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# A new application of nano-graphene oxide as a heterogeneous catalyst in crossed-aldol condensation reaction under solvent-free conditions

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ABSTRACT

Nano-graphene oxide was synthesized by the oxidation of graphite powders. The structural nature of the nano-graphene oxide was characterized by a variety of techniques including XRD, TEM, FT-IR and UV/Vis. The functional groups on its basal planes and edges of nano-grahene oxide play important role in catalytic activity. The catalytic activity of nano-graphene oxide was investigated on Crossed-Aldol condensation reaction. This nanocatalyst was found to be highly efficient in this reaction and products were obtained in good to excellent yields. The recovered nanocatalyst was successfully reused for several runs without significant loss in its catalytic activity.

*Keywords*: *Nano-graphene oxide, Crossed-aldol condensation reaction, Aryl aldehyde.*

## 1. Introduction

In recent years, a two-dimensional single-layered nano-graphene oxide (NGO) has attracted a tremendous amount of attention because of its remarkable properties such as low cost, ease of synthesis, high stability to ambient conditions and novel layered structures [1-3]. NGO exhibits a hydrophilic nature owing to the wide range of oxygen carrying functional groups on its basal planes and edges [4-5]. These functional groups allow NGO to be noncovalently functionalized by DNA [6–8], carbon nanotubes [9] organic molecules [10], and by p-stacking interactions, hydrogen bonding interaction or Vander Waals forces. NGO is readily functionalized with various surfactants, polymeric materials, and nanoparticles in order to provide enormous potential for applications in materials science and engineering [11-12].

Recently, NGO catalyzed reactions such as oxidation of sulfides and thiols, oxidation of benzylic position, and benzyl alcohol, ring opening of epoxides, aza-Michael addition reaction, synthesis of aldehydes or ketones, Friedel–Crafts and addition of indoles to α,β-unsaturated ketones[13-19]. Also, sulfated graphene was tested as catalyst for the esterification of acetic acid, the Beckmann condensation and hydration of propylene oxide [20].

In addition, some studies have demonstrated that immobilizations of transition metal nanoparticles on NGO produce efficient catalysts [21-24].

In continuation with our investigation on crossed-aldol condensation reaction [25], we investigated the new application of catalytic activity of NGO as a heterogeneous catalyst which was synthesized from graphite powder to catalyze crossed-aldol condensation reaction under solvent-free conditions (Scheme 1).

## 2. Experimental

### 2.1. General

All chemicals were purchased from Merck Company and used without purification. Graphite powder was obtained from Aldrich Company. The resulting NGO was characterized by FT-IR, UV/Vis, TEM and XRD patterns. The FT-IR experiments were carried out on a Bruker Vector-22 FT-IR spectrometer (AVATR-370) in a KBr pellet, scanning from 4000 to 600 $cm^{-1}$ at room temperature. The XRD measurements were carried out by using a Bruker $D_8$-advance X-ray diffractometer with Cu $K_\alpha$ radiation (k = 1.5406A°). The TEM measurements were obtained using transmission electron microscopy (TEM) images using Philips CM10 instrument. The UV/Vis spectra were carried out by using a Shimadzu UV-160A spectrometer. The products were also characterized by IR (Perkin-Elmer 783 Infrared spectrophotometer),

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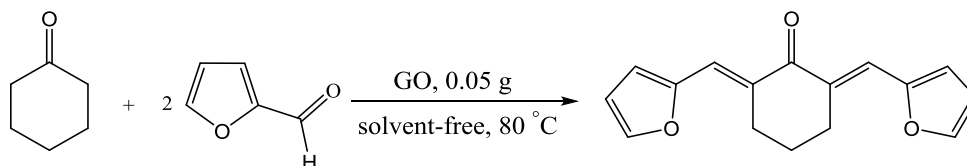
**Scheme 1.** The synthesis of α, ά- bis (substituted-benzylidene) alkanones.

$^1$H and $^{13}$C NMR (Bruker at 400 and 100 MHz in CDCl$_3$ using TMS as internal standard) and Mass spectra (GC-17A Shimadzu & MS-QP 5050 with DI at 70 eV).

### 2.2. Preparation of NGO

The NGO was prepared according to modified Hummers method with small modifications [26,27]. Briefly, to a reaction flask were added graphite powder (3 g), NaNO$_3$ (1.5 g) and concentrated H$_2$SO$_4$ (75 mL), and then cooled on an ice bath. An amount of 9 g of KMnO$_4$ was slowly added over 1 h and stirring for 2 h in an ice-water bath, and the temperature was kept below 20 $^°$C. The mixture was then stirred at 35 (± 3 $^°$C) for 30 min. The flask was then cooled to room temperature and deionized water (150 mL) was slowly added to the mixture, and the temperature was increased to 98 $^°$C. The resultant mixture was further stirred for 2 h at 98 $^°$C. After 15 min, the mixture was further treated with 400 ml of deionized water and 30 mL of 5% H$_2$O$_2$ solution to remove residual permanganate ions. Then, the solution filtered and washed successively with 10% HCl aqueous solution completely until sulfate could not be detected with BaCl$_2$. The resultant solid was recovered and washed with deionized water and ethanol and then dried in air at 40 $^°$C. The brown powder of NGO (4.3 g) was characterized by XRD, TEM, FT-IR and UV/Vis.

### 2.3. General procedure for the synthesis of α,ά-bis (substituted-benzylidene) alkanone derivatives

A mixture of ketone (1 mmol), substituted benzaldehyde (2 mmol) and NGO (50 mg) were stirred at 80$^C$ under solvent-free conditions. The progress of the reaction was monitored by thin layer chromatography. After completion, the product was extracted with ethyl acetate (3×15 mL). The organic layer was dried and concentrated under reduced pressure to obtain the crude product. The product was recrystallized from ethanol to afford pure product and characterized by $^1$H and $^{13}$C NMR, IR and Mass spectroscopy analysis. All of the physical and spectroscopic data were compared with those reported in the literature.

*Selected spectral data:*

*(2E,5E)-2,5-bis (4-methylbenzilidene) cyclopentanone (**Table 2, entry 3**):*

Yellow solid; m.p.= 240-242 $^°$C (lit. [28] 244-246 $^°$C); IR (KBr): $\bar{v}$ = 3080, 3030, 2940, 2880, 2840, 1695, 1630, 1590, 1580, 1550, 1500, 1380, 1277, 1246, 1170, 1124, 980, 810. $^1$H NMR (250 MHz, CDCl$_3$): δ= 2.40 (s, 6H), 3.10 (s, 4H), 7.25 (d, J= 7.5 Hz, 4H), 7.50 (d, J= 7.5 Hz, 4H), 7.58 (s, 2H), $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 21.5, 26.5, 129.5, 130.8, 133.1, 133.7, 136.5, 139.7,196.4, MS: m/z (%) 290 (2.5, M$^+$+2), 277 (100), 263 (23), 247 (65), 199 (56), 184 (25), 167 (47), 153 (96), 145 (55), 128 (96), 115 (96), 102 (45), 91 (28), 77 (92).

*(2E,5E)-2,5-bis (2-nitrobenzylidene) cyclopentanone (**Table 2, entry 6**):*

Deep red Solid; m.p.= 160.0-161.5 $^°$C (lit. [29] 158$^°$C); IR (KBr): $\bar{v}$ = 3080, 3050, 2950, 2880, 1680, 1623, 1600, 1562, 1504, 1465, 1430, 1338, 1236, 1175, 980, 855, 773, 748, 732, 690, 660. $^1$H NMR (250 MHz, CDCl$_3$): δ= 2.89 (s, 4H), 7.57 (d, J= 7.8 Hz, 2H), 7.71 (m, 1H), 7.87 (s, 1H), 8.11 (d, J= 7.8 Hz, 1H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 26.0, 125.1, 129.6, 130.6, 131.2, 132.3, 133.2, 140.1, 148.8, 194.4. MS: m/z (%) 350 (1, M$^+$), 304 (6, M-NO$_2$), 287 (100), 269 (2), 259 (4), 231 (6), 197 (7), 153 (17), 127 (48), 115 (38).

*(2E,6E)-2,6- bis (4- metoxybenzylidene) cyclohexanone (**Table 2, entry 13**):*

Yellow Solid; m.p.= 203-205 $^°$C (lit. [29] 203-204$^°$C); IR (KBr): $\bar{v}$ = 3060, 3040, 2990, 2820, 1650, 1580, 1550, 14964, 1415, 1300, 1240, 1160, 1130, 1010, 960, 830. $^1$H NMR (250 MHz, CDCl$_3$): δ= 1.78 (m, 2H), 2.90 (t, 4H), 3.82 (s, 6H), 6.92 (d, J= 8.75 Hz, 4H), 7.44 (d, J= 8.75 Hz, 4H), 7.76 (s, 2H), $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 23.0, 28.5, 55.3, 113.9, 128.7, 132.2, 134.3, 136.5, 159.9, 190.1. MS: m/z (%) 335 (12, M+1), 334 (100, M$^+$), 319 (10), 277 (21), 246 (17), 215 (8), 167 (11), 153 (26), 145 (15), 121 (33), 115 (54), 102 (64), 91 (44), 77 (69).

*(2E,6E)-2,6-bis (4-chlorobenzylidene) cyclohexanone (**Table 2, entry 15**):*

Yellow Solid; m.p.= 144-146 $^°$C (lit. [29] 147-148$^°$C); IR (KBr): $\bar{v}$ = 3100, 3030, 2950, 2880, 1665, 1600, 1568, 1481, 1400, 1394, 1260, 1156, 1142, 1122, 1085, 1002, 957, 827, 814, 790. $^1$H NMR (250 MHz, CDCl$_3$): δ= 1.82 (quin, J= 6.3 Hz, 2H), 2.91 (t, J= 6.3 Hz, 4H), 7.41 (m, 8H), 7.75 (s, 2H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 22.8, 28.4, 128.7, 131.6, 134.3, 134.6,

135.8, 136.4, 189.9. MS: m/z (%) 342 (6, M$^+$), 344 (2, M+2), 346 (0.6, M+4), 309 (4), 307 (13), 281(5), 279 (15), 244 (15%, M-99), 215 (17), 167 (14), 152 (37), 127 (63), 114 (100).

*(2E,6E)-2,6- bis(2-furylmethylene) cyclohexanone (Table 2, entry 17)*:

Brown crystal; m.p.= 143-145 $^o$C (lit.[30] 140-141$^°$C); IR (KBr): $\bar{v}$ = 3125, 2925, 1680. $^1$H NMR (250 MHz, CDCl$_3$): δ= 1.79 (quin, J=6.2 Hz, 2H), 2.91 (t, J=6.2 Hz, 4H), 6.42–7.46 (m, 8H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 22.04, 28.36, 112.70, 116.43, 123.73, 144.90, 133.42, 153.15, 189.34.

*(1E,4E)-1,5-bis (4-methylphenyl) penta-1,4-dien-3-one (Table 2, entry 23)*:

Yellow Solid; m.p.= 146-148$^°$C (lit.[31] 147-148$^°$C); IR (KBr): $\bar{v}$ = 3080, 3030, 2990, 2880, 1645, 1613, 1587, 1557, 1501, 1405, 1328, 1175, 1094, 987, 814. $^1$H NMR (250 MHz, CDCl$_3$): δ= 2.39 (s, 6H), 7.04 (d, J= 7.5 Hz, 2H), 7.23 (s, 4H), 7.52 (s, 4H), 7.71 (d, J= 7.5Hz, 2H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 21.5, 124.6, 128.4, 129.7, 132.1, 140.9, 143.1, 189.0. MS: m/z (%) 262 (M$^+$, 10), 261 (100, M-1), 247 (80), 232 (7), 218 (19), 203 (14), 170 (16), 145 (24), 115 (32), 105 (15), 91 (20).

*(1E, 4E)- 1, 5- bis (4-metoxyphenyl) penta-1, 4- dien-3-one (Table 2, entry 25)*:

Yellow Solid; m.p.= 131-133$^°$C (lit.[31] 130-132$^°$C); IR (KBr): $\bar{v}$ = 3050, 3030, 2950, 2930, 2830, 1650, 1615, 1630, 1595, 1560, 1501, 1414, 1287, 1246, 1165, 1030, 982, 820. $^1$H NMR (250 MHz, CDCl$_3$): δ= 3.87 (s, 6H), 6.85-6.98 (m, 6H), 7.54-7.59 (m, 2H), 7.66 (s, 2H), 7.73 (s, 2H). $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 55.4, 114.4, 123.5, 127.6, 130.1, 142.6, 161.5, 188.8. MS: m/z (%) 293 (28, M-1), 250 (4), 235 (7), 186 (6), 161 (20), 132 (58), 117 (46), 102 (45), 89 (100), 76 (57).

## 3. Results and Discussion

Nano-graphene oxide was synthesized from natural sources of graphite by Hummers method [26,27]. During the oxidation process, hydroxyl, carbonyl, epoxy, and proxy groups were bonded to the edges of basal planes of the graphite structure. Simultaneously, carbon hydrolyzation occurred and the sp$^2$ bonds changed to sp$^3$ bonds. Fig. 1 shows the model described by Lerf–Klinowski [32] with the omission of minor groups (carboxyl, carbonyl, ester, etc.) on the periphery of the carbon plane of the graphitic platelets of NGO. The high magnification TEM image of NGO (Fig. 2) shows large sheets to be situated on the top of the grid and have the tendency to scroll and wrinkle, illustrating the flake-like shapes of graphene [33].
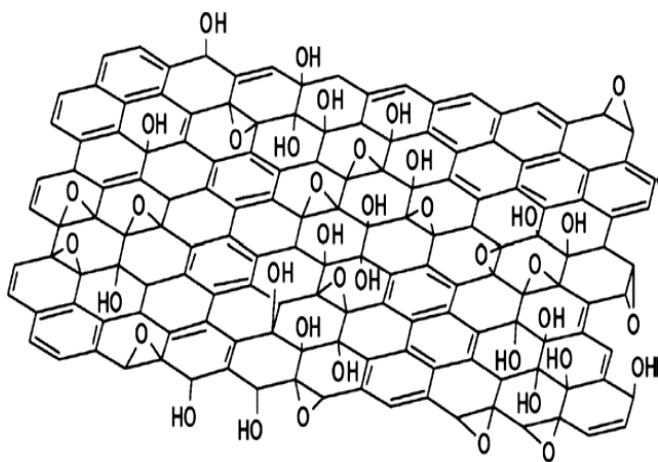


**Fig. 1.** Lerf–Klinowski model of NGO

The powder XRD pattern of graphite has the diffraction characteristic peak appears at 26.5$^°$, corresponding to an interlayer spacing 0.34 nm [20]. While, the XRD patterns of the NGO exhibits a peak (002) centered at 11.73$^°$, corresponding to an interlayer spacing of 0.75 nm (Fig. 3). Further, The UV/Vis spectrum of NGO (Fig. 4) shows a strong absorption peak at 230 nm and a shoulder at about 300 nm which are attributable to the π→π* transition of graphitic C–C bonds and assigned to the n→π * transitions of C=O bonds, respectively. Thus, UV-Vis spectra provided evidence of the presence of hydroxyl, epoxide, carboxylate and carbonyl groups on NGO, similar to the XRD and FT-IR [34]. The FT-IR spectrum of NGO are shown in Fig. 5. An intense and broad peak appeared at around 3446 cm$^{-1}$, assigned to the stretching mode of an O–H bond, reveals the abundance of hydroxyl groups in NGO. The strong band at 1716 cm$^{-1}$ and 1618 cm$^{-1}$ revealed the presence of C=O and C=C functional groups in NGO. Also, the bands at 1280 cm$^{-1}$ and 1066 cm$^{-1}$ are attributed to the presence of C–OH and C–O (epoxy) groups, respectively.
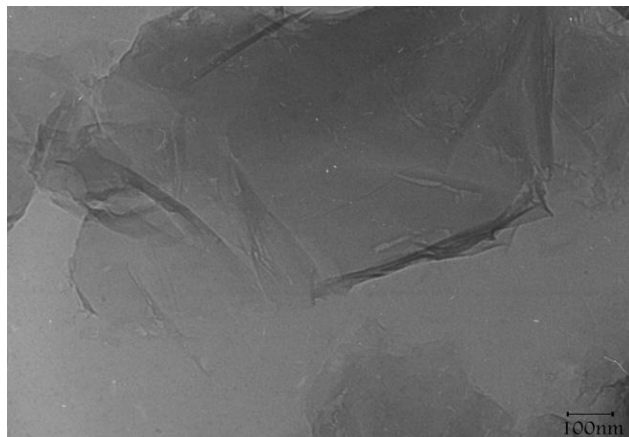


**Fig. 2.** The TEM image of NGO.
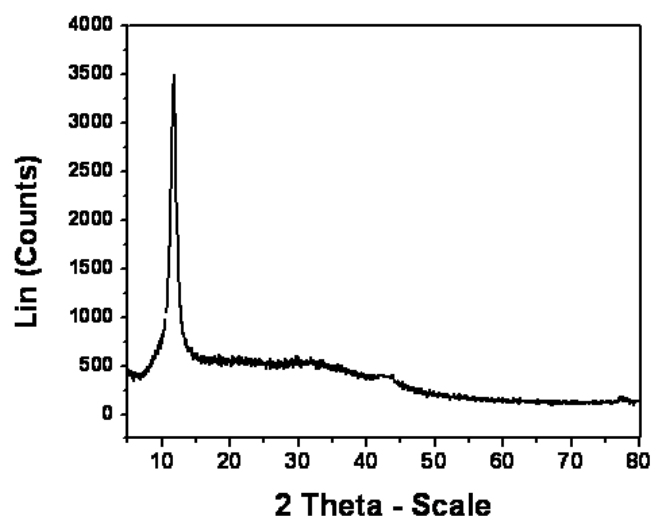
**Fig. 3.** The XRD spectrum of NGO.

**Fig. 4.** The UV/Vis spectrum of the NGO.



The condensation of substituted benzaldehyde (2 mmol) and cyclopentanone (1 mmol) was attempted in the presence of 10-60 mg of NGO at thermal conditions (80 $^{\circ}$C). The results showed that 50 mg of NGO gave the best yield (Table 1, entry 5). Next, the reaction carried out at different temperature (Table 2). As shown in Table 2, the best result was obtained in 80 $^{0}$C (entry 4). Reaction was also carried out in some solvents ($CH_2Cl_2$, $C_2H_4Cl_2$, $CH_3CN$, EtOH, MeOH, THF and $H_2O$). The best results were achieved in solvent-free conditions.

Under the optimal reaction conditions, the generality of the condensation reaction was investigated by reacting aryl aldehydes substituted by either electron-withdrawing or electron–releasing groups with ketones to get the corresponding α,ά- bis (substituted-benzylidene) alkanone (Table 3).



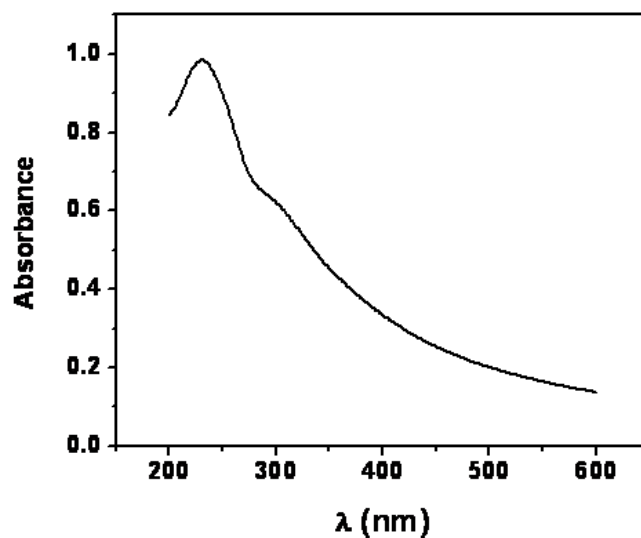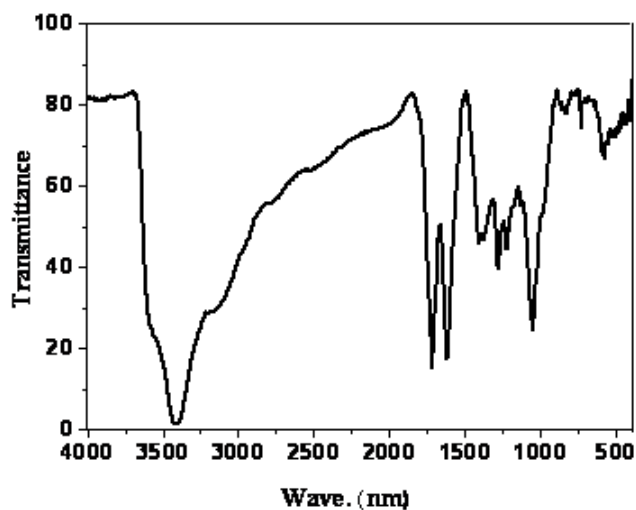**Fig. 5.** The FT-IR spectra of the NGO.

**Table 1.** The effect of NGO loading on the condensation of benzaldehyde and cyclopentanone.[a]

| Entry | NGO (mg) | Temp. ($^{\circ}$C) | Time (min) | Yield (%) |
|-------|----------|---------------------|------------|-----------|
| 1 | 10 | 80 | 45 | 20 |
| 2 | 20 | 80 | 45 | 40 |
| 3 | 30 | 80 | 45 | 55 |
| 4 | 40 | 80 | 45 | 75 |
| 5 | 50 | 80 | 45 | 95 |
| 6 | 60 | 80 | 45 | 96 |

[a]benzaldehyde: cyclopentanone: 2:1.

**Table 2.** The effect of temperature on the condensation of benzaldehyde and cyclopentanone.[a]

| Entry | Temp. ($^\circ$C) | Time (min) | Yield (%) |
|-------|-------------------|------------|-----------|
| 1 | r. t. | 45 | 10 |
| 2 | 50 | 45 | 40 |
| 3 | 80 | 45 | 95 |
| 4 | 90 | 45 | 96 |
| 5 | 100 | 45 | 97 |

[a]benzaldehyde (2 mmol), cyclopentanone (1 mmol), NGO (0.05 gr).

**Table 3.** Graphene oxide catalyzed condensation of aryl aldehydes with cyclic and non-cyclic ketones.[a]

| Entry | Ketone | Ar | Time (min) | Yield (%) |
|-------|--------|-----|------------|-----------|
| 1 | cyclopentanone | $o$-CH$_3$C$_6$H$_5$ | 40 | 95 |
| 2 | " | $m$-CH$_3$ C$_6$H$_5$ | 30 | 95 |
| 3 | " | $p$-CH$_3$ C$_6$H$_5$ | 30 | 95 |
| 4 | " | $o$-Cl C$_6$H$_5$ | 120 | 85 |
| 5 | " | $p$-Cl C$_6$H$_5$ | 120 | 85 |
| 6 | " | o-NO$_2$ C$_6$H$_5$ | 120 | 75 |
| 7 | " | o-CH$_3$O C$_6$H$_5$ | 30 | 90 |
| 8 | " | p-CH$_3$O C$_6$H$_5$ | 30 | 95 |
| 9 | cyclohexanone | o-CH$_3$ C$_6$H$_5$ | 30 | 90 |
| 10 | " | C$_6$H$_5$ | 30 | 95 |
| 11 | " | p-CH$_3$ C$_6$H$_5$ | 30 | 95 |
| 12 | " | o-CH$_3$O C$_6$H$_5$ | 30 | 90 |
| 13 | " | p-CH$_3$O C$_6$H$_5$ | 30 | 95 |
| 14 | " | m-Cl C$_6$H$_5$ | 120 | 85 |
| 15 | " | p-Cl C$_6$H$_5$ | 120 | 85 |
| 16 | " | o-NO$_2$ C$_6$H$_5$ | 120 | 75 |
| 17 | " | 2-furyl | 40 | 90 |
| 18 | " | C$_6$H$_5$CH=CH | 40 | 93 |
| 19 | " | 2-thienyl | 50 | 89 |
| 20 | " | 5-methyl-2-thienyl | 35 | 95 |
| 21 | Acetone | o-CH$_3$ C$_6$H$_5$ | 120 | 85 |
| 22 | " | C$_6$H$_5$ | 120 | 80 |
| 23 | " | p-CH$_3$ C$_6$H$_5$ | 120 | 85 |
| 24 | " | o-CH$_3$O C$_6$H$_5$ | 120 | 85 |
| 25 | " | p-CH$_3$O C$_6$H$_5$ | 120 | 85 |
| 26 | " | o-NO$_2$ C$_6$H$_5$ | 120 | 75 |

[a]The products were isolated and characterized by IR, Mass, ^{1}H and ^{13}CNMR.

As the results are shown in Table 3, aldehydes bearing electron–releasing substituents on phenyl ring favored the formation of product (90-95%) in 30-49 min. (Table 3, entries 1-3 and 7-13). In contrast, aldehydes bearing electron– withdrawing groups gave lower yield (75-85%) in 120 min. (Table 3, entries 4-6 and 14-16). Also, furfural, cinamaldehyde, thiophene-2-carbaldehyde and 5- methylthiophene-2-carbaldehyde were investigated in aldol reaction (Table 3, entries 17-20). The results showed excellent yields. In addition, the reaction was carried out by condensation of several non-cyclic ketones with aryl aldehydes to yields the corresponding products.

It was found that non-cyclic ketones gave corresponding products similar to the aldehydes bearing electron–withdrawing groups (Table 3, entries 21-26).

The efficiency of NGO was compared with several catalysts [35-46]. The results are shown in Table 4. In the presence of NGO, the reaction required shorter time with excellent yield (Table 4, entry 13).

The reusability of n- NGO was also evaluated (Fig. 6). After completion of the reaction, NGO was filtered and washed with EtOH twice, dried in a Vacuum Oven and employed for the next reaction. The catalyst was used up to five cycles with no significant loss of activity. The performance of NGO was consistent and thus validates its recyclability.
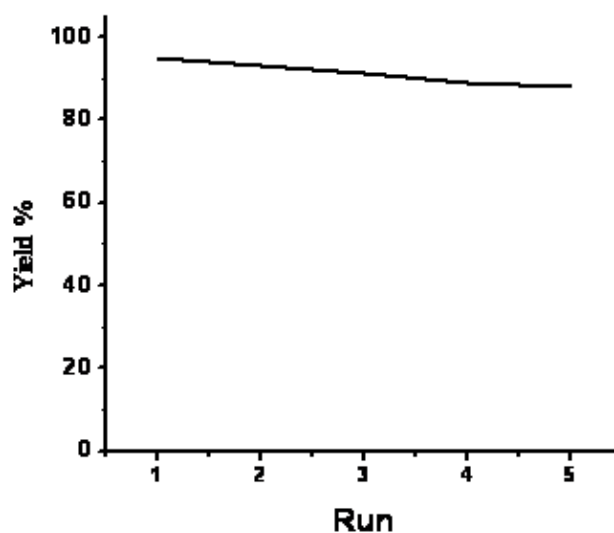


**Fig. 6.** Recyclability of NGO.

## 4. Conclusions

In summary, we have described an efficient method for the synthesis of α, ά- bis (substituted- benzylidene) alkanone derivatives catalyzed by NGO under solvent-free and thermal conditions (80 $^{\circ}$C). Also, NGO is easily synthesized, green, cheap, air and moisture stable, heterogenic and could be easily recovered after the reaction and reused for additional runs.

**Table 4.** Comparison of the efficiency of NGO with different catalysts [a].

| Entry | Reaction Conditions | Temp. (°C) | Time (min) | Yield (%) |
|-------|---------------------|------------|------------|-----------|
| 1 | Carbon- based solid acid /solvent-free | 70 | 85 | 95 |
| 2 | RuCl$_3$/water | 120 | 360 | 95 |
| 3 | I$_2$/CH$_2$Cl$_2$ | r.t. | 270 | 89 |
| 4 | Yb(OPf)$_3$/ perfluorodecalin | 120 | 480 | 92 |
| 5 | Animal bone meal(ABM)/ H$_2$O | reflux | 75 | 76 |
| 6 | Sulfated zirconia/ solvent-free | 170 | 240 | 80 |
| 7 | Sulfamic acid/ solvent-free | 80 | 150 | 90 |
| 8 | ACOH/Acetate | 120 | 480 | 95 |
| 9 | FeCl$_3$·6H$_2$O/ ([bmim][BF4]) | 80 | 360 | 90 |
| 11 | NBS/EtOH | 80 | 960 | 92 |
| 12 | H$^+$Catalyst/H$_2$O | 100 | 120 | 95 |
| 13 | NGO/ solvent-free (This work) | 80 | 30 | 95 |

[a]Reaction conditions: benzaldehyde (2.0 mmol), cyclohexanone.

This procedure has advantageous such as recyclability of the catalyst, easy work up, mild reaction condition, and economic viability; prevent solvent waste and good to excellent yields.

## Acknowledgment

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