

ADSORPTION PROPERTIES AND PORE STRUCTURE OF CARBON AEROGEL

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Introduction

Carbon aerogels prepared by Pekala et al. [1] have the monolith form and their physical properties and applications have been studied. The carbon aerogel has a network structure of primary carbon particles, providing predominantly mesopores. Without change of the skeletal carbon gel structure, activation of carbon aerogel with CO₂ introduces micropores, giving a unique carbon material with a bimodal pore structure; having both microporosity and mesoporosity [2]. This mesoporosity is preserved even after high temperature treatment up to 2800°C. Although pore structure of the carbon aerogel was studied in more details using nitrogen adsorption, organic vapor adsorption is still of interest for interpreting not only adsorption into bimodal pore system but also adsorption mechanism itself. In this study, preliminary results of organic vapor adsorption are reported.

Experimental

Carbon aerogel was derived from pyrolysis of a resorcinol-formaldehyde (RF) aerogel according to Pekala's preparation method [1]. The RF aqueous gel was obtained from the sol-gel polymerization of resorcinol and formaldehyde with a slight amount of sodium carbonate as a catalyst. The molar ratio of resorcinol (R) to catalyst (C) was held at R/C=200. The RF gel was dried under the supercritical condition with CO₂ to give the RF aerogel, followed by the carbonization under argon flow at 1000°C. The resultant vitreous black monolith is carbon aerogel, which are denoted by CA in this study. The activation of the carbon aerogel under CO₂ flow was carried out at 900°C [2]. The activated carbon aerogel is designated as a-CA, the burn-off of which is of 28.3 %.

The adsorption isotherms of nitrogen at 77 K, benzene and methanol at 303 K were measured after evacuation at 383 K under 3 mPa for 2 h.

Results and Discussion

Adsorption isotherms of nitrogen on CA and a-CA at 77 K are shown in Figs. 1(a) and 1(b), respectively. According to the IUPAC classification, both are of type-IV isotherms having type-H1 hysteresis. This means CA is mesoporous material, consisting of carbon particles with almost same size in regular array, and CO₂ activation does not change this mesoporosity. In order to determine their porosity, nitrogen isotherms are analyzed with α_s -plots based on that of non-porous carbon [3], listed in Table 1. CA has both microporosity and mesoporosity, and microporosity of a-CA remarkably increases with the activation. Since the pore distribution of micropore and mesopore is detached each other, microporosity and mesoporosity of carbon aerogels can be determined separately.

Figures 1(c) and 1(d) show benzene adsorption isotherms of CA and a-CA at 303 K, respectively. Both isotherms are also of type-IV, indicating that benzene molecules are adsorbed by the similar mechanism to that of nitrogen at 77 K: micropore filling in low pressure region and pore condensation into mesopore.

Methanol adsorption isotherms of CA and a-CA at 303K, shown in Figs. 1(e) and 1(f), are basically of type-IV. There are small steps around $P/P_0=0.35$. These steps must be associated with micropore filling by formation of molecule clusters, observed as a steep uptake of the isotherm with weak adsorbate-adsorbent interaction system, such as water-activated carbon fibers, water-carbon aerogels [4], and methanol- or water-fluorinated activated carbon fibers [5]. Although the uptake at this step does not correspond to micropore volume, V_{micro} , the adsorption amount above the step is almost same to those of nitrogen and benzene. Since the interaction between polar site of methanol and surface functional group of carbon aerogel helps methanol molecule in adsorbing on the surface at low pressure region, the steep uptake of micropore filling isn't

Table 1. Porosity parameters of carbon aerogels.

Sample	$a_{\text{total}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{total}}/\text{ml}\cdot\text{g}^{-1}$	micropore		mesopore	
			$a_{\text{micro}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{micro}}/\text{ml}\cdot\text{g}^{-1}$	$a_{\text{meso}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{meso}}/\text{ml}\cdot\text{g}^{-1}$
CA	702	1.46 [†]	300	0.10	402 [‡]	1.36 [†]
a-CA	1357	1.92 [†]	837	0.32	520 [‡]	1.60 [†]

[†]) The maximum amount of adsorption used as total pore volume.

[‡]) Including contributions of macropore and external surface, which are negligibly small.

observed. Both methanol adsorption isotherms have hysteresis loop of type-H1, while it does not appear in the case of water adsorption on carbon aerogel. The pressure at which capillary condensation occurs is slightly different from the estimated one by the Kelvin equation (Table 2), in which only adsorbate property is taken into account. For further description of capillary condensation, it is indispensable to take into account the adsorbate-adsorbent interaction.

Conclusions

Adsorption isotherms of nitrogen at 77 K, benzene and methanol at 303 K on carbon aerogel are of type-IV,

Table 2. Pore condensation pressures evaluated from the Kelvin equation.

Sample	R^* / nm	P/P_0		
		Nitrogen	Benzene	Methanol
CA	6.77	0.87	0.75	0.90
a-CA	6.15	0.86	0.73	0.89

*) Average pore radius, R , is calculated geometrically as a cylindrical pore; $R = 2V_{\text{meso}} / a_{\text{meso}}$

having type-H1 hysteresis. In the case of methanol adsorption, the small step around $P/P_0=0.35$ is attributed to the micropore filling with cluster formation. For the explanation for lower shifting of capillary condensation pressure with benzene and methanol, it is necessary to take into account the adsorbate-adsorbent interaction.

References

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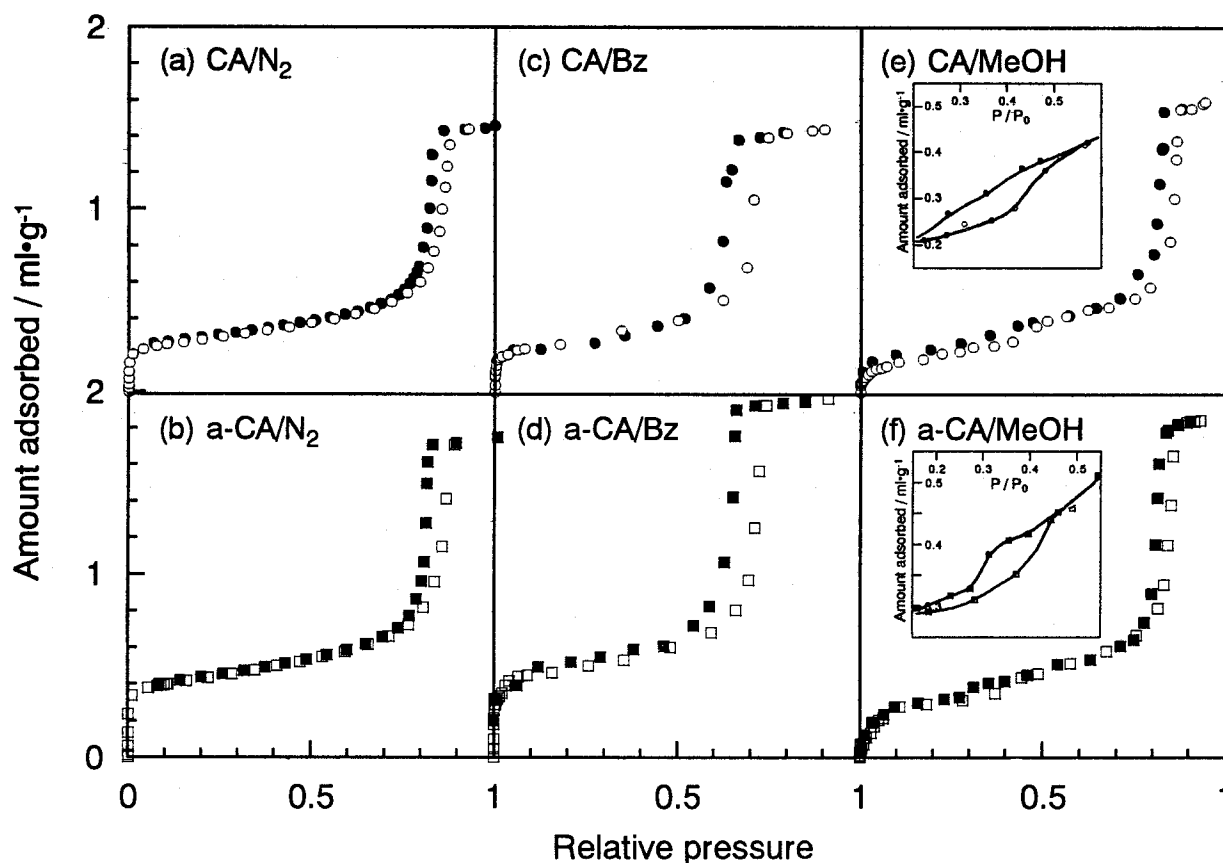


Figure 1. Adsorption isotherms of nitrogen at 77 K, benzene and methanol at 303 K on CA and a-CA. Solid symbols denote desorption.