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Silica-coated multi-walled carbon nanotubes impregnated with polyethyleneimine for carbon dioxide capture under the flue gas condition

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ABSTRACT

In this study, silica-coated multi-walled carbon nanotubes impregnated with polyethyleneimine (PEI) were prepared via a two-step process: (i) hydrolysis of tetraethylorthosilicate onto multi-walled carbon nanotubes, and (ii) impregnation of PEI. The adsorption properties of CO_2 were investigated using CO_2 adsorption–desorption isotherms at 298 K and thermogravimetric analysis under the flue gas condition (15% CO_2/85% N_2). The results obtained in this study indicate that CO_2 adsorption increases after impregnation of PEI. The increase in CO_2 capture was attributed to the affinity between CO_2 and the amine groups. CO_2 adsorption–desorption experiments, which were repeated five times, also showed that the prepared adsorbents have excellent regeneration properties.

1. Introduction

With the worldwide increase in energy requirements, there are serious environmental concerns over the use of large amounts of fossil fuels and possible global warming. CO_2 is considered to be the primary contributor to global warming because of its greenhouse effects. Because greenhouse gases (GHGs) mainly consist of CO_2, post-combustion CO_2 capture and storage from flue gases is considered to be a promising technology for reducing CO_2 emissions [1–7]. Currently, adsorption processes based on, for instance, alkanolamine solutions, are used for CO_2 sequestration; however, they have drawbacks such as equipment corrosion, alkanolamine toxicity, and high energy requirements for CO_2 capture. Furthermore, the loss of adsorbents caused by the latent heat of vaporization of amine solutions may reduce regenerability [8,9]. To solve these issues, dry adsorption, which is based on solid adsorbents that have good adsorption/desorption and superior regeneration properties, has been proposed as a potentially inexpensive alternative technique [10–13].

Solid adsorbents such as silica, carbon, and supported-amine materials have recently been proposed [14–17]. In particular, silica-based materials typically show good CO_2 capacity; however, they are susceptible to thermal degradation, resulting in performance decay. Moreover, silica-based materials are typically hydrophilic; therefore, their use for CO_2 sequestration from flue gases often requires a drying process [18]. To avoid this, significant efforts are needed to remove any hydrophilic sites from the adsorbents [19]. Supported-amine adsorbents show superior CO_2 adsorption capacity via chemisorption; however, the amine groups can undergo degradation at elevated temperatures [20,21]. As chemical adsorbents, supported-amine adsorbents are characterized by a high heat of adsorption (ΔH); this leads to highly exothermic adsorption in large-scale processes [22]. Carbon-based materials have been extensively used as sorbents owing to their highly developed porosity, low cost compared to other solid materials, and hydrophobicity, which imparts a high resistance to water vapor [23–25].

Methods that employ amine-based solid adsorbents are also considered to be an efficient way to reduce GHG emissions via chemisorption of CO_2 [26]. In particular, mesoporous silicas impregnated with polyethyleneimine (PEI) exhibit high CO_2 adsorption capacity, superior CO_2 selectivity, and low energy consumption; such properties make these materials suitable for post-combustion CO_2 capture and storage. However, the low thermal transfer and high ΔH values of chemisorption may cause overheating during CO_2 capture, leading to PEI amine degradation, unstable cycle adsorption, and safety issues [27]. In this work, we report the preparation of porous silica-coated MWCNTs (S-MWCNTs) via a nanocasting technology and the introduction of PEI onto the S-MWCNTs via the wet-impregnation method. The resulting adsorbents exhibit a high loading content and good thermal conductivity, leading to high CO_2 adsorption capacity, efficient diffusion of CO_2, and consequently, good regenerability for CO_2 adsorption/desorption under the flue gas condition.

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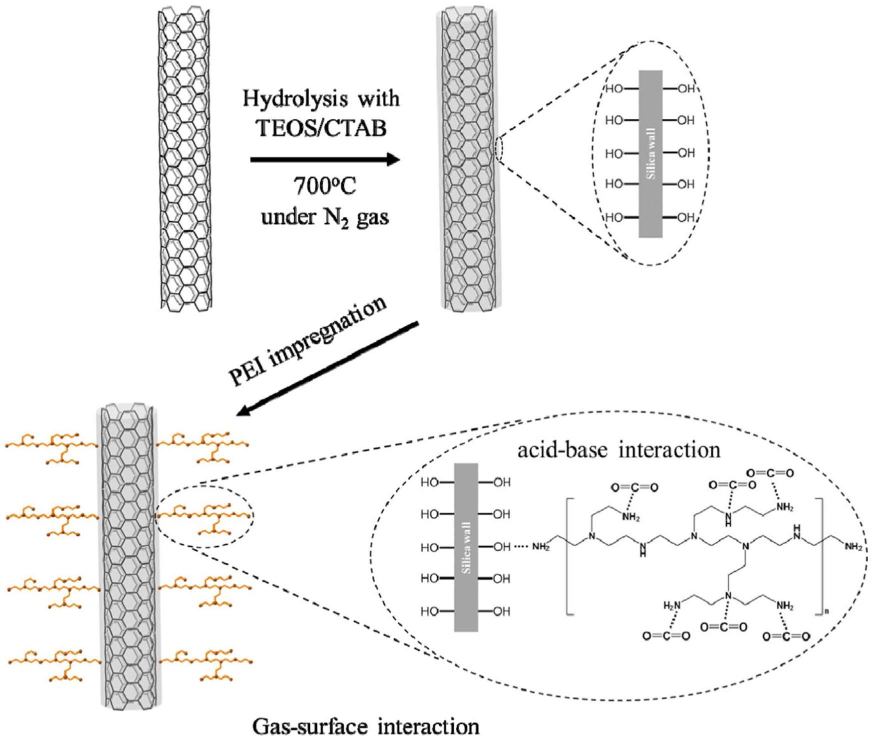

Fig. 1. Fabrication and CO_2 adsorption process of the S-MWCNTs impregnated with PEI.

2. Experimental

2.1. Synthesis of PEI-impregnated porous silica-coated multi-walled carbon nanotubes

The S-MWCNTs were synthesized via the hydrolysis of tetraethylorthosilicate (TEOS, Sigma-Aldrich Co.) onto the surfaces of MWCNTs (Kumho Petrochemical Co., Ltd., Korea) modified with a cationic surfactant. 0.5 g of MWCNTs and 8.8 g of cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich Co.) surfactant were dispersed in a mixture of water (200 mL) and aqueous ammonia (100 mL, 30%) by ultrasonication for 2 h, leading to electrostatic interactions between the negatively charged MWCNTs and cationic surfactant by self-assembly of the surfactant. After complete dispersion, 20 mL of TEOS was slowly added to the mixture under constant stirring for 3 h and subsequently aged at ambient conditions for 24 h. The product was washed with ethanol several times and dried under ambient conditions for 12 h. S-MWCNTs were obtained by calcination at 700 °C for 3 h in a N_2 atmosphere.

PEI-impregnated S-MWCNTs were prepared using the wet-impregnation method. First, the required amount of PEI (M_w=800, Sigma-Aldrich Co.) was dissolved in ethanol (99.9%, Daejung Chemicals, Co.) and stirred for 30 min. The as-prepared S-MWCNTs were added to the solution with continuous stirring at room temperature for 12 h. The product obtained was dried at ambient temperature for 12 h in a vacuum oven. Hereafter, the PEI-impregnated S-MWCNTs are denoted as S-MWCNT/PEI(x), where x represents the weight percentage of PEI impregnated on the S-MWCNTs. The fabrication of the S-MWCNTs impregnated with PEI is schematically illustrated in Fig. 1.

2.2. Characterization

The morphology and microstructure of the adsorbents were investigated using FE-SEM (SU8010, Hitachi Co., Ltd., Japan) and FE-TEM (JEM2100F, JEOL, USA). The surface properties of the samples were determined using X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific Co., USA) with a VG Scientific ESCALAB MK-II spectrometer equipped with a Mg $K\alpha$ (1253.6 eV) X-ray source and high-performance multichannel detector, which was operated at 200 W; Fourier transform infrared (FT-IR, VERTEX 80 V, Bruker Co., Germany) spectroscopy in the range of 400–4000 cm^{-1} was also used. The textural properties of the samples were analyzed via N_2 adsorption–desorption isotherms at 77 K using a gas adsorption analyzer (BELSORP, BEL Co., Japan). Before performing the measurements, the samples were degassed *in vacuo* at 120 °C to remove residual gases and impurities. The specific surface area, which was calculated using the Brunauer–Emmett–Teller (BET) equation, was estimated from the amount of adsorbed N_2 at a partial pressure (P/P_0) of 0.99. In addition, the structures of the mesopores were analyzed using the Barrett–Joyner–Halenda (BJH) model. CO_2 adsorption–desorption isotherms at 298 K were performed using a gas adsorption analyzer and the degassing process described above.

2.3. CO_2 adsorption–desorption experiments under the flue gas condition

A thermogravimetric analyzer (Pyris 1, Perkin Elmer Co., USA) was used to evaluate the CO_2 adsorption and regeneration performance under the flue gas condition (15% CO_2/85% N_2) at 60 °C. The adsorbents were first loaded onto a ceramic pan and degassed at 120 °C for 5 h under pure N_2 flow (60 mL/min). When gas adsorption began, 15% of the N_2 gas flow was immediately switched to CO_2 gas flow; this was maintained for 60 min. When the CO_2 adsorption step was complete, the temperature was increased to 100 °C with a gas-flow change to pure N_2 to degas the samples.

In the cyclic experiments, which were performed to evaluate the regeneration properties of the adsorbents, adsorption and desorption were repeated five times at 60 and 100 °C, respectively, as described above.