



# Graphite and graphene oxides catalyze bromination or alkylation in reaction of phenol with *t*-butylbromide

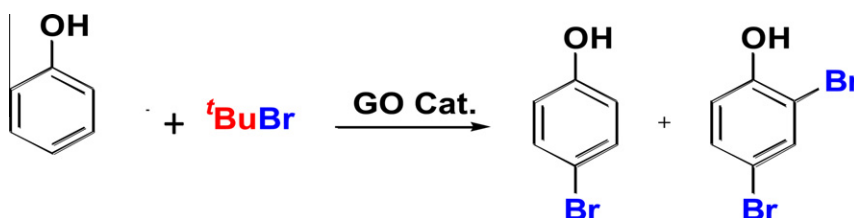
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## HIGHLIGHTS

- ▶ Graphite and graphene oxides catalyze bromination of phenol with *tert*-butylbromide.
- ▶ The bromination occurs on the carbonyl group in the layers of the graphite oxides.
- ▶ Prepared using graphite with nitric acid,  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  and followed by rapid heating.
- ▶ The alkylation occurs during the initial stage and slightly during the reaction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Graphite and graphene oxides, prepared using pure graphite with nitric acid by the Hammers method and followed by rapid heating, were used as a catalyst for bromination or alkylation. The activity test was performed in a batch reactor for 5 h at 323 K with phenol and *tert*-butylbromide as the raw materials. The relationships between the structures and compositions of the graphite and graphene oxides and catalytic activities were studied. The structure and composition of the graphene oxide were analyzed by XRD and X-ray photoelectron spectroscopy. The phenol bromination mainly occurred on the graphite oxide accompanied by Friedel–Crafts alkylation that occurred during the initial stage. The bromination occurred on the carbonyl group in the layers of the graphite oxide based on the XPS and XRD analyses. The mechanism of the phenol bromination on the graphite oxide is discussed.

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## 1. Introduction

The recent interest in graphite and graphene oxides has grown from a proposed application as materials for battery electrodes and the formation of artificial layered nanocomposites containing iron and synthetic polymers. Fully-oxidized graphite and graphene consist of carbonyl, epoxies and hydroxyl groups with no C=C bonds. Little information on the graphite oxide has been reported as catalysts for application in various organic reactions. Graphite oxide was reported to catalyze the Friedel–Crafts addition of indoles to  $\alpha,\beta$ -unsaturated ketones [1]. Graphite oxide also catalyzed the oxidation of thiols, sulfides [2,3], various alcohols and *cis*-stilbene [4,5], the hydration of various alkynes [4–6], the dehydration of xy-

lose [7] and the coupling of acetophenones to benzyl alcohols and arylalkynes to benzyl alcohols [8]. However, no information on the bromination of phenol over graphite and graphene oxides has yet been reported. The other solid acids that have been reported are zeolite H-beta in the presence of bromosuccinic imide [9], and zirconium phosphate using KBr and  $\text{H}_2\text{O}_2$  [10,11]. Tungstate zirconia also catalyzed the bromination of phenol red [12]. On the other hand, an unoxidized graphite containing the aromatic rings of the graphite layers has different surface properties and reactivities than graphite oxide. In a previous study [13], graphite materials catalyzed the Friedel–Crafts alkylation of phenol with *tert*-butylbromide as well as the solid acid of  $\text{AlCl}_3$ . Also, graphite was reported to catalyze the alkylation of *p*-xylene with bromocyclohexane [14] and toluene with benzylchloride [15,16]. Thus, the nonfully oxidized graphite has two functionalities that are the aromatic ring group and an oxygen functional group and, therefore, it is expected

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to have different reactivities. However, no studies on the reactivities of these two parts for bromination and alkylation have been reported using graphite oxides and graphene. Consequently, the study of these two functionalities of the carbon surface will determine the properties and application of the nonfully oxidized graphite and graphene for the organic reactions on the basis of different reaction routes using the same feeds, i.e., Friedel–Crafts alkylation or bromination. In this study, we report that the graphite and graphene oxides with different oxygen functional group contents were prepared and used in the Friedel–Crafts alkylation of phenols to yield *tert*-butylphenol, and the bromination to produce bromophenols with *tert*-butylbromide. The activity and selectivity for the reactions of these catalysts were studied on the basis of their compositions and characteristic oxygen groups and aromatic ring as analyzed by X-ray photoelectron spectroscopy (XPS) and the structures by XRD. The phenol bromination mechanism is also discussed.

## 2. Experimental

Two types of graphite oxides were synthesized from pure graphite (PG, Tokai Carbon Co.; C, 99.99%): PG was oxidized three times with nitric acid to form the graphite oxide denoted as GNO. Several different types of GHOs were prepared by the Hummers and Offemann method by changing the ratio of  $\text{KMnO}_4$  to PG [17]. Samples were prepared by the oxidation of PG by changing the ratio of graphite to  $\text{KMnO}_4$  of 2.0, 3.0 and  $n$ , which denote GHO-2, GHO-3 and GHO- $n$ , respectively. For the graphene oxide, EGHO-2 was prepared from GHO-2 by thermal exfoliation at 673 K for 3 min in air. The bromination activities of the graphite and graphene oxide catalysts were evaluated by the reaction between phenol and *tert*-butylbromide. The activity measurement was made by a batch method; phenol (2 mmol) was mixed with *tert*-butylbromide (2.2 mmol) and graphite oxide (0.5 g) in 5 ml of benzene as the solvent in a 50-ml egg-shaped flask at 50 °C. The *tert*-butylbromide was used without purification. The reaction products were analyzed by GC-FID (Capillary column, DB-WAX) and identified by GC-MS (Series II-JEOL Automass System II, Capillary column, DB-1). The surface composition and structure of the catalysts were analyzed by XPS (Shimadzu Co., ESCA-3200) and XRD (Rigaku Co., RAD-IIC). The XPS O1s, Fe2p, Mn2p, Sn3d, Na2s and Br3p, and C1s spectra were determined according to previously described methods [13,18]. The XPS spectra of the graphite

oxides were deconvoluted to the C–C  $\text{sp}^2$  hybrid (284.5 eV), C–C  $\text{sp}^3$  hybrid (285.4 eV), C–O bond (286.5 eV), and the shape-up satellite due to the  $\pi$ – $\pi^*$  electron transition (290.5 eV). The layer distance ( $d$ ) was calculated using the Bragg equation,  $2d \sin \theta = n\lambda$ , where  $n$  is unity, the X-ray wavelength of the Cu K $\alpha$  radiation ( $\lambda$ ) is 0.154 nm, and  $\theta$  is the angular position of the graphite (002).

## 3. Results and discussion

### 3.1. Reaction of phenol with *tert*-butylbromide over graphite oxide

The reaction of phenol with *tert*-butylbromide over graphite oxide in the benzene solvent is shown in Fig. 1. The phenol concentration decreased from 400 to 290 mmol/L at 1 min after the reaction started. This consumed phenol was related to the phenol adsorbed on the graphite oxide. This result showed that the phenol promptly was adsorbed on the graphite oxide. The *p*-*tert*-butylphenol was produced during the initial period and gradually decreased. *p*-Bromophenol was the major product together with small amounts of the *p*- and *o*-*tert*-butylphenols. The bromination mainly occurred and was accompanied by a slight Friedel–Crafts alkylation during the initial stage. *p*-*Tert*-butylphenol formed along with a small amount of bromophenol after 2 h suggested that the *tert*-butyl cation was active during the initial stage of the reaction and readily reacted with phenol to form the *tert*-butylphenols by the Friedel–Crafts alkylation.

### 3.2. The effects of various graphite oxides

The average concentrations of two types of brominated and *tert*-butylated reaction products at 4–5 h are shown in Fig. 2. The graphites oxidized under various conditions that included nitric acid-treatment, various ratios of  $\text{KMnO}_4$ /graphite (0.5, 1.5, 2, 2.5, 3 and 4.5) and graphene oxide (EGHO) as a rapidly heated GHO-2, were used. The GHO-1.5 and -2 catalysts catalyzed the complete bromination, while the GHO-2.5 and -3 produced an almost complete reaction. For the GHO-4.5, EGHO and GNO, the bromination was nearly half compared and accompanied by the alkylation. The EGHO had a slight activity for the reaction. Pure graphite barely catalyzed this reaction. The reaction of phenol with *tert*-butylbromide on graphite oxides involved several reactions to form *p*-bromophenol, 2,4-dibromophenol, and *o*- and *p*-*tert*-butylphenols. Therefore, the bromination during the phenol reaction

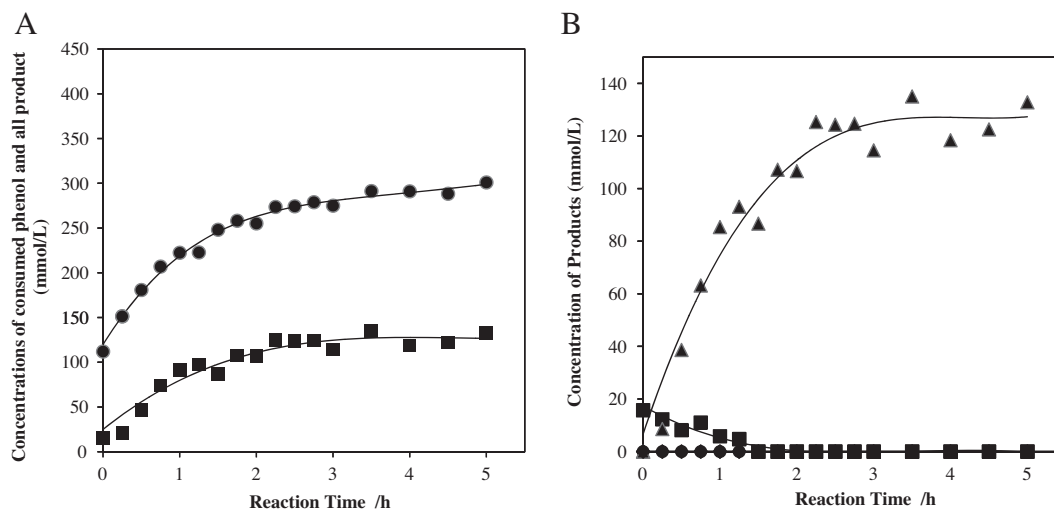


Fig. 1. (A) The reaction of phenol with *tert*-butyl bromide over graphite oxide (GHO-2) at 50 °C. (●) Concentrations of consumed phenol and (■) all products. (B) Concentration of products. (▲) *p*-bromophenol, (◆) 2,4-dibromophenol, (◐) *o*-*tert*-butylphenol and (■) *p*-*tert*-butylphenol.

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