



Amines immobilized double-walled silica nanotubes for CO₂ capture

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HIGHLIGHTS

- ▶ Fabrication of double-walled silica nanotube (DWSNT).
- ▶ Primary, secondary, tertiary, di-, and tri-aminosilanes on DWSNT for CO₂ capture.
- ▶ Maximum CO₂ adsorption capacity and bonding-affinity for various amine types on DWSNT.
- ▶ This work demonstrates the amine type apt for the CO₂ capture.

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ABSTRACT

Novel silica support has been required for high amine loading and good CO₂ molecule diffusion into its pores to increase the performance of CO₂ adsorbents. Herein, amine groups supported on double-walled silica nanotubes (DWSNTs) have been prepared via the immobilization of various aminosilanes (primary, secondary, tertiary, di-, and tri-aminosilanes) on DWSNT, and found to be a very effective adsorbent for CO₂ capture. Amine groups immobilized DWSNTs captured CO₂ reversibly in a temperature swing process at various adsorption temperatures (25 °C, 50 °C, 75 °C, and 100 °C). The amines on modified DWSNTs showed high CO₂ capture capacity in the order of tri-, di-, primary, secondary, and tertiary amines. The CO₂ capture capacity of all aminosilanes immobilized DWSNTs decreased linearly with the increase of the adsorption temperature. We expect that DWSNT would be able to inspire researchers to use it not only as a support for CO₂ capture but also as a promising candidate for various applications.

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1. Introduction

The fossil-fuel-burning power plant is the predominant technology for generating electricity. However, the CO₂ emissions during generating electricity have become a serious concern in relation to global warming [1,2]. At the 2010 United Nations Climate Framework on Change Conference in Cancun, the low carbon emission was the major issue [3]. The CO₂ capture process is one of the most efficient methods to lower CO₂ emission level in atmospheric concentration [4]. Four main approaches to the separation of CO₂ from other gases have been well known: cryogenic process [5], membrane purification [6], absorption with liquids [7], and adsorption using solid adsorbents [8]. In these methods, adsorption processes for gas separation via selective adsorption on solid media have an advantage of regeneration with low energy [9]. In solid adsorbents such as Zeolites [10], carbon materials [11], calcium oxides [12], hydrotalcites [13], metal–organic frame (MOF) materials [14], aminopolymers [15], and organic–inorganic hybrid materials [16],

porous materials modified with amines [17,18] have been found to be a promising adsorbent for achieving the effective adsorption of CO₂ due to the atmospheric adsorption/desorption-operating pressure, no materials corrosion, no loss of the adsorbent, the high adsorption capacity, and the low energy for the regeneration of the adsorbent [19].

High-surface-area silica materials such as SBA-15, SBA-16, MCM-41, MCM-48, and KIT-6 have been widely used as support materials for immobilizing various types of amines for CO₂ capture [20]. In this study, we synthesize new tubular silica as a support material, and suggest that tubular type with large pore is favorable for the mass transfer of large molecules. Therefore, this structure could be useful for various applications.

Although the tubular silica support has good pores for mass transfer, its specific surface area is relatively lower than the SBA-15, SBA-16, MCM-41, MCM-48, or KIT-6. This disadvantage causes the low CO₂ capture capacity. Therefore, we designed and synthesized the double-walled silica nanotube (DWSNT) to solve its shortcoming in this study. We also reported on the effects of amine types (primary, secondary, and tertiary) and amine numbers (mono, di, and tri) for CO₂ capture capacity with (3-aminopropyl) trimethoxysilane (APTMS), [3-(methylamino)

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propyl] trimethoxysilane (MAPTMS), [3-(diethylamino) propyl] trimethoxysilane (DEAPTMS), [3-(2-aminoethyl) aminopropyl] trimethoxysilane (AEAPTMS), and 3-[2-(2-aminoethylamino) ethylamino] propyl-trimethoxysilane (AEAEAPTMS) immobilized on DWSNTs. The goal of this study is to propose a novel adsorbent for the sequestration of harmful gas and toxic chemicals including heavy metal ions in addition to the lowering of CO₂ level in atmospheric condition.

2. Materials and methods

2.1. Preparation of double-walled silica nanotube (DWSNT)

DWSNT was synthesized using a tubular template composed of 2-amino-*N*-dodecylacetamide (ADAA, H₂N-CH₂-CONH-(CH₂)₁₁-CH₃, Thermolon Korea Co.). A 1 mmol of ADAA was dissolved in 20 mL of deionized water (DI water, obtained from a Milli-Q water system as 18.2 MΩ cm) and 2 mL of ethanol (Sigma-Aldrich Chemical Co.) solution, and the solution was well stirred for 2 h at 60 °C. Then, 4 mmol of tetraethyl orthosilicate (TEOS, Aldrich Chemical Co.) was added with stirring, and then resulting mixture was kept at room temperature for 72 h. The solid product was filtered, washed with ethanol and DI water, and dried in an oven at 50 °C for 24 h followed by calcination in air at 550 °C for 5 h to completely remove the ADAA. The calcined DWSNT was subsequently dried at 200 °C under vacuum for 3 h.

2.2. Synthesis of amino-functionalized DWSNT

25 mmol of (3-aminopropyl) trimethoxysilane (APTMS, Aldrich Chemical Co.) was added to 2 g of DWSNT in anhydrous toluene (150 mL, Sigma-Aldrich Chemical Co.). The coupling reaction was allowed to proceed for 24 h at 25 °C with a gentle stirring under a nitrogen atmosphere. After reaction, the amino-functionalized DWSNT was rinsed with ethanol (Sigma-Aldrich Chemical Co.). The assemblies were dried in an oven at 120 °C for 2 h. After drying, it was rinsed three times with toluene (Sigma-Aldrich Chemical Co.), a mixed solution of toluene and ethanol (1:1), and ethanol, in that order. To increase of amount of coupled APTMS on DWSNT, the above procedure was repeated three times. Finally, amino-functionalized DWSNT was freeze-dried under vacuum (pressure lower than 5 mTorr) for 1 week after washing with DI water. The immobilization of [3-(methylamino) propyl] trimethoxysilane (MAPTMS, Aldrich Chemical Co.), [3-(diethylamino) propyl] trimethoxysilane (DEAPTMS, Aldrich Chemical Co.), [3-(2-aminoethyl) aminopropyl] trimethoxysilane (AEAPTMS, Acros Organics Co.), and 3-[2-(2-aminoethylamino) ethylamino] propyl-trimethoxysilane (AEAEAPTMS, Acros Organics Co.) on the DWSNT was carried out by the same procedure with the above APTMS-immobilization method. The all reaction was performed at least three times to verify the reproducibility of the reaction through the X-ray photoelectron spectroscopy (XPS) wide-scan and the XPS high-resolution N1s spectra.

2.3. Instrumentations

High resolution X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 V/PC diffractometer with a high-power Cu Kα source operating at 40 kV and 150 mA. The morphologies of the DWSNT particles were examined using a field emission gun scanning electron microscopy (FEG SEM) (Inspect F50, FEI) at 15 kV. The samples for FEG SEM were prepared by dropping a large number of particles of the DWSNT onto a double-sided adhesive carbon disk and sputter-coated with a thin layer of Pt/Pd (E-1010, Hitachi) to

prevent sample charging problems. The nitrogen amount of amino-functionalized DWSNTs was obtained using an elemental analyzer (EA 1108, FISON Instruments). Transmission electron microscopy (TEM) images were obtained with a Philips CM-30 operating at 200 kV. The samples for TEM were prepared by dispersing a large number of particles of the products through a slurry in ethanol onto a holey carbon-coated copper grid, followed by evaporation. Nitrogen adsorption and desorption isotherms were measured at 77.3 K on a ASAP2420 (Micromeritics) having an accelerated surface area and porosimetry system. Prior to the determination of adsorption isotherm, the sample was evacuated at 1.333 Pa and 423.15 K for 2 h to remove all physisorbed species from the surface of the adsorbent. Surface area was determined by the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) method from the isotherm of adsorption branch. To analyze the surface of amino-functionalized DWSNTs, X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a PHI 5000 VersaProbe (Ulvac-PHI) with an Al Kα X-ray source (1486.6 eV of photons) used at 15 kV and 25 W. The data were recorded at room temperature and at a pressure below 6.7×10^{-8} Pa. All binding energies were referenced to the neutral C1s peak at 285.0 eV to compensate for the surface-charging effects. The peaks were deconvoluted using a curve-fitting method with a series of Gauss-Lorentzian curves allowing for adjustment of FWHM (full width at half maximum) using the software of CasaXPS (version 2.3.12).

2.4. CO₂ adsorption/desorption tests

CO₂ adsorption/desorption measurements for amino-functionalized DWSNTs were performed using a thermogravimetric analyzer (TGA, thermal gravimeter S-1000, SCINCO). A sample weight of ca. 10 mg was loaded into an alumina sample pan in a TG unit and tested for CO₂ adsorption/desorption performances. The initial activation of the samples was carried out at 110 °C for 3 h in a nitrogen atmosphere. Then adsorption run was conducted using highly pure and dehumidified CO₂ gas at 25, 50, 75 and 100 °C under atmospheric condition, and the desorption run was carried out using at 110 °C for 3 h. Both the gases, CO₂ and N₂ were passed through automatic valve, assisted with timer for continuous adsorption and desorption profile.

3. Results and discussion

3.1. Synthesis of amino-functionalized DWSNT

The morphology and pore structure of synthesized DWSNT were observed as shown in Fig. 1. In the FEG SEM (Fig. 1a) and TEM (Fig. 1b) images, the rod configuration and double-walled structure of DWSNT were confirmed. The outer diameters of outer tube and inner tube of DWSNT were ca. 92 nm and ca. 24 nm, respectively. Outer and inner tube walls are almost equal in thickness of ca. 10.3 nm. The nanotube length histogram for DWSNT is shown in Fig. 1c. In XRD pattern of the DWSNT (Fig. 1a), any sharp peak was not observed for the crystal structure at both of the small (0.5–5°) and wide (5–70°) angles of 2θ. The total pore volume and BET specific surface area of DWSNT were 1.11 cm³/g and 348 m²/g, respectively (Fig. 1d). Interestingly, two peaks were observed approximately at 28 Å and 390 Å in the BJH pore diameter distribution curve, which indicate that very uniform double-walled structure can be attained with the simple synthesis (Fig. 1d, inset).

In this study, (3-aminopropyl) trimethoxysilane (APTMS), [3-(methylamino) propyl] trimethoxysilane (MAPTMS), [3-(diethylamino) propyl] trimethoxysilane (DEAPTMS), [3-(2-aminoethyl) aminopropyl] trimethoxysilane (AEAPTMS), and

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