Fractal Analysis of Polymeric and Particulate Titania Aerogels by Adsorption

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Polymeric and particulate titania (TiO_2) aerogels with high surface areas were prepared from sol−gel derived TiO_2 lyogels via freeze-drying as well as CO_2 supercritical drying. The surface fractal dimensions of these aerogels were evaluated with two methods based on physisorption, one by Avnir and Pfeifer, and the other, the modified form of the Frenkel−Halsey−Hill (FHH) equation. The two approaches yielded almost identical results. The surface fractal dimensions measured are approximately 2.7 and 2.8 for polymeric and particulate TiO_2 aerogels, respectively, thereby indicating that the fractal surfaces of particulate aerogels are slightly more irregular than those of polymeric aerogels.

Introduction

A lyogel is a substance which contains a continuous solid skeleton enclosing a continuous liquid phase; it can be characterized as being either polymeric or particulate.[1] Sol−gel synthesis of TiO_2 lyogels typically involves the hydrolysis of a titanium alkoxide, e.g., titanium ethoxide, $Ti(OC_2H_5)_4$, with a controlled amount of water in the presence of an organic solvent. The hydrolysis can be catalyzed by either an acid or a base. As soon as intermediate hydroxy groups appear, polycondensation is initiated, which continues until the lyogel is formed. In general, acid-catalyzed reactions with low water-to-metal alkoxide molar ratios yield polymeric lyogels, whereas base-catalyzed reactions form particulate lyogels. Upon removing the solvent with a drying method capable of preventing collapse of the porous network due to the interfacial tension between the liquid and vapor, these lyogels are converted into their corresponding aerogels.

Fundamental differences exist in the gelling mechanism as well as in the final structure between polymeric and particulate lyogels.[1] The formation of a polymeric network via chemical reactions has been proposed as the gelling mechanism for polymeric lyogels. The formation of a network via particle aggregation induced by attractive dispersion forces has been proposed as the gelling mechanism for particular lyogels; the structure is controlled by the balance between electrostatic repulsion and attractive van der Waals forces.

If the differences between polymeric and particulate TiO_2 aerogels are to be characterized, quantitative measures of the surface features of the aerogels are required. The characterization of surface irregularity is essential in the fields of chemistry, physics, engineering, and related disciplines.

The specific surface area, the micropore volume, and the total pore volume can be evaluated from the adsorption data.[2] The specific surface area can be determined with the BET equation utilizing an adsorption isotherm at low relative pressures. The micropore volume is estimated with the Dubinin−Radushkevich (DR) equation through an adsorption isotherm at very low relative pressures. The total pore volume is determined from the amount of an adsorbate adsorbed at a relative pressure close to unity.

To characterize of surface irregularity, difficulty is encountered in applying conventional techniques based on the notion of isolated deviations from planar surface geometry. It is arduous to identify a limited number of structure parameters that can portray the irregularity for a broad spectrum of purposes. Conventional techniques usually depend on a multitude of model-specific parameters that are cumbersome to access in practice.[3] Fractal geometry, introduced by Mandelbrot in the 1970s,[4] has been successfully applied to characterizing surface irregularity of silver films,[3] silica aerogels,[5,6] carbon particles,[7] and various other objects.

Fractal objects are scale invariant, i.e., self-similar, in that they appear to be similar at all scales of resolution.[7] Experimental techniques for determining surface irregularity include small-angle X-ray scattering (SAXS),[6,8] electronic energy transfer,[6] and adsorption.[3,7,9−13] The thermodynamics of adsorption is fairly well-established, and experimental procedures are relatively simple; thus, adsorption has been the method of choice in many early studies of surface irregularity.[7]

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The pioneering works of Avnir and Pfeifer on surface fractality, conducted via the adsorption technique, have amply demonstrated that the accessible surface area of an adsorbent depends on the cross-sectional area (σ) of an adsorbate.[9-11] The number of moles of an adsorbate in the monolayer (n_m) is assumed to be proportional to $\sigma^{-d/2}$; thus

$$\ln(n_m) = (-d_{SF}/2)\ln(\sigma) + \text{constant} \qquad (1)$$

where d_{SF} is the surface fractal dimension; n_m can be evaluated by fitting an adsorption isotherm at low relative pressures to the BET equation.[2] By employing adsorbates with various molecular sizes and evaluating the corresponding monolayer contents of the surface, d_{SF} can be evaluated from the slope of a log−log plot of n_m vs σ. In this approach, the yardstick is the molecular size of the adsorbate. Small molecules can be adsorbed on the minute irregular surface, while large molecules may have sizes sufficiently large to prevent detection of small surface features. The surface fractal dimension increases with the degree of surface irregularity from 2 for a perfectly smooth surface to nearly 3 for a highly irregular surface.

The surface fractal dimension also can be evaluated from a single adsorption isotherm by utilizing a modified form of the Frenkel−Halsey−Hill (FHH) equation. Conventional FHH theory describes multilayer adsorption through an isotherm equation expressed as

$$n/n_m = \kappa[-\ln(P/P_0)]^{-\nu} \qquad (2)$$

where P and P_0 are the vapor pressure and saturated vapor pressure of the adsorbate, respectively; n is the number of adsorbed moles of the adsorbate at a given relative pressure (P/P_0); κ is a constant; ν is a constant defined to be equal to $^1/_3$. Nevertheless, Halsey[14] has found that ν may vary between $^1/_2$ and $^1/_3$; others have observed that ν ranges between 0 and 1.[14]

Much effort has been expended in employing FHH theory to characterize fractal surfaces. By incorporating a pore-size distribution for a fractal surface into the Dubinin approach for adsorption on porous materials, Avnir and co-workers[13] have proposed the following isotherm equation:

$$n/n_m = \kappa[-\ln(P/P_0)]^{-(3-d_{SF})} \qquad (3)$$

In contrast, Pfeifer and co-workers[3] have proposed the model below after investigating the effects of surface fractality on thick-film adsorption:

$$n/n_m = \kappa[-\ln(P/P_0)]^{-(3-d_{SF})/3} \qquad (4)$$

This expression can be reduced to eq 3 when the effect of surface tension on thick-film adsorption is taken into account.[12,15]

In reality, eq 3 is valid only at high coverage when the interface is controlled by the surface tension between the liquid and gas (capillary condensation). Equation 4 holds only when the van der Waals attraction forces between the gas and solid dominate, i.e., during early stages of the multilayer formation;[12] the surface tension between the liquid and gas is negligible.

Table 1. Conditions for Synthesizing TiO_2 Lyogels

sample	TiO_2 concn in t-C_4H_9OH (wt %)	H_2O/Ti (molar ratio)	catalyst	catalyst/Ti (molar ratio)
polymer lyogels	5	4/1	HCl	0.08/1
particulate lyogels	10	4/1	NH_4OH	0.20/1

Yin[14] has demonstrated that eq 3 also can be obtained by combining the Kelvin equation for capillary condensation with a fractal pore-size distribution on porous materials. Yin's approach supposes that the adsorption process results in the sequential filling of pores from small to large, rather than layer-by-layer surface coverage as assumed in conventional FHH theory. The adsorption process of fractally porous materials, therefore, is dominated by capillary condensation.

Equation 3 indicates that d_{SF} can be obtained from the slope of a log−log plot of n/n_m vs $\ln[(P/P_0)^{-1}]$ through a single adsorption isotherm, regardless of the adsorbate chosen. The value of n is recoverable by dividing the measured volume at STP by 22.4. The value of n_m also is determined via the BET equation.

In the present work, polymeric and particulate TiO_2 aerogels were prepared by sol−gel derived TiO_2 lyogels via freeze-drying as well as CO_2 supercritical drying. The specific surface area, micropore volume, and total pore volume of each aerogel sample were measured. The surface fractal dimensions of these aerogels were determined utilizing the Avnir and Pfeifer's method and the FHH method. The results obtained from the two approaches are compared.

Experimental Section

Preparation of TiO_2 Lyogels. Polymeric TiO_2 lyogels were synthesized by hydrolyzing $Ti(OC_2H_5)_4$, with HCl as the catalyst; t-C_4H_9OH served as the solvent. The organic solvent was divided into two equal portions. $Ti(OC_2H_5)_4$ was dissolved in one portion, and H_2O and HCl were mixed with the remaining one. Subsequently, the two portions were simultaneously transferred to a continuously stirred three-neck flask. The flask was closed immediately. It was heated to and maintained at 323 K by means of a water bath to carry out the hydrolysis and polycondensation reactions. The conditions for synthesizing polymeric TiO_2 lyogels are summarized in Table 1.

A procedure similar to that described above was followed to synthesize particulate TiO_2 lyogels; however, NH_4OH replaced HCl as the catalyst. Moreover, the flask was partially opened so that a portion of the t-C_4H_9OH was removed through evaporation. This accelerated aggregation of TiO_2 particles, thereby giving rise to the formation of particulate lyogels. The conditions for synthesizing particulate TiO_2 lyogels are summarized in Table 1 as well.

Preparation of TiO_2 Aerogels. Polymeric and particulate TiO_2 aerogels (designated as samples 1 and 2, respectively) were prepared by removing t-C_4H_9OH from polymeric and particulate TiO_2 lyogels via freeze-drying. The TiO_2 lyogels were placed in a closed container and rapidly refrigerated; subsequently, the frozen lyogels were transferred to a freeze-dryer. The t-C_4H_9OH then was sublimated by maintaining the temperature and vapor pressure of the frozen lyogels at 263 K and 1 Torr, resulting in conditions below the triple point of t-C_4H_9OH. Although the temperature was gradually increased after a portion of the t-C_4H_9OH was removed, it was always less than the freezing temperature of t-C_4H_9OH during drying.

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Table 2. Specific Surface Areas and Pore Volumes of TiO_2 Aerogels As Determined from Nitrogen Adsorption Data

sample	surface area (m^2/g)	micropore vol[a] (cm^3/g)	total pore vol[a] (cm^3/g)
1	510	0.214	0.307
2	578	0.207	0.953
3	511	0.182	1.363
4	516	0.195	0.897

[a] The equivalent liquid volume.

Polymeric and particulate TiO_2 aerogels (designated as samples 3 and 4, respectively) also were prepared via supercritical drying. The TiO_2 lyogels were pressurized with CO_2 in an autoclave from which all t-C_4H_9OH was removed through a series of CO_2 purges. After t-C_4H_9OH was completely replaced by CO_2, supercritical drying was performed at conditions of 320 K and 110 atm; the critical temperature and pressure of CO_2 are 304 K and 72.9 atm.

Measurements of Adsorption Isotherms. Prior to the adsorption measurements, all aerogel samples were degassed at 400 K for 2 h under flowing nitrogen. Adsorption isotherms were measured with a NOVA-1200 gas sorption analyzer (Quantachrome Corp., Boynton Beach, FL).[16]

Adsorption isotherms at low relative pressures, each comprising six points, were measured for each sample with four adsorbates, N_2 ($\sigma_{N_2} = 0.162$ nm^2), C_2H_6 ($\sigma_{C_2H_6} = 0.259$ nm^2), C_3H_8 ($\sigma_{C_3H_8} = 0.360$ nm^2), and n-C_4H_{10} ($\sigma_{C_4H_{10}} = 0.421$ nm^2), at adsorption temperatures of 77, 189, 228, and 273 K, respectively.[11] To reduce experimental error, the sample cell was calibrated for each adsorbate. A nitrogen adsorption isotherm comprising 20 points, with the relative pressure ranging from 0.05 to 0.95, was measured for each sample as well.

Estimation of Surface Fractal Dimensions and Other Properties. The number of moles in the monolayer for each adsorbate was evaluated with the BET equation, based upon the adsorption isotherms obtained from the four adsorbates at low relative pressures. The surface fractal dimension of each sample was estimated from eq 1 with the n_m's and σ's of the four adsorbates and from eq 3 utilizing a single nitrogen adsorption isotherm at high relative pressures.

The specific surface area was evaluated utilizing the number of moles in the monolayer and the cross-sectional area of nitrogen. The micropore volume was evaluated from the DR equation with nitrogen adsorption isotherm at very low relative pressures. The total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure close to unity.

Results and Discussion

Specific Surface Areas and Pore Volumes. Table 2 lists the specific surface areas of the four aerogel samples. All of the specific surface areas exceed 500 m^2/g.

The micropore and total pore volumes of the four aerogel samples obtained from the nitrogen adsorption data are presented in Table 2 as well. The micropore volumes of the four samples are almost identical. The total pore volumes of the two particulate aerogel samples (samples 2 and 4) are essentially the same; the difference in the total pore volume between two polymeric aerogel samples (samples 1 and 3) is substantial.

On the basis of the analysis of the ratio of the micropore volume to total pore volume, one polymeric aerogel sample (sample 1) from freeze-drying essentially is microporous; approximately 70% of its total pore volume belong to the micropores. The other three samples have only limited microporosity.

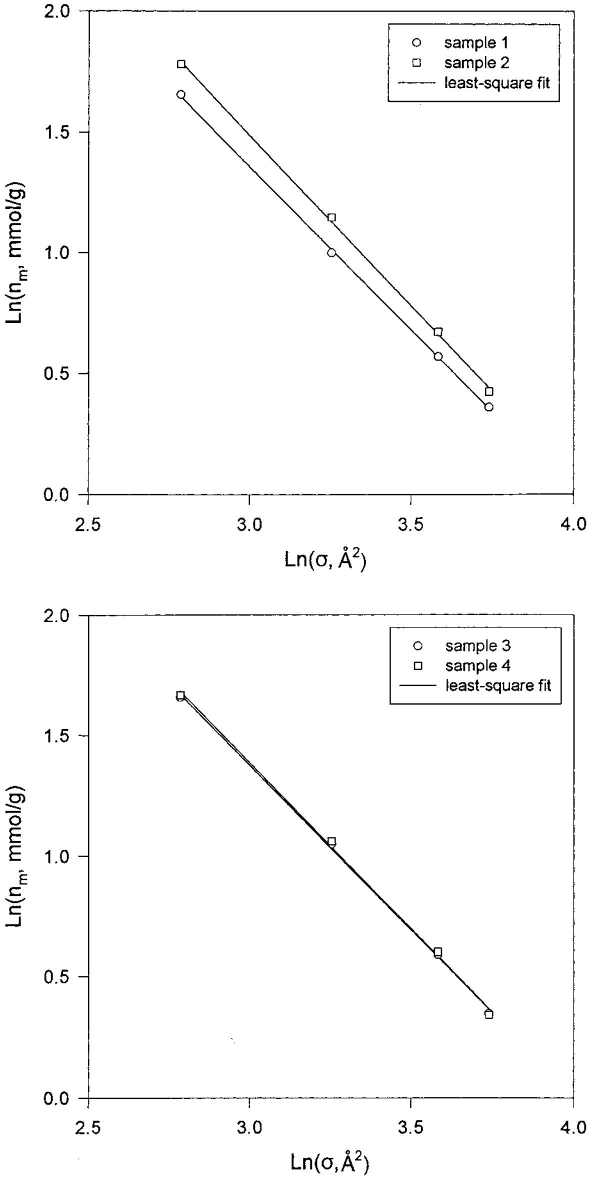

Figure 1. Monolayer content (n_m) versus cross-sectional area (σ) with N_2, C_2H_6, C_3H_8, and n-C_4H_{10} as adsorbates: (a, top) samples 1 and 2; (b, bottom) samples 3 and 4.

Table 3. Surface Fractal Dimensions of TiO_2 Aerogels

	surface fractal dimension	
sample	Avnir and Pfeifer method	FHH method
1	2.70	
2	2.82	2.80
3	2.73	2.61
4	2.76	2.79

Surface Fractal Dimensions. Figure 1a displays the log−log plots of n_m vs σ for samples 1 and 2, in light of the Avnir and Pfeifer's method (eq 1). The surface fractal dimensions of both samples determined from the slopes of the plots are summarized in Table 3. Figure 2a shows the log−log plots of n/n_m vs $\ln[(P/P_0)^{-1}]$ for the same two samples in light of the FHH method (eq 3). The plots are linear at high relative pressures. The surface fractal dimensions evaluated from the slopes of the plots are presented in Table 3.

The log−log plots of n_m vs σ and n/n_m vs $\ln[(P/P_0)^{-1}]$ for samples 3 and 4 are given in Figures 1b and 2b, respectively. The resultant surface fractal dimensions of the two samples are summarized in Table 3 as well.

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[16] Quantachrome Corp., NOVA-1200 Gas sorption analyzer, Version 3.00; Quantachrome Corp., 1994.

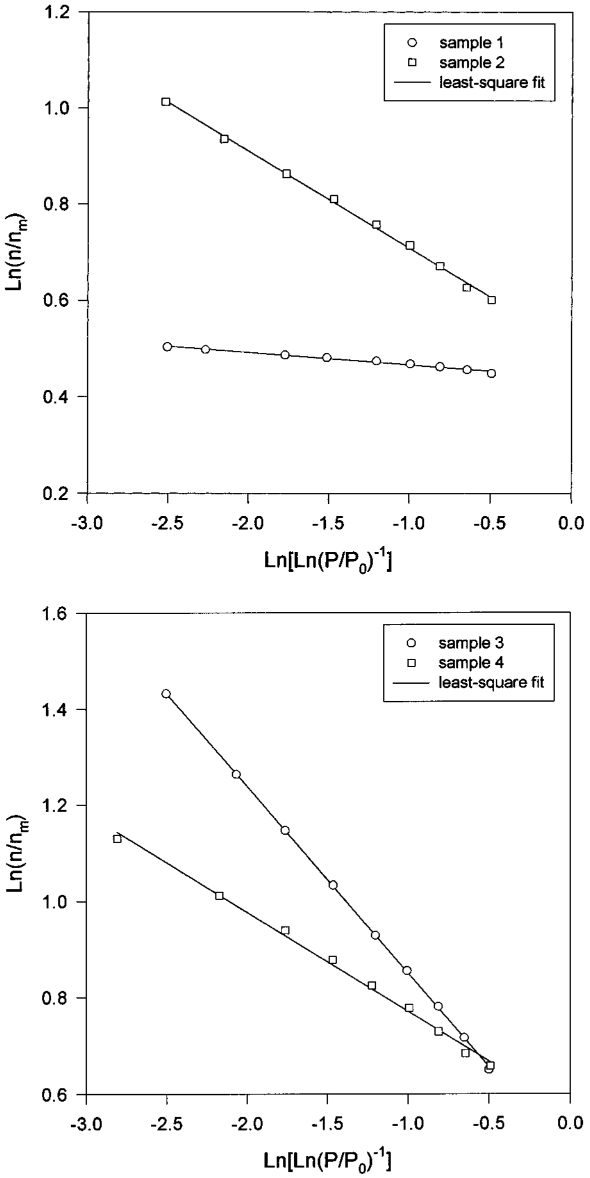

Figure 2. FHH plots for N_2 adsorption on aerogels: (a, top) samples 1 and 2; (b, bottom) samples 3 and 4.

The surface fractal dimensions of the polymeric and particulate aerogel samples, evaluated from the Avnir and Pfeifer's method, are approximately 2.7 and 2.8, respectively; the FHH method yielded almost identical results for both particulate aerogels (samples 2 and 4), and the result for one of the polymeric aerogels (sample 3) was similar, 2.6. Nevertheless, the surface fractal dimension of another polymeric aerogel sample (sample 1) cannot be evaluated from this method; the reasons will be elaborated later. Despite this, the results indicate that the fractal surfaces of particulate aerogels are slightly more irregular than those of polymeric aerogels.

The structures of a lyogel and its aerogel are closely related.[1] Structural differences between polymeric and particulate TiO_2 lyogels were observed with transmission electron microscopy (TEM).[17] Scanning electron micrographs revealed that the surface morphology of polymeric aerogels is unlike that of particulate aerogels when they are prepared via CO_2 supercritical drying.[18]

The specific surface area of an absorbent is highly dependent on its surface irregularity and pore structure. As can be noted in Table 2, polymeric and particulate TiO_2 aerogels prepared here are similar in their surfaced areas and micropore volumes as determined from nitrogen adsorption data, even though they have very dissimilar total pore volumes. The differences in their surface fractal dimensions, however, are observed to be minimal. These data suggest that the surface characteristics of these aerogels are very similar over a length scale of a few bonds. The nanoscale morphology of the aerogels is relatively independent of the initial processes of lyogel formation; the initial stages of hydrolysis and polycondensation are robust to the synthetic conditions. The mesoscale morphology is affected significantly by the synthetic procedure, causing the differences observed in various lyogel and aerogel structures. Adsorption measurements are ineffective in elucidating differences in mesoscale surface features.

Comparison of Two Methods. The surface fractal dimensions of all four aerogel samples can be evaluated with the Avnir and Pfeifer method; however, this method has some drawbacks. One is the uncertainty in molecular size for most adsorbates, which changes with the adsorption temperature and adsorbent. For example, the value of the cross-sectional area for C_3H_8 ranges from 0.32 to 0.40 nm^2.[19] Another drawback is the necessity that the adsorbate molecules employed be similar in shape;[20] ideally, they should be members of a homologous series.

The FHH method can evaluate the surface fractal dimension from a single adsorption isotherm regardless of the adsorbate chosen. No assumptions are required as to the molecular size of the adsorbate. This method is, therefore, simple and convenient. This method, however, cannot evaluate surface fractal dimensions of the microporous materials, e.g., sample 1 in this study. The Kelvin equation, which is the foundation of the modified form of the FHH equation (eq 3), is not expected to hold for small-pore radii due to the large values of the adsorption potential anticipated.[21] In addition, the conventional FHH equation holds when the film thickens beyond two or three molecular layers;[21] however, the multilayer of adsorbate molecules cannot be formed on the microporous materials. Moreover, the slope of a log–log plot of n/n_m vs $\ln[(P/P_0)^{-1}]$ is sensitive to the forces responsible for adsorption. If both the van der Waals attraction forces between the gas and solid and the surface tension between the liquid and gas are appreciable, the slope should have a value between $(d_{SF} - 3)/3$ and $(d_{SF} - 3)$.[12] In practice, the constant ν in the conventional FHH equation can be varied between 0 and 1 to better describe various adsorption isotherms.[14]

As mentioned above, sample 1 has significant microporosity; therefore, the Kelvin equation does not hold

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due to small pore radii. In addition, n/n_m of sample 1 ranges rather narrowly from 1.5 to 1.7, while the magnitude of n/n_m of the other three samples varies widely from 1.8 to 3.0 and even higher as the relative pressure varies from 0.50 to 0.95. It is very plausible, therefore, that the modified form of the FHH equation is incapable of evaluating the surface fractal dimension of sample 1.

Conclusions

The surface fractal dimensions of the polymeric and particulate TiO_2 aerogel samples, obtained from the Avnir and Pfeifer method, are approximately 2.7 and 2.8, respectively. The FHH method yielded almost identical results for the particular aerogel samples (samples 2 and 4), and a similar result, approximately 2.6, was obtained for one polymeric aerogel sample (sample 3).

The nanoscale surface features of the four aerogels are essentially the same. The fractal surfaces of particulate aerogels are only slightly more irregular than those of polymeric aerogels. The similarity in surface fractal dimension implies that the nanoscale morphology is determined during the early stage of the synthetic process; the synthetic procedure seems to have little impact. The close agreement of the surface fractal dimensions obtained from different adsorption techniques corroborates this interpretation. Mesoscale morphology, however, is affected by synthetic conditions. Adsorption studies have limited value in studying features in this regime.

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Notation

d_{SF}	surface fractal dimension
n	number of adsorbed moles of the adsorbate at P/P_0
n_m	number of moles of the adsorbate in the monolayer
P	vapor pressure of the adsorbate
P_0	saturated vapor pressure of the adsorbate

Greek letters

κ	constant of the FHH equation
ν	exponent of the FHH equation
σ	cross-sectional area of the adsorbate

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