Preparation and characterization of aminated graphite oxide for CO$_2$ capture

Yunxia Zhao[a], Huiling Ding[a,b], Qin Zhong[a,*]

[a] *School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China*
[b] *School of Chemistry and Chemical Engineering, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China*

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ABSTRACT

Adsorption with solid sorbents is one of the most promising options for postcombustion carbon dioxide (CO$_2$) capture. In this study, aminated graphite oxide used for CO$_2$ adsorption was synthesized, based on the intercalation reaction of graphite oxide (GO) with amines, including ethylenediamine (EDA), diethylenetriamine (DETA) and triethylene tetramine (TETA). The structural information, surface chemistry and thermal behavior of the adsorbent samples were characterized by X-ray powder diffraction (XRD), infrared spectroscopy (IR), transmission electron microscope (TEM), elemental analysis, particle size analysis, nitrogen adsorption as well as differential thermal and thermogravimetric analysis (DSC–TGA). CO$_2$ capture was investigated by dynamic adsorption experiments with N$_2$—CO$_2$ mixed gases at 30 °C. The three kinds of graphite oxide samples modified by excess EDA, DETA and TETA showed similar adsorption behaviors seen from their breakthrough curves. Among them, the sample aminated by EDA exhibited the highest adsorption capacity with the longest breakthrough time of CO$_2$. Before saturation, its adsorption capacity was up to 53.62 mg CO$_2$/g sample. In addition, graphite oxide samples modified by different amount of EDA (EDA/GO raw ratio 10 wt%, 50 wt% and 100 wt%) were prepared in the ethanol. Their CO$_2$ adsorption performance was investigated. The experimental results demonstrated that graphite oxide with 50 wt% EDA had the largest adsorption capacity 46.55 mg CO$_2$/g sample.

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1. Introduction

Carbon dioxide (CO$_2$) capture and sequestration is considered to be the most efficient way to control greenhouse effect [1]. Coal-fired power plant is one of the greatest CO$_2$ man-made emission sources, so capture of CO$_2$ from coal-fired power plants is an economical and effective means [2]. Absorption process is a very mature method of the various ways for CO$_2$ removal [3], and has been extensively researched for several decades [4]. Furthermore, there are many concrete examples of industrial application at home and abroad [5]. However, some long-existing problems have not been solved, such as volatility, degradability, high regeneration cost, refractory waste absorption liquid and so on [6,7]. As a newly emerged research direction, ionic liquid absorber without the deficiency above is still in the stage of experiment with high cost and high viscosity [8,9]. Compared with absorption method, adsorptive process is featured as less investment, handy manipulation, less adsorbent loss, no corrosion on equipment and no environment pollution [10]. The search for a suitable adsorbent is generally the first step in the

development of an adsorption separation process [11]. Therefore, screening a kind of effective adsorbent is particularly important.

In recent years, many efforts have been made in the research of high efficient adsorbents. Amine-functionalized carbon-based materials and silica-based materials are two kinds of chemosorbent mainly studied now. Yao Shi and co-workers [12] prepared tetraethylenepentamine-loaded KIT-6 as CO$_2$ adsorbents. They found that the dynamic adsorption capacity increased when the amount of TEPA increased at 60 °C. The dynamic adsorption capacity dropped slightly (about 5%) during forty cycles of adsorption/desorption. Serna-Guerrero et al. [13–16] considered triamine-grafted pore-expanded mesoporous silica as a promising adsorbent for acid gas removal and they are closely studying the CO$_2$ adsorption/desorption character. This material exhibited very high CO$_2$ adsorption capacity and high selectivity for CO$_2$ over N$_2$ and O$_2$, even in the presence of moisture. It was also demonstrated that under the proper regeneration conditions, TRI-PE-MCM-41 was stable over 100 adsorption–desorption cycles. Plaza et al. [17] used activated carbons with amines impregnated for CO$_2$ separation. At room temperature, compared to the raw materials without being impregnated, the capture capacity was lower, which was ascribed to a drastic decrease in microporous volume. However, at medium temperatures (70–90 °C), the contribution of chemisorption associated to the incorporated amino groups may improve the performance of the carbon.

* Corresponding author at: School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China. Tel.: +86 025 84315517; fax: +86 025 84315517.

E-mail address: zq304@mail.njust.edu.cn (Q. Zhong).
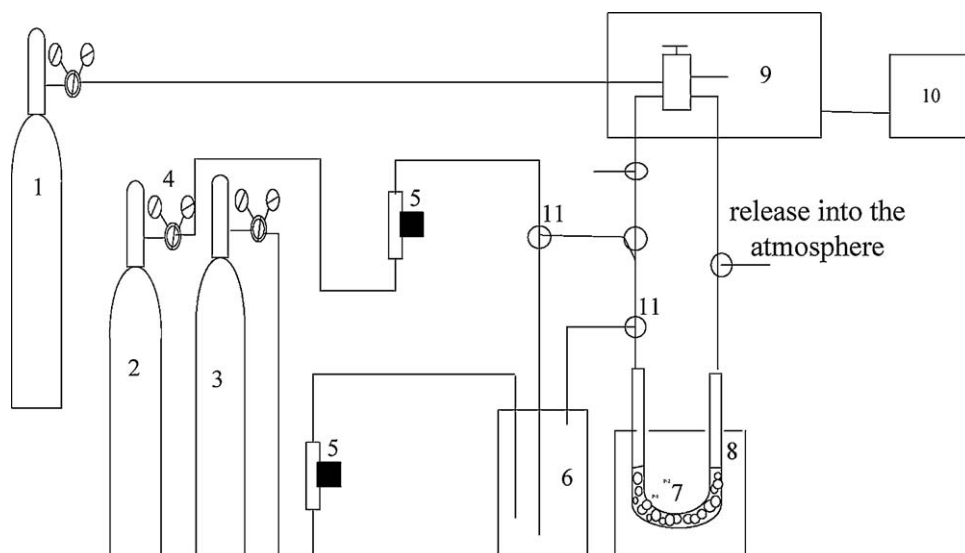
Fig. 1. Scheme of the CO_2 dynamic adsorption unit. 1 – hydrogen cylinder; 2 – nitrogen cylinder; 3 – CO_2 cylinder; 4 – gas pressure relief valve; 5 – mass flow controller; 6 – surge flask; 7 – adsorbent; 8 – water bath; 9 – gas chromatography; 10 – workstation; 11 – three-way valve.

Beyond that, graphene has enjoyed significant attention in recent years. There has been extensive research on gas adsorption properties of graphite/graphene. Yildirim and co-workers [18] developed a kind of graphene oxide framework materials by interlinking graphene oxide with diboronic acid. They exhibited their surface area and gas uptake was many times higher than that of graphene oxide sample. Cabrera-Sanfelix [19] performed density-functional calculations to investigate the adsorption and reactivity of CO_2 on a defected graphene sheet and put forward plausible mechanism, which could motivate further work to solve the same atmospheric problem on other defects in graphite and graphene. Bourlinos et al. [20] synthesized a foam-type graphite oxide-like derivative that was lightweight. It had a high surface area and porosity. The carbogenic foam selectively absorbed CO_2, showing low affinity for the N_2, CH_4 and H_2.

Graphite oxide (GO) is a derivative of graphene and consists of oxygen functional groups on their basal planes and edges [21], so surface modification of GO with amines or amine-containing molecules takes place easily through the corresponding nucleophilic substitution reactions [22]. If polyamines covalently attach to its layers, the residual unreacted amine groups can react with CO_2 and have potential for the removal of CO_2 greenhouse gas from coal-fired flue gas. The aim is to improve the selectivity and capacity of the sorbents to capture CO_2 through introducing basic nitrogen-functionalities into the graphite based materials. In this work, GO was synthesized by Hummers method first, and then it was reduced and surface modified by ethylenediamine (EDA), diethylenetriamine (DETA) and triethylene tetramine (TETA). These resultant materials were used as a new kind of CO_2 trapping agent. In addition, GO with different amounts of EDA was prepared. All the graphite samples were characterized and their CO_2 capture property was investigated by dynamic adsorption tests.

2. Experimental

2.1. Preparation of graphite oxide

GO was synthesized using graphite powder with a modified Hummers method according to the literature [23]. At the preoxidation process, 5.0 g graphite powder was added in a 80 °C solution of 7.5 ml concentrated H_2SO_4, 2.5 g $K_2S_2O_8$ and 2.5 g P_2O_5, then dark blue mixture was obtained, which was washed, filtered and dried

in air after standing at the room temperature for 6 h. The above product was put into 115 ml concentrated H_2SO_4 in the ice water bath. With stirring, 15 g $KMnO_4$ was added gradually. Then the mixture was stirred at 35 °C for 2 h with 230 ml deionized water added during this time. Finally the reaction was stopped by the addition of 0.7 l deionized water and 12.5 ml 30% H_2O_2, which led to bright yellow mixture. After filtering and washing using diluted HCl to remove metal ions, the resulting GO was stable in water solution.

2.2. Surface modification with amines

The above GO products divided into six equal parts were made up certain concentration aqueous solution. 20 ml EDA, DETA or TETA was added into each solution under vigorous stirring. The reaction continued for 24 h under reflux (80 °C). Finally, modified GO was isolated by centrifugation and thoroughly washed with much deionized water, filtered, and dried at 80 °C. The obtained black particles were grinded and griddled using 80 mesh sieves.

2.3. Graphite oxide samples loaded with different amounts of EDA

The GO suspension was centrifuged and dried. Every 1.5 g GO was dispersed into 80 ml ethanol, then the right amount of EDA (EDA/GO raw ratio 10 wt%, 50 wt% and 100 wt%) was added respectively. Ethanol from the GO suspension with EDA could evaporate gradually in 80 °C water bath under mechanical stirring. Finally black dried powders were obtained, referred to as AGO-10, AGO-50 and AGO-100.

2.4. Samples characterization

X-ray powder diffraction (XRD) patterns were taken on a XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China) using Cu Kα radiation (λ = 0.15406 nm). The tube voltage was 35 kV, and the current was 20 mA. The XRD diffraction patterns were taken in the 2θ range of 5–80° at a scan speed of 8°/min. Infrared (IR) spectra were recorded on a MB154S-FTIR spectrometer (Bomem, Canada). The samples were measured in the form of KBr pellets. Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were conducted with a SDTQ600 thermal analyzer (PerkinElmer Pyris Diamond, America). Analyses were done under a nitrogen atmosphere (50 ml/min flow