Fractal Surface Structure of Food Materials Recognized by Different Molecules

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The moles of monolayer adsorption of defatted rice flour, wheat flour, and corn fiber, and of active carbon as a reference, were measured using argon, nitrogen, krypton, ethane, propane, and butane. The relation between the moles of monolayer adsorption and the cross-sectional area of adsorbent molecules was not as expected for the smooth surface, but showed a fractal surface structure. A fractal dimension, D_σ , was calculated from the logarithmic relation between the moles of monolayer adsorption and the cross-sectional area of adsorbent molecules. The values of D_σ were not equal in general to the values of another fractal dimension, D_s , calculated in our preceding paper from the logarithmic relation between the specific surface area and the particle diameter.

The fractal concept proposed by Mandelbrot¹⁾ in 1975 seems to be useful for quantitative understanding of the irregular structure of foods. Pfeifer *et al.*^{2,3)} showed that for active carbon, or silica gel, the relation between the specific surface area and particle diameter was not as commonly believed, but as the following:

$$S_w \propto n_m \propto d_p^{D_s-3} \quad (1)$$

where d_p is the particle diameter, D_s a fractal dimension, n_m the monolayer moles of a gas adsorbed on a gram of solids, and S_w the specific surface area recognized by the gas molecule adsorbed on the solid. They also showed that the value of n_m , which is reversely proportional to the cross-sectional area of molecules for the ideally smooth surface, was not as that for the smooth surface but as the following:

$$n_m \propto \sigma^{-D_\sigma/2} \quad (2)$$

where D_σ is another fractal dimension, and σ the cross-sectional area of the adsorbent molecules. In Eqs. (1) and (2), the values of D_s and D_σ may take any non-integral real number between 2 and 3. Though Pfeifer *et al.*⁴⁾

assumed that D_s is equal to D_σ , it may not to be so in general.

If D_s is independent of D_σ , the combination of Eqs. (1) and (2) gives

$$n_m \propto d_p^{D_s-3} \cdot \sigma^{-D_\sigma/2} \quad (3)$$

Since $S_w \propto n_m \cdot \sigma$, we obtain the following equation from Eq. (3)

$$S_w \propto d_p^{D_s-3} \cdot \sigma^{(2-D_\sigma)/2} \quad (4)$$

Equation (4) suggests that the specific area of a material may be differently recognized by molecules of different size. In our preceding paper⁵⁾ we found that the surface porous structures of rice flour, wheat flour, and corn fiber, before and after defatting, and milk powders, were fractal and their irregularity was evaluated by the fractal dimension D_s . We also showed that the specific surface areas measured using N_2 and Kr were different. Although this is against common sense, in which the surface is implicitly assumed to be smooth, it is acceptable, from the fractal viewpoint, for an irregular surface looked at with molecular-level scales.

As for whether D_s is equal to D_σ , Nagai and Yano⁶⁾ showed that the values of D_s and D_σ

were not equal for dried starch gels.

The purpose of this paper is to study more (1) on the different recognition of the specific surface area by different kinds of molecules, and (2) on whether D_s is equal to D_σ , using the same materials used in our preceding paper.⁵⁾

Materials and Methods

Materials. Rice flour, wheat flour, and corn fiber, before and after defatting, were used. The sample materials were the same as those used in our preceding paper,⁵⁾ although the mean particle diameter was $26\ \mu\text{m}$ for the rice flour and wheat flour, and $45\ \mu\text{m}$ and $71\ \mu\text{m}$ for the corn fiber. Commercial active carbon was also used as a reference.

Moles of monolayer adsorption: using argon, nitrogen, ethane, krypton, propane, and butane, the adsorption isotherms were measured with an Accusorb 2100 (Micromeritics Co.) at temperatures shown in Table I after the sample was completely dried at 40°C under reduced pressure. The moles of monolayer adsorption were calculated from the adsorption isotherms using the following B.E.T. plot:

$$\frac{P/P_s}{V(1-P/P_s)} = \frac{1}{VmC} + \frac{(C-1)(P/P_s)}{VmC} \quad (5)$$

where C [—] is constant, P [mmHg] an adsorption equilibrium pressure of a gas, P_s [mmHg] the saturation pressure of the gas at the given temperature, V [ml/g] an adsorbed volume of the gas per unit weight of solid at the adsorption equilibrium at the standard temperature and pressure (STP), and V_m [ml/g] the value of V for monolayer coverage. The moles of monolayer adsorption n_m [mol/g] were calculated to be

$$n_m = Vm/22400 \quad (6)$$

The purity of the argon and the nitrogen gas used was guaranteed to be 99.9995% that of the other was 99.9%.

Table I. MOLECULAR CROSS-SECTIONAL AREA AND EXPERIMENTAL CONDITIONS

Gas	Molecular cross-sectional area ⁸⁾ (nm ²)	Temp. (°C)	Saturated pressure (mmHg)
Ar	0.147	-196	213
N ₂	0.162	-196	760
Kr	0.202	-196	3.5
Ethane	0.230	-78	1303
Propane	0.364	-78	111
Butane	0.448	0	774

Table I lists the molecular cross-sectional area of the gases and the saturation gas pressure calculated from the Antoine equation⁷⁾ at the temperature of measurement.

Results

Since lipid-containing raw samples absorbed much ethane, propane, and butane, the B.E.T. plots did not give straight lines. Therefore, the monolayer adsorption was measured only for defatted materials.

Figure 1 shows the adsorption isotherms of six gases on the defatted wheat flour. The relative pressure on the abscissa is an equilibrium pressure of a gas divided by the saturation pressure of the gas shown in Table I, and STP on the ordinate means standard temperature and pressure. The smaller the molecule, the larger the adsorption volume. Figures 2 and 3 show the adsorption isotherms of the various gases on the defatted rice flour and defatted corn fiber ($45\ \mu\text{m}$ in the mean particle diameter) in low relative pressure, less than about 0.35, since it was enough to calculate the monolayer value. Though the results for the defatted corn fiber of $71\ \mu\text{m}$ in mean particle diameter are not shown here, the adsorption isotherms were similar to those shown in Figs. 2 and 3. As Figs. 1 through 3

Fig. 1. Adsorption Isotherms of Various Gases on Defatted Wheat Flour (mean particle diameter $26\ \mu\text{m}$). (◆), argon; (●), nitrogen; (▼), krypton; (●), ethane; (■), propane; (▲), butane.

Fig. 2. Adsorption Isotherms of Various Gases on Defatted Rice Flour (mean particle diameter $26\text{ }\mu\text{m}$). ($\circ$), argon; ($\circ$), nitrogen; (Δ), krypton; ($\square$), ethane; ($\diamond$), propane; (∇), butane.

Fig. 3. Adsorption Isotherms of Various Gases on Defatted Corn Fiber (mean particle diameter $45\text{ }\mu\text{m}$). ($\circ$), nitrogen; (Δ), krypton; ($\square$), ethane; ($\diamond$), propane; (∇), butane.

show, the adsorbed volume decreased as the adsorbent molecular size increased, but the point of interest is the dependence of the monolayer moles (n_m) of the gases on the cross-sectional areas (σ) of the gases.

Figure 4 shows sample B.E.T. plots of propane gas for three samples. Good linear relations were obtained. The value of V_m was obtained from the intersection of the ordinate and the slope of the lines according to Eq. (5), from which n_m was calculated by Eq. (6).

Figure 5 shows the relation between monolayer values (n_m) and molecular cross-

sectional area (σ). Linear relations of $\log n_m$ vs. $\log \sigma$ were obtained. Fitting these data to Eq. (2), the fractal dimension D_σ for the defatted materials and active carbon was calculated as shown in Table II. For the defatted corn fibers of $45\text{ }\mu\text{m}$ and $71\text{ }\mu\text{m}$ in particle diameter, the value of n_m was higher for the former than the latter as shown in Fig. 5, but the fractal dimension D_σ was not very different. In Table II, the value of D_s found in our preceding paper⁵ using the same samples as used in this paper is shown for comparison.

Fig. 4. B.E.T. Plot to Calculate Monolayer Values of Propane Gas. Defatted wheat flour, (○); defatted rice flour (△); defatted corn fiber, (□).

Cross-sectional Area of Molecules σ [$\text{\AA}^2$]

Fig. 5. The Relation between Monolayer Values n_m and Cross-sectional Area σ of Molecules.

Defatted wheat flour, (○); defatted rice flour (△); defatted corn fiber, (□) for $45\ \mu\text{m}$ and (■) for $71\ \mu\text{m}$; and active carbon, (◇).

Table II. COMPARISON BETWEEN D_s AND D_σ OF THE SAME MATERIALS

Sample	D_s	D_σ
Defatted rice flour	2.29	2.10
Defatted wheat flour	2.55	2.67
Defatted corn fiber		
$45\ \mu\text{m}$	2.61	1.59
$71\ \mu\text{m}$	2.61	1.50
Active carbon	—	2.10

Discussion

Judging from the value of D_σ , the surfaces of defatted rice flour and active carbon used in this research were relatively smooth, while the surface of defatted wheat flour was irregular and fractal in nature. That is, the specific surface area of the defatted wheat flour was differently recognized by different size molecules. Pfeifer *et al.*³⁾ showed that fractal dimension D_σ of active carbon changed from 3.03 to 1.94 with the progress of the degree of activation. Therefore, the active carbon used in this report was probably a highly activated one.

The value of D_σ is usually considered²⁾ to be between 2.0 and 3.0. However, D_σ for the defatted corn fibers were 1.59 and 1.50. This might happen for two reasons. One is the effect of some remaining lipid that absorbed hydrocarbon gases, making the "monolayer" adsorption incorrect. The defatting of the materials used was not complete, as shown in our preceding paper⁵⁾ by chemical analysis. And, even if the defatting be complete, it would not be certain that the gases were adsorbed only on the "surface" of a fibrous material. The surface structure of biological materials to be measured has an uncertainty in its definition. The other reason may be the effect of molecular shape. A long molecule might not go into a

hole which a sphere of the same cross-sectional area could go into. On the other hand, a long molecule might be packed more densely than the sphere on the surface. The constraint $D_s=2-3$ may have to be examined more carefully.

Comparison of D_s obtained in our preceding paper⁵⁾ with D_σ obtained in this paper (see Table II) shows that, although the differences between D_s and D_σ were not significant for the defatted rice flour and defatted wheat flour, the value of D_s in general may not be equal to D_σ as shown for the defatted corn fiber. This suggests that D_σ does not necessarily evaluate a simple surface structure as previously stated for corn fiber. The inequality between D_s and D_σ was also observed by Nagai and Yano⁶⁾ for xero-gels of starch. The assumption $D_s=D_\sigma$ adopted by Pfeifer *et al.*⁴⁾ may not be applicable in general.

Since the values of D_s and D_σ were estimated as shown in Table II, the monolayer moles of a gas adsorbed on a gram of sample solids, n_m , and so the specific surface area recognized by the gaseous molecule, S_w , were predicted as a whole by Eqs. (3) and (4), respectively, as a function of d_p and σ .

The fractal analyses made in our preceding paper⁵⁾ and in this paper show a way for the

quantitative evaluation of irregular structure of food materials, which may be used in food processings for improvements of adsorption selectivity, mass transfer characteristics including surface diffusion, reaction characteristics on solids, and physical properties including texture.

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