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Fractal Dimensions of Macroporous and Hypercrosslinked Polymeric Adsorbents from Nitrogen Adsorption Data

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The nitrogen adsorption data of macroporous and hypercrosslinked adsorbents at 77 K were measured in the relative pressure range of 10^{-6} to 0.99. The Brunauer−Emmett−Teller (BET) surface area, micropore volume, pore size distribution, and fractal dimension of two adsorbents were evaluated from analysis of N_2 gas adsorption isotherms. The estimated surface fractal dimensions D of macroporous and hypercrosslinked adsorbents using the modified fractal Frenkel−Halsey−Hill (FHH) model were 2.471 and 2.709, respectively. Compared with the results of N_2 adsorption isotherm analysis, it should be noted that the surface fractal dimension D was related to the pore size distribution of the adsorbents. The more well-developed the microporous structure of a polymeric adsorbent, the larger the fractal dimension D. Moreover, the adsorbents were also analyzed by transmission electron microscopy (TEM), confirming the surface irregularities and more sophisticated microporous structure of the hypercrosslinked adsorbent as compared to the macroporous adsorbent.

1. Introduction

Over the past few decades, porous polymeric resin has emerged as a potential alternative to activated carbon due to its controllable pore structure and stable physical and chemical properties, as well as regenerability on site, and is frequently used as an adsorbent in purification and separation processes.[1−3] Permanently porous polymeric resins may be classified into two categories: macroporous and hypercrosslinked. Macroporous resins are produced by suspension copolymerization of a monomer and a cross-linking agent.[4] Hypercrosslinked polymeric adsorbents are produced by cross-linking polymers of macroporous resins in a good solvent and represent a class of predominantly microporous organic materials with high surface areas.[5] The cross-linking tightens the structures and modifies the surface properties of the porous polymeric network.

At present, the adsorption capacities of macroporous and hypercrosslinked adsorbents have been identified from their porosity, specific surface area, and pore size distribution.[2,6−8] The most common and recognized methods of surface analysis are based on standard gas-phase N_2 adsorption isotherms to estimate the surface area and the pore size distribution. In addition to gas adsorption, fractal analysis has become a powerful tool to describe the geometric and structural properties of fractal surfaces and pore structures.[9,10] Fractal analysis, at first a purely mathematical concept, has been introduced into numerous fields of science.[11] The fractal geometry is quantitatively evaluated by the fractal dimension D,[9] which is a measure of the surface and structural irregularities of a given solid. The value of this dimension can vary from 2 to 3, where the lowest value 2 corresponds to a perfectly smooth surface, while the upper limit 3 corresponds to a totally irregular or rough surface.[12,13] Recently, a number of studies have shown that surface fractality has an important influence on physicochemical processes such as diffusion, reaction kinetics, and adsorption,[14,15] and the fractal concept can be adopted to explain the relationship between the surface structure and the adsorption capacity of an adsorbent. So far as we know, there is no report about the fractal dimensions of polymeric adsorbents. Therefore, for a better understanding of the surface and pore structure responsible for adsorption, great interest will be focused on the fractal characterization of polymeric adsorbents.

In this paper, a hypercrosslinked polymeric adsorbent (HPA-1) and a macroporous polymeric adsorbent (XAD-4), which have the same matrix of poly(styrene-divinylbenzene), were chosen as the model adsorbents to discuss the fractal dimension by using nitrogen adsorption isotherms. This work claims to enrich knowledge about the fractal nature of polymeric adsorbents.

2. Experimental Section

The macroporous polymeric adsorbent (Amberlite XAD-4) was purchased from the Rohm & Haas Company (Philadelphia, PA). The hypercrosslinked polymeric adsorbent (HPA-1) was prepared via a postcross-linking step involving the Friedel−Crafts reaction between the chloromethylated copolymer of styrene-divinylbenzene, the synthetic process which has been described in detail in our previous paper.[16] Prior to use, all of the adsorbents were extracted with ethanol (high-performance liquid chromatography, HPLC, grade) for 8 h and then dried under vacuum at 323 K for 10 h. The N_2 gas adsorption−desorption isotherms were measured at 77 K using a gas adsorption analyzer ASAP 2020 (Micromeritics Instrument Co., USA) within the range p/p^0 of 10^{-6} to 0.99. The pore size distributions were obtained using the Horvath−Kawazoe (HK) method and Barrett−Joyner−Halenda (BJH) method. Transmission electron

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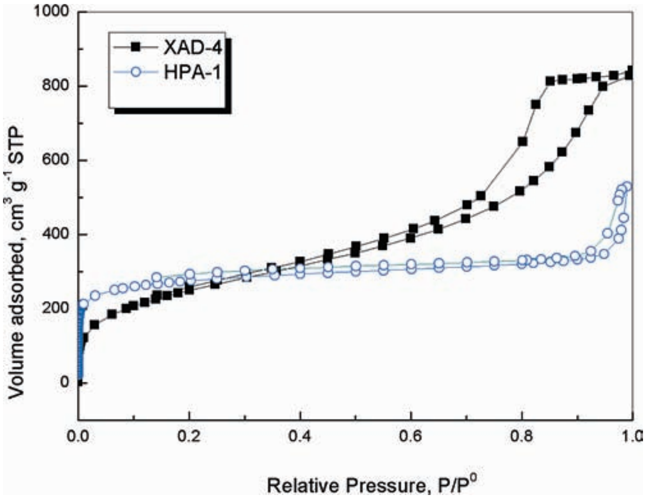

Figure 1. Nitrogen adsorption isotherms at 77 K: ○, HPA-1; ■, XAD-4.

Table 1. Textural Properties of Polymeric Adsorbents

resin	HPA-1	XAD-4
matrix and porosity	poly(styrene-divinylbenzene), hypercrosslinked	poly(styrene-divinylbenzene), macroporous
S_{BET}^{a} ($m^2 \cdot g^{-1}$)	938.6	922.3
S_{BJH} ($m^2 \cdot g^{-1}$)	214.3	676.7
V_{micro}^{b} ($cm^2 \cdot g^{-1}$)	0.538	0.363
V_{meso} ($cm^2 \cdot g^{-1}$)	0.252	1.031
V_t^{c} ($cm^2 \cdot g^{-1}$)	0.819	1.435

[a] BET surface area (S_{BET}) and mesopore surface area (S_{BJH}) were calculated from the adsorption−desorption isotherm of N_2 at 77 K by BET and BJH methods, respectively. [b] Micropore pore volume (V_{micro}) and mesopore pore volume (V_{meso}) were calculated from the adsorption−desorption isotherm of N_2 at 77 K by HK and BJH methods, respectively. [c] Total pore volume (V_t) was estimated to be the liquid volume of nitrogen at a relative pressure of 0.99.

micrographs of XAD-4 and HPA-1 were obtained using a Jeol JEM-1200 microscope.

3. Results and Discussion

3.1. Pore Size Distributions. The nitrogen adsorption isotherms at 77 K of polymeric adsorbents XAD-4 and HPA-1 are shown in Figure 1. It is observed that the adsorption isotherm of the hypercrosslinked polymeric resins (HPA-1) is close to type I of the IUPAC classification, reflecting the domination of micropores in the pore structure. The adsorption isotherm of macroporous adsorbent (XAD-4) was of type II in the same classification, and the existence of a remarkable hysteresis loop confirms the presence of mesopores. A summary of the values of the textural properties of the samples is included in Table 1.

In general, the HK and BJH distributions as a whole reveal the complex nature of adsorbents regarding their micro- and mesoporous structure. Figure 2a shows the distribution of pore size calculated according to the HK model. The distribution corresponding to XAD-4 shows a negligible micropore volume in the mentioned pore size region, while HPA-1 shows comparably high volumes. HK distribution functions clearly indicate the development of an important microporous structure for the hypercrosslinked polymeric adsorbent by an extensive postcrosslinking of macroporous resins. It is also clearly shown in Figure 2b that XAD-4 has a predominant pore size distribution in the mesoporous region compared to HPA-1, and the increase of the pore volume of XAD-4 with respect to that of HPA-1 is obvious. From the Table 1 we also know that the micropore volume was only 25.2 % of the total pore volume for XAD-4, but 65.7 % for HPA-1.

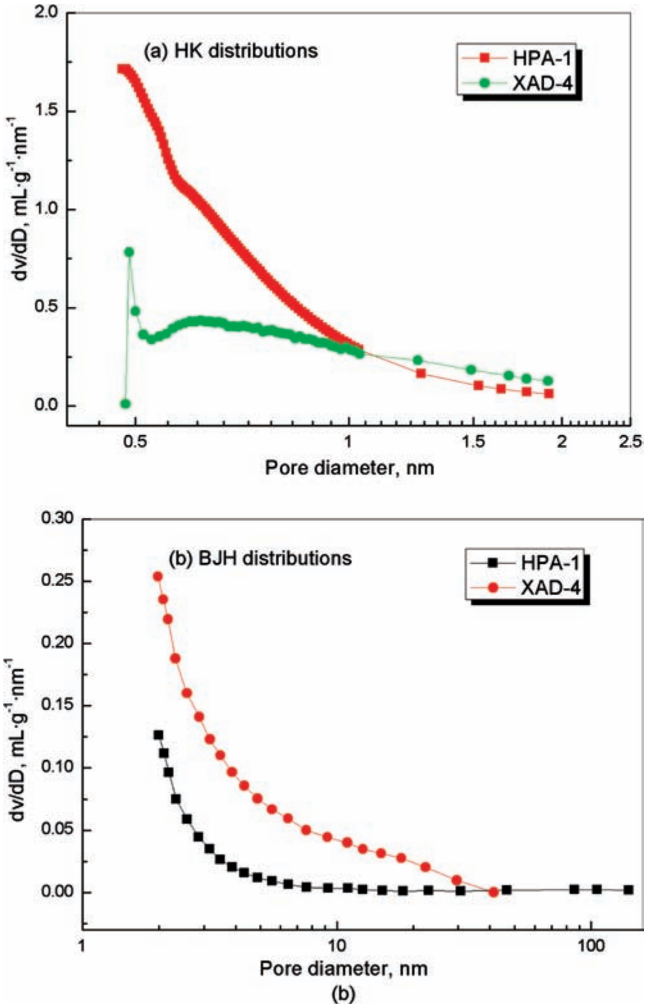

Figure 2. Distributions of pore size for HPA-1 and XAD-4 from the (a) HK model and (b) BJH model.

3.2. Fractal Dimensions. One of the simplest and most popular relationships to determine the fractal dimension of a solid, based on the adsorption data, is the Frenkel−Halsey−Hill equation (FHH). On the basis of the theory of Pfeifer et al., the fractal dimensions are estimated from:[17,18]

$$\ln(v/v_{mono}) = \text{constant} + (D - 3)\ln(\ln(p^0/p)) \qquad (1)$$

where v is the amount of N_2 adsorbed at each equilibrium pressure, p; v_{mono} is the amount adsorbed of monolayer coverage; and p^0 is the saturation pressure. Thus, a plot of $\ln(v/v_{mono})$ versus $\ln(\ln(p^0/p))$ shows a linear trend, and the slope may be used to calculate D.

Figure 3a,b reproduces the plots of $\ln(v/v_{mono})$ against $\ln(\ln(p^0/p))$ from the N_2 gas adsorption isotherms measured on XAD-4 and HPA-1, respectively. For two polymeric adsorbents specimens, one can find clearly that there appeared two or three (several) straight lines with different slopes. It was reported that, as more adsorbed layers are built up, the interface of the adsorbate with the adsorbed molecules becomes smooth, and hence the surface fractal dimension would no longer describe the interface but would describe the adsorbed molecule agglomerates.[19,20] Therefore, to ensure a reliable determination of D, it is therefore recommended to determine D only around monolayer coverage.[20,21] In this work, the slopes of the first

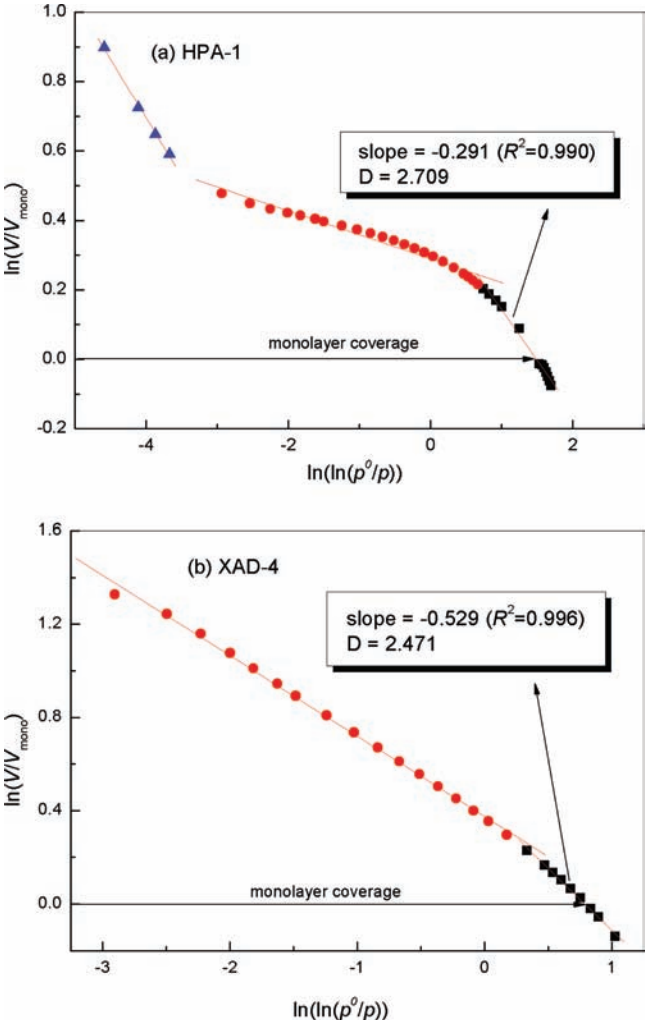

Figure 3. Plots of ln(υ/υ_{mono}) against ln(ln(p^0/p)) reconstructed from the N_2 gas adsorption isotherms obtained from (a) HPA-1 and (b)XAD-4.

linear regions of Figure 3a,b in value, respectively, were taken to determine the surface fractal dimensions of the two kinds of polymeric adsorbents, XAD-4 and HPA-1. The values obtained of *D* for all products prepared in this study are listed in Figure 3. From the above data we calculated, we can see the following: (a) The hypercrosslinked polymeric adsorbent (HPA-1) with a proposed micropore structure has a greater fractal dimension of 2.709, indicating a wealth of pore structure and a more sophisticated pore distribution. These high values suggest that the surfaces are irregular and have strong micropore structures. (b) The macroporous polymeric adsorbent (XAD-4) has a fractal dimension of 2.471, suggesting that XAD-4 could have a partially irregular surface due to its micromesoporous structure.

Clearly, the results obtained on the fractal dimension provide important information on the topography and allow us to obtain a better knowledge of the surface characteristics of these adsorbents. Comparing the results of N_2 adsorption isotherm analysis with those of fractal analysis, it should be noted that the surface fractal dimension *D* is related to the pore size distribution of the adsorbents. The more well-developed the microporous structure of the polymeric adsorbents, the larger the fractal dimension *D*.

On the other hand, the images obtained by transmission electron microscopy (TEM) reveal the difference in the porous structure of both types of the porous adsorbents, macroporous and hypercrosslinked polymeric adsorbents. The TEM images of HPA-1 and XAD-4 are depicted in Figure 4a,b, respectively. The white portions that look bright are considered to be the pores of the polymer specimen, and dark portions are the pore walls encompassing the pores. As can be seen in Figure 4, XAD-4 consisted of more agglomerated pores, revealing a highly developed mesoporosity, while HPA-1 was composed of less agglomerated pores and had the satisfied self-similarity. This observation agrees well with the results from the adsorption−desorption isotherms of N_2. The TEM images provide clear evidence that the increase of the fractal dimension *D* calculated for HPA-1 compared to XAD-4 is the result of a stronger micropore structure.

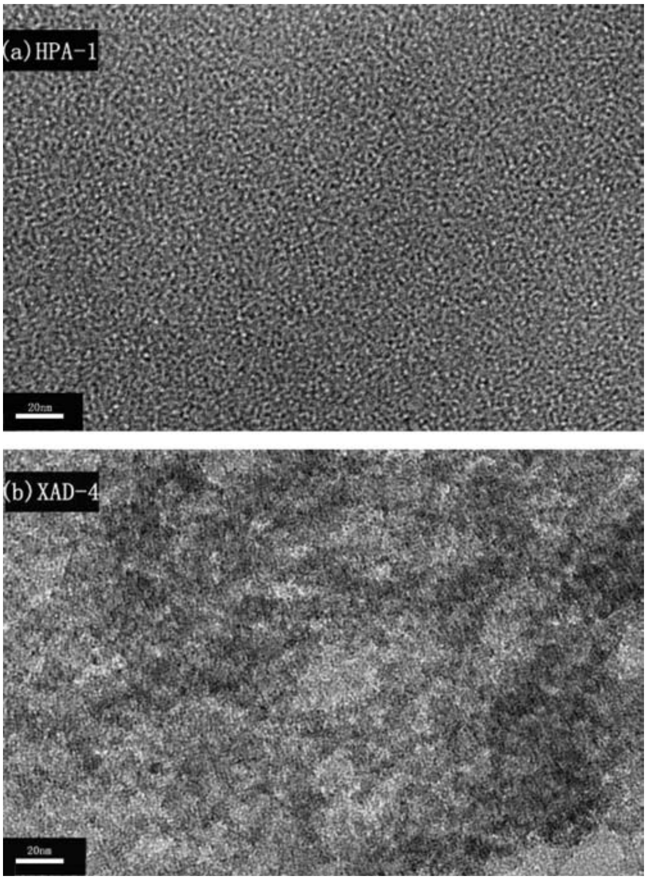

Figure 4. Transmission electron microscopy (TEM) image of the polymeric adsorbents: (a) HPA-1 and (b) XAD-4.

4. Conclusions

The microtopography of macroporous and hypercrosslinked adsorbents, which have the same matrix of poly(styrene-divinylbenzene), has been studied using the fractal dimensions method. Their surface fractal dimensions were calculated using the modified form of the FHH equation. The results showed that a significant increase of the fractal dimension was found for the hypercrosslinked polymeric adsorbent (HPA-1) as compared to macroporous adsorbent (XAD-4). HPA-1 with a well-developed microporous structure has a higher fractal dimension *D* ($D = 2.709$), but XAD-4, which has predominant pore size distribution in the mesoporous region, has a lower fractal dimension ($D = 2.471$). The two adsorbents were also analyzed by TEM, confirming that the more well-developed the microporous structure of polymeric adsorbents, the larger the fractal dimension *D*.

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