RESEARCH NOTES

Estimation of Pore Size Distribution by CO_2 Adsorption and Its Application in Physical Activation of Precursors*

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Abstract The CO_2 adsorption data may show more than one section in the Dubinin-Radushkevich-Kaganer(DRK) plot if samples had been over-activated. Each section in the plot represents a range of pore size. The whole DRK plot provided information on the pore size distribution(PSD) of a sample, which may be used to monitor the effect of activation conditions in activation processes.

Keywords pore size distribution, activated carbon, CO_2 adsorption, activation

1 INTRODUCTION

Activated carbon of high specific surface area assumes prosperous application in adsorptive storage of natural gas or hydrogen. It can be manufactured by chemical activation with KOH from proper precursors. AX-21 carbon was a well-known example, which was originally manufactured by Anderson Company. However, problems concerning corrosion, wastewater treatment and production cost caused close of the production of AX-21. Physical activation with steam or CO_2 as oxidizing agent is simple in process and safe in operation. Nevertheless, product quality of the activated carbon is very sensitive to the activation rate. Fast activation produces macro pores and inducing surface burning. Therefore, optimizing the activation condition is critical for high product quality, productivity, and low cost.

It is quite common to measure nitrogen adsorption at 77 K to get the information of pore size distribution (PSD). However, CO_2 adsorption can detect smaller pores[1]. It was applied to monitor activation process by the authors in this work. The CO_2 isotherm was treated by the Dubinin-Radushkevich-Kaganer(DRK) equation[2]. The reported PSD was compared with the result obtained from a PSD oriented isotherm model. The effect of activation condition was found to fully reflected in the PSD information thus obtained.

2 ACTIVATION EXPERIMENTS

Carbonized coconut shells were the precursors. CO_2 was the oxidizing agent. Activation took place in a vertical tube at temperature 900 ℃. The size of reac-

tion zone was about $\phi 50 \times 150\,\mathrm{mm}$. The flow rate of CO_2 varied from 2 to 80 ml·min^{-1}. Ferrous catalyst was added to the precursor in some batches. Samples with different percentage of burn-off were taken during activation. The effects of CO_2 flow rate, catalysis, and burn-off were quantified by monitoring the adsorption of CO_2.

3 SPECIFICATION OF CARBON QUALITY BY THE DRK PLOT OF CO_2 ISOTHERMS

The DRK equation[2] is usually applied to analyze Type-I isotherms. It is much the same as the Dubinin-Radushkevich (DR) equation, but assumes monolayer adsorption mechanism. Therefore, the percentage of pore-filling was replaced by the percentage of surface coverage

$$\lg(n/n_{\mathrm{m}}) = -D\lg^2(p_0/p) \qquad (1)$$

The plot of $\lg(n)$ *vs.* $\lg^2(p_0/p)$ should be linear. The intercept gives the value of monolayer saturated adsorption. The sectional area of an adsorbed CO_2 molecule is $22 \times 10^{-20}\,\mathrm{m}^2$, which was estimated from liquid CO_2 density. The specific surface area of carbon sample can be calculated by the following equation

$$A = n_{\mathrm{m}}(6.023 \times 10^{23})(22 \times 10^{-20}) = 1.325 \times 10^5 n_{\mathrm{m}} \qquad (2)$$

The pore size can be estimated from the slope, which relates to the characteristic energy of adsorption E_0 (J·mol^{-1}) of the DR equation

$$D = \left(\frac{RT}{\beta E_0}\right)^2 \qquad (3)$$

The affinity coefficient β of CO_2 is $0.35^{[1,3]}$. It has been proved that E_0 was related to the average pore size. A well-known correlation was suggested by Stoeckli and his co-workers[4]

for $E_0 < 20\,\text{kJ} \cdot \text{mol}^{-1}$ $L = 24/E_0$ (4)

for $20\,\text{kJ} \cdot \text{mol}^{-1} < E_0 < 42\,\text{kJ} \cdot \text{mol}^{-1}$

$$L = 10.8/(E_0 - 11.4)$$ (5)

It was proved[5] that the potential well is deeper for smaller pores than for larger ones. The adsorbate molecules are adsorbed preferably in deeper potential wells. Therefore, smaller pores were covered first by adsorbate at lower pressure, and then larger pores covered at higher pressure. As consequence, the DRK plot will show changing slopes for a large PSD carbon in a wide range of pressure. For example, three sections can be identified in the DRK plot of CO_2 adsorption on AX-21 carbon at 25 ℃, as shown in Fig. 1. The intercepts and slopes of the three sections are listed in Table 1. The average pore size and surface area of pores in each section are also listed. It shows that some meso-pores (larger than 2.0 nm) were identified by CO_2 adsorption. However, most meso-pores are inertial for adsorption of supercritical gases.
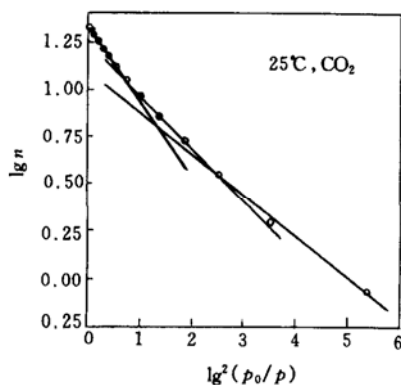

Figure 1   The DRK plot of activated carbon AX-21

4   IDENTIFICATION OF PSD BY A PSD-ORIENTED ISOTHERM MODEL

The amount adsorbed at pressure p is the sum of that adsorbed in all pores of different sizes. Therefore, the isotherm can be written as

$$n(p) = \int_0^\infty w(L,p)f(L)\mathrm{d}L$$ (6)

Where $n(p)$ is the measured amount adsorbed at pressure p; $w(L,p)$ is the local isotherm equation; $f(L)$ is the pore size distribution (PSD) of the adsorbent. The integration of Eq. (6) was approximated by summation of differences over all intervals. Any pore narrower than the molecule diameter of CO_2 (0.33 nm) will be dummy for CO_2 adsorption. Therefore, the range of pore size was thus scaled by the molecular size of CO_2 and divided into 6 intervals: 0.35—0.70, 0.70—1.1, 1.1—1.5, 1.5—2.0, 2.0—2.5 and 2.5—3.0 nm. Pores larger than 3 nm are not important for supercritical adsorption. Suppose the pore volume in the ith interval is v_i, and $w_i(p)$ is the amount adsorbed per unit volume of pores in the ith interval at pressure p, then

$$n(p) = \sum_{i=1}^{6} v_i w_i(p)$$ (7)

The DR equation was used for local isotherm, whose E_0 was related to L by Eq. (4). In terms of Matlab we obtained the expression for $w_i(p)$

$$w_i(p) = \frac{48.13}{(L_{i+1} - L_i)\ln\dfrac{p_0}{p}}\left[\text{erf}\left(0.2951 L_{i+1}\ln\frac{p_0}{p}\right) - \text{erf}\left(0.2951 L_i \ln\frac{p_0}{p}\right)\right]$$ (8)

By substituting Eq. (8) into Eq. (7) one can calculate the amount adsorbed at a given pressure of p. Fitting Eq. (7) to the measured adsorption isotherm, appropriate values of parameter v_i were obtained by nonlinear regression aiming at minimizing the following objective function

$$\sum_{p/p_0=0}^{p/p_0=0.8}\left[n(p) - \sum_{i=1}^{6} v_i w_i\right]^2$$ (9)

The PSD of AX-21 carbon resulted by the model was shown in Fig. 2. The total pore volume is $1.34\,\text{ml} \cdot \text{g}^{-1}$, which is well agreed with $1.32\,\text{ml} \cdot \text{g}^{-1}$ reported by the DRK plot. However, almost all pores are less than 2.1 nm according to the DRK plot. In contrast, about 20% is meso-pore as indicated in Fig. 2.

Table 1   Specification of AX-21 carbon by the DRK plot of CO_2 adsorption at 25 ℃

Pressure	Intercept	Surface area* m²·g⁻¹	Slope	E_0 kJ·mol⁻¹	Pore volume* ml·g⁻¹	Average pore size, nm
Low	1.0769	1582	−0.21424	15.3	0.74	1.6
Medium	1.2474	2342	−0.28157	13.3	1.10	1.8
High	1.3263	2809	−0.3877	11.4	1.32	2.1

* The accumulative value up to this interval of pores.
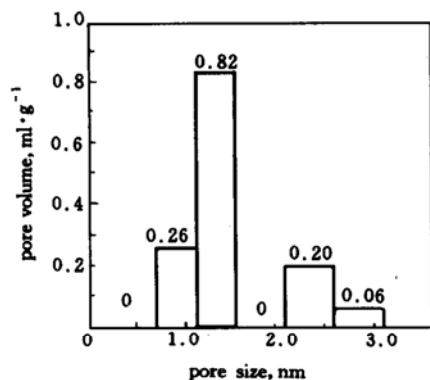
Figure 2 Pore size distribution of AX-21 carbon evaluated by the presented model

Figure 4 The DRK plots of different activation samples of same burn-off

● C1 at burn-off 36.4%; ◆ C3 at burn-off 32.9%;
○ C1 at burn-off 56%; ◇ C3 at burn-off 55.5%;
△ C3 at burn-off 80.1%

5 DISCUSSION ON THE EFFECT OF ACTIVATION CONDITIONS

Precursor burn-off is the most important among other conditions to the quality of activation sample. The isotherms of CO_2 adsorption at different percentage of burn-off of sample C3 are shown in Fig. 3. From the DRK plots of C3 set of data it was discovered that other conditions such as the flow rate of oxidizing agent, with or without catalysis, do not affect PSD of samples before a critical burn-off was reached, provided surface burning had not happened. It was illustrated by the DRK plots of samples C1 and C3 in Fig. 4. Although two precursors were activated under different conditions, they have almost the same DRK plot at the same burn-off. It was noticed in this work that there were two critical burn-offs in the activation process of carbonated coconut shell precursor. They are roughly 35% and 60% respectively. The DRK plot is a single line if burn-off is less than 35%. There will be two sections in a DRK plot if the burn-off is larger than 35% but less than 60%. If the burn-off is larger than about 60%, three sections were identified in the DRK plot (Fig. 5). However, if surface burning happened, the DRK plot could be a single line even for much larger burn-off. This was observed at sample
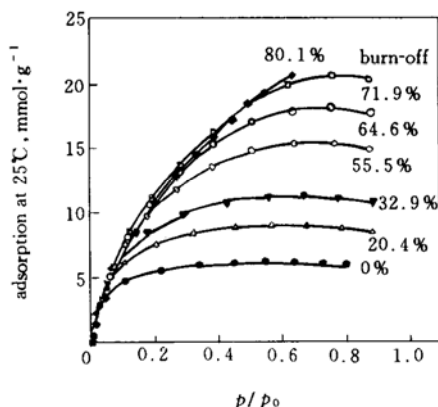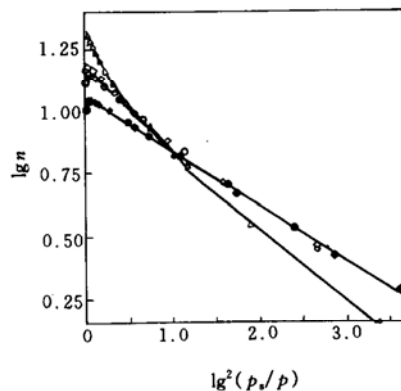
C4, whose DRK plot is still a single line at a burn-off of 63.4%, as shown in Fig. 6. Too large burn-off is of no use for creating new pores, but helpful for enlarging the existing micro-pores. The PSD of sample C3 at the burn-off of 80.1% is shown in Fig. 7. It has nearly the same total pore volume as AX-21, but less small pores. The pores smaller than 1.5 nm account for only 57% of the total pore volume as compared to 80% in AX-21 carbon. As consequence, the adsorption capacity of C3 for methane is 16% lower than AX-21.
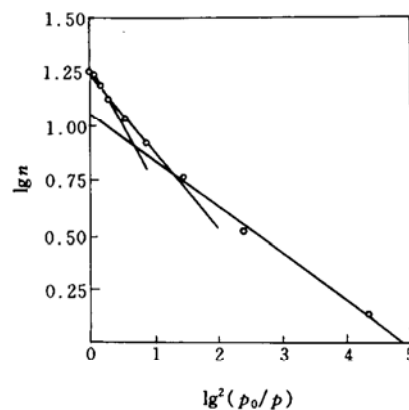

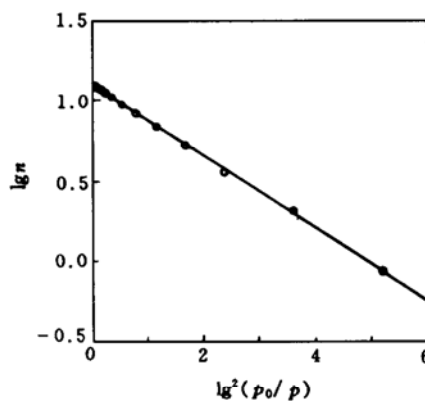**Figure 5** The DRK plot of C3 at burn-off 64.6%

Figure 3 CO_2 adsorption isotherms of precursor C3 at different burn-off (298 K)

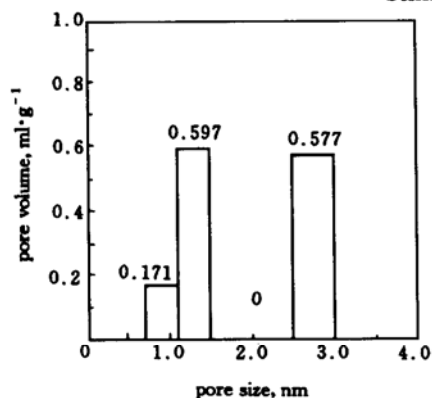**Figure 6** The DRK plot of C4 at burn-off 63.4%

Figure 7   Pore size distribution of sample C3 at burn-off 80.1%

NOMENCLATURE

A	specific surface area of adsorbent, $m^2 \cdot g^{-1}$
D	pore size, nm
E_0	characteristic energy of adsorption, $J \cdot mol^{-1}$
L	average pore size, nm
n	amount adsorbed, $mol \cdot g^{-1}$
n_m	monolayer saturated adsorption, $mol \cdot g^{-1}$
p	equilibrium pressure of adsorption, MPa
p_0	saturated pressure of CO_2 (6.343 MPa at 298.15 K)
R	gas constant, $MPa \cdot m^3 \cdot K^{-1}$
T	equilibrium temperature of adsorption, K
v_i	volume of pores in the ith interval, $ml \cdot g^{-1}$
β	affinity coefficient of adsorbate

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