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Reactive adsorption of acidic gases on MOF/graphite oxide composites

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ABSTRACT

Composites were prepared from metal–organic framework (MOF; copper-containing HKUST-1) and graphite oxide (GO). The synthesized materials were tested as adsorbents of hydrogen sulfide (H_2S) and nitrogen dioxide (NO_2). Their surface was characterized using nitrogen adsorption, Fourier-transform infrared (FT-IR) spectroscopy and thermogravimetric analysis. The results indicate that formation of new small pores in the composites has a positive effect on the adsorption capacity of both acidic species. Physisorption and reactive adsorption are suggested as main adsorption mechanisms. The latter mechanism is related to the presence of unsaturated copper sites in the MOF structure, which bind H_2S and NO_2 molecules. This process is followed by further reactions with the MOF network leading to the formation of either copper sulfide or copper nitrate. Although the overall scheme of adsorption process appears to be similar for both H_2S and NO_2 adsorption, the importance of the surface features governing these mechanisms appears to be different. Consequently, different trends in the performance of HKUST-1 and the composites are observed.

1. Introduction

Air pollution and its adverse impact on the environment and human health has been an on-going issue for many decades. The growing world population and the emergence of recently industrialized countries make this issue even more pronounced. This causes that there is a search for efficient and cost-effective media to remove toxic gases from air. Materials on which researchers place a lot of effort are porous adsorbents [1]. Many types of materials fall into this category. Examples are activated carbons, zeolites, alumina, polymeric resins and metal–organic frameworks (MOFs) [1,2]. All these materials represent the prime candidates for air quality remediation owing to their overall high surface area (ability to store large amount of adsorbed species via physisorption) and surface chemistry, which includes the presence of functional groups and/or catalytic species (possibility of chemisorption/reactive adsorption). Although these compounds fulfill the "basic" requirements of gas adsorbents, the increasing air pollution along with a constant strengthening of air quality regulations call for the use of state-of-the-art materials with high adsorption capacity. Moreover, a real challenge is the vast range of toxic gases, which have to be removed from air at ambient conditions (e.g. H_2S, NO_2, NO, N_2O, SO_2, NH_3, CO, AsH_3, PH_3). All these species exhibit very different physical (e.g. size) and chemical (e.g. acidity) features, which may entail the use of distinct adsorbents. Consequently, while the search for adsorbents with high adsorption capacities is necessary, fundamental aspects of the adsorption process of the target toxic gases should be also taken into considerations. Indeed, the in-depth understanding of the chemistry/physics of each adsorbate, the parameters governing its adsorption as well as its retention mechanisms on different materials are crucial for the design of adsorbents with an enhanced performance.

Considering the diversity of adsorbents available, various research groups focus on improving their filtering capability via modification of the physical and/or chemical properties. Over the past decade, the field of gas adsorption leaped forward with the development of MOF materials [3–5]. They represent highly porous and crystalline 3D networks in which metallic units (ions or oxides) are connected with organic ligands (carboxylates, sulfonates, phosphonates) [2,5,6]. The great interest in these materials, which is fostered by their tunable physical and chemical properties, has fueled extensive research (almost 4000 MOF structures reported in 2006 [7]) and selected MOFs are now commercialized. Nevertheless, MOFs exhibit a few weak points that impede the use of their full potential. These include the poor stability in humid conditions of selected MOFs (a parameter that can be difficult and costly to control) as well as weak dispersive forces owing to their large amount of void space (which lead to a weak gas retention and consequently an increased risk of the release of a toxic adsorbate).

Combining MOF materials with other substrates has been proposed in order to mitigate the above-mentioned drawbacks. These substrates include alumina [8–13], silica [12,14], functionalized self-assembly monolayer (SAM) [12,15], functionalized graphite

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[8,16], graphite oxide (GO) [17–20], carbon nanotubes [21], or amorphous carbon [11]. In particular, the hybrid materials of MOF and GO have shown enhanced dispersive forces compared to the parent MOFs thanks to the presence of graphene layers [22,23]. Such features enabled an increased adsorption capacity for the removal of ammonia [22,23].

This paper focuses on the use of the MOF/GO composites for the removal of two toxic gases, hydrogen sulfide (H_2S) and nitrogen dioxide (NO_2). Although both are acidic and similar in size, certain differences exist, as for instance their water solubility or reactivity/dissociation process. Many studies have reported the use of carbonaceous materials for their removal and the retention mechanisms proposed differ significantly [24–39]. Although some of the results presented here were reported separately in previous papers [40,41], in this study we intend to combine them in order to highlight/generalize the similarities and differences in the adsorption of acidic gases on the particular MOF and MOF/GO composites. This is an important aspect for the target application of these materials as filtration media in the respirators, where the affinity towards the broad spectrum of the chemistry of species to be removed is of paramount importance.

2. Experimental

2.1. Materials

The MOF material selected for this study was a copper-based MOF with copper ions as the metallic component and benzene tricarboxylate (BTC) as the organic bridges. This material is commonly referred to as HKUST-1 and its structure has been fully described by Chui and coworkers [42]. The synthesis of the parent materials, referred to as HKUST-1 and GO, can be found in Ref. [19]. It was done following the syntheses described by Millward and coworkers [43] for HKUST-1 and Seredych and Bandosz [44] for GO. Briefly, HKUST-1 was prepared by dissolving copper nitrate hemipentahydrate and 1,3,5 benzenetricarboxylic acid in a mixture of N,N dimethylformamide (DMF), ethanol and deionized water. The mixture was subjected to stirring and sonication to ensure complete dissolution of the crystals. The mixture was then heated at 85 °C in an oil bath under shaking for about 20 h. After cooling, the crystals were filtered, washed and immersed in dichloromethane. Dichloromethane was changed twice during three days. The crystals were collected after filtration and washing with dichloromethane, and dryed under vacuum at 170 °C for 28 h. The resulting product was kept in a dessicator and is referred to as HKUST-1. GO was prepared according to the Hummers method. Briefly, graphite powder (Sigma–Aldrich) was oxidized using sulfuric acid, potassium permangnate and hydrogen peroxide at room temperature. The mixture was left overnight and GO particles, settled at the bottom, were separated from the excess liquid by decantation followed by centrifugation. The remaining suspension was subjected to dialysis 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. In Ref. [19], the preparation of the composites whose GO content ranges from 5 to 18 wt.% of the final material weight is also described. These composite materials were prepared by dispersing GO powder in the well-dissolved copper nitrate–BTC mixture. The resulting suspension was subsequently stirred and subjected to the same synthesis procedure as for HKUST-1. The resulting composites are referred to as MGO-*n* with $n = 1$, 2, and 3 for the different GO contents (5, 9 and 18 wt.%, respectively).

2.2. Methods

2.2.1. H_2S and NO_2 breakthrough dynamic tests

In order to determine the breakthrough capacities of the materials studied, dynamic breakthrough tests were performed at room temperature. In a typical test, a flow of gas (H_2S or NO_2) diluted with air went through a fixed bed of adsorbent with a total inlet flow rate of 225 mL/min for NO_2 and 250 mL/min for H_2S. The concentration of each species was 1000 ppm. The adsorbent's bed contained about 2 cm^3 of glass beads well mixed with the amount of adsorbent required to obtain a homogeneous bed with minimum pressure drop. The concentration of gas (H_2S or NO_2) in the outlet gas was measured using an electrochemical sensor (Multi-Gas Monitor RAE system). The adsorption capacity of each adsorbent was calculated in mg per gram of the material by integration of the area above the breakthrough curve. For NO_2 adsorption tests, NO_2 was diluted in either dry or moist air whereas for H_2S, only dilution in moist air was performed. Moreover, in the latter case, the adsorbent bed was prehumidified prior to running the breakthrough tests. In all cases, after the breakthrough tests, all samples were exposed to a flow of clean carrier air only (180 mL/min of clean air after NO_2 breakthrough tests, 225 mL/min of clean air after H_2S breakthrough tests) to impose the desorption of the target gas and thus to evaluate the strength of its retention. The suffixes -ED and -EM are added to the name of the samples after the exposure to the gas in dry and moist conditions, respectively.

In the case of NO_2 adsorption, nitrogen monoxide (NO) concentration in the outlet stream was also monitored. NO is often encountered as a by-product [39,45] and, although less toxic than NO_2, its presence is not a desired feature and must be controlled.

2.2.2. Sorption of nitrogen

Nitrogen isotherms were measured at -196 °C using an ASAP 2010 instrument (Micromeritics). Prior to each measurement, initial and exhausted samples were outgassed at 120 °C to vacuum 10^{-5} Torr. The surface area, S_{BET}, (Brunauer–Emmet–Teller method), the micropore volume, V_{mic}, (calculated from the *t*-plot), the mesopore volume, V_{mes}, the total pore volume, V_t, were calculated from the isotherms.

2.2.3. FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet Magna-IR 830 spectrometer using the attenuated total reflectance (ATR) method for H_2S-related samples and the diffuse reflectance method for the NO_2-related samples. The latter method was used to avoid damage of the ATR crystal owing to the strong oxidizing power of NO_2. The spectrum was generated, collected 16 times and corrected for the background noise. For H_2S-related samples, the experiments were done on the powdered materials without KBr addition. For NO_2-related samples, the experiments were done on the powdered materials (2–3 wt.%) mixed with KBr (97–98 wt.%).

2.2.4. 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^{-1}) while the nitrogen flow rate was held constant (100 mL min^{-1}). From the TG curves, differential TG (DTG) curves were derived.