Reactive adsorption of hydrogen sulfide on visible light photoactive zinc (hydr)oxide/graphite oxide and zinc (hydr)oxychloride/graphite oxide composites

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ARTICLE INFO

ABSTRACT

Composites of zinc (hydr)oxide and graphite oxide (GO) with 2, 5, and 20 wt.% of the GO component were obtained by precipitating zinc hydroxide from zinc chloride with dispersed GO present in the solution. The materials were evaluated as adsorbents of hydrogen sulfide at ambient conditions. The surface properties of the initial and exhausted samples were studied by FTIR, XRD, SEM/EDX, TEM, nitrogen adsorption, potentiometric titration, microcalorimetry, and thermal analysis. The adsorption capacity increases with an increase in the content of GO in the composites studied. The lower adsorption capacities measured for the samples with 2 and 5 wt.% of graphite oxide are linked to the zinc (hydr)oxychlorides phase present in these composites. The heats of H_2S adsorption on the zinc (hydr)oxide and its composites were measured in nitrogen and in air flow. The results indicate that highly energetic adsorption centers are formed on the composite surfaces. Exposure to visible light decreases the H_2S adsorption capacity. This behavior is linked to photoactivity that leads to the reduction of the composite and formation of sulfur and sulfites/sulfates. These processes involve active centers, —OH groups, which react with hydrogen sulfide.

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1. Introduction

Hydrogen sulfide is a toxic pollutant present in the atmosphere as a result of anaerobic bacterial reduction of sulfates. The inhalation of hydrogen sulfide can be lethal for humans as it attacks the neural system and important organs [1]. Materials that have been applied for the removal of H_2S at high temperatures include zeolites, modified alumina, or metal oxides [2,3]. Modified activated carbons are typically used at ambient conditions [4]. The modification methods focus on an increase in surface basicity to enhance H_2S dissociation. The approaches used include impregnation with caustics or alkali metal salts [5,6] and the incorporation of nitrogen functional groups [7,8]. Another group of carbonaceous materials studied as adsorbents of hydrogen sulfide are graphite oxide-based materials [7,9–11]. Although the graphite oxide's structure and chemistry depend on various factors like the level of oxidation and on the type of oxidizing agents used, it can generally be represented as distorted graphene layers decorated with different oxygen functional groups [12–15]. These oxygen groups enable GO dispersion in many solvents and they also participate in the formation of various composite materials.

Composites of graphite oxide or graphene with zinc (hydr)oxide were recently studied as adsorbents of H_2S at ambient conditions [9]. The results showed that an addition of graphite oxide or graphene significantly improves the performance of these materials, especially in moist conditions. The conversion of H_2S to SO_2 on the surface was enhanced by photocatalytic activity in visible light. The synergistic effect of the GO component was linked to the structure of the composite where the zinc (hydr)oxide component had more terminal groups than its bulk phase. These groups were shown to take part in oxidation reactions via a photochemical path. The graphite oxide and graphene components also helped in electron transfer leading to oxygen activation. The better adsorption capacity on the GO composites than that on $Zn(OH)_2$ was linked to more terminal OH groups, to the presence of oxygen activating functional groups and to bonds between zinc (hydr)oxide and the graphene oxide in the composites. Products formed on the surface after H_2S adsorption included elemental sulfur, sulfite, sulfate species and zinc sulfide.

The synergistic effect on the surface of cobalt (hydr)oxide/GO composites was also shown to be important for the reactive adsorption of H_2S, especially in moist conditions [10]. The adsorption process was significantly enhanced when a small amount of

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graphite oxide was present in the composite. The new chemical environment at the interface was shown to contribute to the extent of H_2S dissociation. Superoxide ions formed as a result of the incorporation of heteroatoms into the graphene oxide matrix were indicated as important participants in H_2S oxidation reactions. A high adsorption capacity on the composites with the low ratio of GO was explained taking into account a unique structure and chemistry of the composites. The presence of a small amount of highly dispersed graphite oxide sheets resulted in a very amorphous and chemically heterogeneous material with a significant number of oxygen vacancies and terminal hydroxyl groups. These sites helped in the oxidation and reactive adsorption. The presence of cobalt in lower oxidation states in the materials with a higher carbonaceous component content, which was a result of the reducing effect of graphene layers on metal oxide nanoparticles, had a negative effect on the adsorption of H_2S.

This paper aims to further investigate the interactions of zinc (hydr)oxide/GO composites with hydrogen sulfide. Various contents of GO were chosen to evaluate the effect of the amount of GO on the materials' chemical and physical properties and on their performance as hydrogen sulfide adsorbents. The results obtained in ambient light and in dark are expected to shed a new light on photoactivity of the zinc (hydr)oxide/GO composites. This photoactivity might be an important factor for applications of these materials as reactive adsorbents and catalysts [16–18].

2. Experimental

2.1. Materials preparation

Graphite oxide was synthesized by oxidation of graphite (Sigma–Aldrich) using the Hummers method [19]. Graphite powder (10 g) was stirred with cool concentrated sulfuric acid (230 mL at 0 °C). Then, potassium permanganate (30 g) was added slowly to the suspension to prevent a rapid rise in the temperature (less than 20 °C). The reaction mixture was then cooled to 2 °C. After removal of the ice-bath, the mixture was stirred at room temperature for 30 min. Distilled water (230 mL) was slowly added to the reaction vessel to keep the temperature under 98 °C. The diluted suspension was stirred for an additional 15 min and further diluted with distilled water (1.4 L), before adding hydrogen peroxide (100 mL). The mixture was left overnight. GO particles, settled at the bottom, were separated from the excess liquid by decantation followed by centrifugation. The remaining suspension was transferred to dialysis tubes (MW cutoff 6000–9000). Dialysis was carried out until no precipitate of $BaSO_4$ was detected by addition of $BaCl_2$. Then, the wet form of graphite oxide was centrifuged and freeze-dried. A fine brown powder of the initial graphite oxide was obtained. The resulting material is referred to as GO.

The composite material GO/zinc (hydr)oxide was prepared by dispersing GO powder (2, 5 and 20 wt.% of the final mass of the material) in 1.0 L of zinc chloride (0.05 M). The resulting well-dispersed suspension was stirred for 4 h. A sodium hydroxide solution (0.05 M) was then added (2.0 L) to the dispersed graphene-base phases with a rate 2.0 mL/min using a Titronic Universal (SCHOTT). Then, the obtained composites were extensively washed with distilled water until neutral pH and no traces of chlorine ion were found in the leachates. Finally, the suspension was centrifuged and the gel formed was dried at 100 °C for 2 days. The composites are referred to as ZnGO-2, ZnGO-5 and ZnGO-20. The numbers represent the weight percent of graphite oxide in the composites.

The samples after exposure to H_2S in moist conditions have the suffix E added to their name. Letter L refers to the experiments run in ambient light and D- to those run in dark conditions.

2.2. Characterization of materials

2.2.1. FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out using a Nicolet Magna-IR 830 spectrometer using the attenuated total reflectance (ATR) method. The spectrum was generated and collected 32 times and corrected for the background noise. The experiments were done on the powdered samples, without KBr addition.

2.2.2. Thermal analysis

Thermogravimetric (TG) curves were obtained using a TA instrument thermal analyzer. The initial and exhausted samples were exposed to an increase in temperature (10 °C/min) while the nitrogen flow rate was held constant (100 mL/min). From the TG curves, differential TG (DTG) curves were derived.

2.2.3. pH of the surface

A 0.1 g sample of dry adsorbent was added to 5 mL of deionized water and the suspension stirred overnight to reach equilibrium. The pH of suspension was measured using an Accumet Basic pH meter (Fisher Scientific, Springfield, NJ, USA).

2.2.4. Nitrogen adsorption

N_2 isotherms were measured at −196 °C using an ASAP 2020 (Micromeritics, Surface area and Porosity Analyzer Norcross, GA, USA). Prior to each measurement, initial samples were outgassed at 120 °C to vacuum 10^{-4} Torr. The surface area, S_{BET} (Brunauer–Emmet–Teller method was used), the micropore volume, V_{mic} (calculated using the Dubinin–Radushkevich approach) [20] the mesopore volume, V_{mes}, the total pore volume, V_t (calculated from the last point of the isotherms based on the volume of nitrogen adsorbed) were calculated from the isotherms. The volume of mesopores, V_{mes}, represents the difference between the total pore volume and the micropore volume.

2.2.5. Potentiometric titration

Potentiometric titration measurements were performed with a DMS Titrino 716 automatic titrator (Metrohm). Volumetric standard NaOH (0.1 M) was used as the titrant starting from the initial pH of the materials suspension up to pH 11. The experimental data was transformed into a proton binding curves, Q, representing the total amount of protonated sites [21,22].

2.2.6. X-ray diffraction (XRD)

XRD measurements were conducted using standard powder diffraction procedures. Adsorbents were ground with methanol in a small agate mortar. The mixture was smear-mounted and then analyzed by CuK$_\alpha$ radiation (tension −40 kV and current −40 mA) generated in a Phillips X'Pert X-ray diffractometer. A standard glass slide was run for the background. The diffraction patterns were collected from 5° to 70° at absolute scan.

2.2.7. SEM/EDX

Scanning electron microscopy images were obtained using a Zeiss Supra 55 VP with an accelerating voltage of 15.00 kV. Scanning was performed in situ on a powder sample. SEM images with energy-dispersive X-ray (EDX) analysis were done at 10 KX magnifications. The areas analyzed were 456 μm^2 and the difference in the atomic contents of elements on the surface between the results collected from different areas was less than 2–4%.

2.2.8. TEM

Transmission electron microscopy (TEM) was performed on a Zeiss EM 902 instrument. The microscope has a line resolution of 0.34 nm and a point resolution of 0.5 nm; operates in normal,