Separation of biomass using carbon molecular sieves treated with hydrogen peroxide

CrossMark

Seho Cho, Dayoung Lee, Young-Seak Lee *

Department of Fine Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 305-764, Republic of Korea

A B S T R A C T

The effect of functionalized carbon surface on gas separation is investigated in modified carbon molecular sieves (CMSs) with H_2O_2 for CO_2/CH_4 mixed gas. The textural properties of the surface changed slightly, with a greater micropore volume and surface area enhancement. The amount of adsorbed CO_2 increased from 2.57 for the raw sample to 2.68 mmol/g for the modified CMSs. The breakthrough times for CO_2 were after 7.5 min for modified CMSs and 5 min for R-CMS. These effects were due to the interaction between CO_2 and oxide groups on the surfaces of CMSs resulting from the H_2O_2 treatment.

© 2014 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

The increase in the use of fuel resources due to explosive economic growth has resulted in an oil crisis, price increases and pollution of the environment. Wars are being fought around the world, even now in the 21st century, due to the desire to control fuel sources. To solve such significant problems, many researchers have searched for new energy sources and have developed energy-efficient systems and processes [1].

Renewable energy is energy that comes from natural resources, such as wind, sunlight, rain, geothermal heat, and biofuel. Approximately 16% of the energy consumed globally comes from renewable sources. Biogas, one type of renewable fuel, is methane produced by the anaerobic digestion of organic material by anaerobes. Biogas can be produced either from biodegradable waste materials or from energy crops fed into anaerobic digesters to supplement gas yields. The solid byproduct, the digestate, can be used as a biofuel or a fertilizer. To use the biogas as an energy source, the purity of the methane produced must be over 98%. Carbon dioxide in particular must be removed [2,3].

Carbon dioxide can be removed by several methods, including membrane separation, adsorption, and absorption. Among these methods, adsorption processes such as the pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) have many advantages, such as low operating costs and high selectivity [4].

Carbon materials having porosity are widely used as effective adsorbents in such fields because these carbon absorbent materials have an adequate pore size distribution (PSD), a relatively high mechanical strength, high chemical stability and high pressure resistance due to their high specific pore surface areas [5–7]. In addition, carbon-based materials have been developed over a period of recent century, including activated carbon (AC), carbon nanotubes (CNTs), graphite, graphite nanofibers (GNFs), fullerenes, whiskers and carbon molecular sieves [8,9].

The properties of carbon materials are strongly influenced by the presence of chemical species on the surface of these materials. Various surface groups that contain oxygen, hydrogen, nitrogen, sulfur, halogens, and other elements have been identified on carbon materials. These chemical groups can be introduced through various manufacturing processes [10,11]. Carbon–nitrogen complexes are well known to possess surface groups that increase CO_2 adsorption [12]. However, the methods by which nitrogen atoms can be introduced onto carbon adsorbents are not simple; such methods also produce pungent odors and involve compounds that act as irritants. Carbon–oxygen complexes are the most important surface groups that influence the physicochemical properties of carbon materials, including the wettability, chemical reactivity and catalytic and electrical properties of these materials. In addition, various methods are available for the production of surface oxide groups (acidic, basic and neutral) on carbon involving the use of simple and safe processes with compounds capable of

physical oxidation (i.e., O_2, N_2O, CO_2, H_2O, CO, O_3) or chemical oxidation ($KMnO_4$, HNO_3, and KCO_3) [13–15]. Oxygen-containing functional groups (e.g., phenol, carbonyl, carboxyl, quinine, and lactone groups) on carbon surfaces have been produced using such agents [16]. These oxygen-containing functional groups on carbon surfaces are useful and potentially advantageous for the adsorptive storage or separation of CO_2 from biomass that contains methane gas.

The objective of this work was to enhance the separation of CH_4/CO_2 mixed gas and the CO_2 adsorption capacity of modified porous carbon materials using hydrogen peroxide. The surfaces of CMSs were modified by hydrogen peroxide treatment. This treatment was performed within a few minutes using a simple procedure. The chemical components, texture properties and mixed gas (CH_4/CO_2) separation ability of the treated CMSs were analyzed using XPS, gas adsorption analysis, and gas chromatography, respectively.

2. Experimental

2.1. Materials and methods

The carbon molecular sieves (Carbotech, Germany) were prepared by treatment with aqueous hydrogen peroxide (35% H_2O_2, SamJeon, Korea) under atmospheric conditions.

The oxide groups on the carbon surfaces of the CMSs were introduced using H_2O_2 solution (concentration: 5, 10, or 15%) for 60 min at room temperature with stirring. The mixture was filtered to separate out the treated CMSs, which were then washed with deionized water three times. After washing, the samples were dried at 373 K for 48 h. The raw CMSs and the CMSs treated with 5, 10, and 15% hydrogen peroxide solutions are referred to as R-CMS, 5-HCMS, 10-HCMS, and 15-HCMS, respectively.

2.2. Characterization

The chemical components on the carbon surface after H_2O_2 treatment were identified using X-ray photoelectron spectroscopy (XPS, Thermo Electron, MultiLab 2000 spectrometer, England). Al Kα (1485.6 eV) X-rays were used with a 14.9 keV anode voltage, a 4.6 A filament current, and a 20 mA emission current [17]. To investigate the textural properties and the pore structure, CO_2 adsorption was used to determine the microvolume, surface area, and pore size distribution (PSD) using an ASAP 2020 instrument (Micromeritics Ins. Corp.), and the values of these parameters were calculated by density functional theory (DFT) and the Dubinin–Astakhov (DA) equation [18].

The separation behavior of the CO_2/CH_4 mixed gas was analyzed by micro gas chromatography (micro-GC). The ratios of the $CO_2/CH_4/N_2$ gases were set to those typical of landfill gas: 20%, 30%, and 50%, respectively. N_2 (99.999%) gas was used as the purging gas. In this study, the bed used consisted of a steel reactor 10 mm in diameter and 150 mm tall, with a microporous metal plate located at the middle of the column. The pressure inside the fixed bed was controlled using a back pressure system. Ten-gram samples of the untreated and treated CMSs were loaded into the bed and purged under atmospheric conditions for 60 min. The total feed gas flow rate was held at 200 cc/h in the room temperature while the measurements were taken.

3. Results and discussion

3.1. XPS analysis of modified carbon molecular sieves

The XPS spectra of the CMSs after treatment with various concentrations of H_2O_2 and the XPS spectrum of a pristine CMS are shown in Fig. 1. The presence of the main carbon peak (C1s) and a
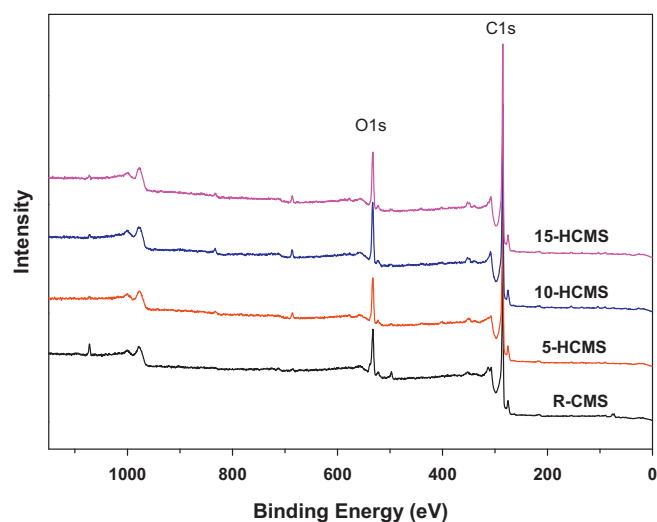

Fig. 1. XPS wide-scan spectra of the CMSs: R-CMS, 5-HCMS, 10-HCMS, and 15-HCMS.

small oxygen peak (O1s) can be observed at approximately 285 eV and 532 eV, respectively, in all samples. The intensity of the O1s peak for the treated samples (see O/C ratios in Table 1) was greater than the intensity of this peak for the untreated sample (O/C ratio: 7.4 at.%) because functional groups were introduced onto the carbon surface by treatment with hydrogen peroxide. Additionally, it was observed that a commercial carbon molecular sieve contained oxygen atoms (6.9%) on the carbon surface.

In addition, the changes in the chemical bonds of the all of the CMS samples were investigated by C1s deconvolution; the results are shown in Fig. 2. The C components on the surfaces of all CMSs are listed in Table 2, along with the assignments, binding energies, and concentrations.

In the C1s deconvolution for R-CMS, five main peaks for C(1), C(2), C(3), C(4), and C(5) were observed at 284.5, 285.4, 286.4, 287.3, and 288.8 eV, respectively, corresponding to sp^2(C–C), sp^3(C–C), C–O, C = O, and (C = O)OH bonds [19]. However, the observed peak positions on the carbon surfaces of all CMSs differed slightly from the values reported by other authors. These slight peak shifts may be caused by differences in the preparation, treatment methods, surface chemical compositions and properties, or crystallization behavior [20]. Treatment with hydrogen peroxide may increase the number of C–OOH groups. Increases in the concentrations of the C(4) and C(5) components are due to the introduction of oxygen and hydroxide by the reaction of hydrogen peroxide with the carbon surface. The increase in the ratio of C–OOH groups on treated CMSs was greater than the increase in the ratio of C = O groups on treated CMSs. These ratios were calculated based on the components on the surface of the raw CMS.

3.2. Textural properties of modified carbon molecular sieves

The changes in the pore textures of the CMSs after hydrogen peroxide treatment were investigated by carbon dioxide adsorption

Table 1
XPS surface composition (at.%) for CMSs chemically treated with H_2O_2.

Treatment	%		Ratio
	C	O	O/C
R-CMS	93.1	6.9	7.4
5-HCMS	89.8	9.2	10.2
10-HCMS	88.7	11.3	12.7
15-HCMS	89.3	10.7	11.9