

1-Amino-2-Naphthol-4-Sulfonic Acid-Functionalized Graphene Oxide: A Heterogeneous Nanocatalyst for the One-Pot Synthesis of Tetraketone Derivatives[†]

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Abstract: Numerous organic and inorganic compounds, as well as transition metals, have been mentioned as homogeneous catalyst, in chemical processes. However, the utilization of these homogeneous catalysts is inhibited by challenges such as separation of the products from the reaction mixtures and the recycling of catalysts, despite their high catalytic activity resulting from the increased contact surface of the homogeneous catalysts with reactants. In recent years, various research have been accomplished on graphene oxide due to its remarkable chemical and mechanical properties. Among these applications, the use of modified graphene oxides as catalysts is of extreme importance. In this work, 1-amino-2-naphthol-4-sulfonic acid-functionalized graphene oxide (GO-ANSA) was employed, as a new and highly effective heterogeneous nanocatalyst, for the preparation of tetraketone derivatives through multicomponent reaction of 1,3-diketones with aromatic aldehydes. This catalyst proceeds rapid conversion of substrates and affords high yields of the products. Furthermore, it is recyclable, easily separable and environmentally friendly.

Keywords: Green Chemistry; Heterogeneous catalyst; Nanocatalyst; MCRs; Modified graphene oxide; Tetraketone derivatives.

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1. Introduction

Multicomponent reactions (MCRs) are the main procedure for synthesizing of organic compounds *via* simple reactions [1]. These reactions have exceptional benefits such as high efficiency, high purity of the products, and atomic economy [2]. Recently, there has been specific attention given to the development of MCRs using metal-free and environmentally friendly catalysts. The goal of the most research in the field of catalyst has been devoted to increase catalyst efficacy and decrease reaction time [3, 4].

Tetraketones and their derivatives are typically synthesized through Knoevenagel condensation and Michael addition, and these compounds have several applications in the field of medicinal chemistry [5, 6]. Tetraketones contain four carbonyl groups and exist in two forms, known as keto-enol tautomerism [7]. Additionally, they serve as major intermediates in the preparation of important heterocycles, including xanthenediones and acridindiones. By eliminating a water molecule, tetraketones can be converted to xanthenediones, which have numerous medicinal and biological uses [8]. Given the extensive usage of these derivatives in the pharmaceutical industry, their synthesis is of great importance, and considerable efforts have been dedicated to developing mild, facile, and environmentally friendly methods for synthesizing of tetraketones (as intermediates in the synthesis of xanthenediones). Green chemistry has utilized efficient and recyclable catalysts for the synthesis of these compounds. Various synthetic methods have been

described, involving the use of different catalysts, temperature conditions, and solvents [9–12].

Graphene oxide (GO) has demonstrated its efficacy as a catalyst in numerous reactions. However, functionalizing it with organic compounds enhances the catalytic properties as a heterogeneous catalyst. Various types of functionalized GO catalysts have been documented [13–18]. In this work, we employed GO-ANSA as a new and highly effective heterogeneous nanocatalyst. The application of GO-ANSA, as a nanocatalyst, for the preparation of tetraketone derivatives enables rapid and high-yield reactions. Furthermore, this catalyst is recyclable and can be easily separated.

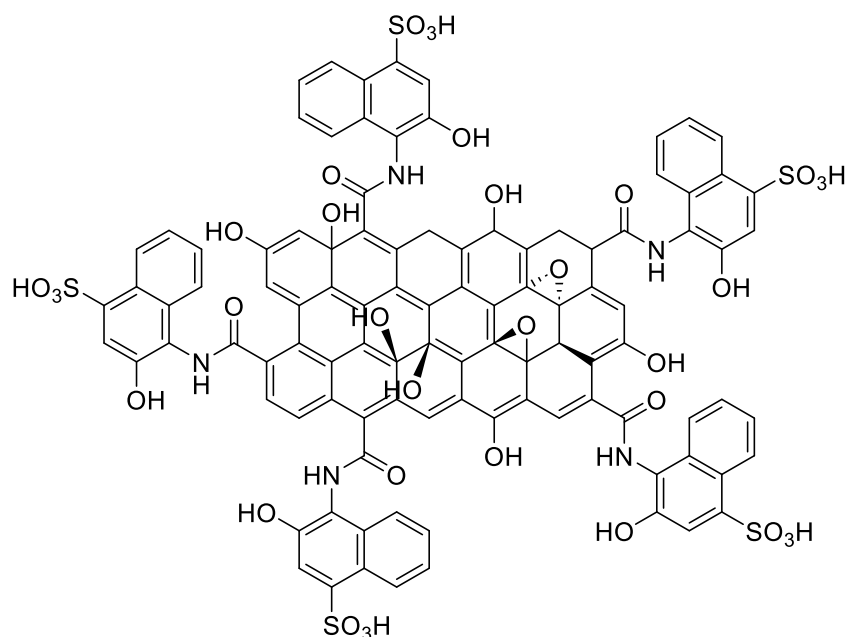
2. Experimental

2.1. Materials

Graphite flakes with a purity of 99.8% was purchased from Merck. Sodium nitrate (NaNO_3) with a purity of 98+ % was purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4) with a purity of 98%, potassium permanganate (KMnO_4) with a purity of 98.5%, hydrogen peroxide (H_2O_2) with a purity of 30%, hydrochloric acid (HCl) with a purity of 35–37%, acetic anhydride, 1-amino-2-naphthol-4-sulfonic acid with a purity of 96%, 1,3-cyclohexanedione, benzaldehyde derivatives, dimethylformamide (DMF) and EtOH with a purity of 96% were purchased from Merck. Distilled water was used in all necessary steps of reactions or purification.

2.2. Synthesis of GO-ANSA

The synthesis of GO was carried out using the modified Hummers' method [14]. The prepared GO was dispersed in DMF as a solvent. Acetic anhydride was added to the flask and placed in an ultrasonic bath for 2 h. Then, 0.4 g of ANSA was added, and the mixture was refluxed for two days. After that, the obtained residue was washed with THF and EtOH. Eventually, the product dried at room temperature (Scheme 1).

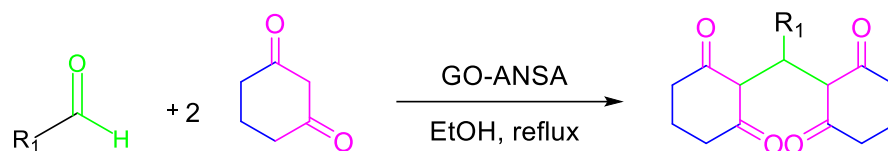


Scheme 1. schematic structure of the ANSA-functionalized GO (GO-ANSA).

2.3. Synthesis of Tetraketone Derivatives by Using GO-ANSA as Nanocatalyst

In a 10 ml flask on a magnetic stirrer, 1.0 mmol of benzaldehyde derivatives, 2.0 mmol of 1,3-cyclohexanedione, 15.0 mg of GO-ANSA and 3.0 ml of EtOH, as a solvent, were

added and mixed. The progress of the reaction was followed by using thin layer chromatography (TLC). After the completion of the reaction, the obtained mixture was filtered to remove the catalyst from the reaction mixture. Then, the filtrate was cooled until the crystals of the product appeared (Scheme 2).



Scheme 2. Synthesis of tetraketone *via* one-pot reaction of benzaldehyde derivatives and 1,3-cyclohexanedione in the presence of GO-ANSA catalyst.

3. Results and Discussion

3.1. Characterization of GO-ANSA

The obtained nanomaterial was characterized by using Fourier transform infrared (FTIR) spectroscopy (Figure 1). First, in FTIR analysis of GO, wide bands at 3600–2400 cm⁻¹ show all the hydroxyl groups of the GO plane as well as those located at the edge of GO including COOH and phenolic functional groups; the band at 1623 cm⁻¹ shows the vibration stretching of C=C bond. In the FTIR analysis of GO-ANSA, bands appeared at 1650 cm⁻¹ and 1544 cm⁻¹, indicating the C=O and C-N in amide groups, respectively. Wide bands at 3600–3100 cm⁻¹ show the vibration stretching of O–H and N–H bonds in the structure of GO-ANSA.

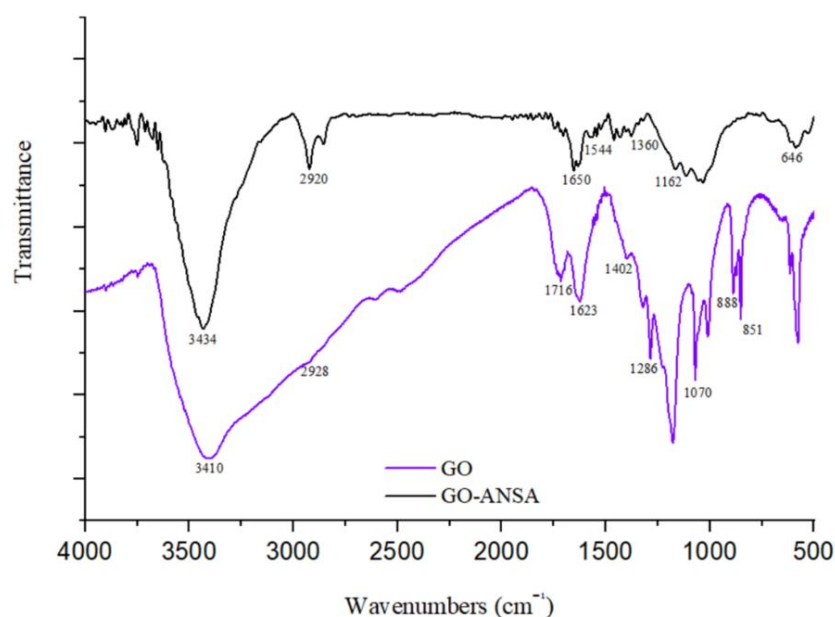


Figure 1. FTIR analysis of GO-ANSA.

Brunauer-Emmett-Teller (BET) analysis was also utilized to determine porosity of the obtained GO-ANSA nanomaterial (Figure 2). The obtained data show the nitrogen adsorption-desorption isotherm of GO-ANSA, which is in consistent with the type (III) adsorption isotherm.

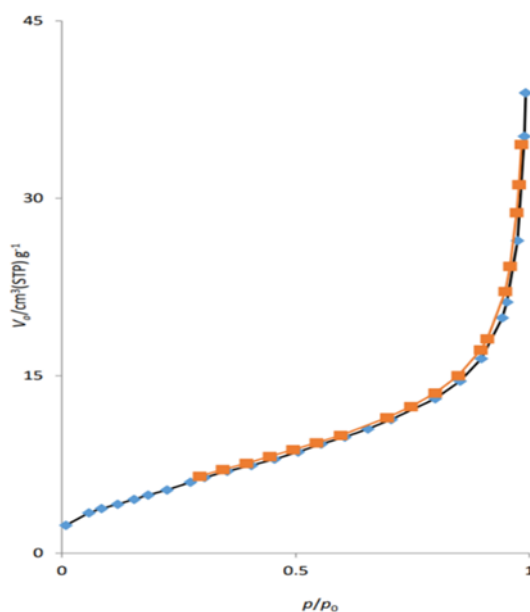
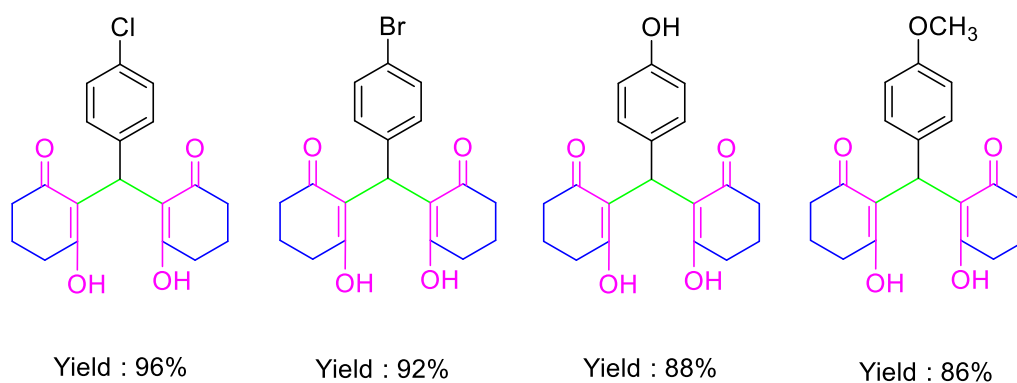


Figure 2. Nitrogen adsorption-desorption isotherm of the GO-ANSA.

3.2. Prepared Derivatives

According to **Scheme 3**, by using GO-ANSA, as a heterogeneous nanocatalyst (15.0 mg), desired products were synthesized in high yield. Possibility of simple method for separation and recycling of the GO-ANSA catalyst from the reaction mixture is another benefit of this nanocatalyst. This catalyst was recycled in at least five reactions without significant loss of the catalytic activity.



Scheme 3. Scope of tetraketone derivatives synthesis catalyzed by GO-ANSA.

4. Conclusion

The major goal of this research was simple preparation of the tetraketone derivatives through the multi-component reaction under eco-friendly conditions. GO-ANSA, as a novel nanocatalyst, was used for this reaction. Indeed, it is easily prepared and has advantages such as appropriate catalytic activity, easy separation, and good recyclability for at least for five cycles. In addition, EtOH is the best solvent for the synthesis of tetraketone derivatives under reflux conditions.

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