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PII:	S1381-1169(14)00289-1
DOI:	http://dx.doi.org/doi:10.1016/j.molcata.2014.06.038
Reference:	MOLCAA 9179
To appear in:	Journal of Molecular Catalysis A: Chemical
Received date:	22-10-2013
Revised date:	21-6-2014
Accepted date:	28-6-2014

Please cite this article as: S.M. Islam, A.S. Roy, R.C. Dey, S. Paul, Graphene based material as a base catalyst for solvent free Aldol condensation and Knoevenagel reaction at room temperature, *Journal of Molecular Catalysis A: Chemical* (2014), http://dx.doi.org/10.1016/j.molcata.2014.06.038

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# Graphene based material as a base catalyst for solvent free Aldol condensation and Knoevenagel reaction at room temperature

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#### Abstract

Graphene oxide (GO) acts as a highly active heterogeneous base catalyst for a wide variety of reactions. Here we have described the catalytic activities of GO in the condensation reaction of various substituted benzaldehydes with acetophenone (aldol condensation) and with active methylene compound malononitrile (Knoevenagel reaction) at room temperature under solvent free condition. GO is characterized by powder x-ray diffraction (XRD), UV-visible spectra, Fourier transform infrared spectroscopy (FT-IR) and AFM. The experimental results showed that the GO had higher catalytic activity and it can be recycled without significant loss of its activity.

*Keywords:* Graphene oxide; Heterogeneous catalysis; Aldol condensation; Knoevenagel reaction; room temperature.

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#### 1. Introduction

The aldol reaction is one of the most powerful methods of forming carbon-carbon bonds and it has tremendous synthetic applications [1]. Biological systems have perfected this stereospecific transformation by using enzymes aldolases. Despite their lack of large-scale compatibility and their narrow substrate specificity, aldolases represent a great source of inspiration for the development of catalysts. In recent years, several aldol reactions using acid or base catalysts have been reported including iron-catalyzed cross-aldol reactions [2], proline-loaded catalysts for stereoselectivity [3], aldol-type reactions of lithium enolate [4] and silvl enolate [5, 6]. Currently, due to low toxicity, operational simplicity and efficiency, compared to traditional metal-based catalysts, there is much interest in organocatalysts [7]. Organocatalysis is the acceleration of chemical reactions with a sub-stoichiometric amount of an organic compound, which does not contain a metal atom. Organocatalysts that can promote aldol reactions have been reported by research groups [8, 9]. However; their drawbacks also have been realized. The major limitations using organocatalyst catalyzed reactions are high catalyst loadings and the difficulty of recovering the catalyst [10, 11]. An alternative strategy is to design recyclable and subsequently reusable versions of organocatalysts [12].

The Knoevenagel reaction of aldehydes with compounds containing activated methylene groups has been widely employed in the synthesis of several fine chemicals, intermediates of anti-hypertensive drugs and calcium antagonists [13-16]. Cinnamic acid, its ester and carboxylic functional derivatives, very important components in flavors, perfumes, synthetic indigo and pharmaceuticals, are synthesized by Knoevenagel condensation. This reaction is conventionally catalyzed by alkali metal hydroxides or by organic bases like primary, secondary and tertiary amines under homogeneous conditions with attendant difficulties in catalyst recovery and recycling [17-19]. Over the last few years, a wide range

of solid catalysts have been investigated for these reactions such as amino-functionalized mesoporous silica [20], diamine-functionalized mesopolymers [21], amine-functionalized mesoporous zirconia [22], Mg–Al mixed oxide on hexagonal mesoporous silica [23], biguanide-functionalized mesoporous silica [24], acid–base bifunctional mesoporous MCM-41 silica [25], amine-functionalized superparamagnetic nanoparticles [26], chitosan hydrogel [27], acrylic resin immobilized lipase [28], organic–inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts [29], IRMOF-3 [30] and ZIF-8 [31].

Nowadays, Graphene oxide (GO) is a hot topic in the fields of materials science and synthetic chemistry due to its unique features. Due to the presence of various functionalities on the surface of graphene oxide, it shows huge catalytic activity. In addition, it has large specific surface area [32-34], good biocompatibility and high adsorption capacity [35, 36]. This large specific surface area and presence of various functional groups are responsible for its enormous catalytic activity in synthetic chemistry. Also high thermal and electrical conductivity [37] and excellent mechanical strength have found enormous applications in the development of composite materials and catalyst. These composites can be used over a wide range of applications, including memory devices [38], energy storage [39], catalysis [40-44], solar cells [45], molecular imaging [46] and drugs delivery [47]. In a recent precedent, sulfated graphene obtained by hydrothermal sulfation of reduced graphene oxide with fuming sulfuric acid at 180 °C was tested as catalyst for the esterification of acetic acid, the Pechmann condensation and hydration of propylene oxide [48]. The difference between the material used in this prior work and the present one is that we are using here directly the GO samples obtained by the modified Hummers method followed by exfoliation in aqueous solution without any subsequent treatment. Our GO is, therefore, more conveniently prepared and does not require additional and hazardous treatments. The activity of GO as a base catalyst was tested for the direct aldol reactions using aldehydes and acetophenone as

reacting substrates and Knoevenagel condensation of aldehydes and active methylene compounds at room temperature under solvent free condition.

#### 2. Experimental

#### 2.1. Materials and reagent

All reagents and solvents were purchased from commercial sources and were further purified by standard procedures. Graphite powder (<20 micron), hydrogen peroxide (30 %) were purchased from Aldrich and used as received. Other reagents were purchased from Merck and used as received.

UV-visible spectra were measured using Shimatzu UV- 2550 spectrophotometer with a quartz cell of 1 cm path length. Fourier transform infrared (FTIR) spectra were measured with Nicolet 6700 (Thermo Scientific) instrument using KBr plates. Diluted graphene oxide (GO) was dropped onto silicon substrate and dried at room temperature to prepare specimens for X-ray diffraction measurements. X-Ray diffraction pattern was measured at room temperature using Shimadzu, XRD-6000, 40 kV, 20 mA with Cu K radiation,  $\lambda = 1.5418$  Å. Diluted GO was deposited on glass slide and then AFM was measured using VEECO DICP II autoprobe (model AP 0100). <sup>1</sup>H NMR spectra were recorded at room temperature on Bruker Avance DPX-400 spectrometers using TMS as internal standard.

#### 2.2. Preparation of colloidal graphene oxide (GO)

Graphene oxide (Fig. 1) was synthesized via a modified Hummer's method. In brief 200 mg graphite powder, 100 mg sodium nitrate and 5 mL concentrated  $H_2SO_4$  were mixed and cooled to 0  $^{0}C$ . The solution was kept under vigorous stirring followed by addition of 600 mg KMnO<sub>4</sub> in a stepwise manner keeping the temperature below 20  $^{0}C$ . Next, the temperature of the solution was slowly raised to 35  $^{0}C$  and kept at this condition for 30 min. This step is important to control the graphene oxide size since longer oxidation leads to smaller graphene oxide sheets. Next, 10 mL water was added to the whole solution leading to

a rise in temperature to ~100  $^{0}$ C and this temperature was maintained for 15 min. The whole solution was then mixed with 30 mL water followed by addition of 500 µL 3% H<sub>2</sub>O<sub>2</sub> that reduces the residual permanganate. The light yellow precipitate was washed with warm water 7–8 times. Finally, this was dispersed in 20 mL distilled water with 15 min sonication at a concentration of 1.5 mg mL<sup>-1</sup>. Longer sonication should be avoided to control the size of graphene oxide. The solution was centrifuged at 3000 rpm to remove large particles and the solution was used as colloidal graphene oxide.



Fig. 1. A schematic model of a single sheet of graphene oxide

#### 2.3. General procedure for the aldol condensation

A reaction mixture containing aldehyde (1.2 mmol), acetophenone (1 mmol) and GO in water (0.5 mL) were stirred at room temperature for appropriate time. The completion of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with dichloromethane followed by subsequent separation of organic and aqueous layers by separating funnel. Organic layer was dried over Na<sub>2</sub>SO4 and concentrated under reduced pressure and obtained crude product was purified by column chromatography using EtOAc/hexane as eluent. All the yields were calculated from isolated products.

#### 2.4. General procedure for Knoevenagel condensation reaction

The organocatalyst GO was stirred with 2 mmol of manolonitrite for 30 min at room temperature in 25 mL RB flask. To this mixture corresponding aldehyde (1 mmol) was added and the resulting mixture was stirred for appropriate time. After completion of the reaction, the reaction mixture was diluted with dichloromethane followed by subsequent separation of organic and aqueous layers by separating funnel. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents, the crude product was purified by column chromatography using EtOAc/hexane as eluent. All the yields were calculated from isolated products.

#### 3. Results and discussion

#### 3.1. Characterization

Here, Colloidal graphene oxide was prepared first using Hummer's method. The presence of various chemical functionalities on graphene oxide nanosheets and their dispersion in water were examined by XRD, FTIR, UV-Vis Spectroscopy. Fig. 2 shows the XRD patterns obtained for graphene oxide powder. A sharp peak at  $2\theta = \sim 10.6^{0}$  for graphene oxide, corresponding to an interlayer spacing of ~0.9 nm (d spacing). The oxidation of graphite powder leads to the introduction of various functional groups. These functional groups are bonded on both basal planes and edges of graphitic layers, as well as the presence of trapped water molecules between these layers, expanding the interlayer spacing in graphene oxide [50].



Fig. 2. XRD spectra of graphene oxide

Further, the nature of the chemical functionalities was characterized by FT-IR (Fig. 3). An intense and broad peak appeared at 3408 cm<sup>-1</sup>, attributed to the stretching mode of an O–H bond, reveals the abundance of hydroxyl groups in graphene oxide. The band at around 2915 cm<sup>-1</sup> appears due to C-H stretching (symmetric and asymmetric) vibrations. The band at 1709 cm<sup>-1</sup> (vC=O) represents carboxylic acid and carbonyl groups. Another band at 1591 cm<sup>-1</sup> represents C=C stretching vibration in grapheme oxide. Furthermore, the bands at 1230 cm<sup>-1</sup> and 1079 cm<sup>-1</sup> are attributed to the presence of C–OH and C–O groups, respectively, in graphene oxide.



Fig. 3. FT-IR spectra of graphene oxide

The UV-Vis spectrum of graphene oxide (Fig. 4) exhibits a strong absorption peak at 230 nm, which is attributable to the  $\pi$ - $\pi$ \* transition of graphitic C–C bonds and a shoulder at ~300 nm is assigned to the n- $\pi$ \* transitions of C=O bonds. Thus, similar to the XRD and FTIR, UV-vis spectra provided evidence of the presence of an ample number of oxygen functionalities, such as hydroxyl, epoxide, carboxylate and carbonyl on graphene oxide. AFM study was conducted for as synthesized GO (Fig. 5). It shows that as synthesized graphene oxide has a typical thickness of ~1 nm and length is around ~1 µm. This result reveals that as synthesized GO is of a single layer and the obtained GO is of micron size.



Fig. 4. UV-vis spectra of graphene oxide



Fig. 5. AFM image and line analysis of graphene oxide

#### 3.2. Catalytic activity of Graphene Oxide

The use of metal-free carbons instead of metal supported catalyst in synthetic chemistry has largely progressed over the last decade. Since GO contains many functional groups (i, e –OH, -COOH, -CO-, -O-), we have decided to investigate the catalytic activity of GO in the base catalysis direct Aldol condensation and Knoevenagel condensation reactions, respectively.

#### 3.2.1. Direct aldol reaction of aldehydes

Initial efforts sought to explore the base catalytic properties inherent to GO as a means to effect C=C bond forming reaction via aldol condensation followed by the elimination of water. In organic synthesis, the aldol reaction is one of the most important carbon-carbon bond forming processes. The  $\alpha,\beta$ -unsaturated carbonyl compounds are subunits of many natural products and often used as precursors in the preparation of flavonoids and isoflavonoids. The efficiency of GO as a base catalyst was first tested in aldol reaction over various electron-withdrawing and electron-donating aromatic aldehydes with acetophenone under solvent free condition. Initially, we optimized the condition using the reaction of acetophenone with benzaldehyde under different experimental conditions.

The condensation of acetophenone and benzaldehyde is illustrated in the reaction Scheme 1. Before attempting a detailed catalytic work, a noncatalytic reaction between acetophenone and benzaldehyde was examined, and it was observed that at room temperature only 3% formation of product was detected, indicating that the reaction is not taking place in the absence of a catalyst (Table 1, entry 1). The condensation of benzaldehydes and acetophenones was reported to be catalyzed by acid or bases [50, 51].



**Scheme 1.** Aldol condensation between acetophenone and benzaldehyde catalyzed by GO

**Table 1.** Room temperature aldol reaction between acetophenone and aromatic aldehydes catalyzed by GO.<sup>a</sup>

		GO RT	R	3
Entry	R	<b>R</b> <sub>1</sub>	Product	Yield (%) <sup>b</sup>
1°	Н	Н	3a	3
$2^{d}$	Н	Н	-	-
3	Н	Н	3a	89
4	Н	-CH <sub>3</sub>	3b	84
5	Н	-OCH <sub>3</sub>	3c	85
6	Н	-OH	3d	87
7	Н	-Cl	3e	91
8	-CH <sub>3</sub>	Н	3f	93
9	-Cl	Н	3g	92

<sup>a</sup> Reaction conditions: acetophenone (1 mmol), aldehyde (1.2 mmol), catalyst (0.5 mL), solvent-free, at room temperature, 4 h. <sup>b</sup> Isolated yield. <sup>c</sup> without catalyst. <sup>d</sup> reaction at 0 <sup>o</sup>C.

The effect of temperature plays an important role in the aldol condensation reaction. It was examined in the temperature range between 0  $^{0}$ C and 50  $^{0}$ C, in the absence of solvent and the results are illustrated in Fig. 6. The above reaction did not proceed at 0  $^{0}$ C even after several hours (Table 1, entry 2). Temperature increase leads to a higher yield. The yield of product for a reaction time of 4 h at 10  $^{0}$ C is only 32%, whereas at room temperature the conversion is 89%. For the same time of 4 h, an increase of only 2% is observed when the temperature is raised from room to 50  $^{0}$ C. For this reason, room temperature was employed as the ideal temperature to continue with the analysis of other reaction variables. However, the

catalytic performance of GO as a function of the reaction time in the condensation of benzaldehyde and acetophenone was studied at three temperatures under solvent-free conditions (Fig. 6). The catalytic activity for the three temperatures was found to increase rapidly with the reaction time up to 4 h, and then remains almost constant. The constant value is probably due to the blockage of the catalytic center by the high concentration of product.



**Fig. 6.** Effect of reaction temperature and time on the catalytic performance of GO in aldol condensation reaction between benzaldehyde and actophenone.

To show the generality of the process, we applied the optimized conditions to reactions of acetophenone with a variety of aryl-benzaldehydes and the results of this study are summarized in Table 1. The results showed that, in general, the reactions were clean and products were isolated by liquid column chromatography in pure form without further purification. Finally, we studied the influence of the substituting groups on the aromatic ring of acetophenones and benzaldehydes. The reactions of aldehydes bearing electron-donating

groups such as -Me, -OMe and -OH gave yields similar to those of the corresponding reaction with unsubstituted benzaldehyde (Table 1, entries 4-6). The presence of electronwithdrawing groups in acetophenone such as -Cl gave a comparable rate of condensation, even when the aldehyde contains an electron-withdrawing group such as -Cl, presumably due to ease of formation of the enolate anion in the first step (Table 1, entries 7 and 9). Then we tested several aldol reactions between various aromatic aldehydes and acetone using GO as the catalyst. As shown in Table 2, the yields of reactions are kept moderate by carrying the reaction at room temperature.

**Table 2.** Room temperature aldol reaction between acetone and aromatic aldehydes catalyzed by GO.<sup>a</sup>

R		+ 1 -	GO RT R	
-	Entry	R	Product	Yield (%) <sup>b</sup>
-	1	Н	5a	72
	2	-CH <sub>3</sub>	5b	67
	3	-OCH <sub>3</sub>	5c	65
	4	-Br	5d	69
	5	-Cl	5e	78

<sup>a</sup> Reaction conditions: acetophenone (1 mmol), aldehyde (1.2 mmol), catalyst (0.5 mL), solvent-free, at room temperature, 4 h. <sup>b</sup> Isolated yield

#### 3.2.2. Knoevenagel condensation reaction

The catalytic activity of the GO was tested for the Knoevenagel condensations of benzaldehyde with malononitrile to produce benzylidene malononitrile as the major product (Scheme 2). Romero [52] reported amine-functionalized SBA-15 giving 98% conversion at 105 <sup>o</sup>C towards the Knoevenagel condensation reaction. However, at room temperature amine-functionalized MCM-41 showed 81% conversion as reported by Sugi [53]. The inherent disadvantages associated with these reports were either higher temperature or longer

reaction time. However, in this study we got better results due to the co-operative effect of the acidic and basic sites present in the GO.



Scheme 2. Knoevenagel reaction of benzaldehyde with malononitrile using the GO catalyst.

As motivated by the principles of green chemistry, it was decided to carry out the reaction under room temperature and solvent free conditions. Initially it was found that no reaction occurred in the absence of GO, whereas GO effectively catalyzed Knoevenagel condensation reactions producing benzylidene malononitrile in high yields. This may be due to the presence of basic sites in GO, which is responsible for the activity.

With such results in hand, we then decided to investigate the effects of various reaction parameters on the condensation of benzaldehyde with malononitrile to produce benzylidene malononitrile using GO as a catalyst. The effect of a benzaldehyde to malononitrile molar ratio on the reaction conversion was studied by carrying out the reaction at molar ratios of 1:4, 1:3, 1:2, and 1:1 respectively (Fig. 7). At a benzaldehyde: malononitrile molar ratio of 1:2, the catalyst gave the best conversion of 97% in 4 h. The selectivity towards benzylidene malononitrile was 99%. However, on further increasing the malononitrile concentration, though the conversion remains almost the same, the product selectivity decreased. This suggests that the self-condensation of malononitrile takes place when its concentration in the reactant mixture increases.



**Fig. 7.** The effect of molar ratios of benzaldehyde: malononitrile towards Knoevenagel condensation.

Results showing the influence of reaction time on conversion and product selectivity in the condensation reaction over the GO catalyst are presented in Fig. 8. As can be seen from the figure, the conversion and selectivity are increasing with time up to 4 h. Then the reaction became slower and reached a plateau. The conversion and selectivity values show no appreciable change with further rise in reaction time.

The GO was employed in the reaction, where the catalyst activity is mainly due to the structural basicity. In order to demonstrate the versatility of GO for Knoevenagel condensation, we submitted various substituted aldehydes and substrates containing active methylene groups with the molar ratio 1:2. In the case of substituted benzaldehyde containing electron donating groups (–CH<sub>3</sub>), the conversion decreased while the electron withdrawing substituents (-NO<sub>2</sub>) on the aromatic ring substantially increased the conversion (Table 3).



Fig. 8. Influence of reaction time on Knoevenagel condensation







<sup>&</sup>lt;sup>a</sup> Reaction conditions: malononitrile (2 mmol), aldehyde (1 mmol), catalyst (0.5 mL), solvent-free, at room temperature,. <sup>b</sup> Isolated yield

In the case of electron withdrawing groups the possibility of attack of the carbanion (generated from the active methylene group) on the carbonyl carbon is more when compared to that of electron donating groups. Condensation of various benzaldehydes with various substrates possessing active methylene groups is shown in Table 4. The substituents with electron withdrawing nature stabilize the carbanion (due to resonance) compared to those having electron donating nature. So malononitrile displays the maximum conversion among all other substrates.

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	() + н₂с			_X
	R	Υ KI	Y Y	
Entry	R	Y	X	Yield (%) <sup>b</sup>
1	Н	COOEt	COOEt	90
2	Н	CN	CN	97 (99) <sup>c</sup>
3	Н	CN	COOEt	94 (100/0) <sup>d</sup>
4	OCH <sub>3</sub>	CN	COOEt	93 (100/0) <sup>d</sup>
5	Cl	CN	COOEt	92 (100/0) <sup>d</sup>
6	NO <sub>2</sub>	CN	COOEt	95 (100/0) <sup>d</sup>
7	ОН	CN	COOEt	94 (100/0) <sup>d</sup>
8	Н	CN	Cl	90 <sup>c</sup>
9	Н	CN	СООН	89 <sup>c</sup>
10	Н	CN	Ph	84 <sup>c</sup>

**Table 4.** Effect of various active methylene groups towards Knoevenagel condensation.<sup>a</sup>

<sup>a</sup> Reaction conditions: active methylene compound (2 mmol), aldehyde (1 mmol), catalyst (0.5 mL), solvent-free, at room temperature, 4 h. <sup>b</sup> Isolated yield. <sup>c</sup>Yield determined by GC analysis.  ${}^{d}E/Z$  ratio, Determined by <sup>1</sup>H NMR of the product.

#### 3.3. Comparison with other reported system

Base catalyzed Aldol condensation of benzaldehyde with acetophenone or Knoevenagel condensation of benzaldehye with malononitrile under heterogeneous conditions over a variety of catalysts has been studied. Table 5 provides a comparison of the results obtained for our present catalytic system with those reported in the literature [20, 29, 54-58]. From Table 5, it is seen that present catalyst exhibited higher yields compared to the other reported system [20, 29, 54-58]. Reactions conducted at room temperature, shorter reaction time was required for these reactions and most importantly above coupling reactions occurred under solvent free condition using GO catalyst.

**Table 5.** Comparison of catalytic activity of the GO catalyst in the Aldol condensation and

 Knoevenagel condensation with other reported systems

Reaction	Catalyst	<b>Reaction Conditions</b>	Yield (%)	Ref.
Aldol condensation	aminopropyl-functionalized silica sol–gel	1.3 mmol benzaldehyde, 1 mmol acetophenone, 100 mg catalyst, 140 <sup>0</sup> C, 4 h, solvent free	87	54
	Fe <sub>3</sub> O <sub>4</sub> @Fe(OH) <sub>3</sub>	0.2 mmol aldehyde, 1 mmol acetophenone, 128 mg catalyst, toluene, RT, 20 h	38	55
	GO	1.2 mmol benzaldehyde, 1 mmol acetophenone, 0.5 mL catalyst (1.5 mg/mL), RT, 4 h, solvent free	89	This study

Knoevenagel condensation	amino-functionalized mesoporous silica	1 mmol benzaldehyde, 1 mmol malononitrile, 20 mg catalyst, RT, 6 h, ethanol	90	20
	М3	4.61 mmol benzaldehyde, 5.24 mmol malononitrile, 0.0297 g catalyst, $100^{0}$ C, 6 h, solvent free	93	29
	HAP-γ-Fe <sub>2</sub> O <sub>3</sub>	2 mmol benzaldehyde, 2 mmol malononitrile, 0.025 g catalyst, $30^{0}$ C, 1 h, water	64	56
	GO	1 mmol benzaldehyde, 2 mmol malononitrile, 0.5 mL catalyst (1.5 mg/mL), RT, 4 h, solvent free	97	This study
	mp-PBI	1 mmol benzaldehyde, 1 mmol malononitrile, 50 mg catalyst, RT, 20 h, acetonitrile	100	57
	mpg-C <sub>3</sub> N <sub>4</sub> -tBu	1 mmol benzaldehyde, 1 mmol malononitrile, 50 mg catalyst, $70^{0}$ C, 2 h, acetonitrile	67	58

### 3.4. Recycling of the catalyst

Furthermore, we checked the recycling of the graphene oxide catalyst by choosing the reaction of benzaldehyde with acetophenone or with malononitrile as a model reaction. After

completion of the reaction, the catalyst could easily be recovered by simple extraction of the reaction mixture with dichloromethane, the as-obtained aqueous layer containing catalyst used for the subsequent experiments (5 runs). The results of these experiments are shown in the Fig. 9. As shown, the yield of the product was found to be similar during these experiments, establishing the efficient recycling of the catalyst, as well as the heterogeneous nature of the developed methodology.



Fig. 9. Results of recycling tests of GO.

#### 4. Conclusion

In summary, we have synthesized a grapheme oxide through a modified Hummer's method, which can effectively catalyse the aldol reaction as well as knoevenagel condensation reaction. This organocatalyst shows excellent catalytic activity towards direct aldol reactions of different substituted benzaldehydes with acetophenone and acetone at room temperature. GO showed high reactivity with 97% conversion and 99% product selectivity in 8 h towards the Knoevenagel condensation reaction at room temperature under solvent free

condition. Furthermore, the organocatalyst GO can be recovered and reused as the catalyst in the subsequent runs without any loss of activity. In a broader perspective, these results establish GO's potential for use in synthetic chemistry, and it could open new catalytic applications especially in the development of metal free methodologies in future.

#### Acknowledgement

SMI acknowledges Council of Scientific and Industrial Research (CSIR) and Department of Science and Technology (DST), New Delhi, India for funding. ASR acknowledges CSIR, New Delhi, India for his senior research fellowship. We thank the Indian Association for the Cultivation of Science, Kolkata for providing the instrument support.

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### Graphene based material as a base catalyst for solvent free Aldol

### condensation and Knoevenagel reaction at room temperature

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#### **Research Highlights**

- Graphene oxide (GO) was prepared by the modified Hummers method.
- The activity of GO as a base catalyst was tested for the Aldol reaction.
- GO was also used as catalyst for Knoevenagel condensation.
- The activity of GO was tested at room temperature under solvent free condition.
- GO can be reused upto five times.

### **Graphical Abstract**

Graphene based material as a base catalyst for solvent free Aldol

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