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Hydrogen sulfide adsorption on nano-sized zinc oxide/reduced graphite oxide composite at ambient condition

Hoon Sub Song[a,d], Moon Gyu Park[b], Soon Jin Kwon[c], Kwang Bok Yi[b], Eric Croiset[a,*], Zhongwei Chen[a], Sung Chan Nam[d,**]

[a] Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L3G1, Canada
[b] Department of Chemical Engineering Education, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea
[c] Graduate School of Green Energy Technology, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea
[d] Greenhouse Gas Department, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 305-343, Republic of Korea

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ABSTRACT

This paper presents new insights on the synthesis of nano-ZnO on reduced graphite oxide (rGO) composite via a microwave-assisted route and its use as a potential sorbent to adsorb hydrogen sulfide (H_2S) at ambient conditions. Depending on the synthesis methods, the nano-sized ZnO on rGO presents different characteristics, in particular the degree of nano-ZnO dispersion on the surface of the rGO. Microwave-assisted reduction was able to offer a mild reduction to the oxygen-containing functional groups attached on the surface of graphite oxide (GO). Those oxygen-containing functional groups provide the bridge and the terminal groups between zinc oxide and the rGO surface. Because those functional groups act as anchor sites for metal ions, it was possible to achieve uniformly distributed nano-sized ZnO particles on the surface of the rGO sheets. In addition, they accelerate oxygen activation for H_2S adsorption. H_2S adsorption tests at ambient conditions were conducted. The 1-D carbon nanotubes (CNTs) had been used for reference in order to investigate the functionality of 2-D rGO substrate. Also, the effects of the different synthesis methods (microwave vs. reflux) were evaluated for H_2S adsorption. The adsorption capacity increased dramatically for the microwave-assisted composite compared to the composite manufactured using the reflux method.

1. Introduction

Hydrogen sulfide (H_2S) is one of the most common sulfur-containing compounds found in natural gas and syngas [1]. H_2S is a toxic gas and a known major contributor of acid rain. Due to environmental regulations and to protect downstream processes, increasingly deeper H_2S removal is necessary. One of the methods for removing H_2S is by adsorption. Extensive studies have been performed in order to determine appropriate metal oxides (or metal hydroxide) as H_2S adsorbents or adsorbent's supports [2–5]. Many different adsorbents have been studied for H_2S adsorption, such as zeolite [6], metal oxides (or hydroxide) [2,7,8] and activated carbon [9]. It is known that sulfur interacts with a metal or an oxygen atom by transferring electrons from H_2S orbitals into unoccupied orbitals of the metals [10]. Zinc oxide (ZnO) is very effective in limiting poisoning by the removal of hydrogen sulfide (H_2S) from gas steams with the formation of zinc sulfide (ZnS) [11]. This reaction produces a metal sulfide or sulfate, as shown in equation 1 in the case of zinc oxide [12]. The mechanism of H_2S adsorption on an ionic solid such as ZnO has been introduced earlier [12] starting with the dissociation of H_2S into H^+ and HS^-, followed by diffusion of HS^- into the oxide lattice and migration of oxide and water to the surface. Therefore, the diffusion of S^{2-} and HS^- ions into the ZnO is required in order to convert ZnO to ZnS by proton transfers from H_2S to the chemisorbed OH groups on the Zn–O surface [13].

$$ZnO_{(s)} + H_2S_{(g)} \rightarrow ZnS_{(s)} + H_2O_{(g)} \quad (1)$$

Graphene has received increasing attention both in fundamental science and applications because of its excellent electronic properties, chemical stability, and high surface area [14]. Recently, graphene-based composites with metal oxide has sparked considerable interest since graphene can be used as adsorbent due to its unique 2-D layered structure [15,16]. Because of its mechanical and electrical properties, most of graphene studies have focused on the electro-chemistry field, such as super-capacitor [17,18] and battery [19–21]. In this study, the unique characteristics of graphene have been applied to desulfurization. In addition, among various metal oxides, ZnO is one of the most commonly used for H_2S adsorption at

* Corresponding author. Tel.: +1 519 888 4567x36472; fax: +1 519 888 4567.
** Corresponding author. Tel.: +82 42 860 3645; fax: +82 42 860 3645.
E-mail addresses: ecroiset@uwaterloo.ca (E. Croiset), scnam@kier.re.kr (S.C. Nam).

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high temperatures [8,10]. Most recently, several studies using zinc (hydro)oxide with graphene (or graphite oxide) composites have been conducted in order to investigate the interaction characteristics between the graphene-related composites and H_2S or NO_2 gases. Therefore, it has been known that zinc (hydro)oxide with graphite oxide composites are quite active for those H_2S and NO_2 adsorption at room temperature [22–24].

The object of this study is to investigate the effect of a substrate for active metal oxide (zinc oxide for this study). The unique beneficial characteristics of rGO containing oxygen functional groups to increase the H_2S adsorption capacity have been studied. In addition, the structure and morphology of the adsorbent (i.e. particle size of active metal oxide and oxygen functional groups on the surface of rGO) could be controlled depending on the reduction process from graphite oxide to reduced graphite oxide. Therefore, the effects of the different reduction processes (i.e. microwave vs. reflux) to the H_2S adsorption capacities should be evaluated. Although most of H_2S adsorption experiments using ZnO have been conducted at high temperature, the present study investigates this novel ZnO/graphene adsorbent as a candidate for low temperatures H_2S adsorption.

2. Experimental

2.1. Preparation of adsorbents

The following chemicals, graphite powder (Sigma–Aldrich, <45 μm, ≥99.99%), sulfuric acid (Sigma–Aldrich, ACS reagent, 95.0–98.0%), hydrochloric acid (Sigma–Aldrich, ACS reagent, 37%), hydrazine solution (Sigma–Aldrich, 35 wt% in H_2O), potassium permanganate (Samchun Chemical, 99.3%), hydrogen peroxide (OCI Company Ltd, 30 wt% in H_2O), sodium hydroxide (Sigma–Aldrich, ACS reagent, ≥97.0%), zinc acetate dehydrate (Sigma–Aldrich, ACS reagent, ≥98%) and phosphoric acid (Sigma–Aldrich, ACS reagent, ≥85 wt% in H_2O), were used.

2.1.1. Synthesis of graphite oxide

A modified graphite oxide (GO) synthesis procedure is based on our previous work [25]. Briefly, graphite oxide was synthesized as follows: a sulfuric acid (360 mL) and phosphoric acid (40 mL) mixture was prepared in an ice bath; and then 3.0 g of graphite powder was added. When the temperature reached ~5 °C, 18.0 g of $KMnO_4$ was added slowly. The mixture was stirred for 1 h and then transferred to a heating mantle to provide isothermal conditions at 50 °C. The oxidation process was conducted for 18 h. The system was then cooled to room temperature, and then placed in an ice bath again. 400 mL of de-ionized water and 15 mL of 30% H_2O_2 were added gradually. The mixture turned bright yellow and generated copious bubbles. The mixture was stirred for 1 h and then centrifuged at 3500 rpm for 3 min. The remaining solid paste was washed with a mixture of 100 mL of de-ionized water and 100 mL of 30% HCl for 1 h, and this washing was repeated twice. The product was then rinsed twice again with 200 mL of de-ionized water. The mixture was centrifuged again at 3500 rpm after the washing procedure. After the washing steps, the paste was freeze and vacuum-dried overnight.

2.1.2. Synthesis of nano-zinc oxide/reduced graphite oxide composite

400 mg of GO was dissolved in 200 mL of ethylene glycol (EG) and then underwent ultra-sonication for 30 min. 100 mL of 1.0 M aqueous NaOH solution was added, followed by 30 min of sonication again. Then, 100 mL of 0.069 M aqueous zinc acetate solution (ZnAc) was added into the mixture drop wise (2.0 mL/min) for 50 min. For the reduction process, two different methods (reflux and microwave) were performed to produce zinc oxide (ZnO)/rGO composites. 300 μL of hydrazine solution was added before the reduction process. For the reflux method, the ZnAc/GO mixture was heated at 105 °C for 18 h. For the microwave method, the ZnAc/GO mixture was microwaved for 30 s (with 30 s interval) 6 times. These two methods resulted in ZnO/rGO mixtures. After cooling down to room temperature naturally, those ZnO/rGO mixtures were filtered and washed with DI water three times until the pH reached around 7.0. Finally, the pastes were dried in a vacuum-oven at 40 °C overnight. The ZnO/rGO composites from reflux and microwave method are named as ZnO/rGO-R and ZnO/rGO-M, respectively. For reference, graphene itself synthesized from reflux and microwave also were prepared without adding the zinc acetate aqueous solution. In addition, zinc oxide/carbon nanotube (CNT) composites were also prepared using identical way for reflux and microwave methods.

2.2. H_2S adsorption breakthrough tests

Dynamic breakthrough capacity tests were conducted at ambient temperature. The adsorbents were packed into a quartz tube (internal diameter 10 mm). 0.5 cm^3 of the adsorbents were diluted with 1.0 cm^3 of Al_2O_3 (total 1.5 cm^3 of bed). The mass of the adsorbent was between 0.147 and 0.201 g. For the pre-humidified process, moist air (281.4 mL/min) went through the fixed bed of adsorbent for 1 h. In a typical test, a flow of hydrogen sulfide (2.4 mL/min with 3.01 vol% of H_2S balanced with N_2) was mixed with the moist air before passing through the adsorbent bed. Therefore, the initial H_2S concentration was 254.5 ppm with total flow rate of 283.8 mL/min. After the H_2S stream passes through the bed, the product stream was diluted with 1716.2 mL of dry air before being injected in the H_2S analyzer due to the limitation of the H_2S analyzer (Fluorescence H_2S Analyzer, Model 101E, Teledyne). The experiments were carried out until the output H_2S concentration reached ~10 ppm. After the moisture pre-treatment, the ZnO/rGO-R and ZnO/rGO-M samples were labeled as ZnO/rGO-R-W and ZnO/rGO-M-W, respectively. In addition, after the H_2S adsorption tests, samples are named as ZnO/rGO-R-H_2S and ZnO/rGO-M-H_2S, respectively.

2.3. Characterizations

X-ray diffraction (XRD, Rigaku, 40 kV/100 mA of X-Ray (step size: 0.02°) was used for adsorbent characterization; 5–60° of 2θ range was tested. Raman (Model: NTEGRA Spectra, NT-MDT) was carried out with spectra of 2/cm resolution and 473 nm wavelength. X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo) was carried out with number of scan of 4, source type of Al K Alpha, spot size of 500 μm and energy step size of 0.1 eV. Fourier-transform infrared (FT-IR) spectroscopy was carried out a Nicolet 6700 (Thermo Scientific) with KBr dilution at 1:300 weight ratio. TEM analysis (Model: JEM-2100F HR, Jeol Ltd., Japan) was conducted with accelerating voltage of 200 KeV, point resolution of 0.23 nm and resolution of STEM of 0.2 nm.

3. Results and discussions

3.1. Characterizations of nano-ZnO/rGO composite

The crystal structures of the graphite oxide (GO), reduced graphite oxide (rGO), and zinc oxide/rGO composites were characterized using XRD (see Fig. 1). The 2θ of GO is located at 9.62°. The interlayer spacing of GO (d_{002} = 9.18 Å) is larger than graphite (3.4 Å) implying that oxygen containing functional groups, such as hydroxyl, epoxy and carboxyl, are intercalated between the graphite layers [26]. Since the surface functional groups on the surface of rGO act as active sites for guest materials [20,27], the rGO is