

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.

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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 silyl 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

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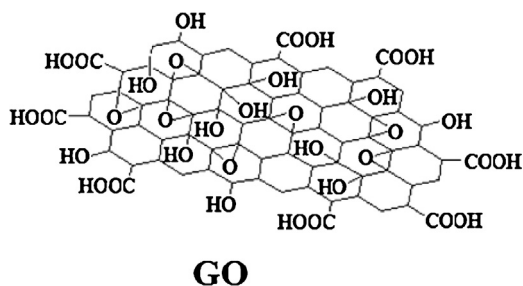


Fig. 1. A schematic model of a single sheet of graphene oxide.

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 μm), 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 Shimadzu 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, $\lambda = 1.5418 \text{ \AA}$. Diluted GO was deposited on glass slide and then AFM was measured using VEECO DICP II autoprobe (model AP 0100). ^1H 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 °C. The solution was kept under vigorous stirring followed by addition of 600 mg KMnO_4 in a stepwise manner keeping the

temperature below 20 °C. Next, the temperature of the solution was slowly raised to 35 °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 °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_2O_2 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. 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.

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_2SO_4 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 manolonitrile 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_2SO_4 . 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 $2\theta = \sim 10.6^\circ$ for graphene oxide, corresponding to an interlayer spacing of $\sim 0.9 \text{ nm}$ (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 [49].

Further, the nature of the chemical functionalities was characterized by FT-IR (Fig. 3). An intense and broad peak appeared at 3408 cm^{-1} , 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^{-1} appears due to C–H stretching (symmetric and asymmetric) vibrations. The band at 1709 cm^{-1} ($\nu\text{C=O}$) represents carboxylic acid and carbonyl groups. Another band at 1591 cm^{-1} represents C=C stretching vibration in graphene oxide. Furthermore, the bands at 1230 cm^{-1} and 1079 cm^{-1} are attributed

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