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A new method of determining the fractal surface dimension of porous media by TG-DTA technique

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Abstract

Based on the new equation rigorously derived from Mandelbrot's relationship between the surface area S and the volume V of a solid, TG-DTA technique can be used to determine the fractal surface dimension of porous media. The experimental results show that the new method is reliable, simple and practicable. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fractal dimension; Porous media; TG-DTA

1. Introduction

Many surface phenomena, for example, in heterogeneous chemistry, surface science and materials engineering, have been observed to display statistical or random self-similarity in scales [1,2], which can be described and analysed by fractal geometry [3]. Determining the fractal surface dimension of porous media is important for understanding reaction and diffusion mechanisms in porous reactants or catalysts [1,2,4–7,24], percolation of fluids in permeable materials [8], and fractured causes of materials [9] and so on. Experimental determinations of the fractal dimension have been obtained by frozen adsorption [10–15], mercury porosimetry [16–19], scanning electron microscopy [20,25], small-angle X-ray scattering [21–26], and nuclear magnetic relaxation [27,28]. However, these measurements have been often interrupted by multi-layer condensation of adsorbates, pore collapse under a high pressure and various postulates in deriving the equation with fractal dimension, which brings about not only some fractal information relevant to the surface pattern and pore structure of porous media losing partly, but also complicating the measuring processes. In the present work, therefore, the author shows that the fractal surface dimension of porous media can be determined by a new method of activation–nonisothermal adsorption with TG-DTA technique.

2. A new equation

Based on the Mandelbrot's relationship [3] between the surface area S and the volume V of a solid:

$$S^{1/D} \propto V^{1/3} \tag{1}$$

where D is the fractal surface dimension of the solid. Substituting $V = \frac{m}{\rho}$ into Eq. (1), where m and ρ are the mass and the apparent density of the solid, respec-

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tively, and considering S as the Euclidean area of the fractal surface S_E, then Eq. (1) becomes

$$S_E^{1/D} = K_\delta \left(\frac{m}{\rho}\right)^{1/3} \tag{2}$$

where K_δ is the geometric factor related to the measurement scale δ. According to the dimensional analysis, the dimension of Eq. (2) is

$$[S_E^{1/D}] = \frac{2}{D} = [K_\delta] + 1 \quad \text{or} \quad [K_\delta] = \frac{2}{D} - 1 \tag{3}$$

where [ ] expresses the dimension of a physical quantity. Thus, Eq. (2) becomes

$$[S_E^{1/D}] = K'\delta^{2/D-1}\left(\frac{m}{\rho}\right)^{1/3} \quad \text{or}$$

$$S_E = K\delta^{2-D}\left(\frac{m}{\rho}\right)^{D/3} \tag{4}$$

where K' or K is a constant of independent on the measurement scale δ. Here, we have two methods to determine the D values of porous media, on the basis of the following equation from Eq. (4):

$$\ln S_E = \ln K + (2-D)\ln\delta + \frac{D}{3}\ln\left(\frac{m}{\rho}\right) \tag{5}$$

Firstly, D can be obtained by measuring the S_E values correspondent to the variable mass m with the same scale δ. Secondly, D can be determined by measuring the S_E values correspondent to the variable δ with the same mass m. The former is simpler, because varying the scale values in a molecular size, which means preparing some kinds of adsorbates, is much more troublesome than changing the mass of a solid sample in experiments. Therefore, the first method has been adopted in this study.

3. Experimental results

Based on Eq. (5), the TG-DTA technique used to determine the fractal dimension of porous media involves the vaporisation of gas species (mainly the water molecules at physical adsorption) from the sample into a carbon dioxide flow of 60 ml min^{-1} under a procedure heating of 10 K min^{-1} and up to a constant temperature of 573 K, and the adsorption ofÂcarbon dioxide from a carbon dioxide flow onto the surface of the sample under natural cooling from 573 K to 298 K, as shown schematically in Fig. 1.

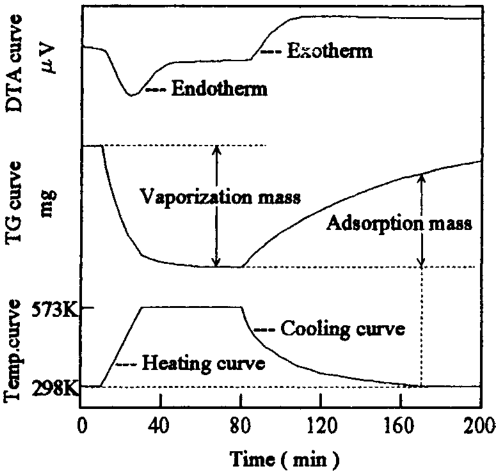

Fig. 1. Schematic diagram of the TG-DTA experiment.

In the experiment, an alumina crucible containing the sample was placed on the plate of TG and DTA. Then, the carbon dioxide valve was opened after vacuum-pumping until the air residual pressure of the TG-DTA system was less than 2 Pa. The constant flow of carbon dioxide was held until the experiment finished. The TG-DTA curves were obtained by using a Beijing LCT thermobalance. The measuring limit of TG is 10 ± 0.01 mg, of DTA is ± 10μV, and the reference is 100 mg of α-Al_2O_3 analytical reagent. The time of constant temperature at 573 K usually is 30–60 min, which depends on the time of constant mass of the sample at 573 K.

The experimental results are listed in Table 1. The molecular mass of carbon dioxide is 44 g mole^{-1} of carbon dioxide divided by Avogadro constant 6.022×10^{23} mole^{-1} equals 7.307×10^{-23} g per carbon dioxide. The cross section [29] of carbon dioxide is 2.53×10^{-15} cm^2 per carbon dioxide, and then the diameter of a carbon dioxide molecule is 1.612×10^{-8} cm, which is the measurement scale δ. The area per gram carbon dioxide is 2.53×10^{-15} cm^2 per carbon dioxide divided by 7.307×10^{-23} g per carbon dioxide, which equals 3.4624×10^7 cm^2 g^{-1} carbon dioxide. The Euclidean area of the fractal surface of a porous carbonic solid $S_E = (3.4624 \times 10^7$ cm g^{-1} carbon dioxide) × (the

Table 1
Thermogravimetry experiment data of porous carbonic samples

Runs	Initial mass at 298 K (g, $\times 10^{-3}$)	Vaporisation mass at 573 K (g, $\times 10^{-3}$)	m at 573 K (g, $\times 10^{-3}$)	Adsorption mass at 298 K (g, $\times 10^{-3}$)	S_E at 298 K (cm^2 $\times 10^4$)
A1	60.30	5.77	54.53	3.36	11.6337
A2	53.30	5.48	47.82	3.05	10.5603
A3	46.70	4.39	42.31	2.54	8.7945
A4	40.48	4.19	36.29	2.34	8.1020
A5	33.66	3.95	29.71	1.87	6.4747
A6	27.84	2.65	25.19	1.54	5.3321
A7	25.07	2.61	22.46	1.36	4.7089
A8	22.15	2.32	19.83	1.28	4.4319
A9	19.50	1.88	17.62	1.10	3.8086
A10	15.05	1.42	13.63	0.85	2.9430
A11	12.42	1.32	11.10	0.80	2.7699
A12	10.35	1.18	9.17	0.68	2.3544
B1	45.72	4.55	41.17	1.83	6.3362
B2	38.63	4.02	34.61	1.50	5.1936
B3	33.15	3.06	30.09	1.32	4.5704
B4	27.38	2.53	24.85	1.10	3.8086
B5	24.90	2.37	22.53	0.95	3.2893
B6	21.73	2.14	19.59	0.84	2.9084
B7	19.86	2.05	17.81	0.79	2.4583
B8	17.45	1.79	15.66	0.71	2.4583
B9	15.81	1.48	14.33	0.64	2.2159
B10	14.86	1.40	13.46	0.63	2.1813
B11	12.81	1.35	11.46	0.54	1.8697
B12	11.55	1.24	10.31	0.49	1.6966
C1	131.84	3.28	128.56	0.80	2.7699
C2	103.49	2.88	100.61	0.66	2.2852
C3	80.86	2.42	78.44	0.49	1.6966
C4	60.80	2.18	58.62	0.38	1.3157
C5	41.18	1.33	39.82	0.30	1.0387

mass of carbon dioxide adsorbed by the carbonic sample or the adsorption mass, g) cm^2.

The A1–A12 group stands for grainy activated carbon, analytical reagent, fixed carbon on dry basis: $\geq$98%, and apparent density $\rho = 0.847$ g cm^{-3}. The B1–B12 group stands for powder activated carbon, chemically pure, fixed carbon on dry basis: $\geq$97%, and apparent density $\rho = 0.809$ g cm^{-3}. The C1–C5 group stands for powdered coke, grain size: $-180 + 200$ mesh, fixed carbon on dry basis: 75.38%, and ash content: 22.86%, and apparent density $\rho = 1.137$ g cm^{-3}.

4. Discussion

Eq. (5) deals with the data of Table 1, and the results are shown in Fig. 2.

It can be seen from the figure that the plots of ln S_E versus $\ln\left(\frac{m}{\rho}\right)$ have good linear relationship, which shows that the method of determining the fractal surface dimension of porous media by the TG-DTA technique in common use is much more reliable, simple and practicable than those [10–29] reported, and, thus, has a prospect of widespread application.

The reason that the method was used successfully, is that a lot of activation sites remained on the fractal surface of the porous medium after physical adsorption vaporised the gas species and transported out in a flow of carbon dioxide in a process of heating and constant temperature, which just provided a chance available for adsorption of carbon dioxide in a process of cooling naturally. Therefore, the method may be called activation–nonisothermal adsorption.

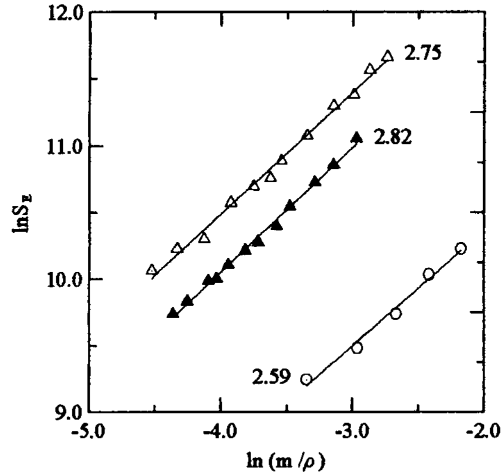

Fig. 2. Plots of ln S_E versus $\ln\left(\frac{m}{\rho}\right)$ (△: data of A1–A12, ln $S_E = 0.916\ln\left(\frac{m}{\rho}\right) + 14.155$, $R^2 = 0.9935$, $D = 2.75$; ▲: data of B1–B12, ln $S_E = 0.940\ln\left(\frac{m}{\rho}\right) + 13.818$, $R^2 = 0.9958$, $D = 2.82$; ○: data of C1–C5, ln $S_E = 0.863\ln\left(\frac{m}{\rho}\right) + 12.095$, $R^2 = 0.9866$, $D = 2.59$. The D values are marked at the correspondent lines in the figure).

5. Conclusion

The results show that the derivation of the equation $S_E = K\delta^{2-D}\left(\frac{m}{\rho}\right)^{D/3}$ is distinct and rigorous. Based on it, the new method of activation–nonisothermal adsorption with TG-DTA technique is reliable, simple and practicable.

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