



Vapor adsorption on coal- and wood-based chemically activated carbons (II) adsorption of organic vapors

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Abstract

The present investigation was undertaken to determine the adsorption properties and evaluate the adsorption capacities of several coal- and wood-based chemically activated carbons using the Dubinin–Radushkevich (DR) characteristic adsorption analysis. Limiting micropore volumes (W_0), determined from CCl_4 and acetone adsorption isotherms at room temperature, were generally in good agreement with the development of surface area. An effect of adsorbate polarity on the adsorption capacity was found in the case of lower surface area activated carbons rather than higher surface area carbons. This can be attributed to higher density of surface oxygen and carbon surface oxygen functional groups on the lower surface area carbon samples. Characteristic adsorption energy (E_0) values obtained from coal-based KOH activated carbons were generally higher than those obtained from wood-based H_3PO_4 activated carbons. These results indicate that the coal-based KOH activated carbons have narrower micropores and uniform micropore size distributions. The average micropore sizes were mostly affected by the degree of surface area development which depended on the heat treatment temperature during the synthesis process. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Microporous adsorbents are widely used to remove chemical species from the gas or liquid phase through their excellent adsorption capacities, which are closely related the large internal surface areas and micropore volumes that are generally associated with microporosity. For practical industrial use, adsorptivity is one of the most important properties of activated carbons with similar surface chemistry.

In recent research, coal- and wood-based activated carbons were prepared using a chemical activation route with varying heat treatment temperatures employing KOH and H_3PO_4 as chemical activants [1–3]. The physical adsorption characteristics of these carbon

samples with CCl_4 and acetone vapors as adsorbates have been investigated. Limiting micropore volumes and characteristic adsorption energies were obtained by applying the Dubinin–Radushkevich (DR) equation [4].

The resulting adsorption characteristics of the activated carbons investigated will be discussed and correlated with the heat treatment temperature, emphasizing organic vapor adsorption.

2. Experimental

2.1. Materials

Eight different types of activated carbons were prepared at the Center for Applied Energy Research at the University of Kentucky [1–3]. The carbon samples were synthesized from Illinois bituminous coals and white oaks using a chemical activation process with potassium

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hydroxide (KOH) and phosphoric acid (H_3PO_4), respectively, as chemical activation agents, and low and high temperature heat treatments. The preparative procedure and carbon numbering procedure has been described previously [5]. Their Brunauer, Emmett, Teller (BET) and mesopore surface areas, and average micropore sizes are listed in Table 1.

2.2. Adsorption measurements

2.2.1. Gravimetric adsorption experiments

The gravimetric adsorption procedure has been described previously [5]. Samples were exposed to equilibrium relative pressures of CCl_4 and acetone vapor in the relative pressure range of 10^{-4} to 0.8 to obtain isotherms. The experimental isotherm data were analyzed using the DR equation to obtain adsorption parameters for each carbon sample.

2.2.2. Application of the DR equation to the adsorption isotherms

The DR equation was used to estimate the maximum limiting micropore volume per gram of adsorbent (W_0):

$$\ln(W) = \ln(W_0) - \left(\frac{A}{\beta E_0} \right)^2 \quad (1)$$

Affinity coefficients for each adsorbate were estimated theoretically from the molar volume of each vapor taking benzene as a reference vapor [6,7]. Micropore volumes (W_0) of the carbon samples for each adsorbate were evaluated from the intercept at $A=0$ from $\ln(W)$ versus $(A/\beta)^2$ plots. Characteristic adsorption energies (E_0) were evaluated from the slope of the $\ln(W)$ versus $(A/\beta)^2$ plots. Average micropore size (L) was estimated from the value $L=k/E_0$ where k was taken to be $17.25 \text{ kJ nm mol}^{-1}$ [8–11]. The estimated micropore volumes and the characteristic adsorption energies were then correlated with the BET surface areas.

Table 1
BET and mesopore surface areas, and percentage of the total surface area associated with mesopores

Sample No.	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	S_{mesopore} ($\text{m}^2 \text{ g}^{-1}$)	Percentage of area due to mesopores
1 ^a	580	54	9
2 ^a	835	37	4
3 ^a	1081	42	4
4 ^a	1583	46	3
5 ^a	1605	55	3
6 ^b	783	38	5
7 ^b	1075	38	4
8 ^b	1807	238	13

^aCoal-based, KOH activated.

^bWood-based, H_3PO_4 activated.

3. Results and Discussion

3.1. Adsorption isotherms

3.1.1. CCl_4 adsorption isotherms

Weight increases in gram per gram of the five coal-based KOH chemically activated carbon samples on exposure to CCl_4 vapor are plotted versus relative vapor pressure (P/P_0) in Fig. 1. Similar CCl_4 adsorption isotherms for the three wood-based H_3PO_4 chemically activated carbon samples are shown in Fig. 2. The maximum relative pressures investigated in the case of CCl_4 adsorption were in the range of 0.7–0.8.

Typical Type I adsorption isotherms were obtained for the coal- and wood-based chemically activated carbon samples. In the case of sample 8, the saturation plateau is not parallel to the relative pressure axis compared to the other carbon samples. Most of the micropores in sample 8 are filled up below $P/P_0=0.2$ and larger mesopores influence the adsorption at $P/P_0>0.2$, resulting in increased adsorption as P/P_0 increases. This result implies that sample 8 is a microporous adsorbent which contains a large portion of mesopores. Samples 6 and 7, and the coal-based KOH activated carbons show mostly microporous structures with very little mesoporosity.

3.1.2. Acetone adsorption isotherms

The acetone adsorption results were compared with the CCl_4 adsorption isotherm data in order to ascertain similar adsorption trends even though acetone has polar characteristics while CCl_4 is non-polar. The adsorption properties of each carbon sample were again charac-

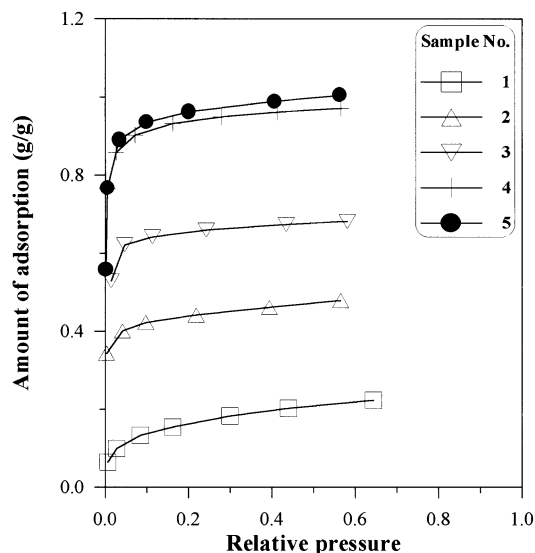


Fig. 1. CCl_4 adsorption isotherms (coal-based KOH chemically activated carbons).

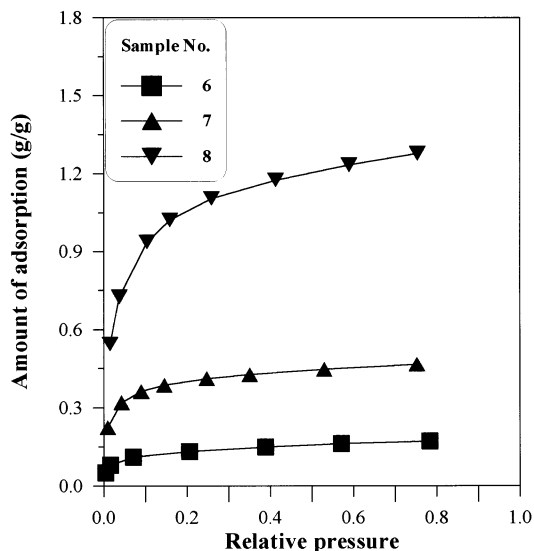


Fig. 2. CCl_4 adsorption isotherms (wood-based H_3PO_4 chemically activated carbons).

terized in terms of microporosity/mesoporosity. Acetone adsorption isotherms on the coal-based KOH activated carbon samples are shown in Fig. 3. Typical Type I adsorption isotherms were again obtained. The acetone adsorption isotherms show similar trends as the CCl_4 adsorption isotherms for most of the coal-based activated carbon samples. The adsorption amounts of most of the KOH carbon samples correlate well with the surface area, implying consistent microporous structure for these carbon samples.

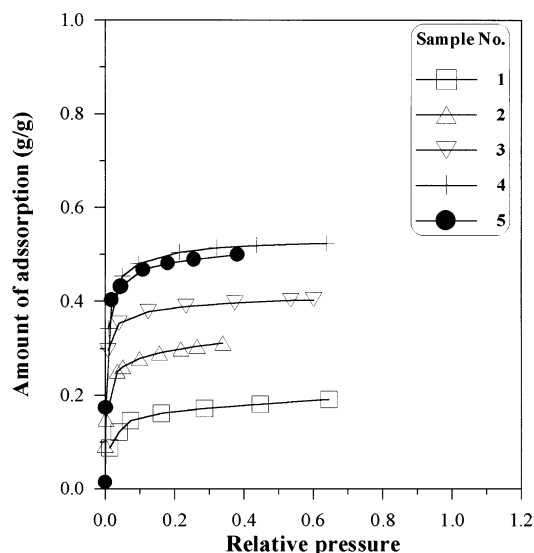


Fig. 3. Acetone adsorption isotherms (coal-based KOH chemically activated carbons).

Acetone adsorption isotherms on the three wood-based H_3PO_4 chemically activated carbon samples also showed similar trends as the CCl_4 adsorption isotherms. As in the case of the CCl_4 adsorption isotherms, the saturation capacities increased as P/P_0 increased in the case of Sample 8. Samples 6 and 7 were quite similar to those of the coal-based KOH carbon samples, implying consistent microporous structures.

To further evaluate the effects of porosity on the shape of the adsorption isotherm, the mesoporosity of each activated carbon was obtained [1–3]. The mesopore surface areas were determined by mercury porosimetry. The obtained values of the mesopore surface area (S_{mesopore}) are listed in Table 1. The percentage of total surface area on each carbon sample associated with mesopores was determined from $(S_{\text{mesopore}}/S_{\text{BET}}) \times 100$ and is also listed in Table 1. Most of the coal-based KOH activated carbon samples show highly microporous structures with very low mesoporosity (% of $S_{\text{mesopore}} = 3$ –9). Most of the wood-based activated carbon samples showed also highly microporous structures with the percentage of surface area associated with mesopores ranging from 2 to 5. On the other hand, sample 8 showed a microporous structure with an increased amount of mesoporosity (13%). The different position of the flat plateau region and increasing saturation capacity with P/P_0 of sample 8 can be therefore be attributed to the larger amount of mesopore surface area. The inflection point which signifies completion of the micropore filling process can be delayed by the effect of mesoporosity.

3.2. Limiting micropore volumes, characteristic adsorption energy and average micropore size from the DR characteristic adsorption isotherms

3.2.1. Limiting micropore volume

The resulting W_0 values for all the coal- and wood-based chemically activated carbon samples are listed in Table 2 for each adsorbate. The standard deviation of

Table 2

Micropore volumes of coal- and wood-based chemically activated carbons (CCl_4 and acetone adsorption)

Sample No.	W_0 ($\text{cm}^3 \text{g}^{-1}$)	
	CCl_4	Acetone
1	0.14	0.24
2	0.30	0.39
3	0.43	0.51
4	0.61	0.61
5	0.63	0.64
6	0.11	0.25
7	0.28	0.33
8	0.76	0.78

the W_0 values was in the range of 1–4%. The resulting data show that the W_0 values obtained from CCl_4 and acetone adsorption on each activated carbon sample are generally in good agreement with the development of surface area. As expected, the microporous structure of the activated carbon sample is the most important factor that affects the adsorption properties.

The W_0 values obtained from CCl_4 adsorption were somewhat lower than those obtained from the acetone adsorption in the case of carbon samples 1, 2, 3 and 6. In general, the amount of acetone adsorption (W) is less than that of CCl_4 adsorption for most of the coal-based carbon samples. This difference can be attributed to their different liquid densities (ρ for $\text{CCl}_4 > \rho$ for acetone). The effect of adsorbate polarity on the adsorption amount was found to be more significant in the case of adsorbents with lower surface areas. This in turn affects the limiting micropore volume.

To investigate the polarity effect on the adsorption capacity, surface oxygen concentrations of each carbon sample were obtained using the X-ray photon spectroscopy (XPS) technique [5]. The resulting data showed that higher oxygen concentrations were found on the lower surface area carbon samples. It was also found that the lower surface area carbon samples contain a higher density of carbon surface oxygen functional groups such as C–O and C=O, resulting in more active polar adsorption sites. In Fig. 4, it can be seen that the difference in W_0 values for acetone and CCl_4 vapors becomes more significant in the case of lower surface area carbon samples. The effect of polarity on the adsorption capacity can thus be significantly higher in

the lower surface area carbon samples. This can be attributed to the higher density of surface oxygen species and carbon surface oxygen functional groups such as C–O and C=O in the lower surface area carbon samples. However, polarity did not significantly influence the W_0 values in the case of the high surface area samples.

3.2.2. Characteristic adsorption energy and average micropore sizes

Affinity coefficient (β) values for CCl_4 and acetone vapors were estimated to be 1.08 and 0.82 by taking benzene as a reference vapor, respectively. The resulting characteristic adsorption energies for all the coal- and wood-based chemically activated carbon samples are listed in Table 3. The standard deviation of the E_0 values was again in the range of 1–4%.

It was found that the E_0 values obtained from CCl_4 and acetone adsorption generally correlated inversely with the development of surface area in the case of both coal-based KOH and wood-based H_3PO_4 activated carbon samples. Generally, the E_0 values obtained from organic vapor adsorption on the coal-based KOH activated carbon samples were somewhat higher than those obtained on the wood-based H_3PO_4 activated carbon samples. This result implies that the coal-based KOH activated carbons have more highly developed microporous structures, producing higher characteristic adsorption energies.

The average micropore width (L) in nanometers being filled with each adsorbate in the activated carbon samples was evaluated and listed in Table 3. The characteristic adsorption energy data yielded average micropore sizes in the range of 0.72–1.88 nm, when the average value of k was taken as $17.25 \text{ kJ nm mol}^{-1}$. These values are in good agreement with the size of typical micropores ($< 2 \text{ nm}$). The average micropore sizes of the coal-based KOH activated carbon samples were found to be lower (0.72–1.02 nm) than those of the wood-based H_3PO_4 activated carbon samples

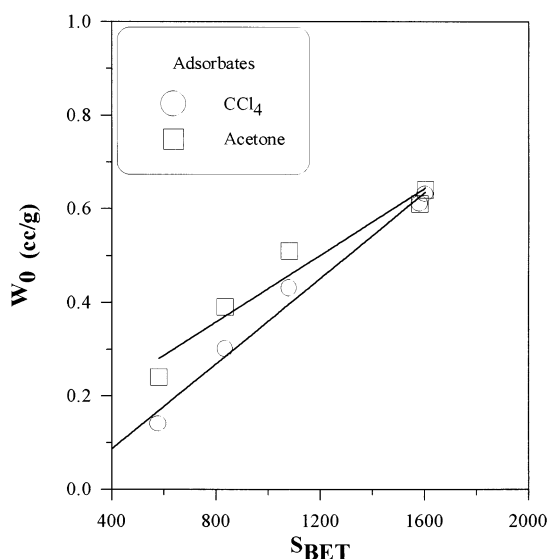


Fig. 4. Plots of W_0 versus S_{BET} obtained from the CCl_4 and acetone adsorption isotherms (coal-based KOH activated carbons).

Table 3

Characteristic adsorption energy and average micropore size of coal- and wood-based chemically activated carbons (CCl_4 and acetone adsorption)

Sample No.	E_0 (kJ mol ⁻¹) [L (nm)]	
	CCl_4	Acetone
1	23.9 (0.72)	23.6 (0.73)
2	23.9 (0.72)	23.5 (0.73)
3	20.2 (0.85)	22.7 (0.76)
4	19.9 (0.87)	21.8 (0.79)
5	16.9 (1.02)	18.9 (0.91)
6	11.6 (1.49)	12.0 (1.44)
7	10.4 (1.66)	12.7 (1.36)
8	8.2 (2.10)	9.2 (1.88)

(1.36–2.1 nm). It can thus be again concluded that the coal-based KOH activated carbon samples have highly developed microporous structures with smaller average micropore sizes than the wood-based H_3PO_4 activated carbon samples. This also results in the higher characteristic adsorption energies.

3.3. Correlation of the surface area with micropore volume, characteristic adsorption energy and average micropore size

3.3.1. Correlation of the surface area development with limiting micropore volume

To evaluate the relationship between surface area and limiting micropore volume, Fig. 4 plots BET surface area versus W_0 for CCl_4 and acetone adsorption on the coal-based KOH activated carbon samples. The straight lines indicate that there is generally a good correlation between surface area development and micropore volume. It can be concluded that the limiting micropore volume is closely related to the surface area development. This produces more adsorption sites for the micropore filling process. In Fig. 4, adsorbate polarity leads to an increase in the value of the limiting micropore volume, especially in the case of activated carbon samples with low surface area. The wood-based H_3PO_4 activated carbon samples showed similar S_{BET} versus W_0 plots. The different slopes associated with the S_{BET} versus W_0 plots for the carbon samples can be attributed to the effect of polarity on the W_0 values in the case of lower surface area carbon samples which contain higher oxygen concentrations.

3.3.2. Correlation of the surface area development with characteristic adsorption energy and average micropore size

Plots of the BET surface area versus characteristic adsorption energy obtained from CCl_4 and acetone adsorption on the KOH activated carbon samples are shown in Fig. 5. The results indicate that the E_0 values for both CCl_4 and acetone adsorption decrease slightly with increasing BET surface area. Similar results were obtained in the case of the wood-based activated carbon samples. This result implies that the average micropore size of the carbon samples increases with increasing the degree of heat treatment temperature in the chemical activation synthesis process.

It was found that the heat treatment temperature was a critical parameter in changing the properties of the carbon sample in synthesizing the activated carbon samples investigated. A high heat treatment temperature generally increased the development of surface area and also the limiting micropore volume of each activated carbon sample. From current research, it can be seen that the average micropore sizes are also affected by the heat treatment temperature. Higher heat treatment tem-

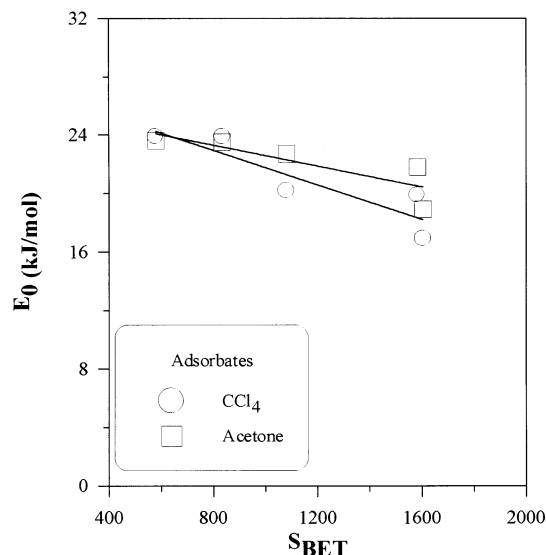


Fig. 5. Plots of E_0 versus S_{BET} obtained from the CCl_4 and acetone adsorption isotherms (coal-based KOH activated carbons).

peratures generally leads to micropore widening phenomenon.

4. Summary and conclusions

W_0 values of coal- and wood-based activated carbons determined from CCl_4 adsorption isotherms were generally found to be lower than those obtained from the acetone adsorption isotherm data in the case of lower surface area activated carbons. Significant influence of adsorbate polarity on the adsorption capacity especially in the lower surface area carbon samples was attributed to higher oxygen concentrations, resulting in more polar adsorption sites. However, adsorbate polarity did not significantly influence the W_0 values in the case of high surface area carbon samples.

E_0 values obtained for acetone adsorption were in good agreement with those obtained from CCl_4 adsorption. E_0 values obtained from KOH activated carbons were generally higher than those obtained from wood-based H_3PO_4 activated carbons. This can be attributed to the more uniform micropore distribution and narrower micropore sizes obtained with coal-based KOH activated carbons. A higher heat treatment temperature generally increases the surface area, micropore volume and average micropore size of carbon samples investigated in the chemical activation synthesis process.

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