

Porous Structure and Liquid-Phase Adsorption Properties of Activated Carbon Aerogels

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ABSTRACT: In this article, activated carbon aerogels (ACAs) were prepared by CO₂ activation. Their pore structures were investigated by N₂ adsorption–desorption analysis. ACAs have excellent microporosity (e.g. 0.36 cm³/g) and mesoporosity (e.g. 1.72 cm³/g). Adsorption characteristics of phenol, methylene blue, I₂, and VB₁₂ on ACAs in the liquid phase were studied by static adsorption experiments. Results showed that CO₂ activation process is an effective way to introduce micropores in carbon aerogels, which is enhanced with the increase of activa-

tion time. As a result, the adsorption capacities of the four mentioned adsorbates on ACAs were improved gradually with the increase of activation time. However, mesopore volume is also a factor on improving adsorption properties for the relatively giant molecules methylene blue and VB₁₂. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2775–2779, 2007

Key words: carbon aerogels; activation; pore structure; adsorption

INTRODUCTION

Carbon aerogel (CA) is one kind of novel porous carbon material. The high surface area, controllable porosity, and narrow pore size distribution make CAs good candidates as adsorbents. Basically, CA has a network structure of primary carbon particles, providing predominant mesopores. These carbon particles have a few micropores relative to their precursory organic aerogels (AGs) which are mainly mesoporous materials and have nearly no micropores. Hanzawa et al. successfully denoted a uniform microporosity to mesoporous CAs without change of their skeletal carbon gel structure by activation.¹ Activation increased noticeably the pore volume and the surface area. Activated carbon aerogels (ACAs) had a bimodal pore size distribution of uniform micropores and mesopores, which would have a wide variety of functions. Subsequently, the study on application of ACAs has been attracting much attention on the material for electric double-layer capacitor.^{2–5} Besides CO₂ activation, steam activation also was used.^{6,7}

In previous studies,⁸ the adsorption property of organic vapors on ACAs was investigated. Results

showed that the adsorption capacities of organic vapors on the prepared ACAs were about 2–3 times larger than those on sulfonic-group-containing polyacrylonitrile-based activated carbon fiber (SNACF) and pitch-based activated carbon fiber (PACF). However, to the authors' knowledge, thus far, there was very little work that reported the adsorption properties of adsorbates on ACAs from aqueous solution. The purpose of this article is to investigate the effect of pore structure on adsorption property, such as whether the bimodal pore size distribution of samples is good at adsorption of different dimension molecules in liquid phase or not. In addition, the investigation of structure and adsorption property of ACAs can also develop the application of CAs as new adsorbent.

EXPERIMENTAL

Materials

AGs were synthesized by sol-gel polymerization of resorcinol and formaldehyde, followed by ambient pressure drying (24 h at room temperature, 12 h at 60°C, and 5 h at 110°C). Subsequently, the resultant AGs were heated to 400–900°C with a heating rate of 5°C/min and kept at predetermined carbonization temperature for 3 h in N₂ flow (800 mL/min). After cooled down, CAs were obtained.⁹ The CAs were referred to CA-xxx, where xxx denotes the carbonization temperature. Then, CAs were ground into powder and heated with a heating rate of 5°C/min to 900°C by a quartz tube furnace under an N₂

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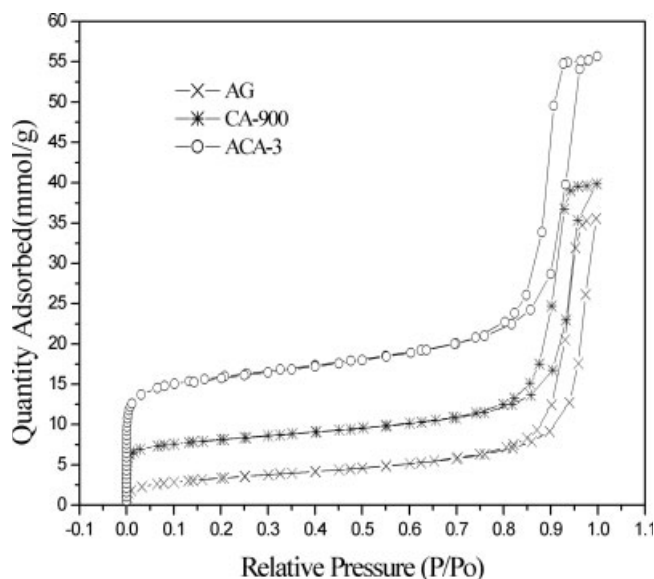


Figure 1 The N_2 adsorption–desorption isotherms of AG, CA-900, and ACA-3.

atmosphere, and then activated with 25 vol % CO_2 for a predetermined activation time. After cooled down, ACAs were obtained, which were denoted as ACA-*yy*, where *yy* denotes activation time.

Characterization of aerogels

The nitrogen adsorption and desorption isotherms of the samples obtained were taken using an ASAP 2010 Surface Area Analyzer (Micromeritics Instrument Corporation, Atlanta, GA). The BET specific surface area (S_{BET}) was analyzed by Brunauer–Emmett–Teller (BET) theory. The specific micropore volume (V_{mic}) and specific micropore surface area (S_{mic}) were analyzed by *t*-plot theory. The micropore diameter (D_{mic}) was analyzed by Horvath–Kawazoe (HK) theory. The specific mesopore volume (V_{mes}) and mesopore diameter (D_{mes}) were analyzed by Barrett–Johner–Halendar (BJH) theory. The pore size distribution was analyzed by density functional theory (DFT) theory.

Adsorption experiment

Adsorption amounts of phenol, methylene blue, I_2 , and Vitamin B_{12} (VB_{12}) on aerogel samples were obtained by measuring their concentrations before and after adsorption at $30^\circ C$. A certain concentration of phenol, methylene blue, I_2 , and VB_{12} solutions were respectively added to a vial containing a known amount of aerogels. All solutions were shaken for 24 h to reach adsorption equilibrium. Just prior to use, adsorbents were dried at $110^\circ C$ under vacuum until the samples kept at constant weight.

The methylene blue and VB_{12} solutions concentration were determined by UV Spectroscopy at 665 and 361 nm with a 756 Spectrophotometer, respectively. Phenol and I_2 solutions concentration were determined following the method of national standards of P. R. China GB/T 12496.5-90 and GB/T 12496.7-90.

RESULTS AND DISCUSSION

The N_2 adsorption and desorption isotherms of AG, CA-900, and ACA-3 at 77 K are shown in Figure 1. According to the IUPAC classification, the adsorption isotherms of the three typical samples exhibit similar type IV characteristic, indicating that the samples are typical mesoporous materials. In these materials, capillary condensation normally takes place, leading to hysteresis loops with type H1. The type H1 hysteresis loop is typical of pores in agglomerates of spheroidal particles of fairly uniform size and array. In particular, the uptake at relatively low pressure (P/P_0) increases noticeably when AG was carbonized and CA was activated. At low relative pressures, micropore filling occurs. It can be seen that activation treatment invites more micropores than carbonization process. Such an activation treatment does not change the basic network structure, so that ACA has both abundant micropores and mesopores. This conclusion can be confirmed from the pore size distribution of AG, CA-900, ACA-1, and ACA-3 shown in Figure 2. It can be seen that AG has a single mesopore peak, while CA-900 and ACAs have two groups of micropore peak besides a mesopore peak. The main micropore peak of CA and ACAs concentrates at ~ 0.5 nm and the mesopore distribution peak is shifted from ~ 21 to ~ 18 nm

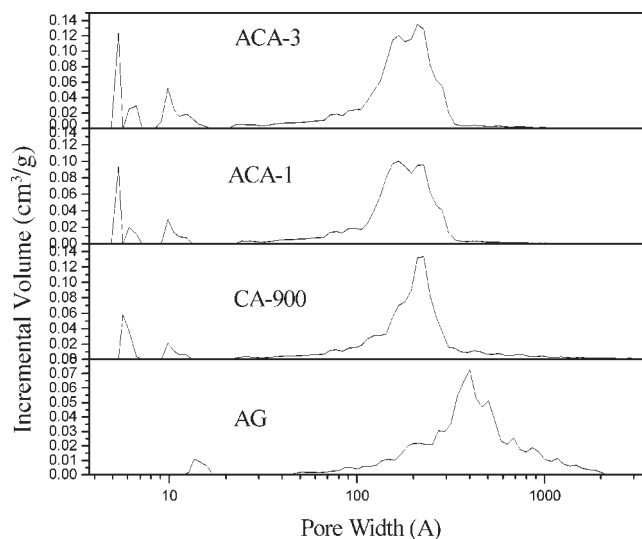


Figure 2 DFT pore size distribution of AG, CA-900, ACA-1, and ACA-3.

TABLE I
Textual Characteristics of CAs with Different Pyrolysis Temperatures

Sample	S_{BET} (m ² /g)	S_{mic} (m ² /g)	V_{mic} (cm ³ /g)	D_{mic} (nm)	V_{mes} (cm ³ /g)	D_{mes} (nm)
CA-400	420.4	126.9	0.056	0.72	1.171	16.5
CA-500	564.2	263.6	0.121	0.57	1.207	15.8
CA-600	654.4	352.2	0.163	0.52	1.247	15.7
CA-700	625.0	348.8	0.162	0.52	1.146	14.8
CA-800	612.3	343.8	0.160	0.53	1.085	14.7
CA-900	620.2	352.7	0.164	0.54	1.248	16.5

S_{BET} : BET surface area; S_{mic} : *t*-plot area; V_{mic} : *t*-plot volume; D_{mic} : HK median pore width; V_{mes} : BJH desorption cumulative pore volume of pores between 1.7 and 300 nm diameter; D_{mes} : BJH average pore width.

after carbonization and further activation. Carbonization introduces micropores into CA, which results in the prominent increase of surface area (see Table I). It is clear that activation can also donate abundant micropores in aerogels, which makes a contribution on the S_{BET} , S_{mic} , and V_{mic} (see Fig. 3).

Table I shows the porous structures of AG and CAs prepared with different carbonization temperatures. It can be seen that AG is a typical mesoporous material having a large mesopore volume exceeding 1.2 cm³/g and having nearly no micropore volume and small surface area. After carbonization, the S_{mic} and V_{mic} increase and S_{BET} increases correspondingly. Under the carbonization temperature of 600°C, the S_{BET} of aerogels increases gradually with the increase of carbonization temperature and reaches a high value of 654.4 m²/g. Also, the V_{mic} and S_{mic} increase from 0.01 to 0.16 cm³/g and from 28.4 to 352.2 m²/g, respectively. Over 600°C, the S_{BET} , V_{mic} , and S_{mic} of CAs seem to keep unchanged when further increasing the carbonization temperature from 700 to 900°C. The micropores volume increases about 1.9 times when carbonization temperature rises from 400 to 900°C, while the mesopores volume changes a little during carbonization process. But carbonization process results in a decrease of mesopores diameter because the carbon particles pile more closely during this process.

Figure 3 shows the effect of activation time on textural parameters of ACAs. It is obvious that S_{BET} , S_{mic} , V_{mes} , and V_{mic} have climbing trends when activation time prolongs. But the diameter of mesopores decreases with the increase of activation time. It can also be explained that some of mesopores collapsed and the carbon particles piled more closely during activation process, which resulted in the shrink of mesopores. It can be concluded from Figure 3 that it is an effective way to improve the pore volume and surface area by extending the activation time. After 3-h activation, the surface area is over 1200 cm²/g and the micropore volume reaches about 0.36 cm³/g, which are greater than those of the samples without activation.

As discussed earlier, activation has improved the pore volume and surface area of CAs. Therefore, the activation would be helpful for the application of CAs as adsorbents. The liquid-phase adsorption characteristics of CAs with different carbonization temperatures and those of ACAs with different activation times were measured and compared. The results are shown in Figure 4. Liquid-phase adsorption experiments were conducted using phenol, methylene blue, I₂, and VB₁₂ as adsorbates. Figure 4 shows the trends of adsorption of four adsorbates on CAs and ACAs. To explain the relation of the texture characteristic and adsorption properties of the samples, we compared the adsorption amounts of the adsorbates on the CAs with different carbonization temperatures at first. From Figure 4, we can see that the adsorption amounts increase as the carbonization temperature becomes high. From 400 to 700°C, there is a prominent increase on the adsorption amount. Over 700°C, it seems to keep unchanged when further increasing carbonization temperature to 900°C. These results can be explained by the porous properties of the samples (see Table I).

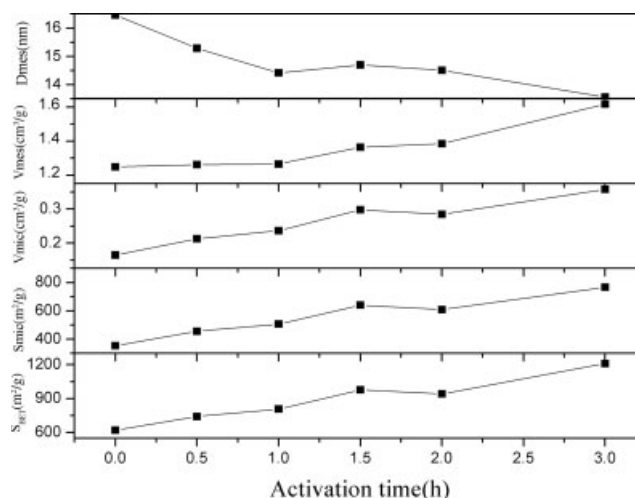


Figure 3 Effect of activation time on S_{BET} , V_{mes} , V_{mic} , S_{mic} , and D_{mes} .

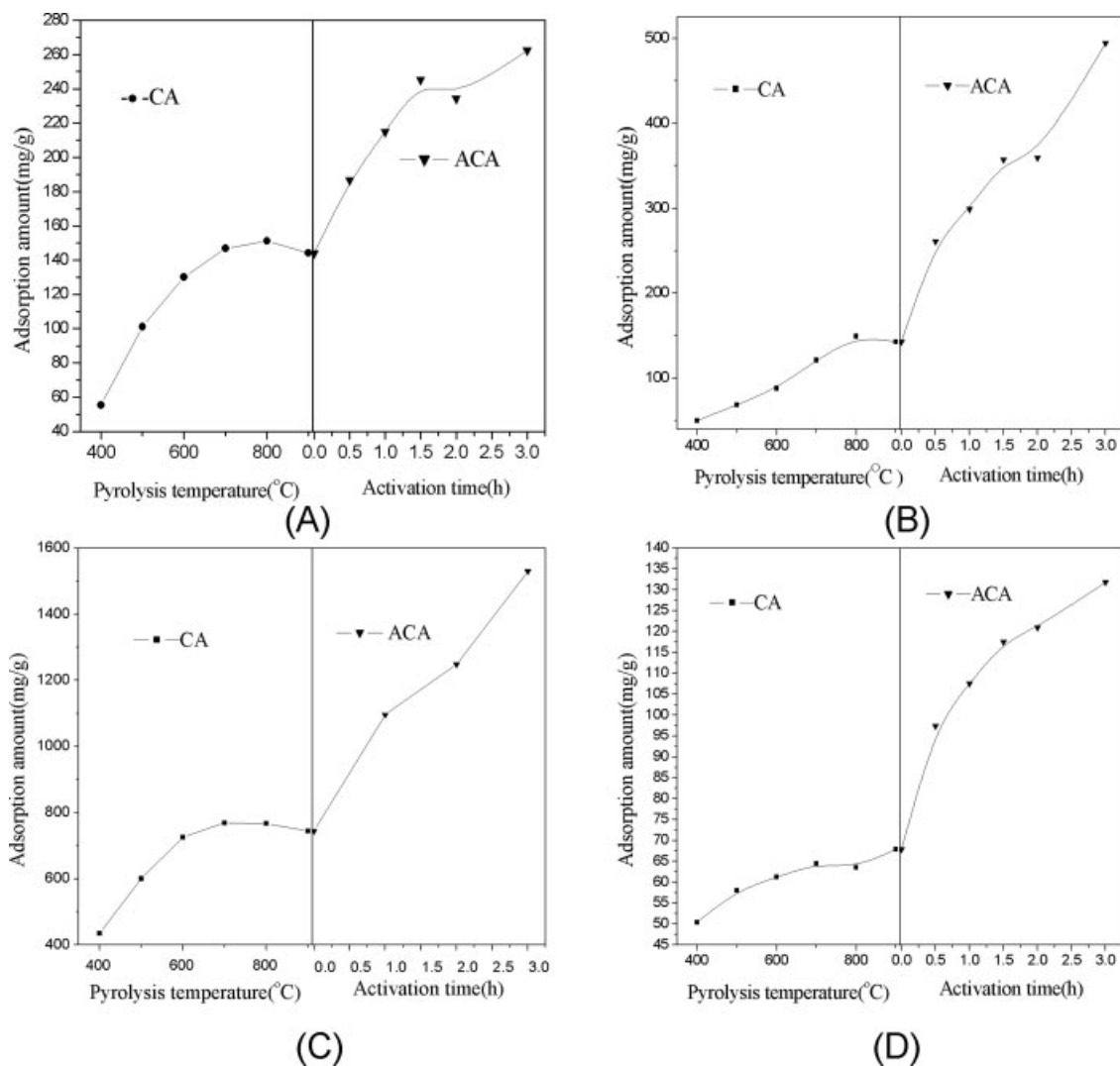


Figure 4 Adsorption of (A) phenol, (B) methylene blue, (C) I_2 , and (D) VB_{12} on CAs and ACAs.

Generally speaking, surface area plays an important role on adsorption. The S_{BET} value of CA-400 is only $420.4 \text{ m}^2/\text{g}$, which can reach over $600 \text{ m}^2/\text{g}$ on increasing carbonization temperature. It also has been known from Table I that the increase of surface area is mainly attributed to the increase of micropores area. So the increase of micropores is an important factor on improving the adsorption amounts of samples. CA-400 has few micropores (V_{mic} value is only $0.06 \text{ cm}^3/\text{g}$). Due to its lower S_{BET} and V_{mic} , it possesses low adsorption amount. Also, the unchanged adsorption amounts of CAs carbonized from 700 to 900°C attribute to their similar surface area and micropores volume. So, it is reasonable to conclude that the V_{mic} of the samples plays an important role in the adsorption. The results of adsorption of four adsorbates on subsequent activation samples confirm the conclusion. Figure 4 shows that the adsorption properties of CAs improve greatly after activation. And the adsorption amounts of ACAs

increase with the increase of activation time, which is consistent with the change of S_{BET} , V_{mes} , and V_{mic} (see Fig. 3). The adsorption characters of different adsorbates on CAs and ACAs are related to the structures of both adsorbates and adsorbents. Phenol, which is often encountered in wastewater treatment, has a maximum dimension of 0.80 nm .¹⁰ Methylene blue, which is a relatively large molecule with the dimension¹¹ of $1.70 \times 0.76 \times 0.325 \text{ nm}^3$, is usually used to evaluate the mesopores of carbon and also serves as a model compound for adsorption of organic contaminants from aqueous solution. The value of the iodine number is always used to evaluate adsorption properties of activated carbon, which defines the activated carbon's power to adsorbates of about 1 nm size from solutions.¹² VB_{12} has the greatest molecule size with a diameter¹³ of 2.09 nm in the four adsorbates, which has caught much attention on its separation and purification by polymeric adsorbents and activated carbon. The CAs and

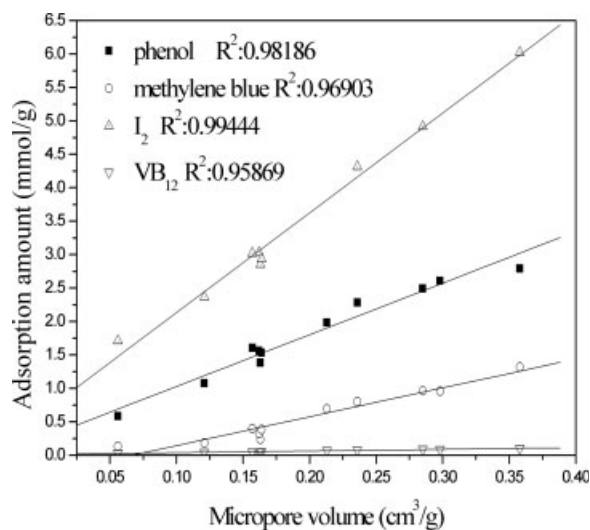


Figure 5 Effect of micropore volume on adsorption of four adsorbates.

ACAs have a bimodal pore size distribution of uniform micropores and mesopores. The diameters of micropores are about 0.5 nm for all the samples and the diameters of mesopores for different samples varies slightly as mentioned earlier. The effect of micropore volume on adsorption amount (expressed in mmol/g) of four adsorbates is shown in Figure 5. It can be seen that the adsorption amounts of the four adsorbates increase linearly with the increase of micropores volume. The correlation coefficient (R^2) of the lines are all over 0.95, and for phenol and I_2 , R^2 of the lines are greater than 0.98, indicating good linearity. Furthermore, the slopes of these lines have the following order: $I_2 > \text{phenol} > \text{methylene blue} > \text{VB}_{12}$, which shows the rate of adsorption amount of the four adsorbates increases with the increase of micropore volume and indicates the effect of micropores on adsorption process for adsorbates with different molecule dimensions. As we know, for small molecules the adsorption occurs mainly in micropores, whereas for relatively bigger molecules the adsorption occurs mostly on the external surface, so the reason for the increase of adsorption amount of bigger molecules with the increase of micropore volume is mostly the increase of the adsorption power of micropores and not the effect of micropore filling. So the increase of adsorption amount of bigger molecules with the increase of micropore volume is less than that of smaller molecules, as shown in Figure 5 that for small molecule I_2 , the adsorbed molecules amounts increase sharply with the increase of micropores volume, whereas for VB_{12} with bigger molecule dimension, the adsorption amount has no clear increase with the increase of micropore volume, since the diameter of micropores is too small to

allow the VB_{12} molecule through. And it also can be seen that the increased portion of adsorption amounts of VB_{12} on ACAs is greater than that on CAs because of the increase of mesopore volume of ACAs, which indicates that mesopores also play a role in the adsorption of bigger molecules. So it is obvious that activation process developed better porous structure which is effective to adsorption not only of small molecules but also of relatively giant molecules.

CONCLUSION

Activation is an effective way to improve the pore volume and surface area of CAs. After 3-h activation, the surface area reaches over $1200 \text{ cm}^2/\text{g}$, the micropore volume reaches about $0.36 \text{ cm}^3/\text{g}$, and the mesopore volume also increases to $1.72 \text{ cm}^3/\text{g}$, which are greater than those of the samples without activation. According to adsorption tests, ACAs exhibit excellent adsorption properties compared to CAs. The high micropores volume is an important reason for the increase of adsorption properties of ACA, especially for small molecules, such as phenol and I_2 , whereas for bigger molecules, mesopore volume also plays a role in improving adsorption capacity of samples. Results show that CO_2 activation can produce CAs with better porous structures, which are favorable to adsorption not only of small molecules but also of relatively giant molecules.

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