



Carbon dioxide adsorption performance of ultramicroporous carbon derived from poly(vinylidene fluoride)



Seul-Yi Lee, Soo-Jin Park*

Department of Chemistry, Inha University, 100 Inharo, Incheon, Republic of Korea

ARTICLE INFO

Article history:

Received 11 November 2013

Accepted 18 January 2014

Available online 28 January 2014

Keywords:

Carbon dioxide capture

Microporous carbon

Activation-free method

Heat-treatment

Pore size

ABSTRACT

This study examined the properties of ultra-microporous carbon synthesized by the pyrolysis of poly(vinylidene fluoride) as a function of the heat-treatment temperature, and evaluated the CO₂ adsorption capacity by pressure swing analysis. X-ray photoelectron spectroscopy confirmed the specific elements of the heat-treated carbon (HTC) surfaces. The textural properties were analyzed using N₂ adsorption isotherms at 77 K. The CO₂ adsorption capacity was measured by CO₂ isothermal adsorption at 298 K and under increasing pressure up to 100 kPa. The CO₂ adsorption capacity increased with increasing heat-treatment temperature to 873 K (HTC-873, 155 mg/g), and then decreased at 973 K (HTC-973), which correlated with their micropore volume. Interestingly, HTC-773 with a smaller pore size had higher CO₂ adsorption capacity than HTC-873 at pressures up to 30 kPa. This results show that the CO₂ adsorption capacity at a certain pressures (in particular <30 kPa) is strongly affected by the pore size of the HTC samples but not by the micropore volume or specific surface area.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Global warming is considered one of the grand challenges of the 21st century. The greenhouse effect can be attributed to an increase in the emission of the greenhouse gases, such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbons (CFC), and sulfur hexafluoride (SF₆) since the beginning of industrialization. Among them, CO₂ is the main greenhouse gas that causes global warming.

As published in the International Energy Agency (IEA)'s CO₂ emissions from fuel combustion highlight report (2013) [1], the global atmospheric CO₂ concentration has increased from a pre-industrial value of ~280 parts per million in volume (ppmv) to ~394 ppmv in 2012. Most of the CO₂ emissions into atmosphere might originate from the combustion of fossil fuels (~99% in global annual CO₂ emissions of approximately 32 Gt).

CO₂ capture and storage (CCS) technology is attracting increasing interest to reduce the ever-increasing amount of CO₂ released into the atmosphere and its impact on global climate change [2]. Three main technologies are currently under discussion for CO₂ capture from power plant flue gases: pre-combustion capture, oxy-fuel technology, and post-combustion capture. The post-combustion capture technology has attracted interest because existing plants can be equipped relatively easily with the technology [3–6].

As an efficient alternative technology for post-combustion CO₂ capture, adsorption processes are considered a promising technology for capturing CO₂ from flue gases in commercial applications [7]. This technology has some advantages over other methods, such as absorption with a physical or chemical solvent, cryogenic separation, membrane separation, etc., as well as low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures [8–11].

Porous carbon materials are used widely as gas-phase and liquid-phase adsorbents, catalyst supports, electrode materials for supercapacitors, etc. [12–15], owing to their hydrophobic nature, high surface area, good thermal and mechanical stability, chemical inertness, and high physisorption capacity.

Recently, porous carbon materials have been considered a potential candidate for CO₂ adsorption from combustion flue gas in industrial applications. These materials have attracted considerably more attention in CO₂ adsorption than any other type of adsorbent, such as carbon materials [16–18], zeolites [19,20], micro or meso silica [21], metal oxide [22], metal-organic frameworks [23–26], etc., on account of their availability, large surface area, viable CO₂-friendly sites on the pore structure, reasonable production cost, and low energy requirements for regeneration through their moderate heat of sorption, higher hydrophobic surface properties [27].

Normally, porous carbon materials are synthesized by the carbonization of carbon precursor [28,29]. Furthermore, to obtain well-developed microposity with a large surface area, activated carbon materials can be prepared by two methods, *i.e.* physical activation [30,31] and chemical activation [32–34]. Physical activation

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

E-mail addresses: sjpark@inha.ac.kr, psjin@kriict.re.kr (S.-J. Park).

implies the pyrolysis of the precursor at high temperatures with gas including carbon dioxide, steam, etc. Chemical activation also involves pyrolysis, but at lower temperatures, as well as impregnation of the parent materials with chemical activation agents, such as alkaline hydroxide and transition metal oxides. Some novel activation-free methods have been reported, including polymer blend pyrolysis [35] and casting method using a micro or mesopore hard template [36,37].

In particular, the nanoporous synthetic carbon materials by thermal-decomposition of polymers are known to be efficacious for gas adsorption and storage. The adsorption of small molecules, such as CO₂, H₂, CH₄ and other gases, in a porous material requires strict control and tuning of the synthesis and preparation of porous structure. Thus, the structural and textural designs for the specific adsorbent have been obtained by selecting the suitable polymers for the optimization of porosity characteristics (such as size and volume), which has also the advantage of easy and simple process [38,39].

This study synthesized ultra-microporous carbon by pyrolyzing poly(vinylidene fluoride) without a chemical or physical activation process, and evaluated the CO₂ adsorption capacity by a pressure swing analysis at 298 K. In addition, the pore formation mechanism of the heat-treated carbon (HTC) samples was examined as a function of the heat-treatment temperature. The relationship between the textural properties of HTC and the CO₂ adsorption capacity was also evaluated.

2. Experimental

2.1. Sample preparation

Poly(vinylidene fluoride) (PVDF, CH₂CF₂, Mw: 534,000, m.p.: 444 K, purchased from Aldrich Co.) was used as the precursor. To obtain ultra-microporous carbon, 1 g of PVDF was mixed homogeneously in suspension with acetone. Subsequently, the PVDF suspension was dried at 353 K for 24 h. The dried PVDF film form was transferred to a furnace and heated to the required heat-treatment temperature at 2 K/min in ultra-pure N₂ gas flow. The temperature was maintained for 2 h. The samples were prepared at various heat-treatment temperatures ranging from 673 to 973 K. Based on previously published papers [40,41], this temperature range was chosen considering the thermal degradation behavior of PVDF during the heat-treatment process. After cooling, the samples consisting of black powder were washed thoroughly with distilled water and dried in a vacuum oven at 393 K for 24 h. The heat-treated ultra-microporous carbon samples derived from PVDF (HTC) were labeled according to the heat-treatment temperature: HTC-673, HTC-773, HTC-873, and HTC-973.

2.2. Characterization

The X-ray photoelectron spectra (XPS) were obtained using a monochromatic MgK α X-ray source operated at 150 W. Survey scans were collected with a pass energy equal to 20 eV. The vacuum system pressure was maintained at approximately 10⁻⁹ kPa throughout the XPS experiments. A non-linear least squares curve fitting program (Peak-Fit version 4) with a Gaussian-Lorentzian mix function and Shirley background subtraction was used to deconvolve the XPS subpeaks. The binding energies of all peaks were corrected relative to the reference peak (graphite C_{1s}, 284.5 eV).

The X-ray diffraction (XRD) patterns were obtained with CuK α radiation operating at 40 kV and 40 mA (Rigaku Model D/MAX diffractometer). The patterns were recorded with a scan step time of 2 s and a step size of 0.02°.

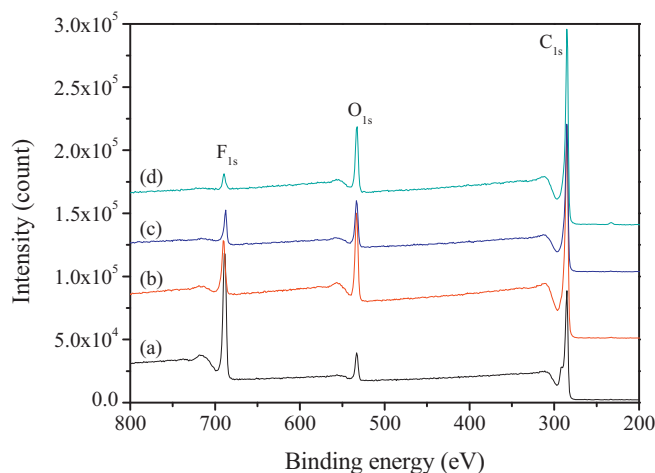


Fig. 1. XPS spectra of the HTC samples as a function of the heat-treatment temperature; (a) HTC-673, (b) HTC-773, (c) HTC-873, and (d) HTC-973.

The specific surface areas of the HTC samples studied were measured by N₂ gas adsorption at 77 K using an automated adsorption apparatus (BELSORP Mini, BEL Co., Japan). The system and sample were out-gassed at 573 K for 6 h to obtain a residual pressure of <10⁻⁴ kPa prior to making the determinations.

CO₂ adsorption was carried out using a volumetric adsorption measurement (BEL HP, BEL Co., Japan). Prior to adsorption analysis, the sample (approximately 0.5 g) was degassed at 573 K for 6 h. After cooling the sample to room temperature, ultra-high purity grade (99.9999%) CO₂ gas was introduced from 0.1 to 100 kPa. The CO₂ adsorption experiments were performed at 298 K by pressure swing analysis.

3. Results and discussion

XPS was used to provide information on the surface chemical species of the synthesized HTC samples as a function of the heat-treatment temperature. The correlation between the chemical species and the pore structures of the HTC samples was examined. As shown in Fig. 1, all spectra exclusively exhibited F_{1s}, O_{1s}, and C_{1s} peaks. The C_{1s} peak intensity increased significantly with increasing heat-treatment temperature but the F_{1s} peak intensity decreased dramatically. Table 1 lists the surface compositions. The value of C_{1s}/(O_{1s} + F_{1s}) increased steadily with increasing heat-treatment temperatures. The pyrolysis residue is made up of largely aliphatic and fluoro-aromatic structures. In addition, the surface characteristics of the HTC surfaces depended on the amount of chemical species remaining (atom and their compounds of fluorine and oxygen), which might affect the pore structures [42].

Fig. 2 illustrates the XRD patterns of HTC samples. There are two broad diffraction peaks around 2 θ = 23° and 43° in each spectrum correspond to the (002) and (100) reflection planes, interlayered spacings between adjacent graphite layers and in-plane orderings, respectively. These diffraction peaks were slightly shifted upward with an increase in the heat-treatment temperature. It was found

Table 1
Chemical compositions of samples studied.

Specimens	C1s (%)	O1s (%)	F1s (%)	C1s/(O1s + F1s)
HTC-673	67.7	7.41	24.2	2.14
HTC-773	76.2	14.0	8.1	3.45
HTC-873	81.5	12.5	4.8	4.71
HTC-973	83.2	12.9	2.1	5.55

Download English Version:

<https://daneshyari.com/en/article/1196869>

Download Persian Version:

<https://daneshyari.com/article/1196869>

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