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Enhanced adsorption of hydrogen sulfide and regeneration ability on the composites of zinc oxide with reduced graphite oxide

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HIGHLIGHTS

- Reduced graphite oxide (rGO) promotes the H_2S adsorption efficiency of metal oxide.
- Oxygen functional groups on rGO affect the chemical state of zinc oxide.
- ZnO/rGO composite shows about 5 times higher H_2S adsorption capacity.
- ZnO/rGO composite shows stable regeneration efficiency over 8 cycles.

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ABSTRACT

Interaction of oxygen-containing functional groups on reduced graphite oxide (rGO) surface and zinc oxide (ZnO) has been investigated; and critical functionalities of rGO for enhancing H_2S adsorption were studied. The abundant oxygen functional groups attached on the surface of rGO promoted the dispersion of nano-sized ZnO; then a higher surface area on the adsorbents was achieved. In addition, they prevented the aggregation of ZnO particles during regeneration at 600 °C. Beside those physical property changes, the presence of rGO modified the chemical properties of ZnO, as confirmed by XPS analysis. Due to those oxygen functional groups, the amount of zinc ions (Zn^{2+}) are placed at the oxygen vacant sites, not only in the Zn–O lattice on ZnO/rGO composite. It was determined that the amount of oxygen ions in the Zn–O lattice decreased; and loosely bonded oxygen ions near the Zn–O lattice and on the surface were generated. Therefore, it was found that the presence of rGO plays a critical role to provide appropriate conditions for H_2S adsorption, which was confirmed through the H_2S adsorption breakthrough and regeneration tests. The ZnO/rGO composite showed about fivefold that of pure ZnO. The capacity after 1st regeneration for ZnO/rGO decreased by about 57% but then was maintained constant over 8 recycles while that on ZnO decreased dramatically to reach nearly zero capacity after 5 cycles.

1. Introduction

Hydrogen sulfide (H_2S) is one of the most common sulfur components and is considered as an undesirable component in most industrial applications since sulfur impurities rapidly deactivate or poison catalysts, which are widely used in the chemical or petrochemical industries [1]. Therefore, the removal of sulfur-containing gases (i.e. SO_2, H_2S etc.) has become a critical issue. Various approaches to remove H_2S, such as sorption, catalysis or condensation, have been applied [2]. Among those approaches, different adsorbents, such as activated carbon, zeolites [3,4], modified alumina [5] or metal oxides [6,7], have been investigated. Zinc oxide (ZnO) has been widely used as an adsorbent for removal of H_2S from hot gas steams (in range of 500–800 °C) with the formation of zinc sulfide (ZnS) by the following reaction ($ZnO_{(s)} + H_2S_{(g)} \rightarrow ZnS_{(s)} + H_2O_{(g)}$) [8]. There is a critical drawback, however, to use ZnO for hot-gas H_2S removal process. Due to its thermal instability,

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the ZnO adsorbent has a risk of evaporating as volatile metallic zinc [9]. For lower temperature applications, the thermal stability is not an issue and ZnO can be converted to ZnS at even ambient condition [10]. To date, several studies have been conducted under moist and dry conditions [11] for H_2S adsorption. It has been proposed that water is critical since moisture is able to dissociates H_2S into HS^- and S^{2-}; and the dissociated H_2S ions are chemically adsorbed on the surface [12,3]. It was confirmed that the carboxylate groups on a composite significantly decreased after H_2S exposure [13]. Different mechanisms, however, govern the adsorption for dry condition since direct replacement of the dissociated HS^- ions with –OH groups on oxide particles are dominant for sulfide formation.

Graphite oxide (GO) has been widely studied as an adsorbent since it contains various oxygen functional groups, such as hydroxides, epoxides, and carboxylic groups on the surface of GO plane [14,15]. Those negatively charged oxygen functional groups, which are known to anchor positively charged metal ions (i.e. Zn^{2+} or Cu^+) through hydrogen bonds, can be controlled quantitatively by varying the reduction processes. Reduced graphite oxide (rGO) has thus received dramatic attentions as a substrate for metal oxide deposition [14–18]. Using those benefits, active researches regarding metal oxides (copper [12], zirconium [17] cobalt [13] or zinc [19,20]) with rGO composites for acid gas (i.e. H_2S, SO_2 or COS) adsorption processes have been extensively studied recently.

As discussed above, many studies for H_2S adsorption have been conducted using metal oxide attached on the rGO surface. However, in-depth investigation of the effects of those oxygen functional groups on the metal oxide chemical states has not been studied. Therefore, in this study, the critical functionalities of those oxygen functional groups for H_2S adsorption were studied by investigating the change of the chemical status of metal oxides attached on rGO. In addition, from a practical point of view, regeneration of the sorbent is critical and this study also investigates the regenerability of the developed composite ZnO/rGO sorbent.

2. Experimental

2.1. Synthesis of graphite oxide

The synthesis of GO was based on our previous work [21]. GO was synthesized using a mixture of 360 mL of sulfuric acid (Sigma–Aldrich, ACS reagent, 95.0–98.0%) and 40 mL of phosphoric acid (Sigma–Aldrich, ACS reagent, ⩾85 wt.% in H_2O), and 3.0 g of graphite powder (Sigma–Aldrich, <45 μm, ⩾99.99%). This mixture was placed in an ice bath. When the temperature reached below 5 °C, 18.0 g of $KMnO_4$ (Samchun Chemical, 99.3%) was added slowly. The mixture was stirred for 1 h and then maintained at isothermal conditions at 50 °C for 18 h. The system was then cooled to room temperature naturally. The mixture was then placed in an ice bath again; and 400 mL of de-ionized water and 15 mL of 30% H_2O_2 (OCI Company Ltd., 30 wt.% in H_2O) were added gradually. The mixture turned then 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 (Sigma–Aldrich, ACS reagent, 37%) twice. The product was then rinsed twice again with 200 mL of de-ionized water. After the washing steps, the paste was freeze- and vacuum-dried overnight.

2.2. Synthesis of ZnO/rGO composites

400 mg of GO was dissolved in 200 mL of ethylene glycol (Sigma–Aldrich, ReagentPlus®, ⩾99%) and 100 mL of 0.1 M aqueous NaOH (Sigma–Aldrich, ACS reagent, ⩾97.0%) solution; then underwent ultra-sonication for 30 min. 0.07 M aqueous zinc and copper acetate (Sigma–Aldrich, ACS reagent, ⩾98%) solutions were prepared. Then, 100 mL of 0.07 M Zinc acetate solution was prepared and mixed with the GO solution; then sonicated for another 30 min. 300 μL of hydrazine solution (Sigma–Aldrich, 35 wt.% in H_2O) was added before the reduction process. The Zn/GO mixture was reduced by microwave irradiation for 3 min (1 min irradiation with 1 min break, 3 times). After cooling down, the mixture was filtered and washed with DI-water three times using centrifuge. Finally, the paste was freeze- and vacuum-dried overnight.

2.3. H_2S adsorption breakthrough and regeneration tests

Dynamic breakthrough tests were conducted at 300 °C. 0.5 cm^3 of the adsorbents diluted with 1.0 cm^3 of Al_2O_3 (Sigma–Aldrich, ~150 mesh) for a total of 1.5 cm^3 of bed were packed into a quartz tube (internal diameter 10 mm). In a typical test, a flow of H_2S (5 mL/min, 3.01 vol% of H_2S balanced with N_2) was mixed with 195 mL/min of N_2 gas before passing through the adsorbent bed. The initial H_2S concentration was 750 ppm with a total flow rate of 200 mL/min. For regeneration, N_2 only was flowed through the spent adsorbent at 600 °C for 1 h. The product stream was further diluted with 1800 mL/min of N_2 before injection to the H_2S analyzer due to the limitation of the H_2S analyzer (Fluorescence H_2S Analyzer, Model 101E, Teledyne) which could accommodate H_2S concentration only up to 10 ppm. The experiments were carried out until the output H_2S concentration, after dilution, reached ~5 ppm. The experimental breakthrough time was determined when the outlet H_2S concentration, after dilution, reaches 0.1 ppm. The amount of sulfur adsorbed per gram of adsorbent was calculated by Eq. (1):

$$\frac{\text{g of S}}{\text{g of Ads.}} = \frac{0.15\ \text{mL H}_2\text{S}}{\text{min}} \times \frac{1\ \text{mol H}_2\text{S}}{22,400\ \text{mL H}_2\text{S}} \times \frac{34.06\ \text{g S}}{1\ \text{mol H}_2\text{S}} \times \frac{32.06\ \text{g S}}{34.08\ \text{g H}_2\text{S}} \times t\left(\frac{\text{min}}{\text{g Ads.}}\right) \tag{1}$$

where t is the experimental breakthrough time (min/g of adsorbent).

2.4. 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 measured. X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, KRATOS Inc.) was used with mono chromatic A1 Ka (1486.6 eV) for X-ray source, 0.1 eV/step; and no surface treatment were used. Scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-4700 with an accelerating voltage of 5.0 kV.

3. Results and discussions

3.1. H_2S adsorption and regeneration ability

From an industrial point of view, regeneration of the adsorbent is critical. Multiple regeneration cycles for pure ZnO and ZnO/rGO composite were then studied. For all cases, identical sulfidation conditions (300 °C and 750 ppm H_2S) were used; and a temperature of 600 °C (in N_2 only) was used for regeneration. Fig. 1 shows the regeneration capacities (mg of sulfur adsorbed per gram of adsorbent) for pure ZnO (up to 5 cycles) and ZnO/rGO samples (up to 8 cycles).

The initial sulfur adsorption capacity for pure ZnO (31.7 mg S/g ads) corresponds to that reported in the literature [7,22]. The initial sulfur adsorption capacity for ZnO/rGO composite (172.6 mg S/g ads) was about 5.5 times higher than that from pure ZnO. After the first regeneration, the decrease in sulfur capacity for both