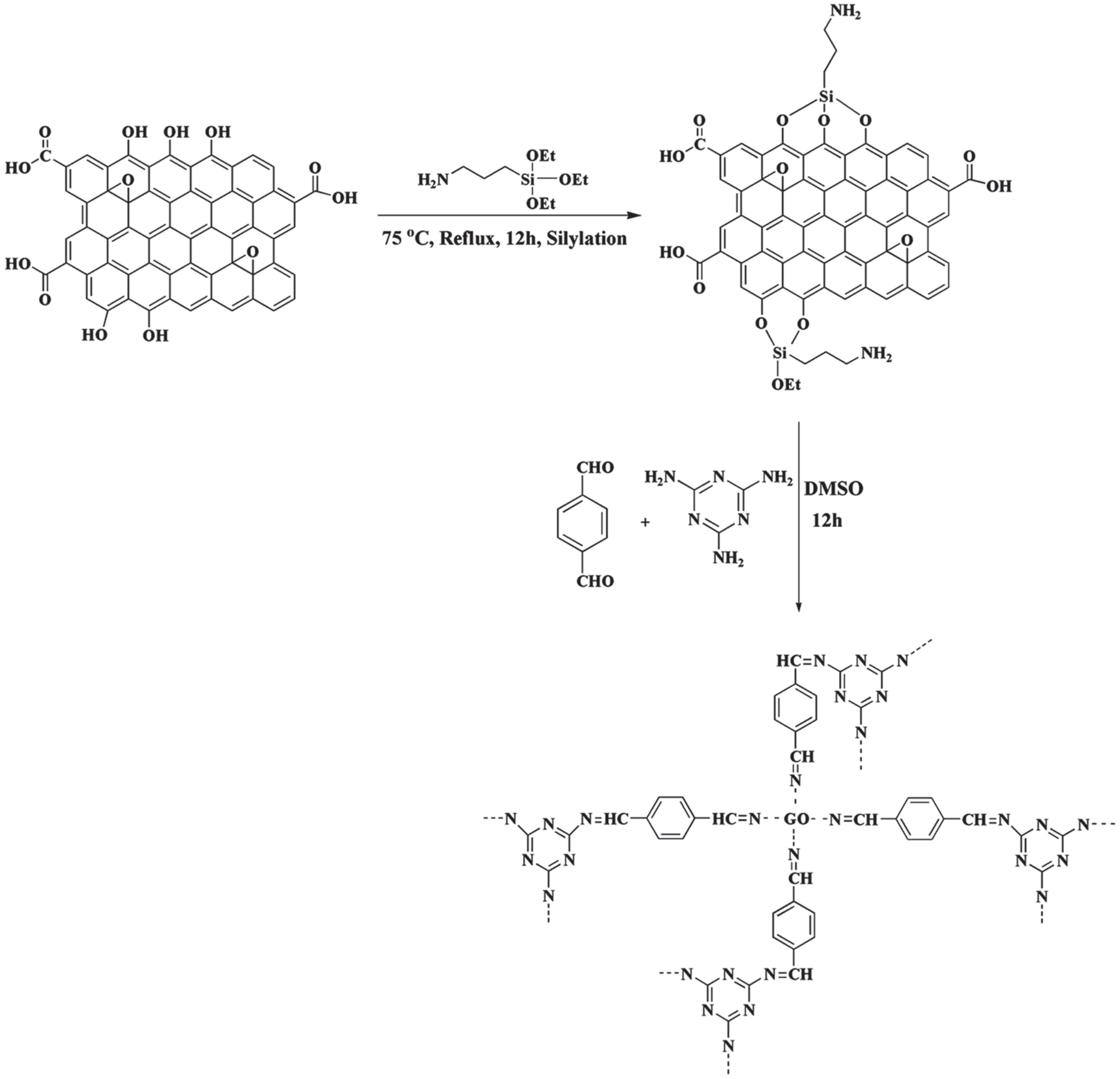


FIGURE 1 Schematic representation of the preparation of GO/COF

2.6 | General procedure for the Knoevenagel condensation using GO/COF as a catalyst

A mixture of various aldehydes (1 mmol), malononitrile (1.5 mmol) and GO/COF (15 mg) was stirred at room temperature. TLC was utilized to monitor the progress of the reaction. After the completion of the reaction, the catalyst was centrifuged. Then, the catalyst was recycled, washed several times with ethanol and water, and reused after drying. Then, the recovered catalyst was reused in eight runs under similar conditions as the first run to exhibit the recyclability and stability of the prepared catalyst.

3 | RESULTS AND DISCUSSION

3.1 | Fabrication of GO/COF

GO/COF hybrid material was prepared using the solvothermal technique. After the preparation of GO, it was functionalized with APTES, to form amine-functionalized GO. Then, COF was synthesized on the surface of $GO-NH_2$ by covalently linking melamine and terephthaldehyde through the condensation reaction to form the GO/COF hybrid material (Figure 1).

3.2 | Characterization of GO/COF

Figure 2 indicated the FT-IR spectra of GO, $GO-NH_2$ and GO/COF, the absorption band around 3430 cm^{-1} in GO is contributed to O-H stretching vibration and the absorption bands appeared at 1708 and 1039 cm^{-1} correspond to C=O and C-O stretching vibrations in carboxyl and epoxy groups. An absorption peak at 1623 cm^{-1} is contributed to C=C skeletal vibrations. In the FT-IR spectrum of $GO-NH_2$, two additional absorption bands at 2940 and 2880 cm^{-1}, revealing of the asymmetric and symmetric stretching vibrations of C-H bonds. The additional absorption bands at 1547 and 797 cm^{-1} are assignable to the symmetric stretching and out-of-plane bending vibrations of N-H band, respectively. The two absorption bands observed at 1116 and 1030 cm^{-1} correspond to the Si-O-Si and Si-O-C stretching vibrations. Besides, the intensity of the absorption band around 3400 cm^{-1} that is characteristic of the surface OH groups considerably decreased, signifying that the silylation happened through reaction with surface OH groups. From the obtained spectral data, it can be realized that APTES has been grafted on GO. The FTIR spectrum of GO/COF revealed a series of new stretching vibrations at 1562, 1500, and 1357 arising from the C=N, C=C, and C-N bonds, respectively, were observed showing condensation and tautomerization.

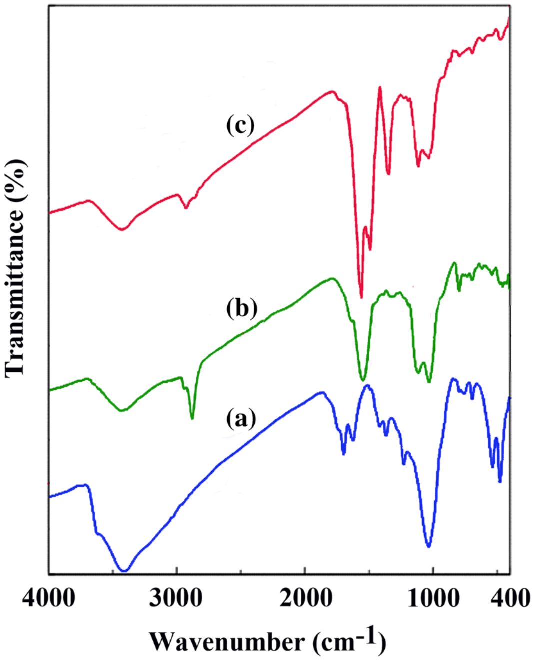


FIGURE 2 FT-IR spectra of GO (a), $GO-NH_2$ (b) and GO/COF (c)

The XRD patterns of GO and GO/COF hybrid are shown in Figure 3. The diffraction peak of GO is observed at 10.2° revealing of the (001) plane of GO. The diffraction pattern of GO/COF hybrid is indicated the three peaks at 9.0, 26.0° and 43.0°. Compared with the pure GO peak, there are no diffraction peaks belonging to the GO sheets in GO/COF. This result is ascribed to the formation of COF between the layers of GO, which

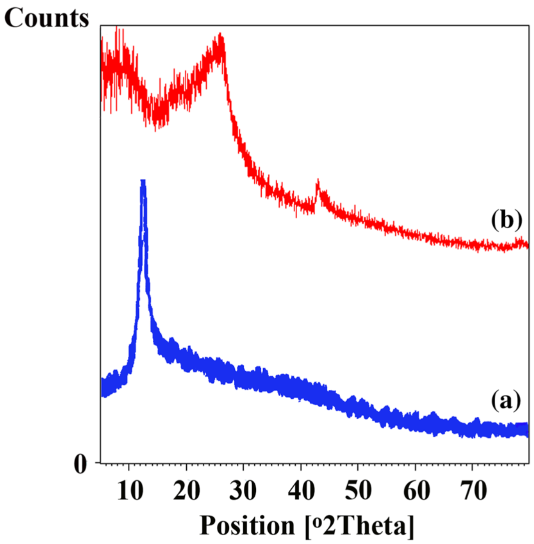


FIGURE 3 XRD patterns of GO (a) and GO/COF (b)

might destroy the regular layer stacking of GO and exfoliate the GO nanosheets, resulting in the disappearance of the GO peak.

Figure 4 shows FE-SEM images of GO (a) and GO/COF (b). FE-SEM image of GO/COF shows the puffy nanoparticles growth of COF on GO surfaces. Furthermore, the puffy nanoparticles of COF are located between GO plates, which prevent from collapsing of the GO plates and provide a suitable surface area. In addition, the EDX analysis of the prepared catalyst confirms the presence of carbon, nitrogen, oxygen, and Si (Figure 5).

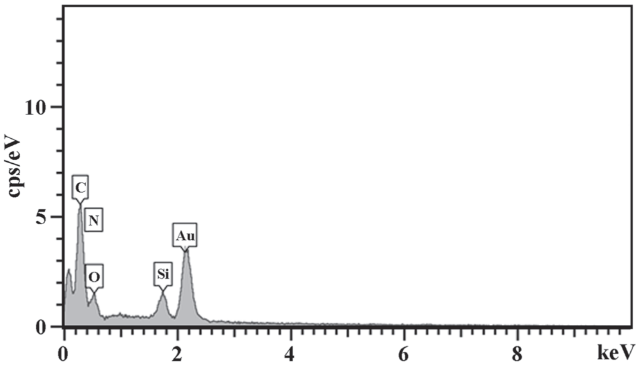


FIGURE 5 EDX spectrum of GO/COF

3.3 | Catalytic activity test

The catalytic application of GO/COF was examined in the Knoevenagel reaction under diverse conditions (Table 1). For the optimization of the reaction conditions, the reaction between malononitrile with benzaldehyde in the presence of GO/COF as a catalyst was designated as a test reaction. The reaction was performed at 5, 10, 15 and 20 mg of GO/COF loading. With increasing of catalyst loading from 5 to 15 mg, the yield was enhanced and the best result in an appropriate time was obtained using 15 mg of catalyst (Table 1, entry 4). By increasing the catalyst loading to 20 mg no change in the yield of the product is observed (Table 1, entry 5). The effect of different solvents such as H_2O, EtOH, CH_2Cl_2 and CH_3CN and solvent-free conditions is also investigated and the results reveal that the yields in H_2O and EtOH solvents are lower than solvent-free conditions (Table 1, entries 6 and 7). It might be attributed to the solvation of the active functional groups by these solvents and hydrogen-bonding between active protonic sites of GO/COF and these solvents which declines the catalytic efficiency. Hence, the use of 15 mg of the catalyst under the solvent-free conditions at room temperature is designated as optimum conditions. After the optimization of the conditions, the generality and the scope of this system are examined using several aromatic aldehydes bearing both electron-donating and electron-withdrawing groups. Based on the obtained results all substrates give the corresponding products in relatively high yield in very short reaction time as reveal in Table 2. The benzaldehyde derivatives containing electron-withdrawing groups such as -NO_2, and -Cl are transformed to the corresponding products with a high yield (Table 2, entries 2–4), whereas the benzaldehyde derivatives possessing electron-donating moieties including -OCH_3, -CH_3, and -OH provide the lower yields (Table 2, entries 5–7). This result proves that the benzaldehyde derivatives having electron-withdrawing groups are slightly reactive compared to those with electron-donating moieties.

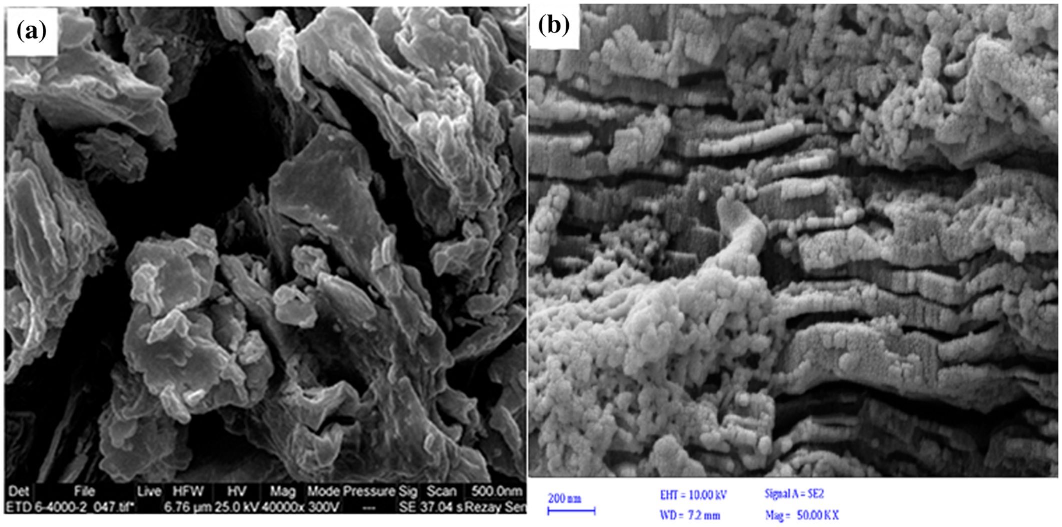
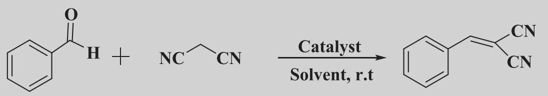


FIGURE 4 SEM images of GO (a) and GO/COF (b)

TABLE 1 Effect of catalyst loading and solvent in the Knoevenagel condensation of malononitrile with benzaldehyde



Entry	Catalyst (mg)	Solvent	Time (min.)	Yield (%)
1	-	-	240	-
2	5	-	10	75
3	10	-	10	89
4	15	-	10	98
5	20	-	10	96
5	15	H_2O	10	84
6	15	EtOH	10	91
7	15	CH_2Cl_2	10	38
8	15	CH_3CN	10	43

Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.5 mmol), catalyst (15 mg), room temperature.

TABLE 2 The Knoevenagel condensation of aldehydes with malononitrile in the presence of GO/COF

Entry	R	Time (min.)	Yield (%)
1	H	90	98
2	4-NO_2	45	100
3	4-Cl	28	99
4	2-Cl	55	93
5	4-MeO	60	89
6	4-Me	60	87
7	4-OH	60	84
8	2-OH	50	86
9	4-Br	30	98

Reaction conditions: aldehyde (1 mmol), malononotrile (1.5 mmol), catalyst (15 mg), room temperature and solvent-free.

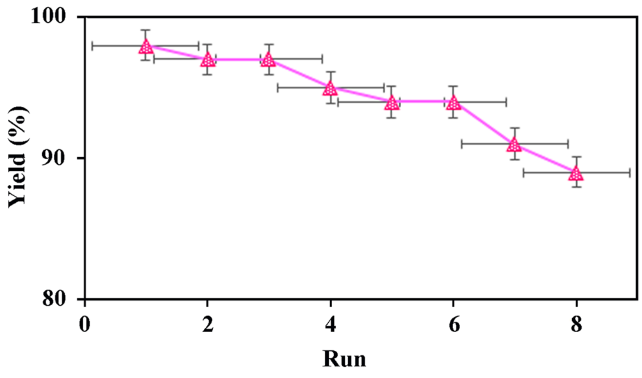


FIGURE 6 Reusability of the GO/COF

TABLE 3 Comparison of the proposed catalyst with reported catalysts for the Knoevenagel condensation of benzaldehyde and malononitrile

Catalyst	Amount	Time	Solvent	Temp.(°C)	Yield (%)	Ref.
KOH/SnO_2	50 mg	15 min	DMF	r.t.	97.0	[35]
ZIF-8	20 mg	3 hr	Toluene	r.t.	100.0	[36]
Amino-functionalized Zn-MOF	0.02 mmol	6 hr	Solvent-free	60	99.9	[37]
KGCN-RGO	10 wt%	5 min	Ethanol	50	99.0	[38]
RhPt/TC@GO NPs	2 mg	10 min	water/methanol	r.t.	99.0	[39]
GO/COF	15 mg	10 min	Solvent-free	r.t.	98.0	Our work

In order to prove the heterogeneity of the catalyst, the filtration experiment of GO/COF was performed. The catalyst was separated from the reaction mixture after 5 min, and the resulting filtrate was further stirred for 5 min. The conversion yield of the benzaldehyde remains unchanged for the filtrate even at extended time, indicating that the catalytic process is heterogeneous and there is not any progress for the reaction in the homogeneous phase.

3.4 | Reusability of GO/COF

To examine the reusability of GO/COF, after the completion of the reaction, the catalyst was collected and separated and then reused under similar conditions as the first run. This experiment was repeated eight times and it was found that GO/COF is stable under the applied conditions and can be reused at least eight times without a considerable decreasing in its catalytic activity (Figure 6).

3.5 | Comparison of the proposed catalyst with previously reported catalysts for the Knoevenagel condensation

The comparison between the performance of the Knoevenagel condensation based on the GO/COF catalyst and some previously reported catalysts involving the Knoevenagel condensation is listed in Table 3. It was found that GO/COF exhibited advantages in terms of cost-effectiveness and simplicity and low temperature.

4 | CONCLUSIONS

In this work, GO/COF catalyst was constructed and characterized by FT-IR, XRD, EDX and SEM techniques. The SEM images displayed that the COF nanoparticles are well dispersed on the surfaces of GO. This study examined the Knoevenagel condensation and synthesis of benzylidenemalononitrile derivatives in the presence of GO/COF as a powerful heterogeneous catalyst. The Knoevenagel products were achieved in high yields under moderate conditions and short reaction time (10 min). The other features of the present study include straightforward preparation and cost-effective of catalyst, accomplishing reaction at room temperature, solvent-free media and low loading of catalyst.

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