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Article

Nanoscale graphene oxide sheets as highly efficient carbocatalysts in green oxidation of benzylic alcohols and aromatic aldehydes

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ABSTRACT

Nanoscale graphene oxide (NGO) sheets were synthesized and used as carbocatalysts for effective oxidation of benzylic alcohols and aromatic aldehydes. For oxidation of alcohols in the presence of H₂O₂ at 80 °C, the NGOs (20% mass fraction) as carbocatalysts showed selectivity toward aldehyde. The rate and yield of this reaction strongly depended on the nature of substituents on the alcohol. For 4-nitrobenzyl alcohol, <10% of it was converted into the corresponding carboxylic acid after 24 h. By contrast, 4-methoxybenzyl alcohol and diphenylmethanol were completely converted into the corresponding carboxylic acid and ketone after only 9 and 3 h, respectively. The conversion rates for oxidation of aromatic aldehydes by NGO carbocatalysts were higher than those for alcohol oxidation. For all the aldehydes, complete conversion to the corresponding carboxylic acids was achieved using 7% (mass fraction) of NGO at 70 °C within 2–3 h. Possible mechanisms for NGO carbocatalyst structure-dependent oxidation of benzyl alcohols and structure-independent oxidation of aromatic aldehydes are discussed.

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1. Introduction

Because of the mass production and utilization of various organic materials in the modern world, effective and green catalytic approaches are required to reduce the risks of these chemicals to humans and the environment [1–8]. The most widely explored catalytic nanomaterials are different forms of transition metals, such as metal oxides [9] and hybrid materials [10], which need ultraviolet (UV)-visible irradiation to work efficiently. However, these catalytic nanomaterials may induce toxic effects, and can also be complex to remove from the environment [11,12]. Consequently, recent research has focused on development of metal-free catalysts.

Recently, carbocatalysts have been proposed as promising metal-free alternatives to transition metal catalysts [13–16].

Different carbon allotropes have been investigated and used as carbocatalysts [1,13,17–26]. The various carbon allotropes have the same basic graphene-based structure [14,23,24], and in recent years, graphene-based materials have attracted attention as carbocatalysts. Graphene-based structures such as pure graphene, doped graphene, and graphene oxide (GO) have been used as carbocatalysts in various reactions, but the graphene-based carbocatalytic field is still in its infancy [1,18,27–29]. Because of its acidic nature, the most common uses of GO are in organic reactions such as Michael addition, Friedel-Crafts reaction, aza-Michael addition, and ring opening polymerization [30–38]. The first reported application of graphene as a carbocatalyst was of GO for the oxidation of benzyl alcohol [39]. Since then, applications of graphene and/or reduced GO (rGO) sheets to reduction of nitrobenzene [40], oxi-

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dation of 9H-fluorene [41], and oxidation of benzene to phenol [42] have been reported. Although graphene-based carbocatalysts are promising, they require harsh conditions, long reaction time, high catalyst concentrations, and produce low yields. Because defects in carbonaceous skeletons act as effective active sites for carbocatalysis [18,43,44], research on graphene-based carbocatalysts has concentrated on producing defects by adding heteroatoms such as boron, nitrogen, and sulfur [1,18,45]. These defective graphene structures have been widely used in oxidation reactions and produce higher yields than pure graphene or rGO [46–51]. However, synthesis of these structures is often complex, requiring doping reagents and specialized equipment, which makes their widespread application in catalysis difficult [18]. Therefore, more effective carbocatalysts need to be developed.

To date, no one has reported increasing the carbocatalytic activity of graphene sheets by decreasing the dimensions of the sheets. In addition, all previous reports on graphene-based materials have been for solvent free and/or heterogeneous catalytic systems. There have been no reports on the application of graphene-based materials as colloidal dispersion systems, that is, systems at the boundary between homogeneous and heterogeneous catalyst systems, to carbocatalysis. It is expected that a reduction in the size of GO will increase the peroxidase-like activity of the graphene skeleton. This is because any reduction in size will increase the density of defects, especially vacancies at edges, and it has been determined that lone pairs in the zigzag structure of sp^2 bonds at vacancies at edges, which have high delocalization states, are active sites for the peroxidase-like activity of carbonaceous structures [42,52–58]. It is important to retain oxygen functional groups of the graphenic sheets during any size reduction, because they contribute to the ability of nanoscale graphene oxide (NGO) to disperse in aqueous solutions and form a colloidal dispersion system. Both the method for decreasing the size of GO sheets and the magnitude of the size reduction could affect the catalytic performance of the NGO. It has been determined that sonication can provide energy for oxidative cleavage of the C–C bond of GO sheets by O_2 from air [59], but does not lead to physical breaking of the sheets. Moreover, in comparison with thermodynamic methods, sonication results in only partial cleavage at oxygen containing functional groups [60].

The aims of this work were to investigate reducing the dimensions of GO to NGO with minimum loss of oxygen functional groups, and to prepare a colloidal dispersion of a carbocatalysts for oxidation reactions. Because of the benefits of sonication discussed above, we used sonication for the synthesis NGO from GO. After physical and chemical characterization of NGO, its ability to catalyze oxidation of benzylic alcohols was examined in an aqueous medium using H_2O_2 as an oxidant. Further information was obtained by applying the NGO catalyst to oxidation of aromatic aldehydes.

2. Experimental

2.1. Preparation of NGO sheets

A modified Hummers' method [61] coupled with a lengthy sonication step was used for synthesis of the NGO sheets, as reported in another study [62]. Briefly, 0.5 g of graphite and 0.5 g of $NaNO_3$ were stirred in 23 mL of H_2SO_4 for 12 h at room temperature (RT). The mixture was then placed in an ice bath and 3 g of $KMnO_4$ was slowly added with stirring for 2 h. The temperature was then increased to 40 °C with stirring for 1 h. Next, 40 mL of deionized (DI) water was added to the suspension, and temperature was increased to 90 °C and held at this temperature for 1 h. Then, 100 mL of DI water was added, and after decreasing the temperature to 30 °C, 3 mL of H_2O_2 was added to the mixture. To remove sulfate and manganese ions, the reaction product was repeatedly washed with a 5% (volume fraction) HCl solution and DI water. The solid product was retained and 100 mL of DI water was added, followed by sonication for 8 h. The mixture was then centrifuged at 5000 r/min for 10 min, and the pellet was removed. The supernatant was retained and washed two more times with 100 mL of DI water followed by sonication for 8 h. The second and third centrifugation steps were at 7000 rpm (10 min) and 10000 rpm (30 min), respectively. These washing steps separated out any large particles and/or clusters and the supernatant changed from a turbid brown solution to a clear brown solution, which was used in the carbocatalytic reactions.

2.2. Oxidation of benzylic alcohols by NGO

To study the catalytic effect of the NGO sheets on the oxidation of benzylic alcohols, we used H_2O_2 as an oxidant in an aqueous solution. Various mass fractions of the NGO sheets ((5–200)%) and different reaction temperatures (RT to 100 °C) were investigated. In a preliminary experiment, benzyl alcohol was heated in the presence of H_2O as solvent, an excess amount of H_2O_2 as oxidant, and 200% (mass fraction) of NGO as catalyst at 100 °C for 24 h. To ensure that the only oxidant present was H_2O_2 , the reaction was carried out under N_2 atmosphere. To study the role of H_2O_2 , the oxidation of benzyl alcohol was also conducted with different concentrations of H_2O_2 (10, 2.2, 1, 0.5 and 0 equivalents (eq.)) in the presence of 100% (mass fraction) NGO in 2 mL of DI water at 100 °C for 24 h. To optimize the different reaction parameters, the effects on the yield were investigated for different benzyl alcohol derivatives (benzyl alcohol, and 4-chloro, 4-methoxy, and 4-nitro derivatives), NGO mass fractions ((10–200)%) reaction temperatures (RT to 100 °C with (20–100)%) (mass fraction) of NGO and 2.2 eq. of H_2O_2), and reaction time (1–24 h with 20% (mass fraction) of NGO and 2.2 eq. of H_2O_2 at 80 °C). The role of substituents on the benzylic carbon in the oxidation process was investigated by studying the oxidation of 1-phenylethanol and diphenylmethanol in the presence of 20% (mass fraction) of NGO and 1.1 eq. of H_2O_2 at 80 °C for 24 h. Finally, to highlight the catalytic performance of the NGO, the oxidation reactions of all of the benzyl alcohol derivatives were conducted with H_2O_2 but without NGO at 100 °C for 24 h. The progress of all reactions was monitored by thin layer chromatography (aluminum sheets, 20 × 20 cm, Merck Millipore) and gas chromatography (PHILIPS PU4500). After completion of the reaction the prod-

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