



# Structural elucidation of physical and chemical activation mechanisms based on the microdomain structure model



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## ABSTRACT

Activated carbons (ACs) prepared by chemical activation commonly show higher specific surface areas and higher yields than those prepared by physical activation. In this study, the differences in the pore development mechanisms between physical and chemical activation processes for AC preparation were studied from a structural point of view, based on the microdomain structure model. Phenol resin-based spherical carbon was used as the starting material. AC preparation *via* potassium hydroxide (KOH) activation (chemical activation) did not induce noticeable changes in the particle or microdomain sizes, despite the abundant development of pores. On the other hand, ACs produced *via* steam activation (physical activation) showed remarkable reductions in both particle and microdomain sizes, depending on the activation temperature. Considering the differences in activation yield and degree of developed porosity between chemical and physical activations, we concluded that, in the case of KOH activation, pore development homogeneously progressed overall for all microdomains consisting of carbon particles without apparent morphological change; however, steam activation caused inhomogeneous gasification from the outer surface of the carbon particles and microdomains. For this reason, KOH-ACs showed higher yield and superior pore development.

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## 1. Introduction

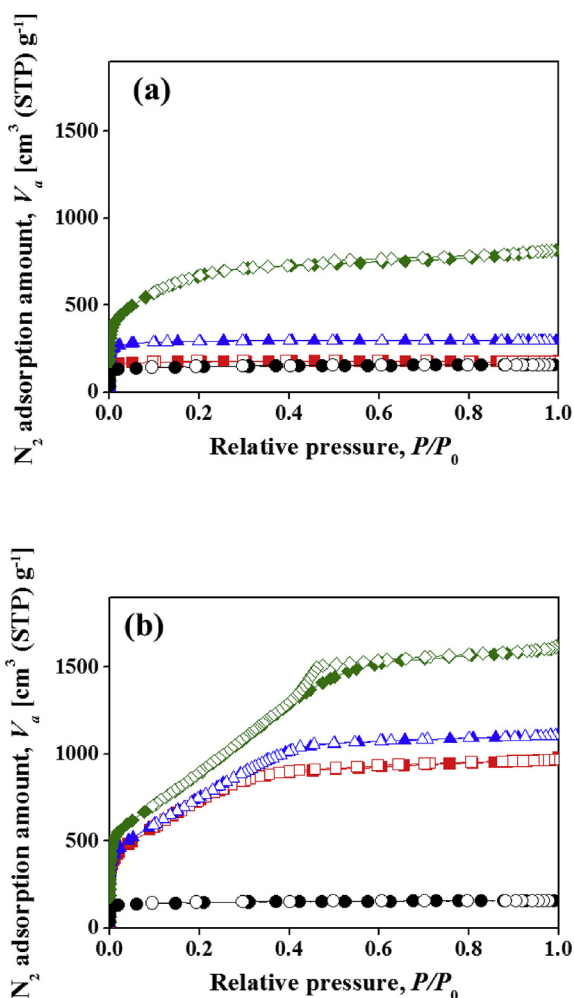
Activated carbons (ACs) are used as adsorbents in water and air purification [1,2] and gas separation [3], as catalysts or catalyst supports [4], and as electrodes in supercapacitors [5]. A wide range of pore characteristics of ACs, such as the specific surface area, pore size distribution, and pore volume, can be controlled through the selection of raw materials and adjustment of the carbonization and activation conditions [6,7]. In particular, the activation process, which is divided into physical and chemical activation, is a key process to obtain ACs with highly developed pores. The advantages of ACs prepared by chemical activation include a higher specific surface area and higher yield, compared with those produced by physical activation [8–10]. For example, MAXSORB, an AC having one of the highest specific surface areas among commercial ACs and prepared by chemical activation using potassium hydroxide (KOH)

as an activating agent, shows threefold higher Brunauer–Emmett–Teller surface area at the same yield of 50% than that by steam activation (physical activation) [11].

Many studies have been performed to clarify the reasons for superior pore development in chemically activated ACs. Marsh et al. described the activation process by KOH as involving two main mechanisms: (1) catalytic gasification of carbon into carbon monoxide and carbon dioxide, and (2) intercalation of potassium metal between graphitic layers, followed by rapid removal [7]. Chemical reaction equations describing KOH and NaOH activations have also been proposed [11–13]. Structural investigations of the pore development mechanism of physical and chemical activations have been attempted using gas adsorption [14], X-ray diffraction [15–17], and transmission electron microscopy (TEM) [14,18–20]. Observation and analysis of pore structure of activated carbon fibers from various precursors, such as isotropic pitch, polyacrylonitrile, cellulose, phenol, and rayon, have been also carried out by using high-resolution TEM and image processing [21–23]. However, a direct comparison of the differences in the pore development mechanisms of these two activation processes is

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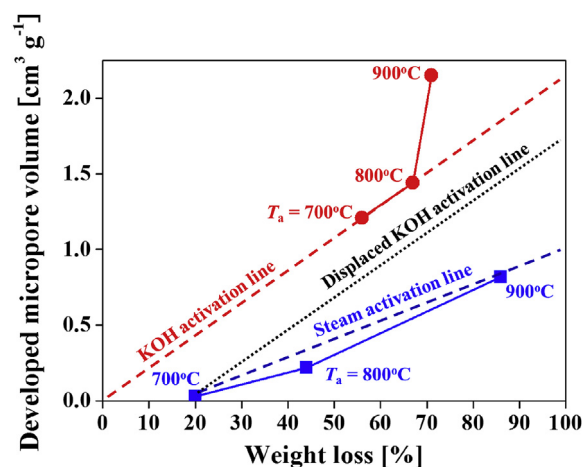
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**Fig. 1.**  $N_2$  adsorption/desorption isotherms at 77 K of C6 and (a) steam- and (b) KOH-activated carbons (ACs). The solid and open symbols denote adsorption and desorption isotherms, respectively. (Circle) C6; (square) C6S7 or C6K7; (triangle) C6S8 or C6K8; (diamond) C6S9 or C6K9. (A colour version of this figure can be viewed online.)

lacking, especially from a structural point of view.

The objective of this study was thus to elucidate the differences in the structural mechanisms of physical and chemical activation processes for AC preparation. Self-same phenol resin-based spherical carbon was used as the starting material because the activation degrees of produced ACs are largely influenced by raw materials and the carbonization conditions [6,7,12,24]. A new structural model, the microdomain structure model, which was recently proposed by some of the present authors [25], was adopted to resolve the AC structure. In this previous study, it has been revealed by scanning tunneling microscopy (STM) observations



**Fig. 2.** Relationship between weight loss and developed micropore volume of (square) steam- and (circle) KOH-ACs prepared at different activation temperatures,  $T_a$ . (A colour version of this figure can be viewed online.)

that each AC particle consists of numerous spherical microdomains, a basic structural unit,  $\sim 2$ – $10$  nm in diameter [25]. Furthermore, unlike the conventional hierarchical pore structure model, in the microdomain structure model, micropores develop in each microdomain, and mesopores form between adjacent microdomains (i.e., in inter-microdomain space).

In this study, based on the microdomain structure model, a structural model to explain the difference in the pore development mechanisms between steam (physical) and KOH (chemical) activations is presented for the first time, through STM and scanning electron microscopy (SEM) structural analyses of the shape and size changes of microdomains and particles together with the observation of correlations between weight loss and the degree of pore development by different activation processes.

## 2. Experimental

### 2.1. Sample preparation

Spherical carbon (C6), prepared by the carbonization of a spherical phenol resin (BEAPS series, Asahi Yukizai Corporation, Japan) at  $600$  °C for 1 h in a flow of  $N_2$ , was used as the starting material. For AC preparation by physical activation, steam was used as the activating agent. C6 was heated to  $700$ – $900$  °C at a ramping rate of  $5$  °C  $min^{-1}$  in  $N_2$  flow ( $100$  mL  $min^{-1}$ ); the sample was held at the desired temperature for 1 h in a steam flow containing  $N_2$  gas (relative humidity = 90%), which was produced by bubbling  $N_2$  through boiling distilled water. After steam activation, the collected sample was dried at  $150$  °C for 12 h in a vacuum oven. AC preparation via chemical activation was performed using KOH (purity > 85.0%; Wako Pure Chemical Industries, Ltd., Japan) as an

**Table 1**  
Pore structural parameters and activation yield of C6 and steam- and KOH-ACs.

Sample	Specific surface area [ $m^2 g^{-1}$ ]	Micropore volume [ $cm^3 g^{-1}$ ]	Average pore width [nm]	Activation yield [%]
C6	655	0.24	0.73	–
C6S7	878	0.27	0.61	80
C6S8	1409	0.46	0.65	56
C6S9	2213	1.06	1.02	14
C6K7	2189	1.45	1.34	44
C6K8	2349	1.68	1.44	33
C6K9	2878	2.39	1.69	29

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