

Short communication

# Direct hydroxylation of benzene to phenol over metal oxide supported graphene oxide catalysts



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## ABSTRACT

A series of metal oxide (V, Fe, Cu) supported graphene oxide (M/GO) catalysts have been prepared by the impregnation method. The catalysts were characterized by TEM, XRD, FT-IR, and Raman spectroscopies and the results showed that the metal oxide nanoparticles were highly dispersed and successfully incorporated on graphene oxide sheets. Among the catalysts, V/GO exhibited the highest efficiency in direct hydroxylation of benzene using H<sub>2</sub>O<sub>2</sub> as an oxidant in acetic acid solvent with a phenol yield of 22.7% and a selectivity of 98.4% under the optimized condition along with good recycle performance.

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## 1. Introduction

Phenol is an important organic intermediate used as a precursor to synthesize many useful chemical materials, such as resins, pesticides, medicine and dyestuffs. Currently, phenol is mainly produced with a relatively low yield through the three-step cumene process, accompanying the production of by-product acetone, high pollution and high energy consumption [1]. Therefore, it is desirable to explore efficient, economic and environment-friendly reaction routes. The direct one-step hydroxylation of benzene has become a research hotspot and gained important progress. Many attempts have been made to employ molecular oxygen, nitrous oxide, hydrogen peroxide and a mixture of oxygen and hydrogen as oxidants in the oxidation of benzene to phenol [2–5]. However, using molecular oxygen as an oxidant requires the existence of reducing agents while nitrous oxide is of high cost and difficult to store, which limits their application in the benzene hydroxylation. By contrast, hydrogen peroxide is a clean and mild oxidant with water as the only by-product and widely used in the study of liquid phase hydroxylation of benzene [4].

Carbon nanomaterial is one of the most commonly used materials in catalysis mainly due to their distinct structure and inherent nature including easy surface modification, remarkable chemical inertness and high specific surface areas [6]. Graphene, a monolayer carbon material, consists of sp<sup>2</sup> hybridized carbon atoms which are arranged in hexagonal structure with a two-dimensional (2D) honeycomb lattice. Ever

since its discovery, graphene has attracted a remarkable attention in the field of catalysis because of its unique thermal, mechanical and chemical properties [7]. Frank et al. reported that pristine graphene could be a promising catalyst for selective oxidation of acrolein to acrylic acid [8]. Nevertheless, the graphene with unfunctionalized carbons limits its application in catalysis. The functionalization of graphene is expected to introduce sufficient O-containing groups on the graphene sheet, which plays an important role in further chemical modification. Graphene oxide (GO), which has a graphene-like structure, containing plentiful functional groups, including hydroxyl, carboxyl, carbonyl and epoxy groups, shows great potential as an efficient catalyst support [9]. Dreyer et al. reported high activity of GO in the selective catalytic oxidation of various alcohols, alkenes and alkynes to aldehydes, acids and ketones, respectively, under relatively moderate conditions, where GO not only acted as the catalyst, but also as the assisted oxidant in addition to ambient oxygen [10]. Furthermore, the open  $\pi$ -electron system of GO may especially promote the interaction between GO and reactants possessing a  $\pi$ -electron system [11]. Our previous work indicated that the increase of hydrophobicity of supports facilitated the adsorption of benzene to enhance the catalytic activity of catalysts in the titled reaction [12]. Therefore, it is anticipated that the hydrophobicity of GO and the  $\pi$ - $\pi$  interaction between GO and benzene will further enhance the adsorption and activation of benzene to improve the catalytic performance of direct hydroxylation of benzene to phenol. Many kinds of transition metal species have been used in the benzene hydroxylation reaction, such as Fe, Cu, V, Co, and Ti [13,14]. Among them, Fe-, Cu-, and V-containing catalysts have shown good catalytic activity.

In this work, we report a facile approach to prepare metal oxide (V, Fe, Cu) supported GO nanocomposites. Their catalytic performance and

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stability were tested in the hydroxylation of benzene with hydrogen peroxide as an oxidant.

## 2. Experimental

Graphite powder,  $\text{NH}_4\text{VO}_3$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were purchased from Aladdin Reagent Inc. Graphite oxide was prepared by the Hummers method [15]. To prepare V/GO, 0.20 g of dried graphite oxide was dispersed in 50 mL of deionized water by sonication for 2 h to form a stable graphene oxide suspension. Then 0.05 g of  $\text{NH}_4\text{VO}_3$  was added, followed by vigorous stirring for 3 h, and drying at 60 °C for 16 h. The resulted solid sample was transferred into a porcelain boat and calcined in  $\text{N}_2$  at 550 °C for 3 h with a heating rate of 1.5 °C·min<sup>-1</sup>. The product was washed with 0.10 mol·L<sup>-1</sup> HCl and deionized water to remove the residue, and then dried at 60 °C in air overnight. To prepare Fe/GO and Cu/GO, the same procedure of preparing V/GO was followed except using the equimolar of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  instead, respectively.

XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu-K $\alpha$  radiation with a voltage of 40 kV and a current of 40 mA. FT-IR spectra were recorded on a Nicolet iS10 infrared instrument using KBr discs. TEM images were obtained from a JEOL JEM2011 microscope operated at 200 kV. Thermogravimetric (TG) measurements were carried out on a Perkin-Elmer TGA 7 thermal analyzer at a heating rate of 10 °C·min<sup>-1</sup> under a 40 mL/min air flow. Raman spectra were recorded on a Dilor LABRAM-1B spectrometer with a 514 nm laser excitation. Elemental analysis was performed on a Thermo Elemental IRIS Intrepid ICP atomic emission spectrometer.

The experiments of benzene hydroxylation to phenol were carried out as follows. Typically, 40 mg of catalyst, 1 mL of benzene and 10 mL

of 80 wt.% acetic acid were added into a 25 mL three-necked flask connected with a reflux setup. After heating to 65 °C, 3.5 mL of 30 wt.%  $\text{H}_2\text{O}_2$  was added dropwise for 30 min with vigorous stirring, the reaction was continued for another 3 h. After reaction, the mixture was separated by centrifugation. The content of liquid products was analyzed by gas chromatography (GC) using toluene as the internal standard. The conversion of benzene, the selectivity of phenol and the yield of phenol were calculated as  $n$  (converted benzene) /  $n$  (initial benzene),  $n$  (phenol) /  $n$  (converted benzene) and  $n$  (phenol) /  $n$  (initial benzene), respectively.

## 3. Results and discussion

The morphology of GO, V/GO, Fe/GO and Cu/GO nanocomposites was characterized by TEM. As shown in Fig. 1a, the large lamellar nano-sheets with low contrast grade can be identified to be multi-layer GO sheets. TEM images exhibit that vanadium oxide (Fig. 1b), iron oxide (Fig. 1c), and copper oxide (Fig. 1d) nanoparticles (the dark dots in the white circles) with different particle sizes are dispersed on the GO sheets. Also, it can be seen that most of the metal oxide nanoparticles are dispersed on the edge or rough area of GO sheets, leading to the inhomogeneous distribution of active species on the GO surface and the nonuniform decoration of GO sheets with metal oxide nanoparticles. The corresponding EDX images of V/GO, Fe/GO and Cu/GO were also listed in Fig. 1 (SI).

The XRD patterns of V/GO, Fe/GO, Cu/GO and GO are presented in Fig. 2. All the samples show the characteristic peak at  $2\theta$  of ca. 13°, corresponding to the (001) crystalline planes of GO [16]. After introducing metal oxide species on GO sheets, the intensity of the peak at 13° decreases whereas a new sharp diffraction peak at 26.5° appears; the latter

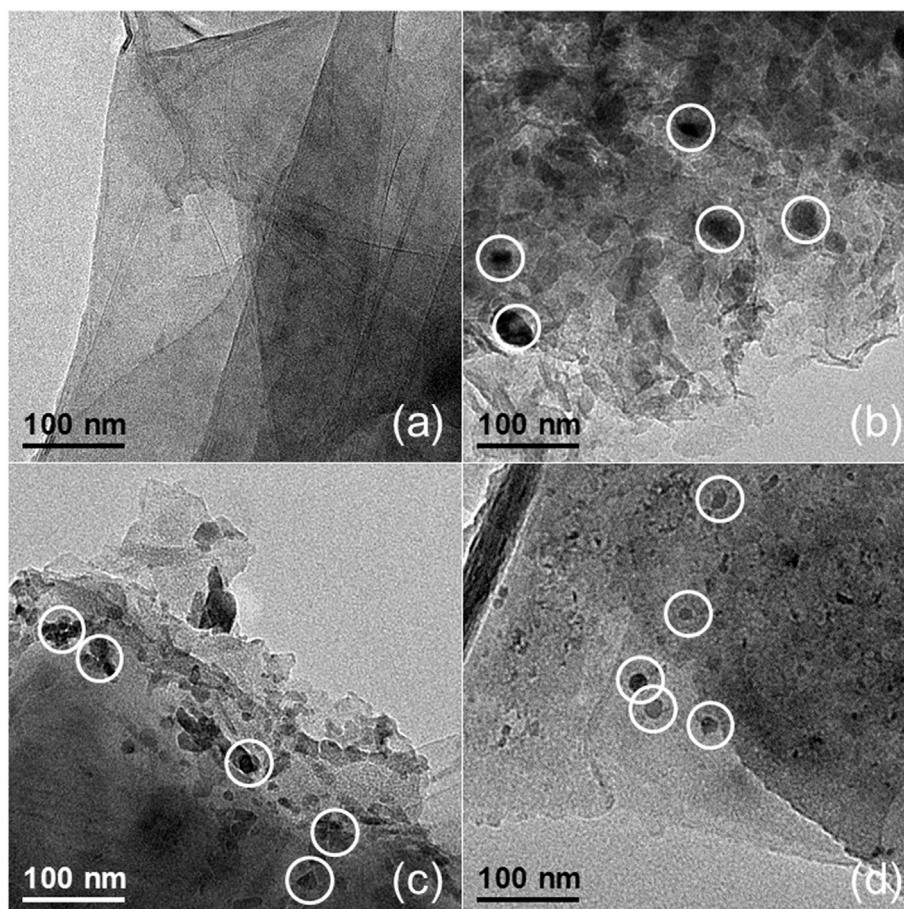


Fig. 1. TEM images of (a)GO, (b) V/GO, (c) Fe/GO, (d) Cu/GO. Some metal oxide particles are exemplified in circle.

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