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Fractal Surface Analysis by Using Capillary Condensation Data

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Both the Neimark equation and the recently proposed modified version (Wang and Li, *Ind. Eng. Chem. Res.* **1997**, *36*, 1598) were used to determine the surface fractal dimension D of coprecipitation methods, and low water sol–gel processes derived alumina and aluminum borate samples calcined at different temperatures. It was found that both D_a (from the adsorption isotherm) and D_d (from the desorption isotherm) values obtained from the Neimark equation are larger than those evaluated from its modified version, respectively, and the scaling range, where fractal behavior is observed, of the Neimark method is smaller than that of its modified version. However, both methods indicated that thermal effects may decrease D for all examined porous samples and pointed out that $D_d < D_a$ in our samples, which is in contrast to the earlier fractal surface analysis report for some porous solids with the modified thermodynamic method (Wang and Li). The relative magnitude between D_d and D_a , and then, the applicability of the relation D_{real} (real surface fractal dimension) = D_m (from mercury intrusion data) – ($D_d - D_a$) proposed by Wang and Li were discussed.

Introduction

It was recently recognized that fractal geometry could be applied to describe the structure heterogeneity of porous solids. Among the different ways to define a fractal geometry, the term “surface fractal” has been extensively used by Avnir and co-workers to identify the fractal dimension D derived from adsorption measurements.^{1–3} There are several ways to evaluate the D value from adsorption data,^{1–5} and the easiest way is to fit a single adsorption isotherm to some fractal isotherm equation having D as a parameter.

Several fractal isotherm equations have been proposed for such a purpose. They are all the generalizations of the classical theories for multilayer adsorption and capillary condensation in a medium with flat surfaces. Among them, the classical Frenkel–Halsey–Hill (FHH) theory on multilayer adsorption has been extended to fractal surfaces. Two types of fractal isotherm equations have thus been proposed. The fractal version of the FHH equation is a popular method and has been applied to determine the surface fractal dimensions for a number of porous solids.⁶ However, some practical difficulties have been met when applied to real adsorbents. Recently, Sahouli et al.⁷ gave a detailed discussion on the applicability of the fractal FHH equation. Another popular method for evaluating D is the so-called thermodynamic fractal isotherm equation recently proposed by Neimark.⁸ The basis for this equation is a very simple relationship between the area of the gas–liquid interface, S , and the mean radius of the curvature of this interface, r ,

$$\ln S = \text{const} - (D - 2) \ln r \quad (1)$$

In this equation, the area of the gas–liquid interface can be calculated according to the Kiselev equation:

$$S = (RT/\gamma) \int_{N(P/P_0)}^{N_{\text{max}}} \ln(P_0/P) dN \quad (2)$$

where N_{max} denotes the amount adsorbed when P/P_0 tends to unity. On the other hand, the Kelvin equation is used to convert the equilibrium pressure P to the mean radius of the curvature r . Applications of Neimark's equation to evaluate D have been demonstrated in some papers.^{9–13}

Recently, Wang and Li¹⁴ proposed a modified version of the Neimark equation by taking into account the effect of volume encompassed by the fractal surface and obtained the following expression:

$$\ln A = \text{const} + D \ln B \quad (3)$$

where

$$A(P/P_0) = \frac{\int_{N(P/P_0)}^{N_{\text{max}}} \ln(P_0/P) dN}{r^2(P/P_0)},$$

$$B(P/P_0) = \frac{[N_{\text{max}} - N(P/P_0)]^{1/3}}{r(P/P_0)} \quad (4)$$

They used the equation to estimate the surface fractal dimension of several kinds of porous media and compared these with the results obtained from mercury porosimetry data. Their results showed that D_a (from adsorption data), D_d (from desorption data), and D_m (from mercury porosimetry data) are different and $D_m > D_d > D_a$. It was also found that the scaling range, where the fractal behavior is observed, of eq 3 is larger than that of eq 1. Finally, it was concluded that owing to the shielding effect of the small pores on the large one existing on both the mercury intrusion process and desorption process, and the effect of the surface tension on both the adsorption and desorption process, the real surface fractal dimension could be calculated from the relationship $D_{\text{real}} = D_m - (D_d - D_a)$. Equation 3 is attractive because it covers a long scaling range and is model-independent. However, some further experimen-

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Table 1. Surface Fractal Dimensions Calculated from Equation 1

sample	calcination temp. (°C)	D_a	applicable range of P/P_0	applicable range of r (nm)	D_d	applicable range of P/P_0	applicable range of r (nm)
S10A	500	2.53	0.09–0.46	0.40–1.24	2.46	0.07–0.64	0.34–2.17
	700	2.55	0.09–0.60	0.40–1.91	2.49	0.07–0.74	0.34–3.17
	900	2.47	0.09–0.61	0.40–1.95	2.39	0.07–0.72	0.34–2.86
	1100	2.41	0.09–0.65	0.40–2.21	2.29	0.06–0.74	0.34–3.14
S9A1B	500	2.65	0.09–0.60	0.40–1.87	2.56	0.06–0.72	0.34–2.96
	700	2.70	0.09–0.60	0.40–1.87	2.67	0.06–0.70	0.34–2.70
	900	2.35	0.09–0.62	0.40–2.03	2.28	0.06–0.75	0.34–3.37
	1000	2.27	0.09–0.64	0.40–2.18	2.27	0.06–0.82	0.34–4.87
C10A	500	2.99	0.09–0.60	0.40–1.88	2.88	0.06–0.45	0.34–1.20
	700	2.78	0.09–0.54	0.40–1.57	2.66	0.06–0.40	0.34–1.01
	900	2.54	0.09–0.55	0.40–1.59	2.44	0.06–0.70	0.34–2.71
	1000	2.59	0.09–0.72	0.40–2.97	2.36	0.06–0.89	0.34–8.27
C9A1B	500	2.86	0.09–0.35	0.40–0.91	2.80	0.06–0.42	0.34–1.11
	700	2.75	0.09–0.40	0.40–1.03	2.68	0.06–0.50	0.34–1.35
	900	2.46	0.09–0.69	0.40–2.55	2.43	0.06–0.69	0.34–2.58
	1000	2.54	0.09–0.69	0.40–2.55	2.33	0.07–0.80	0.34–4.42

Table 2. Surface Fractal Dimensions Calculated from Equation 3

sample	calcination temp. (°C)	D_a	applicable range of P/P_0	applicable range of r (nm)	D_d	applicable range of P/P_0	applicable range of r (nm)
S10A	500	2.40	0.01–0.78	0.19–3.84	2.33	0.01–0.70	0.19–2.72
	700	2.41	0.01–0.82	0.19–4.95	2.35	0.01–0.74	0.19–3.17
	900	2.41	0.01–0.88	0.19–7.38	2.30	0.01–0.76	0.19–3.60
	1100	2.38	0.01–0.88	0.19–7.67	2.32	0.01–0.83	0.19–5.08
S9A1B	500	2.47	0.01–0.83	0.19–5.27	2.38	0.01–0.76	0.19–3.53
	700	2.53	0.01–0.78	0.19–3.90	2.43	0.01–0.71	0.19–2.77
	900	2.29	0.01–0.86	0.19–6.59	2.22	0.01–0.80	0.19–4.38
	1000	2.26	0.01–0.87	0.19–6.92	2.24	0.01–0.78	0.19–3.85
C10A	500	2.83	0.01–0.96	0.19–25.07	2.57	0.01–0.60	0.19–1.90
	700	2.59	0.01–0.77	0.19–3.67	2.51	0.01–0.65	0.19–2.27
	900	2.46	0.01–0.86	0.19–6.73	2.38	0.01–0.78	0.19–3.91
	1000	2.50	0.01–0.88	0.19–7.53	2.30	0.01–0.91	0.19–10.42
C9A1B	500	2.69	0.01–0.75	0.19–3.31	2.54	0.01–0.58	0.19–1.77
	700	2.56	0.01–0.77	0.19–3.68	2.48	0.01–0.66	0.19–2.30
	900	2.39	0.01–0.83	0.19–5.09	2.31	0.01–0.74	0.19–3.19
	1000	2.44	0.01–0.85	0.19–6.04	2.26	0.01–0.85	0.19–5.71

tal examinations are still needed to more clearly define the limits of applicability of the method and the reliability of surface fractal dimension obtained from that equation.

In this study, a series of well-measured nitrogen adsorption isotherms were used to test the modified version of the thermodynamic method. We take also the opportunity to examine the difference between the Neimark equation and its modified version from an experimental point-of-view. The isotherms were obtained for alumina and aluminum borate samples (prepared from the coprecipitation method and sol–gel process) calcined at different temperatures. These samples provide a wide range of pore structure and surface irregularity. We think they are an ideal platform to critically examine the applicability of these two methods.

Experimental Section

Alumina and aluminum borate samples are synthesized with the coprecipitation method and sol–gel process. The detail synthetic and calcination procedures are described in our previous paper.¹⁵ We denote that the coprecipitation method derived alumina and aluminum borate as C10A and C9A1B while the sol–gel-derived counterparts are denoted S10A and S9A1B, respectively. Nitrogen adsorption isotherms and desorption hysteresis loops were measured at 77 K with a Micromeritics ASAP-2000. All samples were out-

gassed at 350 °C for 24 h under vacuum prior to the adsorption measurement.

Results and Discussion

In our fractal analysis of the nitrogen isotherms of alumina and aluminum borate under a wide variety of calcination temperatures, we strive to examine the applicability of both eq 3 and the formula $D_{\text{real}} = D_m - (D_d - D_a)$ from an experimental point-of-view. Also examined is the difference between eqs 1 and 3. Thus, both eqs 1 and 3 are used to evaluate the surface fractal dimension from the adsorption and desorption isotherm. The results were collected in Tables 1 and 2. Also given were the range of P/P_0 and the length scale where fractal characteristics (i.e., a linear behavior in double logarithmic scales) were observed. In Figure 1, the evaluation of D from eq 3 for C10A is taken as the example to be illustrated.

Some key features are seen directly from Tables 1 and 2. The D values evaluated by means of eqs 1 and 3 for all alumina and aluminum borate samples totally fall in the range of $2 < D < 3$, indicating all examined samples do indeed possess fractal geometry in a limited range of length scale. Effects of calcination on the surface roughness of all examined samples predicted by eqs 1 and 3 are the same (i.e., both methods pointed out that thermal effects may decrease the D values). This result is similar to the effect of heating on the surface fractal dimensions of ZrO_2 reported by Rubio

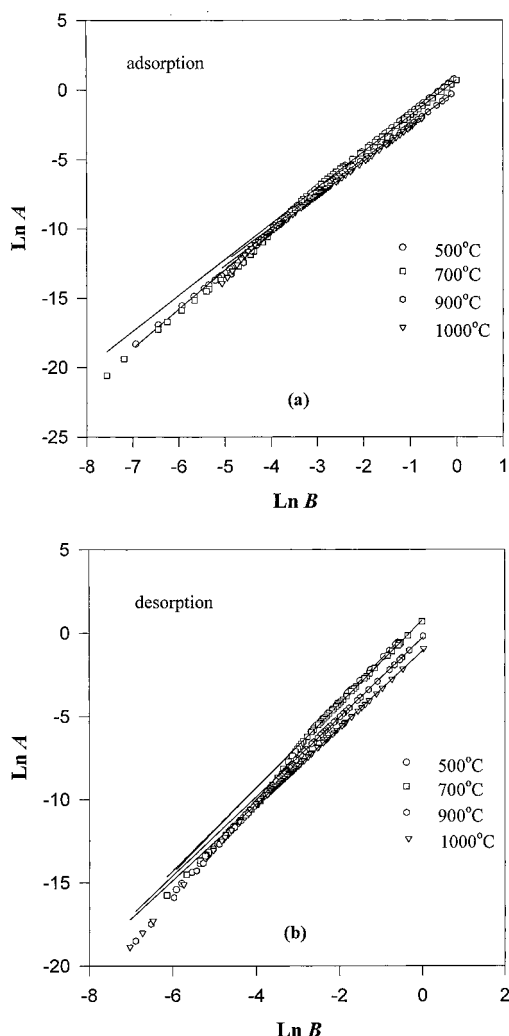


Figure 1. The plots drawn with the standard coordinates of eq 3, $\ln A$ versus $\ln B$, from the measured isotherms on C10A and the straight lines correspond to the linear regression in the scale range of possible fractality: (a) adsorption and (b) desorption.

et al.¹⁶ On the other hand, both D_a and D_d values evaluated from eq 1 are larger than those from eq 3, implying the inclusion of volume circumscribed by the fractal surface may decrease the D values. The scaling range where fractality is exhibited is different for the adsorption and desorption processes. For eq 1, the desorption process possesses a larger value than adsorption, while for eq 3, a reverse result was observed. For the latter, the $\ln A$ versus $\ln B$ plots of all isotherms exhibit two linear sections with an inflection near the location where a steep riser occurs in the isotherm (see Figure 1). Accordingly, the outer cutoff of the scaling regime is in the vicinity of the inflection point and the scaling ranges of adsorption process are larger than those of the desorption process since the "knee" formed by the desorption process moves more left than that of the adsorption process. It was also found that the scaling range using eq 3 is indeed larger than that using eq 1. Finally, both eqs 1 and 3 anticipated that D_a is larger than D_d for all examined samples. Because this is in contrast to the result of Wang and Li,¹⁴ some further discussion is needed.

In the adsorption process, as the pressure is increased from zero, an adsorbed film of nitrogen begins to form on the walls of the pores and the isotherm is governed by a combination of attractive and repulsive gas/solid

interactions and thus cannot probe the surface geometry effectively. As the pressure increases, the thickness of the film increases (multilayer adsorption) and the van der Waals attractions between the solid and adsorbed film, which tend to make the gas/film interface replicate the surface roughness, are the dominating factors. This process continues until the condensation pressure, where a step increase in the adsorption isotherm occurs, is reached and the liquid/gas surface tension (capillary force), which tends to move the interface away from the surface to reduce the interface area, is more important. It is noteworthy that the adsorption process between the multilayer mechanism and capillary condensation may be associated with the coexistence of the surface tension and van der Waals force effects. Since the surface fractal dimension determined by eqs 1 and 3 covers a long P/P_0 range, the competition between the van der Waals force and surface tension will induce $D_a < D_{\text{real}}$, as proposed by Wang and Li.¹⁴

In the desorption process, the liquidlike pore fluid vaporizes from the pores. Initially, a linear decrease of the desorption isotherm was found, corresponding to the vaporization in pores connected to the surface of the solid and/or the decompression of the pore liquid (however, it is difficult to separate one effect from the other). As a rule, the desorption isotherm does not always retrace the adsorption one but rather lies above it over a range of relative pressures, forming a hysteresis loop, before eventually rejoining the adsorption isotherm. The observed hysteresis may be the result of two mechanisms.⁵ One is an intrinsic property of the phase transition, where a vapor phase may be present at pressures above the condensation, and a liquid phase below the condensation pressure. This is called the "single-pore" mechanism for the hysteresis behavior. The second mechanism is related to the topology of the pore network (i.e., pore block effects). The structure of the pore network (its connectivity and accessibility), while irrelevant for adsorption, is very critical in the desorption processes. Some more detailed discussion about the role of the connectivity of the pore in the nitrogen desorption process may see the work of Liu and Seaton.¹⁷ The relative contributions of the single-pore and pore network effects to the hysteresis loop are difficult to ascertain and certainly vary from one solid to another. It is also worth noting that the effects existing in the adsorption process (i.e., the attractive van der Waals gas–solid interaction and the surface tension of nitrogen film) also act on the desorption process.

Because both the surface roughness and structure heterogeneity, which is generated by the existence of pore size distribution, can contribute to the surface fractal dimension,^{18–20} the D_d may be larger than D_a (as observed by Wang and Li), and thus, the relation $D_{\text{real}} = D_m - (D_d - D_a)$ is well-established if the dominating factor in the desorption process is the pore network effects. However, if the thermodynamic contribution to the adsorption hysteresis loop is dominant, the relative magnitude between D_a and D_d may be controlled by the surface tension effects existing in both the adsorption and desorption processes, and the larger one is closer to D_{real} . In our samples, D_d is smaller than D_a , implying the thermodynamic factor is not negligible which is consistent with our previous percolation analysis of nitrogen isotherms of the same samples.¹⁵ In this

case, the relation $D_{\text{real}} = D_m - (D_d - D_a)$ no longer operates effectively and we can only say D_a is closer to D_{real} .

Conclusion

Both Neimark's thermodynamic method, eq 1, and its modified version, eq 3, have been tested with well-measured nitrogen isotherms on alumina and aluminum borate samples. It was found that the modified version of the thermodynamic method predicts smaller D values either from adsorption process data or from desorption process data and possesses a larger scaling range than the Neimark method does. However, both methods indicated that heat treatment may decrease D for four examined porous samples. On the other hand, we also have shown how experimental arguments lead to the conclusion that the relation $D_{\text{real}} = D_m - (D_d - D_a)$, proposed by Wang and Li, holds only in the case where both the nitrogen desorption and mercury intrusion processes are dominated by the pore network effects and that the relative magnitude between D_d and D_a is determined by the surface tension effects existing in both adsorption and desorption processes and the larger one is closer to D_{real} if the thermodynamic factor is the dominating factor in the desorption process.

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Nomenclature

D = fractal dimension of pore surface

N = adsorption quantity, mol

P = current pressure of nitrogen, Pa

P_0 = saturation pressure of nitrogen, Pa

r = mean curvature radius calculated from the Kelvin equation, m

S = area of the gas-liquid interface at capillary condensation, m^2

T = absolute temperature of the adsorption, K

Greek Symbol

γ = surface tension between liquid and gas of nitrogen, J/m

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