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Preparation and characterization of multi-walled carbon nanotubes impregnated with polyethyleneimine for carbon dioxide capture

Min-Sang Lee, Seul-Yi Lee, Soo-Jin Park*

Department of Chemistry, Inha University, 100 Inharo, Incheon 402-751, South Korea

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ABSTRACT

In this work, multi-walled carbon nanotubes impregnated with polyethyleneimine (MWCNT/PEI) have been prepared by wet-impregnation method with various PEI loadings for CO₂ capture. The surface features and morphology were observed by scanning electron microscopy (SEM) and the textural properties were analyzed by N₂/77 K adsorption–desorption isotherms. The CO₂ adsorption capacity was evaluated by thermogravimetric analysis (TGA) method at 15% CO₂ partial pressure. The MWCNT/PEI exhibited higher CO₂ adsorption capacity than pristine MWCNTs. This result suggested that amine groups were attached on carbon surfaces in the impregnation process, leaving CO₂ affinity sites on MWCNT surfaces. MWCNT/PEI exhibited superior cycle stability for CO₂ capture, indicating great potential for application in post-combustion technology.

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Introduction

Public awareness of global climate change has led to a growing need for low cost and efficient technologies to sequester greenhouse gas (GHG) emissions. Fossil fuel power plants are responsible for about 40% of total carbon release into the atmosphere [1–7]. Carbon capture and sequestration (CCS) has been widely recognized as a potential strategy for removal of CO₂ [8,9]. The flue gases of conventional power plants have a CO₂ concentration of 10–15% by volume. Post-combustion gas capture has gained tremendous attention in recent years and various dry CO₂ sorbents have been investigated such as carbonaceous materials, zeolites, and metal organic frameworks (MOF) [10–13]. Although aqueous amines are used as industrial CO₂ scrubbing agents, they have some drawbacks.

The major problem with amine solutions is the high energy requirement during adsorption–desorption processes as a result of the strong chemical bonds between CO₂ and amine groups [14]. In case of zeolites and MOFs, relatively high CO₂ adsorption capacities have been achieved in recent research with their unique porous structure. Liu et al. [15] reported that a zeolite named AlPO₄-53 adsorbed 0.7 mmol/g of CO₂ at 0.1 CO₂ partial pressure. Luebke et al. [16] presented their rht-MOF-7 which showed 1.2 mmol/g of CO₂ uptake at 0.1 CO₂ partial pressure, demonstrating the potential of MOFs for CO₂ capture. However, there are some drawbacks to zeolite and MOF adsorbents. Water resistance of adsorbents is a serious problem because flue gases in power plants contain water vapor. When moisture comes into contact with zeolites or MOFs, decomposition of adsorbents could occur [17].

* Corresponding author. Tel./fax: +82 32 860 8438.

E-mail address: sjpark@inha.ac.kr (S.-J. Park).

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Carbonaceous materials such as activated carbon, carbon nanotubes (CNTs), and activated carbon fibers for CO₂ sequestration are characterized by their high specific surface area, unique pore structures, and their excellent regeneration over multiple CO₂ adsorption processes [18]. Among various carbonaceous materials, CNTs have been proposed for gas adsorption in specific conditions owing to their mechanical strength, thermal stability, hollow structure, high specific surface area, and chemical stability [19,20]. These superior properties have led to increased attention for use of CNTs in CO₂ capture. Recently, Jin et al. reported that amino-functionalized CNTs exhibited high CO₂ capture capacity with physical and chemical adsorption [21]. The chemical adsorption of amino-functional groups improves the selectivity as well as CO₂ adsorption capacity [22].

It was previously reported that the amine groups in PEI have basic properties; therefore, CO₂ could be adsorbed onto PEI by acid–base interaction between CO₂ and PEI [23]. In this work, multi-walled carbon nanotubes (MWCNTs) were used as the supporting carbon material for adsorbents, and PEI was successfully introduced onto the surface of MWCNTs by a wet-impregnation method. The adsorption and regeneration behaviors of PEI/MWCNTs with CO₂ under flue gas conditions will be discussed in detail.

Experimental

Materials

MWCNTs were purchased from Kumho petrochemical Co., Ltd., Korea. The specific surface area of CNTs, pore volume, and average pore diameter are 272 m²/g, 2.681 cm³/g, and 32 nm, respectively. H₂SO₄ (Sigma–Aldrich Co., 95%) and HNO₃ (Sigma–Aldrich Co., 60%) were used for washing metal particles from MWCNTs. Ethanol (Sigma–Aldrich Co., 99%) was used as a solvent and polyethyleneimine solution ($M_w \approx 750,000$, 50 wt.% in H₂O, Sigma–Aldrich Co.) was used as the precursor of amine functionalized groups.

Pre-treatment and PEI impregnation of MWCNTs

PEI impregnated MWCNTs were prepared by pre-treatment of MWCNTs with HNO₃ and H₂SO₄ (HNO₃/H₂SO₄ at a volume ratio of 1:3) and a subsequent wet-impregnation step. First, pre-treatment was performed to remove metal impurities and introduce carboxyl acid groups onto the surface of the MWCNTs. Carboxylated MWCNTs were washed with water and ethanol several times until the pH reached a neutral value. PEI was added to ethanol (10 mL) and stirred while heating at 70 °C for 30 min. The carboxylated MWCNTs were also stirred in ethanol solution for 30 min, and then reacted with the PEI solution. The PEI/carboxylated MWCNT solution was continuously stirred for 12 h at 40 °C. The PEI/carboxylated MWCNTs were recovered as a solid and dried at room temperature.

Characterization

Surface chemical properties of the carboxylated and PEI-impregnated MWCNTs were analyzed using Fourier

transform infrared spectroscopy (FT-IR) (VERTEX 80V; Bruker Co., Ltd., Germany), scanning the range of 400–4000 cm⁻¹. Scanning electron microscopy (SEM) (SU8010; Hitach Co., Ltd., Japan) was used to confirm the surface features and morphology. N₂ adsorption–desorption isotherms were performed to investigate specific surface area and pore structure using an automated adsorption apparatus (BELSORP Mini, BEL Co., Japan). Before measurements were carried out, the samples were heat-treated under vacuum at 120 °C for 12 h in order to out-gas any remaining moisture or organic species.

CO₂ adsorption–desorption experiment at a specific condition

CO₂ adsorption–desorption experiments were performed using a TGA (Pyris 1; Perkin Elmer Co., Ltd., USA) under 15% CO₂/85% N₂, which is similar to the composition of flue gas in fossil fuel power plants. At first, the sample was transferred to the ceramic crucible and degassed at 120 °C for 600 min under N₂ flow. Next, it was cooled to 40 °C and 15% of N₂ flow was changed to CO₂ gas for the CO₂ adsorption process. CO₂ gas flow was maintained for 60 min to stabilize the sample weight. When the adsorption process finished, CO₂ gas was changed to N₂ gas again and maintained for 120 min in order to degas and dehydrate the sample.

Results and discussion

Functional group analysis of the as-prepared samples

The FT-IR spectra of the pristine MWCNT and chemically modified MWCNTs are shown in Fig. 1. The effect of pre-treatment with nitric acid and sulfuric acid was analyzed by comparing FT-IR spectra of MWCNT with carboxylated MWCNT. In Fig. 1b the peak at 1384 cm⁻¹ corresponds to the H–C=O bend frequency, while the peak observed at 1705 cm⁻¹ is ascribed to the COO⁻ group generated by oxidation from HNO₃ and H₂SO₄ in the pre-treatment process. This

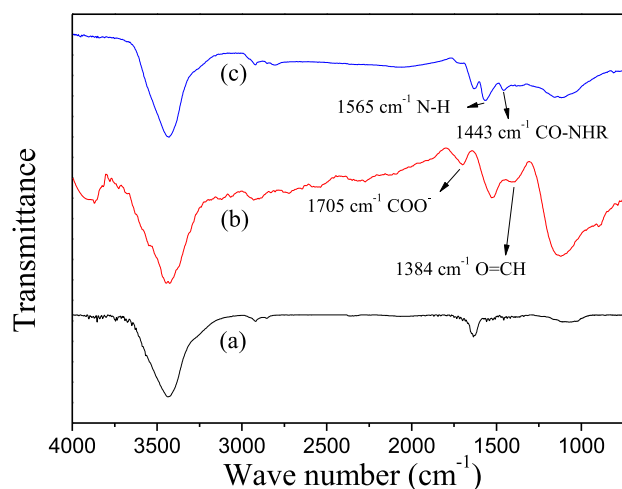


Fig. 1 – Fourier transform infrared (FT-IR) spectroscopy of pristine MWCNT (a), carboxylated MWCNT (b), and MWCNT/PEI-4.50 (c).

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