Pore Structure Characterization of Poly(vinylidene chloride)-Derived Nanoporous Carbons

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Abstract

Poly(vinylidene chloride) (PVDC)-derived nanoporous carbons were prepared by various activation methods: heat-treatment under an inert atmosphere, steam activation, and potassium hydroxide (KOH) activation at 873, 1073, and 1273 K. The pore structures of PVDC-derived nanoporous carbons were characterized by the N₂ adsorption technique at 77 K. Heat treatment in an inert atmosphere increased the specific surface area and micropore volume with elevating temperature, while the average micropore width near 0.65 nm was not significantly changed, reflecting the characteristic pore structure of ultramicroporous carbon. Steam activation for PVDC at 873 and 1073 K also yielded ultramicroporosity. On the other hand, the steam activated sample at 1273 K had a wider average micropore width of 1.48 nm, correlating with a supermicropore. The KOH activation increased the micropore volume with elevating temperature, which is accompanied by enlargement of the average micropore width from 0.67 to 1.12 nm. The average pore widths of KOH-activated samples were strongly governed by the activation temperature. We expect that these approaches can be utilized to simply control the porosity of PVDC-derived nanoporous carbons.

Key words: nanoporous carbon, activation, pore structure, adsorption

1. Introduction

Nanoporous carbons have strong potential for application in various fields, including energy and environmental fields in particular [1,2]. Extensive research has been carried out to develop efficient storage media of supercritical gases as a clean energy and a realistic alternative to the compression and liquefaction storage techniques of gases. Nanoporous carbons are considered a promising candidate for supercritical gas storage [3,4]. As the interaction of a supercritical gas molecule with the pore wall of nanoporous carbon is not strong enough, highly ultramicroporous (pore width < 0.7 nm) carbons are predicted to be efficient adsorption sites for supercritical gases [4]. Supercapacitors, another promising candidate for application of nanoporous carbons, have attracted much attention as energy storage devices for electric vehicles and hybrid electric vehicles [5]. For obtaining high-performance supercapacitors, several parameters of nanoporous carbons are recognized as key factors in terms of their application as electrode materials: specific surface area, pore size, conductivity, and surface chemical state. The selection of an optimal electrolyte has also been demonstrated to be an important factor for maximizing the performance of supercapacitors [6,7]. In particular, the relationship between the pore size of the nanoporous carbons and electrolyte ion size is an important parameter in enhancing the specific capacitance of supercapacitors [8].

Table 1. Activation conditions of PVDC-derived nanoporous carbons

Sample ID	Pre-annealing temperature (K) /atmosphere	Activation method/atmosphere	Activation temperature (K)
HT-873K	673/ N ₂	Heat-treatment/N ₂	873
HT-1073K	673/ N ₂	Heat-treatment/N ₂	1073
HT-1273K	673/ N ₂	Heat-treatment/N ₂	1273
Steam-873K	673/ N ₂	Steam/N ₂	873
Steam-1073K	673/ N ₂	Steam/N ₂	1073
Steam-1273K	673/ N ₂	Steam/N ₂	1273
KOH-873K	673/ N ₂	KOH/ N ₂	873
KOH-1073K	673/ N ₂	KOH/ N ₂	1073
KOH-1273K	673/ N ₂	KOH/ N ₂	1273

PVDC: poly(vinylidene chloride), KOH: potassium hydroxide.

Pore size and pore geometry of nanoporous carbons are important governing factors in the adsorption behaviors of various guest molecules [9–11]. The pores of nanoporous materials are classified according to the pore width w , which is the shortest distance in three-dimensional geometry, as recommended by the International Union of Pure and Applied Chemistry (IUPAC). The micropores have two subgroups of ultramicropores and supermicropores ($0.7 \text{ nm} < \text{pore width} < 2 \text{ nm}$). The maximum size of ultramicropores corresponds to the bilayer thickness of the adsorbed N₂ molecules. Although the importance of ultramicropores has been emphasized in molecular sieving and supercritical gas adsorption, an accurate evaluation of the ultramicroporosity is very difficult due to the blocking near the pore entrance. Recently, many researchers have often used the term “nanopores,” which is not recommended by the IUPAC. Nanopores can be defined as having size less than 5 nm, which is convenient owing to the inherent adsorption characteristics according to recent progress in adsorption science and technology.

Poly(vinylidene chloride) (PVDC) has been proposed as a promising precursor material for obtaining nanoporous carbons [8,12–22]. It is well known that PVDC-derived nanoporous carbons could be prepared by simple heat-treatment without an additional activation process [8,12–20]. The PVDC-derived nanoporous carbons prepared by heat-treatment alone provide an ultramicroporous structure. In this study, various activation methods for PVDC were performed in order to control the porosity of the PVDC. The effects of the activation conditions on the porosity changes were investigated by the N₂ adsorption technique at 77 K.

2. Experimental

2.1. Materials and methods

Homogeneous PVDC (Asahi Kasei Co.) with a crystallite size of 26.7 nm was annealed at 673 K in a N₂ atmosphere for 1 h before the activation process. Activation of PVDC was performed by three methods. First, for the heat-treatment method, the pre-annealed PVDC samples were further heat-treated at 873, 1073,

and 1273 K in a N₂ atmosphere for 1 h, respectively. Second, for the steam activation method, the pre-annealed samples were further heat-treated at the same temperature in a steam atmosphere for 1 h. N₂ was used as a carrier gas. Third, for the KOH activation method, mixtures of pre-annealed PVDC samples and potassium hydroxide (KOH) were further heat-treated at the same temperature in a N₂ atmosphere for 1 h. The weight ratio of KOH to PVDC was 2:1. The N₂ flow rates for all experiments were 100 mL min⁻¹. The sample names and treatment conditions are summarized in Table 1.

2.2. Characterization

The electrical conductivity of PVDC-derived porous carbons was measured with a powder resistivity measurement system. The powder samples were compressed in a cylinder cavity with a diameter of 21 mm under controlled pressure in a range of 3.6–125.4 MPa at room temperature. The pore structures were determined by N₂ adsorption at 77 K using volumetric equipment (Micromeritics ASAP 2010) after preevacuation at 423 K for 2 h, while maintaining the base pressure at 10⁻⁴ Pa. Pore structure parameters were obtained by the subtracting pore effect (SPE) and Dubinin-Radushkevich (DR) methods. The SPE method was performed by using high-resolution α_s -plots, which are constructed using the standard adsorption data for nonporous carbon black [23,24].

3. Results and Discussion

3.1. Electrical conductivity of PVDC-derived nanoporous carbons

Fig. 1 shows the powder resistivity of PVDC-derived nanoporous carbons as a function of applied pressure. The electrical conductivities of all samples increased with an increase in applied pressure, suggesting that the contact area between adjacent particles of the nanoporous carbon increases with increasing applied pressure. The relationship between the electrical conductivity of pressed particles and activation temperatures is also

Fig. 1. Powder resistivity vs. applied pressure plots for PVDC-derived nanoporous carbons: (a) PVDC pre-annealed at 673 K, (b) PVDC heat-treated in N_2 atmosphere, (c) steam-activated PVDC, and (d) KOH-activated PVDC. PVDC: poly(vinylidene chloride), KOH: potassium hydroxide.

shown in Figs. 1b–d. The electrical conductivity of all samples increases with the activation temperature. Therefore, the electrical conductivity strongly depends on the activation temperature of the PVDC. In general, the electrical conductivity of porous carbons decreases with increasing porosity, which is associated with the formation of isolated conducting pathways. However, thermal decomposition of PVDC eliminates non-carbon atoms and develops a more layered carbon structure by carbonization behavior, resulting in enhanced electrical conductivity. In our results, as heat-treatment at higher temperature accelerates the carbonization as well as the development of a porous structure of the PVDC, the electrical conductivity of the samples should be enhanced. Therefore, to obtain nanoporous carbons with better electrical conductivity, it is important to control the activation temperature for PVDC.

3.2. Pore structure of PVDC-derived nanoporous carbons

Fig. 2a shows N_2 adsorption isotherms (77 K) of PVDC-derived nanoporous carbons heat-treated under an inert atmosphere. All adsorption isotherms are of Type I, suggesting the presence of uniform microporosity. The saturated amounts of N_2 adsorption at relative pressure (P/P_0) = 1 increase with heat-treatment temperature. The N_2 adsorption isotherms of all samples show steep uptake at low P/P_0 due to monolayer adsorption on the micropore walls. Fig. 2b shows the high-resolution α_s -plots for N_2 adsorption isotherms at 77 K. The slope of the line passing through the origin and the point at $\alpha_s = 0.5$ leads to the specific surface area. The intercept and slope

of the line above $\alpha_s = 1$ with the ordinate gives the micropore volume and the external surface area, respectively [23,24]. The average micropore width was obtained by simple geometrical slit pore approximation. Typically, the α_s -plot for microporous materials has one or two upward swings below $\alpha_s = 1.0$. The swings at the lower α_s region (f-swing) and at the higher α_s region (c-swing) are indicated as filling and cooperative swings, respectively. The f-swing originates from monolayer adsorption on the micropore walls. The c-swing is an adsorption process in the residual space after the completion of monolayer adsorption on the micropore walls. Therefore, the c-swing indicates a micropore system with pore width larger than the thickness of trilayer N_2 molecules. All samples show only a f-swing below $\alpha_s = 0.5$, suggesting the presence of only ultramicropores. The α_s -plots of heat-treated porous carbons show a typical shape of ultramicroporous carbon. The pore structure parameters of the porous carbons, determined through the α_s -plots, are summarized in Table 2. The total surface area and micropore volume increase with heat-treatment temperature. All samples have a narrow average micropore width of about 0.65 nm, close to an ultramicropore. Table 2 also shows the micropore volume determined from the DR-plots ($V_{\text{micro-DR}}$) for comparison with the values from the α_s -plots ($V_{\text{micro-SPE}}$). Generally, the $V_{\text{micro-DR}}$ value corresponds only to ultramicropores, whereas the $V_{\text{micro-SPE}}$ value provides information about the total micropores. $V_{\text{micro-SPE}}$ and $V_{\text{micro-DR}}$ values of all samples are similar, reflecting the ultramicroporosity of the heat-treated samples, in excellent agreement with the average pore width results determined by the SPE method. Therefore, heat-treatment of PVDC is an effective method for the preparation of ul-

Fig. 2. (a) N_2 adsorption isotherms (77 K) and (b) their high-resolution α_s -plots for heat-treated PVDC-derived nanoporous carbons. The open and solid symbols indicate adsorption and desorption branches, respectively: $\circ$ (HT-873K), $\triangle$ (HT-1073K), $\square$ (HT-1273K). PVDC: poly(vinylidene chloride)

tramicroporous carbons. The formation of an ultramicroporous structure of the PVDC-derived nanoporous carbon heat-treated in an inert atmosphere is thought to be closely related to complete release of hydrogen and chlorine atoms during thermal decomposition of the PVDC at high temperature [25].

Fig. 3a shows N_2 adsorption isotherms of PVDC-derived nanoporous carbons activated under steam. The N_2 adsorption isotherms of activated samples at 673 and 873 K are also Type I, which is due to the presence of uniform microporosity. The saturated amounts of N_2 adsorption at $P/P_0 = 1$ increase with elevated activation temperature. The N_2 adsorption isotherm of the activated sample at 1273 K shows gradual adsorption uptake until $P/P_0 = 0.4$ due to a second layer adsorption on the micropore walls adsorbed by the monolayer. This stems from the presence of supermicropores on porous carbon activated at higher temperature. The N_2 adsorption isotherm for the HT-1273K sample exhibits a hysteresis loop that can be assigned to type H4. It is well known that type H4 is generally obtained from slit-shaped pores in various activated carbons, but the pore size distribution is mainly in the micropore range. The high-resolution α_s -plots for activated samples at 673 and 873 K show only a f-swing below $\alpha_s = 0.5$, suggesting the presence of only ultramicropores (Fig. 3b). On the other hand, the α_s -plot of the activated sample at 1273 K shows a f-swing and c-swing in the α_s region of 0.5 to 1.0, suggesting the presence of both ultramicropores and supermicropores. As shown in Table 2, the total surface area and micropore volume increase with the steam activation temperature. The steam activated samples at 873 and 1073 K have a narrow average micropore width less than 0.7 nm, close to that of an ultramicropore, and similar to that of heat-treated samples. On the other hand, the steam activated sample at 1273 K has a wider average micropore width of 1.48 nm. The average micropore width increased about two-fold compared to the samples treated at lower temperatures. $V_{\text{micro-SPE}}$ and $V_{\text{micro-DR}}$ values of samples treated at 873 and 1073 K in steam are similar, indicating ultramicroporosity. On the other hand, the ratio of $V_{\text{micro-DR}}$ to $V_{\text{micro-SPE}}$ for the sample

Table 2. Pore structure parameters of PVDC-derived nanoporous carbons determined by SPE method. Micropore volumes ($V_{\text{micro-DR}}$) were determined by the DR method

Sample	a_t ($\text{m}^2 \text{g}^{-1}$)	a_{ext} ($\text{m}^2 \text{g}^{-1}$)	a_{micro} ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{micro-SPE}}$ ($V_{\text{micro-DR}}$) (mL g^{-1})	w (nm)
HT-873K	1514	4	1510	0.48 (0.49)	0.64
HT-1073K	1589	2	1587	0.51 (0.51)	0.64
HT-1273K	1635	2	1633	0.53 (0.54)	0.65
Steam-873K	1560	2	1558	0.50 (0.52)	0.64
Steam-1073K	2201	22	2179	0.76 (0.75)	0.69
Steam-1273K	2371	434	1937	1.43 (0.99)	1.48
KOH-873K	1061	8	1053	0.35 (0.36)	0.67
KOH-1073K	2704	38	2666	1.13 (0.97)	0.85
KOH-1273K	2429	108	2321	1.30 (0.90)	1.12

PVDC: poly(vinylidene chloride), SPE: subtracting pore effect, DR: Dubinin-Radushkevich, KOH: potassium hydroxide, a_t : total surface area, a_{ext} : external surface area, a_{micro} : micropore surface area, $V_{\text{micro-SPE}}$: micropore volume determined by SPE method, $V_{\text{micro-DR}}$: micropore volume determined by DR method, w : average micropore width.

Fig. 3. (a) N_2 adsorption isotherms (77 K) and (b) their high-resolution α_s -plots for steam-activated PVDC-derived nanoporous carbons. The open and solid symbols indicate adsorption and desorption branches, respectively: $\circ$ (Steam-873K), $\triangle$ (Steam-1073K), $\square$ (Steam-1273K). PVDC: poly(vinylidene chloride)

treated at 1273 K dramatically decreases to about 0.7, which is associated with the presence of supermicropores, in good agreement with the average pore width determined by the SPE method. Therefore, steam activation at higher temperature has advantages for creating supermicropores. This should be attributed to pore formation by the elimination of hydrogen and chlorine atoms and to successive pore widening due to the attack of more oxidative steam at higher temperature.

Fig. 4a presents N_2 adsorption isotherms of PVDC-derived nanoporous carbons chemically activated with KOH. The N_2 adsorption isotherms of all samples are defined as type I. However, the isotherm of the sample treated at 1273 K shows a gradual adsorption uptake until $P/P_0 = 0.4$ due to a second layer adsorption, originating from the presence of supermicropores. The N_2 adsorption isotherm for the KOH-1273K sample also exhibits a hysteresis loop that can be assigned to type H4, which is similar to that for HT-1273K. The N_2 adsorption isotherm of the sample treated at 1073 K shows a steep uptake at a low P/P_0 due to monolayer adsorption, resulting in a high specific surface area of 2704 m²/g, as shown in Table 2. The

Fig. 4. (a) N_2 adsorption isotherms (77 K) and (b) their high-resolution α_s -plots for KOH-activated PVDC-derived nanoporous carbons. The open and solid symbols indicate adsorption and desorption branches, respectively: $\circ$ (KOH-873K), $\triangle$ (KOH-1073K), $\square$ (KOH-1273K). KOH: potassium hydroxide, PVDC: poly(vinylidene chloride).

α_s -plot of the sample treated at 1273 K shows a f-swing and c-swing in the α_s region of 0.5 to 1.0, suggesting the presence of both ultramicropores and wider micropores, as shown in Fig. 4b, which reflects more heterogeneous microporosity. The micropore volume increases with activation temperature. In contrast, the specific and micropore surface areas of the sample treated at 1273 K slightly decrease compared to those of the sample treated at 1073 K. The chemical activation at higher temperature also results in widened average micropore width. The average micropore width is linearly proportional to the activation temperature, indicating a strong dependence on the activation temperature of the pore structure. As shown in Table 2, the ratio of $V_{\text{micro-DR}}$ to $V_{\text{micro-SPE}}$ decreases with activation temperature, suggesting that porous carbons with higher KOH-activation temperature have more supermicropores. This result should be related to pore widening due to permeation of potassium species into the interlayer space or small pores and the subsequent chemical reactions of KOH, which are accelerated at higher temperature.

4. Conclusions

Nanoporosity control of PVDC-derived porous carbons was successively achieved by various activation methods. Heat-treatment in an inert atmosphere for PVDC provided an ultramicroporous structure. On the contrary, steam activation at 1273 K provided a supermicroporous structure with average micropore width of 1.48 nm. With elevated KOH activation temperature, the average micropore width was gradually enlarged from 0.67 to 1.12 nm. Therefore, the average pore widths of KOH-activated samples were strongly governed by the activation temperature. Consequently, PVDC-derived nanoporous carbons with controllable pore size can find useful applications as electrode materials for energy storage devices.

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