



Probing the intrinsic active sites of modified graphene oxide for aerobic benzylic alcohol oxidation

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ABSTRACT

The graphene-based materials, particularly graphene oxide (GO) with rich oxygenated groups, exhibit high catalytic performance in various metal-free oxidation reactions. However, the intrinsic active site is still unclear, which greatly retards to further develop advanced catalysts. Here, the modified graphene oxide (abGO) was synthesized by sequential base and acid treatment and employed in the aerobic oxidation of benzyl alcohol to benzaldehyde. This novel catalyst displayed much higher activity, selectivity and stability than that of conventional GO. 93.1% conversion and 100% selectivity were achieved over abGO. More importantly, it is shown that the yield of benzaldehyde is linearly proportional to the content of surface phenol hydroxyl groups. Experimentally observed reactivity trends, structure-behavior correlation, molecule mimicking and characterization results strongly confirm that the surface phenol hydroxyl groups are the intrinsic active sites.

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1. Introduction

The selective oxidation of alcohols to aldehydes is fundamentally important both in academic laboratories and industry. These products are valuable fine chemicals and versatile intermediates for perfume, pharmaceuticals, agrochemicals and polymers [1,2]. The conventional oxidation of alcohols is usually performed using toxic stoichiometric reagents, such as chromate or permanganate [2–4]. During the last decade, the heterogeneous metal-based catalysts including Au, Pt and Pd have been extensively employed for aerobic oxidations of alcohols owing to their outstanding catalytic performances under mild conditions. Hutchings et al. [1] showed that Au-Pd/TiO₂ catalyst gave unprecedented high turnover frequency for the oxidation of several kinds of alcohols. Kobayashi et al. [5] developed an efficient polymer incarcerated gold (PI Au) with excellent performance at room temperature in O₂ with the aid of K₂CO₃. Tsukuda et al. [6] described the thiolate-mediated selectivity control by hierarchically porous carbon nanosheets supported Au. The other relatively feasible catalysts include Au/Ga₃Al₃O₉ [7], Au/CuO [8], Pd/CNS [9], PtBi/CNT [10], Pd@N-doped carbon [11],

Pd/HAP [12], ARP-Pt [13], Pd on graphene [14] and encapsulated Pd in ionic copolymer [15]. Nevertheless, these metal catalysts suffer from expensive cost, limited availability and toxic properties. Therefore, the development of environmental benign and cost-effective procedures for the oxidation of alcohols continues to gain great interest. In this respect, it is highly desirable to devise effective metal-free catalyst and use O₂ as oxidant together with water as solvent. As a result, the nanocarbon-based catalysis has been shown to be potential alternative to meet the requirements of sustainable chemistry [16–19]. Kakimoto et al. [17] reported that nitric acid assisted nanoshell carbon smoothly oxidized benzyl alcohol in 1,4-dioxane and afforded high conversion and good selectivity to aldehydes. However, the use of nitric acid increased the difficulty of product separation and also corroded the reactor. Peng et al. [19] claimed that carbon nanotubes could selectively oxidize benzyl alcohol to benzaldehyde in the absence of nitric acid, but the conversion was only 30.3% even under relatively high temperature (130 °C) and O₂ pressure (1.5 MPa). The nitrogen doping mildly improved the conversion of benzyl alcohol to 44.7%. Interestingly, the authors deduced that the surface carboxylic acid groups were greatly detrimental for the catalytic reactivity while the graphene skeletons played a crucial role in activate O₂.

Graphene and its derivative graphene oxide (GO) have attracted tremendous attention, and have been widely applied in the field

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of electronic and photonic devices, catalysis, sensors and energy-storage materials due to their exceptional physical properties and chemical tunability [20–24]. Because of the exhaustive oxidation process in Hummer's method, GO unavoidably possesses several kinds of surface functional groups, such as phenol hydroxyl, carbonyl, and carboxylic acid groups, which provide its moderate acidic and oxidizing properties [25–29]. Dreyer et al. [30] pioneered the use of GO as a metal-free carbon-based catalyst to catalyze the oxidations of various alcohols and hydration of alkynes. Since then, GO or modified materials have been gradually adopted as oxidizing catalysts for the oxidations of amines [31], alcohols [30,32,33], aldehydes [34], benzene [35] and ethylbenzene [36,37]. Porous GO fabricated by Su et al. [36] gave 65% conversion for the oxidative dehydrogenation of ethylbenzene to styrene at 400 °C. They insisted that the unpaired electrons at the edges of defects can activate oxygen molecules and promote the reaction. Liu et al. [33] identified the carboxyl groups as the active sites and the reduced form could be reoxidized by O₂. Owing to the non-stoichiometric and inhomogeneous nature of GO, the intrinsic active sites are still unclear and controversial, making it impossible to study the detailed reaction mechanism or compare the performance of GO bearing different structures objectively and fairly. The surface carbonyl, carboxylic acid, epoxide groups or even graphene skeletons have been regarded as active sites [30,31,33–36]. Therefore, it is urgent to explore the intrinsic active species in governing the reaction rate and activate O₂. Additionally, GO usually suffers from low activity and stability in liquid-phase reaction, which greatly limits its wide applications.

In this work, we have presented a facile method to regulate the surface oxygen-containing groups of GO by the sequential treatment of base and acid. The modified GO with enhanced phenol hydroxyl groups greatly improved the activity as well as stability, and showed good substrate adaptability in the oxidation of benzylic alcohols. More importantly, the structure-behavior relationship and intrinsic active sites were well revealed.

2. Experimental

2.1. Chemicals and reagents

Graphite power (Aladdin), H₂SO₄ (98 wt.%, Xilong Chem. Co. Ltd, China), NaNO₃ (Kermel Chem. Reagent Co. Ltd, China), KMnO₄ (Kermel Chem. Reagent Co. Ltd, China), H₂O₂ (30%, Dong Fang Chem. Co. Ltd, China), NaOH (Sinopharm Chemical Reagent Co., Ltd, China (SCRC)), bromoacetic acid (Aladdin), NaBH₄ (SCRC), hydrochloric acid (SCRC), benzyl alcohol (SCRC), 4-methyl and 4-methoxyl benzyl alcohols (SCRC), 4-nitrobenzyl alcohol (SCRC), cinnamic alcohol (Shanghai Shuangxiang Reagent Co. Ltd, China), furfuryl alcohol (SCRC), 2-thiophene methanol (Tokyo Chemical Industry Co. Ltd (TCI)), anthraquinone (SCRC), 1-naphthalenecarboxylic acid (SCRC), 1-pyrenebutyric acid (SCRC), 1-naphthol (SCRC), guaiacol (SCRC), 4-ethylguaiacol (TCI) and vanillin (SCRC).

2.2. Catalyst preparation

GO was synthesized by a modified Hummer's method [25]. 5 g graphite and 2.5 g NaNO₃ were stirred in 115 mL 98 wt.% H₂SO₄ under ice bath condition. 15 g KMnO₄ was added into the reaction solution and heated to 35 °C under vigorous stirring for 30 min. The system was diluted by 230 mL deionized water, heated to 98 °C, and introduced additional 700 mL water. After adding 50 mL H₂O₂, the suspension was filtered, washed and dried at 50 °C. The dispersed graphite oxide in water was processed by sonication for 60 min, centrifuged and dried at ambient temperature.

10 g NaOH and 15 g bromoacetic acid were added into 200 mL GO aqueous solution (1 mg/mL) with vigorous stirring and sonication for 5 h at room temperature. Subsequently, the mixture was neutralized to pH = 7 by adding hydrochloric acid and stirred for 2 h. After dialyzing 72 h by cellulose ester dialysis membranes (molecular weight cut-off 8000–10000, Solarbio corporation), the mixture was rinsed repeatedly, centrifuged, and dried at 80 °C. The as-synthesized sample was denoted as abGO, while the sample was denominated as bGO without the neutralization of hydrochloric acid. The preparation procedures of abGO are illustrated in Scheme S1 in Supporting Information.

1 g NaBH₄ was added to 200 mL abGO aqueous solution (1 mg/mL) under stirring for 3 h. Subsequently, the suspension was neutralized to pH = 7 by adding hydrochloric acid and stirred for 2 h. Subsequently, the mixture was centrifuged, and dried at 80 °C. The obtained material was named as arabGO, while the sample was denoted as rabGO without the neutralization of hydrochloric acid.

2.3. Catalyst characterization

N₂ adsorption-desorption isotherms were performed at –196 °C on a Micromeritics TriStar 3000 instrument. Prior to the measurements, the catalysts were evacuated under vacuum at 150 °C for 8 h. The IR spectra were obtained from Vertex 70 (Bruker) FT-IR spectrophotometer in the range of 400–4000 cm^{–1} with a resolution of 4 cm^{–1}. Raman spectroscopy was exhibited using a Renishaw UV-vis Raman System 1000 with a multichannel air-cooled CCD detector at room temperature. An Nd-Yag laser operating at 532 nm was utilized as the excitation source with a power of 30 MW. The solid-state C¹³ NMR spectra were measured on a Bruker Avance spectrometer with MAS spin rate at 9000 HZ. XPS spectra were collected from a Kratos AXIS ULTRA DLD spectrometer with Al K α radiation and a multichannel detector. The binding energy was calibrated by C 1s peak at 284.6 eV with ± 0.1 eV error. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were performed in JEM 2011F apparatus operating at 200 kV voltages. The samples were dispersed in ethanol under ultrasonic conditions for 30 min and then deposited on carbon-coated copper grids.

2.4. Catalytic tests

The reactions were performed in a Teflon-lined stainless steel autoclave containing 0.25 mmol feed, 10 mL water and 0.05 g catalyst. The reactor was purged by flushing O₂ with five times, and maintained at 100 °C and 0.2 MPa O₂ for designated time. When the reaction was terminated, the reactor system was quickly cooled to room temperature in an ice-water bath. The solid catalyst was separated by repeatedly centrifugation and then dried at 80 °C. The spent catalyst was conducted for reusability test under the same conditions as above. The liquid mixture was extracted with ethyl acetate, and ethyl benzoate was used as internal standard. The products were analyzed by gas chromatography (Shimadzu GC-2010) using a flame ionization detector with a DB-1 capillary column (60 m \times 0.25 mm \times 0.25 μ m). The C-mass balance was estimated in the range of ca. 97%–101%. All the products were identified by GC–MS.

3. Results and discussion

3.1. Catalyst characterization

TEM and HRTEM images of GO and modified samples are illustrated in Fig. 1. All the samples displayed typical nanosheet structure of graphene with ca. 2–10 layers. Compared to GO, the

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