

Amine-functionalized low-cost industrial grade multi-walled carbon nanotubes for the capture of carbon dioxide

Qing Liu^a, Yao Shi^a, Shudong Zheng^a, Liqi Ning^b, Qing Ye^c, Mengna Tao^a, Yi He^{a*}

a. Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China; b. Department of Earth and Planetary Sciences, Washington University in St. Louis, MO 63130, St. Louis, USA;

c. Department of Life Sciences, Shaoxing University Yuanpei College, Shaoxing 312000, Zhejiang, China

[Manuscript received August 7, 2013; revised September 12, 2013]

Abstract

Industrial grade multi-walled carbon nanotubes (IG-MWCNTs) are a low-cost substitute for commercially purified multi-walled carbon nanotubes (P-MWCNTs). In this work, IG-MWCNTs were functionalized with tetraethylenepentamine (TEPA) for CO₂ capture. The TEPA impregnated IG-MWCNTs were characterized with various experimental methods including N₂ adsorption/desorption isotherms, elemental analysis, X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric analysis. Both the adsorption isotherms of IG-MWCNTs-*n* and the isosteric heats of different adsorption capacities were obtained from experiments. TEPA impregnated IG-MWCNTs were also shown to have high CO₂ adsorption capacity comparable to that of TEPA impregnated P-MWCNTs. The adsorption capacity of IG-MWCNTs based adsorbents was in the range of 2.145 to 3.088 mmol/g, depending on adsorption temperatures. Having the advantages of low-cost and high adsorption capacity, TEPA impregnated IG-MWCNTs seem to be a promising adsorbent for CO₂ capture from flue gas.

Key words

CO₂ adsorption; multi-walled carbon nanotubes (MWCNTs); tetraethylenepentamine (TEPA); heat of adsorption; amine modification

1. Introduction

Growing concerns for global warming and climate change in recent years have motivated research activities toward developing more efficient and improved processes for carbon dioxide (CO₂) capture and sequestration (CCS) from large point sources, such as coal-fired power plants, natural gas processing plants, and cement plants [1]. The conventional technology for CCS with aqueous solutions of amine such as monoethanolamine (MEA), diethanolamine (DEA), diglycol-amine (DGA), N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP) not only requires a great amount of energy but also has serious corrosion issues with its equipment [2]. Therefore, as an alternative approach, CO₂ capture with solid sorbents has attracted much attention in recent years [3–7].

The solid sorbents for CO₂ capture include activated carbons [8], carbon molecular sieves [9,10], carbon nanotubes [11,12], zeolites [13–16], alkali-based sorbents [17], polymers [18,19] and metal-organic frameworks (MOFs) [20–24]. Among them, carbon nanotube-based solid sorbents

have shown some promising results for the separation of CO₂ from gas mixtures over the last several years.

One viable method of synthesizing solid sorbents designed for CO₂ capture involves the grafting of molecules with amino groups onto carbon nanotubes (CNTs). A paper by Lu et al. [11] compared the CO₂ capture capabilities of CNTs, granulated activated carbons (GAC), and zeolites with 3-aminopropyltriethoxysilane (APTES). The modified CNTs demonstrated the greatest improvement in adsorption capacity among the three. Su et al. [25] also investigated the CO₂ adsorption capacity of APTES-functionalized CNTs at various temperatures and discovered that adsorption capacity increased with water content while decreased with temperature, which reflected the exothermic process of adsorption. Their experimental CO₂ adsorption capacity of ~2.59 mmol/g at 293 K for CNT (APTES) is the evidence for the potential of CNTs as low-temperature adsorbents. Single-walled nanotubes (SWNTs) synthesized with another amine functional group, PEI, by Dillon et al. [26] reached a maximum adsorption capacity of 2.1 mmol/g at 300 K. In order to trim down the regeneration time, a combination of vacuum and thermal

* Corresponding author. Tel/Fax: +86-571-88273591; E-mail: yihezj@zju.edu.cn

This work was supported by Zhejiang Provincial Natural Science Foundation of China (Grant No. LZ12E08002).

desorption was proposed by Hsu et al. [12]. They were able to sustain adsorption/regeneration of CNT (APTES) for twenty cycles at 493 K while maintaining the CNTs' physiochemical properties and adsorption capacity.

The other method of preparing CO₂ capture CNTs is impregnation. It carries the benefits of high adsorption capacity, more convenient synthesis and less corrosiveness than grafting [27]. Impregnation incorporates amine non-covalently onto the surfaces and into the pores of CNTs [28]. CO₂ adsorption capacity was found to vary with the loadings of amine. Measured against other amine-impregnated adsorbents, tetraethylenepentamine (TEPA)-functionalized sorbents possess one of the highest adsorption capacities [29,30].

In our previous work [31], a solid adsorbent for CO₂ capture was prepared by impregnating P-MWCNTs with tetraethylenepentamine (TEPA) for confined spaces, such as submarines and space capsules. An adsorption capacity of approximately 3.87 mmol/g was achieved at 313 K, CO₂ 2.0 vol%, H₂O 2.1%, and 50 cm³/min. One of the major obstacles for potential industrial applications of P-MWCNTs is its high cost [31]. Therefore, it is important to find a low-cost substitute. IG-MWCNTs, at one-tenth the price of P-MWCNTs, are one such substitute that has not been previously studied. Similar to P-MWCNTs, IG-MWCNTs possess unique, topological, hollow, tubular structures and offer many advantages such as large pores, reduced mass and volume, good thermal conductivity and chemical stability [32,33]. More importantly, IG-MWCNTs are much less costly than the P-MWCNTs, which make them a promising material for capturing CO₂ from large point sources. The major difference, however, is that it is still not clear what the impact of impurities on CO₂ adsorption and desorption of solid sorbents made from IG-MWCNTs. Therefore, we systematically examined the performance of solid sorbents made from IG-MWCNTs. The IG-MWCNTs were impregnated with TEPA and characterized with various experimental methods including N₂ adsorption/desorption isotherms, elemental analysis (EA), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The optimal working temperature of the sorbent was investigated. In addition, we measured the performance of the sorbents made from IG-MWCNTs by examining the adsorption capacities, dual-component isotherms, and enthalpy of adsorption.

2. Experimental

2.1. Preparation of adsorbents

Solid sorbents for CO₂ capture were prepared by impregnating TEPA in solution onto MWCNTs. Commercially available P-MWCNTs (TNM8, Organic Chemical Co., Ltd., China) and IG-MWCNTs (TNIM8, Organic Chemical Co., Ltd., China) were selected as the supports. The purity of P-MWCNTs is over 95% while the purity of IG-MWCNTs is only 90% or more. TEPA [NH₂(CH₂CH₂NH)₃CH₂CH₂NH₂] (90%, Sinopharm Chemical Reagent Co., Ltd., China) was in-

corporated into the P-MWCNTs and IG-MWCNTs supports by wet impregnation. The impregnation was performed in a sealed vessel under atmospheric pressure. Specifically, a desired amount of TEPA was dissolved in 50 g of ethanol (99.7%, Sinopharm Chemical Reagent Co., Ltd., China) and stirred for 30 min at room temperature before the addition of 2 g of MWCNTs supports. After stirring for 3 h, the mixture was evaporated at 353 K and subsequently dried at 373 K in open air for 1 h. Finally, the samples were grinded into powder and sealed in a vial. These samples were denoted as P-MWCNTs-*n* and IG-MWCNTs-*n*, where *n* represented the weight percentage of TEPA in the composites.

2.2. Characterizations of adsorbents

The morphology of sorbents was analyzed by a high-resolution transmission electron microscope (HR-TEM, JEM-2010, JEOL, Tokyo, Japan). The surface area and pore volume were measured with static volume adsorption system (Model-ASAP 2020, Micromeritics Inc., USA) by obtaining the N₂ adsorption/desorption isotherms at 77.4 K. Prior to the adsorption measurement, the samples were out-gassed at 473 K for 24 h. The N₂ adsorption/desorption data were recorded at the liquid nitrogen temperature (77 K) and then used to determine the surface areas with the Brunauer-Emmett-Teller (BET) equation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with a thermogravimetric analyzer (SDT Q600, TA Instruments, Inc., New Castle, DE) under a dynamic N₂ atmosphere from 303 to 873 K, with a heating rate of 10 K/min. The elemental analysis (C, N, H) was conducted on an elemental analyzer (Flash EA 1112, ThermoFinnigan, Italy). The crystal phase and the surface functional groups of sorbents were characterized by a powder X-ray diffractometer (XRD, Rigaku D/Max 2550/PC, Rigaku Co., Ltd., Japan) using Cu K_α radiation (40 kV, 30 mA) and by an Fourier transform infrared spectrometer (FTIR, NICOLET 6700, thermal scientific, USA), respectively.

2.3. Adsorption experiment

The experimental setup for CO₂ adsorption was carried out using the protocol reported by Liu et al. [34]. The adsorption column was made of quartz glass with a length of 14 cm and an inner diameter of 1.5 cm. The adsorption column was placed into a temperature-controlled heating jacket and filled with 2.0 g of adsorbents. CO₂ was mixed with N₂ (99.99%) at a predetermined composition. The concentration of CO₂ was measured by a gas chromatograph (GC), connected to the outlet of the adsorption column. In a typical experimental setting, adsorbents were treated under a nitrogen flow of 50 cm³/min at 423 K for 1.5 h and then cooled to test temperatures. The nitrogen flow was then switched to a CO₂-containing simulated flue gas at a flow rate of 50 cm³/min. The mole fraction of CO₂ was kept at 10 vol% at atmospheric pressure.

The adsorption capacity of CO₂ on adsorbents at a given

Download English Version:

<https://daneshyari.com/en/article/64046>

Download Persian Version:

<https://daneshyari.com/article/64046>

[Daneshyari.com](https://daneshyari.com)