



Full Length Article

Graphene oxide for acid catalyzed-reactions: Effect of drying process



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ABSTRACT

Graphene oxides (GOs) were prepared by Hummers method through various drying processes, and characterized by XRD, SEM, FTIR, XPS and N₂ adsorption. Their acidities were measured using potentiometric titration and acid-base titration. The catalytic properties were investigated in the alkylation of anisole with benzyl alcohol and transesterification of triacetin with methanol. GOs are active catalysts for both reaction, whose activity is greatly affected by their drying processes. Vacuum drying GO exhibits the best performance in transesterification while freezing drying GO is most active for alkylation. The excellent catalytic behavior comes from abundant surface acid sites as well as proper surface functional groups, which can be obtained by selecting appropriate drying process.

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1. Introduction

Solid acid catalysts have served as important functional materials for the production of chemicals due to their environmentally benign nature with respect to corrosiveness, safety, less waste and ease of separation and recovery [1,2]. The application of solid acid catalysts started in the late 1930s with Houdry cracking process, in which acid-washed clay was used as a catalyst. Since then, a number of new solid acid catalysts have been developed for various industrial processes [3,4]. However, conventional solid acid catalysts usually lose their activities in water participating reactions because of strong chemisorption of water on their active sites. Therefore, water-tolerant solid acid catalysts with high efficiency are desperately needed to be developed [4].

Functionalized carbonaceous materials have emerged as a promising water-tolerant solid acid, given that their inherent advantages, in terms of resistance to acidic and basic media and easily tunable properties [5–7]. Nowadays, various carbon-based solid acids and their application as catalysts have been extensively studied [8–15]. Among them, graphene oxide (GO) has received considerable interest recently owing to its unique structural and surface properties [16]. Prepared by exhaustive oxidation of graphite, GO possesses rich oxygen-containing functionalities, such as carboxyl, hydroxyl and epoxide groups, which endows it with moderate acidic and oxidizing properties [17]. In addition,

it has large specific surface area [16] and high adsorption capacity [18]. This kind of material has already exhibited good catalytic activities for several organic transformations, including hydration [17], oxidation [19], esterification [20], Aza-Michael addition [21], Friedel–Crafts addition [22] and ring opening polymerization [23]. However, in many cases high catalyst loading was necessary to obtain the reaction product in good yield. Thus, further improvements are still needed in activity or selectivity.

In the present work, a series of graphene oxides (GOs) were prepared by Hummers method through various drying processes. Their textural and acidic properties were characterized by XRD, SEM, FTIR, XPS, N₂ adsorption and acid-base titration. The catalytic activities for transesterification and Friedel–Crafts alkylation over these catalysts were investigated. The effect of the nature of the GO surface on the catalytic behavior was also discussed.

2. Material and methods

2.1. Materials

All chemical reagents were of analytical grade and used as received without further purification. Graphite powder (99.95%) (Aladdin), sodium nitrate (NaNO₃) (Sinopharm Chemical Reagent Ltd. China), potassium permanganate (KMnO₄) (Shanghai Chemical Reagent Ltd. China), 30% hydrogen peroxide (H₂O₂) (Jiangsu Tongsheng Chemical Reagent Ltd. China), concentrated sulfuric acid (H₂SO₄) (Sinopharm Chemical Reagent Ltd. China)

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2.2. Synthesis

Graphene oxides (GOs) were synthesized from natural graphite by the Hummers method [24]. 4.0 g graphite powder was mixed with 92 ml concentrated H₂SO₄ with stirring under an ice-water bath, and 2.0 g NaNO₃ was put into the mixture. Then 12 g KMnO₄ was added slowly into the mixture, and maintained at low temperature for 2 h and then at 35 °C for another 2 h. The color changed from dark green to brown and reddish brown gas released. 180 ml of deionized water was added then. 15 minutes later another 560 ml deionized water and 20 ml 30% H₂O₂ was added. This suspension was stirred at high temperature for 1 h. The product was separated by centrifuged, washed twice with 5% HCl solution and later with warm water until no SO₄²⁻ anion was detected. The final product was obtained through various drying processes, including vacuum under the pressure of 100 Pa at 50 °C for 48 h, freezing drying at -25 °C under pressure of 5 Pa for 40 h, drying in air at 50 °C for 48 h, which were denoted as GO-V, GO-F and GO-A respectively.

2.3. Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded on a Persee XD-2 X-ray diffractometer using nickel-filtered Cu-K_α ($\lambda = 0.15418$ nm) at 40 kV and 30 mA with range of 5°–50°. Scanning electron microscopy (SEM) was recorded digitally on a Philips XL 30 microscope operating at 30 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PerkinElmer PHI 5000C spectrometer with Mg K_α radiation ($h\nu = 1253.6$ eV) as the excitation source at a pressure lower than 1029 Torr. All binding energy values were referenced to the C_{1s} peak at 284.6 eV. The BET surface area and pore volume of the catalysts were analyzed by N₂ adsorption at -196 °C using a Micromeritics ASAP 2000 instrument. Infrared spectra (FTIR) of the samples were recorded on a Nicolet iS10 spectrometer.

2.4. Acidity measurement

The density of surface acid site was measured by potentiometric titration [25]. GO powders were suspended in acetonitrile, agitated for 3 h, and then titrated with butylamine (0.1 mol/l in acetonitrile). The electrode potential variation was recorded with a METTLER TOLEDO FE20 potentiometer. The density of strongly and weakly acidic groups was measured by neutralization titration [26,27]. For strongly acidic groups, GO powders were added into an aqueous solution of NaCl (excess) and stirred for 4 h. An aliquot of the solution was removed and titrated with standardized 0.1 mol/l sodium hydroxide solution using a phenolphthalein indicator. For a combined measurement of strongly and weakly acidic groups, GO powders were added into sodium hydroxide solution (excess) and stirred for 4 h. The solution was then back titrated with standard 0.1 mol/l hydrochloric acid solution using a phenolphthalein indicator.

2.5. Catalytic testing

Transesterification of triacetin with methanol was performed in a 25 ml round-bottom flask equipped with a reflux condenser under magnetic stirring. 50 mg catalyst was added into the mixture of 1.135 g triacetin and 1.5 g methanol. The reaction was carried out at 60 °C for 8 h. Friedel-Crafts alkylation of anisole with benzyl alcohol was carried out in a stainless steel autoclave with a PTFE liner using magnetic stirring at stir rate of 900 rpm. Typically, 50 mg catalyst, 0.338 g benzyl alcohol and 5 g anisole were added in the autoclave. The reaction lasts 2 h at temperature of 120 °C. The products of both reactions were analyzed with a

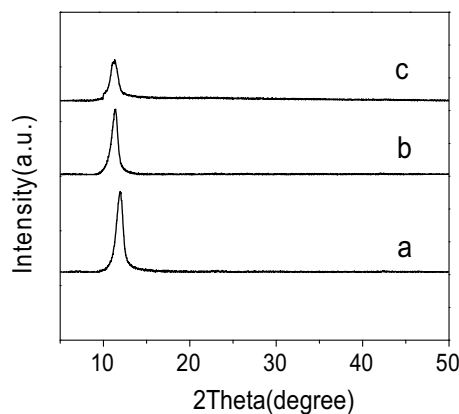


Fig. 1. XRD patterns of (a) GO-A; (b) GO-V; (c) GO-F.

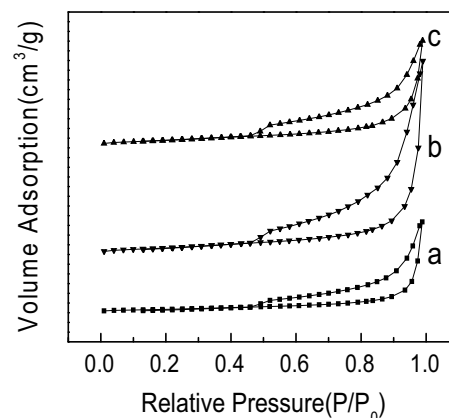


Fig. 2. N₂ adsorption-desorption isotherms of (a) GO-A; (b) GO-V; (c) GO-F.

Table 1
Textural properties of GO catalysts.

sample	BET surface area/(m ² g ⁻¹)	Pore volume/(cm ³ g ⁻¹)	Pore diameter/nm
GO-A	194	1.94	40.0
GO-V	413	3.16	30.6
GO-F	348	1.74	20.0

GC122 gas chromatograph equipped with a SE-30 capillary column (30 m × 0.25 mm × 0.25 μm).

3. Results and discussion

3.1. Structural characterization

Fig. 1 illustrates the XRD patterns of the prepared GOs through various drying processes. All samples exhibit one characteristic peak at $2\theta = 11^\circ$, corresponding to the typical graphene oxide reflection. The diffraction peak of graphite at about 26° was not observed, indicating the successful oxidation of graphite into graphene oxide. However, different drying methods lead to different degrees of exfoliation. The interlayer distances of GOs obtained by freeze drying, vacuum drying and air drying were 0.79, 0.78 and 0.74 nm, respectively.

The N₂ adsorption-desorption isotherms of various GOs were recorded and depicted in Fig. 2. Similar isotherms were observed for all the samples, showing that the drying methods have little effect on the pore structure of GOs. Table 1 summarizes the textural properties of the prepared GO samples. It can be seen that the surface area as well as the pore volume is quite different through various

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