



Correlation between the microstructures of graphite oxides and their catalytic behaviors in air oxidation of benzyl alcohol



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ABSTRACT

A series of graphite oxide (GO) materials were obtained by thermal treatment of oxidized natural graphite powder at different temperatures (from 100 to 200 °C). The microstructure evolution (i.e., layer structure and surface functional groups) of the graphite oxide during the heating process is studied by various characterization means, including XRD, N₂ adsorption, TG-DTA, in situ DRIFT, XPS, Raman, TEM and Boehm titration. The characterization results show that the structures of GO materials change gradually from multilayer sheets to a transparent ultrathin 2D structure of the carbon sheets. The concentration of surface C—OH and HO—C=O groups decrease significantly upon treating temperature increasing. Benzyl alcohol oxidation with air as oxidant source was carried out to detect the catalytic behaviors of different GO materials. The activities of GO materials decrease with the increase of treating temperatures. It shows that the structure properties, including ultrathin sheets and high specific surface area, are not crucial factors affecting the catalytic activity. The type and amount of surface oxygen-containing functional groups of GO materials tightly correlates with the catalytic performance. Carboxylic groups on the surface of GO should act as oxidative sites for benzyl alcohol and the reduced form could be reoxidized by molecular oxygen.

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1. Introduction

Catalytic oxidation of alcohols and carbohydrates with molecular oxygen (O₂) as the terminal oxidant has attracted considerable attention from the viewpoint of green sustainable chemistry [1–6]. A variety of supported noble metal (e.g. Ru, Pt, Pd, Au) or metal oxides (Co₃O₄, MnO, Fe₂O₃, CuO, MgO, etc.) [7–12] catalysts are active for these aerobic oxidation reactions. However, due to toxicity concerns and separation problems, many of these metal-mediated processes are not applicable in pharmaceutical or biotechnological applications [13,14]. Development of metal-free catalysts for oxidation reaction with O₂ as terminal oxidant is of high actual interest both for the academic research and for the industrial application.

Graphite oxide (GO) is an oxygen rich derivative of graphite, consisting of one or few-layer sp² network of carbon atoms [15–20]. The catalytic application of GO has focused primarily on the use of these materials as supports for catalytically active transition metals or metal oxides [21–26]. Recently, a few reports showed that metal-free GO could also be directly used as metal-

free catalysts to a few synthetic oxidation processes [27–31]. For example, Huang et al. found that GO is active for the direct transformation of amines to afford the corresponding imines under mild and neat conditions with molecular oxygen as the terminal oxidation [29]. Bielawski and his co-workers showed that GO is capable of oxidizing alcohols to corresponding carbonyl compounds in the presence of molecular oxygen [31]. Although the catalytic oxidation behaviors of these carbon catalysts are generally attributed to their surface functional groups, the nature of the active sites participating in the reaction and the detail correlation between the microstructure (structure, texture and surface properties) of GO and its catalytic behavior is currently lacking [32]. Understanding these factors is highly desirable for designing more efficient metal-free carbon catalysts for oxidation reaction.

In this work, GO was prepared by oxidizing natural graphite powder based on a modified Hummers method. Thermal treatment was carried out to obtain GO materials with different structure, texture and surface properties. The detailed physico-chemical properties of these GO materials were investigated with a series of characterization methods, including XRD, N₂ adsorption, TG-DTA, in situ DRIFT, XPS, Raman, TEM and Boehm titration. Benzyl alcohol oxidation with air as oxidant source was carried out to detect the catalytic behaviors of different GO materials. The correlation

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between graphite oxide microstructure and their catalytic behavior was discussed basing on these characterization results.

2. Experimental

2.1. Materials

All chemical reagents used were obtained from commercial sources and used without further purification. Graphite powder was purchased from Tianjin Guangfu fine chemical industry research institute. The purity of graphite was larger than 98 wt% and the main ash impurities were Fe 0.45 wt% and S 0.2 wt%. The crystallite size L_c and L_a of graphite is 8.9 and 23.6 nm, separately.

2.2. Catalysts preparation

Graphite oxide (GO) was prepared by oxidizing natural graphite powder based on a modified Hummers method [22,33]. Typically, 2.5 g of natural graphite was mixed with 1.25 g of sodium nitrate and added to 58 mL of cold (<278 K) concentrated H_2SO_4 in an ice-water bath. $KMnO_4$ (7.5 g) was added gradually with vigorous stirring and the temperature of the mixture remained below 293 K. After the mixture was stirred at 308 K for 1 h, distilled water (115 mL) was slowly added and the temperature rose to 371 K. The mixture was allowed to remain at this temperature for 15 min. The reaction was terminated by the addition of 180 mL of distilled water and 25 mL of H_2O_2 (30 wt%). The mixture was filtered by using a Buchner funnel, and the solid material (GO) was washed successively with 5% HCl and excess deionized water until the filtrate obtained a pH value of 7. The resulting material was dried at 100 °C for 12 h and denoted as GO-100. The thermal treatment of GO was carried out in Ar flow at desired temperature (T °C) and resultant materials were denoted as GO- T ($T = 100, 130, 140, 150, 170, 200$).

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer using $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). N_2 -adsorption/desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 373 K for 20 h before measurements. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) model. Pore size distributions were evaluated from adsorption branches of nitrogen isotherms using the Barret–Joyner–Halenda (BJH) model. XPS was performed on a Thermo ESCA LAB 250 system with $Mg K\alpha$ source (1254.6 eV). In situ diffused infrared Fourier transform (DFTIR) spectra were recorded on Thermo Nicolet 6700 FT-IR spectrometer. In a standard procedure, fresh sample was first calcined at 373 K in Ar stream for 30 min, and the temperature of the cell was increased to the desire temperature with the rate of 10 K min^{-1} . Raman spectra were recorded on a Bruker RFS 100 Raman spectrometer with an argon laser (514.5 nm) as an excitation source. Extended scans from 500 to 3000 cm^{-1} were performed to obtain the first-order Raman spectra with typical exposure times of 20 s, and 5 measurements were carried out on different parts of each sample. A mixed Gaussian–Lorentzian curve-fitting procedure was used to fit the spectra in order to get I_D/I_G normalization of Raman spectra. Thermogravimetry and differential thermogravimetry (TG–DTA) measurements were performed using NETZSCH STA 449c thermal station in nitrogen stream with a heating rate of 10 K min^{-1} . Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-2010 electron microscope with an operating voltage of 200 kV. Boehm titration method was used to determine the amounts of

surface groups [34]. GO sample (0.1 g) was placed in 10 mL of 0.05 mol/L solution of the following: sodium hydroxide, sodium carbonate, sodium bicarbonate. The vials were sealed and shaken for 24 h and filtrated, and then a known quantity of hydrochloric acid was added to each filtrate. The excess acid left in the solution was titrated with NaOH. The amounts of acidic sites were calculated with the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups, $NaHCO_3$ neutralizes carboxylic groups, and Na_2CO_3 neutralizes carboxylic and lactonic groups.

2.4. Catalytic test

The aerobic oxidation of benzyl alcohol was carried out in a 50-mL two-neck flask at atmospheric pressure. A quantity of 0.3 g GO materials was used as catalyst. After a suspension of GO in toluene (10 mL) was treated at 353 K, 1.0 mmol benzyl alcohol was added into the reactor. The mixture was contacted with air and the reaction temperature was kept at 353 K. The products were taken via a sampling pipe and analyzed by a gas chromatograph equipped with a capillary column. The oxygen free test was carried out in Ar atmosphere. GO was firstly treated under vacuum atmosphere for 60 min and moved to the reactor swept by Ar flow under 373 K. Then 10 mL toluene and 1.0 mmol benzyl alcohol was squirted into the reactor and the reaction temperature was kept at 353 K.

3. Results and discussion

Fig. 1 shows the thermogravimetry and differential thermogravimetry (TG–DTA) curves of GO-100 measured in N_2 flow. It can be observed that there are three stages in the process of mass loss, which are attributed to the removal of adsorbed water below 100 °C, decomposition of oxygen-containing functional groups in the range of 100–230 °C, and combustion of graphite oxide above 500 °C [35–37]. The corresponding DTA curve shows a strong exothermic peak at 220 °C, corresponding to the decomposition of oxygen-containing functional groups [36]. Basing on these results, the thermal-treating temperatures of 100–200 °C were adopted in this work, aiming to tune the amounts and types of oxygen-containing functional groups on the surface of GO materials.

Fig. 2 shows the XRD patterns of pristine graphite and GO- T samples thermal-treated at different temperatures. The characteristic (002) diffraction peak (at 26.6°, d-space 0.334 nm) of graphite almost completely disappeared in the patterns of GO samples. Simultaneously, a new diffraction peak (001) at 11.4° (corresponding to a d-spacing of 0.779 nm) appeared in the patterns of fresh GO (GO-100), indicating that graphite was totally transformed into GO and most oxygen was bonded to the planar surface of graphite

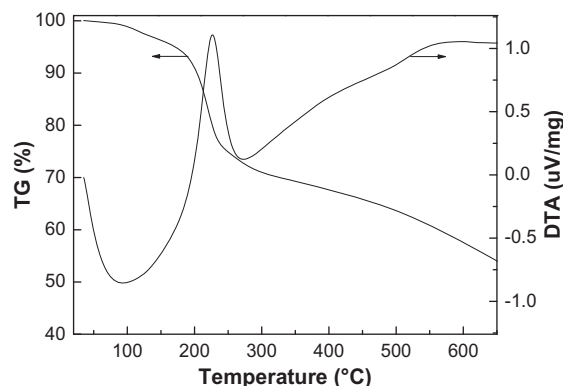


Fig. 1. TG–DTA curves of GO-100.

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