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ORIGINAL CONTRIBUTION

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Surface structural analysis of fine silica powder modified with butyl alcohol

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Abstract The surface structure of modified silica powder has been studied by various experiments and simulations. In addition, the effect of surface structure on wettability has also been investigated. Nonporous silica powder was modified with *n*-and *t*-butyl alcohol. Two series of the modified silica surfaces were characterized by fractal dimension analysis from isotherms with some kinds of adsorptives. The fractal dimensions of the two series of modified surfaces were different from each other with an increase in modified ratio. The fractal dimension of the surface modified with *t*-butyl alcohol (t-modified surface) increased monotonously with butoxy group density. It is thought that the structure of the *t*-butoxy group is rigid and that the *t*-butoxy group cannot change its conformation. On the other hand, the variation of the surface fractal dimension value for the surface modified with *n*-butyl alcohol (n-modified surface), whose structure is flexible, was unique compared with the t-modified surface. Such discrepancy was assumed to be caused by the difference in the structure of the modifier and the assembled state of modifiers between the t- and n-modified surfaces. In order to investigate the variation of surface structure of the surface modified by the butoxy group with an increase in modified ratio, molecular dynamics simulations were performed. By comparing the results of these simulations with experimental results, it has been clarified that the variation in the mobility of the methyl group in the *n*-butoxy groups was closely related to the change in the surface fractal dimension value for the n-modified surface. It was then elucidated that this mobility change was caused by steric hindrance among the groups. Furthermore, the variation of conformation in the *n*-butoxy groups, which was obtained from molecular dynamics simulations, was in good agreement with the change in the wettability of the n-modified surface. It is suggested that the surface density of the modifier, the covering structure and the bulkiness significantly influence the wettability of the modified surface.

Key words Adsorption · Surface fractal · Silica · Chemical surface modification · Molecular dynamics simulation

Introduction

Surface modification of powders with alcohol and alkylsilane is one of the most significant methods for industrial use because it prevents particle aggregation and adhesion. Recently, powder size has progressed to the micron size to produce highly functional and highly efficient materials. For studying the surface modification of powders, macroscopic or microscopic techniques and investigations have been developed. On the other hand,

questions arising from observations on a molecular scale of the modified surface structure have remained unresolved. For more functional and efficient application, it is necessary to evaluate the details of such nanoscopic modified surface structures.

The effects of surface roughness on wettability have been discussed by many investigators [1–3] who have studied the microscopic surface structure and the wettability, information on which was obtained from scanning electron microscopy and contact-angle experiments, respectively. Geometric structure was also studied nanoscopically using several techniques: scanning tunneling microscopy (STM), atomic force microscopy, gas adsorption isotherms. Avnir and coworkers [4–7] researched the fractal dimension of various oxides and the adsorption mechanisms onto their adsorbents. Fractal dimension was introduced by Avnir and coworkers to evaluate solid surface roughness geometrically. Williams and Beebe [8, 9] obtained the surface fractals of graphite and mica from STM images. Ismail and Ismail [10] attempted to combine fractal data from several adsorption isotherms with STM results in order to investigate carbon fiber surfaces.

Molecular dynamics (MD) simulations were used to evaluate the structure in the molecular order, for example, rotation and conformation about the alkyl chain in alkanes, Langmuir–Blodgett (LB) films, monolayers and bilayers [11–17]. Yarovsky et al. [17] performed MD simulations on the silica-based stationary phase of reversed-phase liquid chromatography. They concluded that the thickness of the butyldimethyl sililated layer increased at higher ligand density: this mechanism was responsible for the flexibility of butyldimethyl ligand conformations. However, they obtained only an understanding by chromatography and did not characterize the surface geometrical structure.

Nanoscopic observation is so difficult that one experiment alone cannot necessarily determine the surface structure on a molecular scale; therefore, it is necessary to combine two methods to obtain more detailed information. In this study, we researched the surface fractal dimensions of alkoxyated silica derived from a series of adsoprtion isotherms. MD simulations were performed in order to confirm the structure of the alkoxy groups on the silica surface. In addition, the effect of such surface structure on wettability was also investigated.

Experimental

Materials and surface modification

Fine silica powder (Aerosil 200) was obtained from Nippon Aerosil Co. Because the sample is nonporous and its surface is smooth, it is available to investigate the fractal degree of modified surface structures. Alkoxiation is the reaction of *n*- and *t*-butyl alcohol with the hydroxyl groups of the silica substrate. This reaction was carried out using the acutoclave method [18, 19] at 235 °C and under 30 atm for 1 h. The degree of surface modification was controlled by the alcohol content for 2.8 $-OH/nm^2$ surface density of the hydroxyl groups [20]. Before the measurements, the sample was degassed at 160 °C for 4 h. In this report, the samples modified by *n*- and *t*-butyl alcohol are named the n- and t-modified samples, respectively.

Determination of the surface density of the modifier

The surface density of the modifier was estimated from the number of modifiers and the specific surface area. The number of butoxy groups was determined using a TG/DTA 300 (Seiko Instrument) as shown in Fig. 1. The measurement was carried out under air at a flow rate of 250 ml/min. The value was calculated from the difference in the weight loss between modified sample (W_{CH}) and unmodified sample (W_{OH}). The combustion range in the differential thermal analysis curves was determined from the range of exothermic peaks. The specific surface area was obtained by nitrogen adsorption measurements.

Dispersion test

In order to judge the wettability of the alkoxylated silica surface, a dispersion test was performed [21]. It was a simple method in which the sample was introduced into water and stirred. Wettability was judged by visual observation. The hydrophilic sample powders dispersed in water, and the hydrophobic ones floated on water.

Fractal dimension analysis

The fractal dimension was examined from a series of adsorption isotherms [4–7]. Four adsorptive gases, nitrogen, xenon, *n*-propane

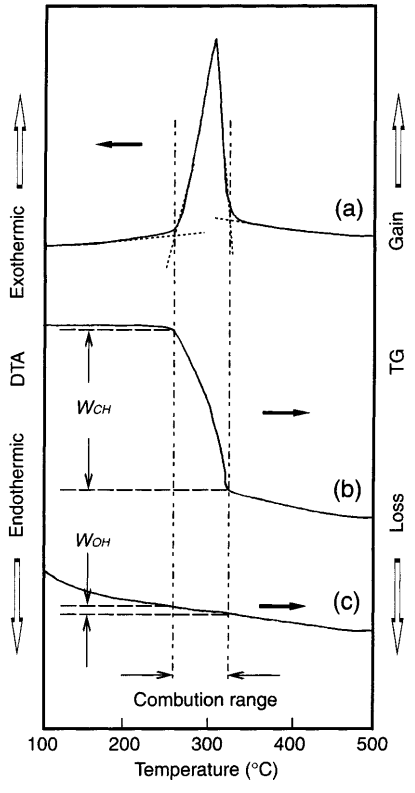

Fig. 1 Estimation of the number of butoxy groups introduced onto the silica surface from thermogravimetric analysis (*TG*) differential thermal analysis (*DTA*) *a* DTA curve for modified silica, *b* TGA curve for modified silica, *c* TGA curve for unmodified silica

and neopentane, were used as listed in Table 1. The monolayer adsorption capacity, V_m, was determined using the Bruneuer–Emmatt–Teller (BET) method. The nitrogen cross-sectional area, σ_{N2}, was taken to be 0.162 nm^2. The fractal dimension, D, was obtained from the following equation:

$$V_m = k\sigma_x - D/2 \ , \quad (1)$$

where σ_x is the cross-sectional area of the adsorbate, and k is a constant. A series of four adsorption isotherms brought about four V_m values using the BET method; therefore, D was calculated using Eq. (1) with the least-squares method.

MD simulation method

A molecular model was created as follows. The silica substrate contained 300 silicon and 570 oxygen atoms with a total surface −OH group density of 2.80 $-OH/nm^2$, which is similar to that for Aerosil [10, 20, 22]. Atom cooridnates for the amorphous silica substrate were fixed during the simulation. Model creation and MD calculations were performed using software from the CAChe work system (CAChe Scientific). The calculation was performed using MM2 parameters. A summary of the models is shown in Table 2.

The MD calculations were carried out as follows. The temperature of the simulation was set to 300 K. The energy of the molecular system is described by the sum of simple potential-energy functions which contain bond stretches, bond angles, dihedral angles, improper torsions, van der Waals forms, electrostatic interactions and hydrogen bonds. The van der Waals interaction for one pair of atoms separated by a distance greater than 0.9 nm was neglected. Methyl and methylene groups were treated as united atoms. The calculation step was every 1 fs, and atom configurations were saved every 100 time steps. Simulations were continued for 100 ps, and all 1000 sampling steps were stored in the trajectory file. Each calculation was carried out 3 times. The average of these three values was taken as a datum.

Results and discussion

Surface modification and determination

Surface modifications on silica powder with *n*- and *t*-butyl alcohol were completed well. The surface butoxy group density, d_B, was calculated using Eq. (2),

$$d_B(-OR/nm^2) = \frac{(\Delta w_{CH} - \Delta w_{OH})N_A}{M_w\ S_{N2}} \times 10^{18} \ , \quad (2)$$

where Δw_{CH} and Δw_{OH} are the ratio of weight loss for the modified and unmodified samples measured by thermogravimetry, M_w is the molar weight of the butyl group, S_{N2} is the BET specific surface area measured from the nitrogen adsorption isotherm and N_A is Avogadro's number. The relationships between alcohol content for sample weight and surface density of modification groups are shown in Fig. 2. The modification ratio is the fraction of converted hydroxyl groups in all amount of hydroxyl group. Prepared samples had various alkoxy group densities. Each conversion rate of the surface silanol was different. As shown in Fig. 2, a high-concentration sample was obtained in the n-modification. The highest butoxy group densities were 1.37 and 1.09 $-OR/nm^2$ for the n- and t-modified samples, respectively. These alkoxy groups have isomeric structures. The results of the maximum surface density investigations suggested that the cross-sectional area of the *n*-butoxy group on the surface was less than that of the *t*-butoxy group due to its flexible structure.

Table 1 Cross-sectional area of adsorbate

Adsorbate	Nitrogen	Xenon	Propane	Neopentane
Adsorption temperature (K)	77	183	183	273
$\sigma_x(nm^2)$	0.162	0.302	0.417	0.614

Table 2 Simulation model properties

Model	Butoxy group density ($-OR/nm^2$)	Silanol density ($-OR/nm^2$)
A	0.31	2.49
B	0.63	2.17
C	0.94	1.86

Dispersion test

If the sample disperses in water, the surface property is estimated to be hydrophilic; on the other hand, if the powder floats on the water surface, the surface is hydrophobic. The results of the dispersion test are shown in Table 3. The surface property change from hydrophilic to hydrophobic was observed at a density

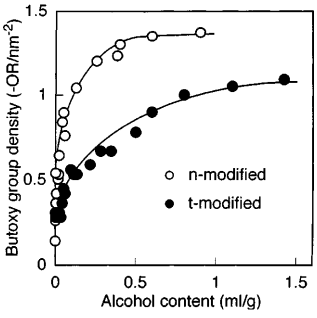

Fig. 2 The relationship between alcohol content for sample weight and surface density of modification groups

Table 3 Results of dispersion test

n-modified		t-modified	
Density ($-OR/nm^2$)	Dispersion state	Density ($-OR/nm^2$)	Dispersion state
0.53	Dispersion	0.56	Dispersion
0.76	Dispersion	0.67	Dispersion
0.84	Partial dispersion	0.70	Partial dispersion
1.04	Float	0.76	Partial dispersion
1.20	Float	0.90	Float

of 0.70 and 0.80 $-OR/nm^2$ for t-modified silica and n-modified silica, respectively. These results prove that the effect of hydrophobicity per butoxy group on the wettability of the t-modified sample was greater than that on the n-modified sample.

Fractal dimension analysis

The fractal dimension has been used to evaluate the geometric structure of surfaces, such as silica gel, carbon black, etc., which have complicated roughness and structural irregularities. The fractal dimension of surfaces modified with short-chain alcohols was also estimated using Eq. (1). To estimate the surface fractal dimension from the adsorption method using various adsorptives, the cross-sectional area, σ_x, and the monolayer capacity, V_m, were required for each adsorptive. Adsorptive properties are listed in Table 1. Each cross-sectional area of adsorbate except for nitrogen was estimated using the following method. The unmodified silica surface area calculated from each adsorption isotherm was assumed to agree with that obtained by nitrogen adsorption, since the Aerosil surface was expected to have a two-dimensional flat surface. The monolayer adsorption capacity was calculated from the adsorption isotherm for various modified samples. Logarithmic plots of V_m as a function of σ_x are shown in Fig. 3: a straight-line fit resulted. All the samples exhibited the same behavior, indicating that alkoxilated silica had a fractal structure.

The results of the fractal dimension analysis are shown in Fig. 4. The plots for the t-modified sample are linear, and the fractal dimension increased monotonously with butoxy group density. The structure of the *t*-butoxy group is rigid and the *t*-butoxy group cannot change its conformation. On the other hand, the *D* value for the n-modified surface does not indicate a monotonous increase because of the ability for conformational change in the alkyl chain. The curve for n-modification surfaces was divided into three regions at about 0.40 and 0.70 $-OR/nm^2$. These facts suggest that the conformation of *n*-butoxy groups changes in the three regions. The curve in region I shown in Fig. 4 indicates that the *n*-butoxy groups tend to lie parallel to the surface because of low surface density; however, the curve in region III shows that the *n*-butoxy groups stand perpendicular to the surface because the space of the *n*-butoxy group to move freely is limited by steric hindrnce among the *n*-butoxy groups. Region II is designated as the transition state form I to III. The conceptual chart for the variation of surface structure is illustrated in Fig. 5. The increase in *D* in region III would be related to the assembled state of the *n*-butoxy group. It is assumed that the assembled state of the *n*-butoxy group is not one monolayer, like a LB monolayer, but some divided blocks, such as a table mountain, for the random distribution and high density of the *n*-butoxy group. The change in number and bulkiness would cause an increase in *D* in region III.

The wettability of t- and n-modified silica changes at *D* values of 2.41 and 2.24, respectively. It is suggested that an appropriate height of the modifier is needed for a change in wettability [21]. Furthermore, it is interesting that the change in the wettability for n-modified silica in comparison with t-modified silica was observed at a low

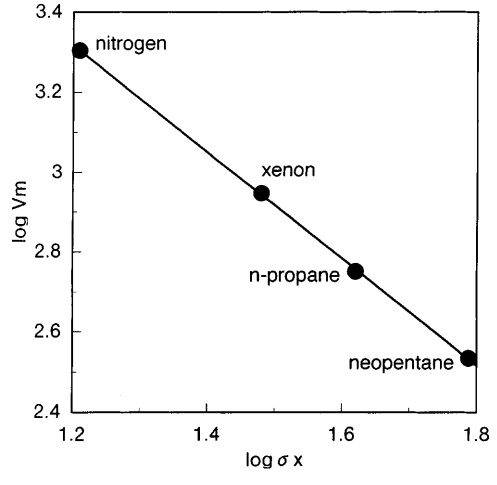

Fig. 3 Monolayer volume, V_m, as a function of the cross-sectional area, σ_x, at a concentration of 1.09 $-OR/nm^2$

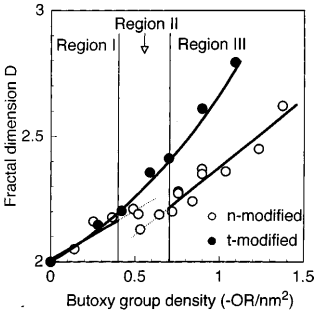

Fig. 4 The fractal dimension values as a function of the *n*-butoxy group density on the silica surface

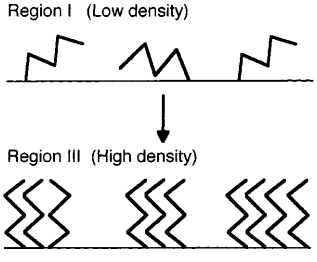

Fig. 5 Change in surface structure with surface modification

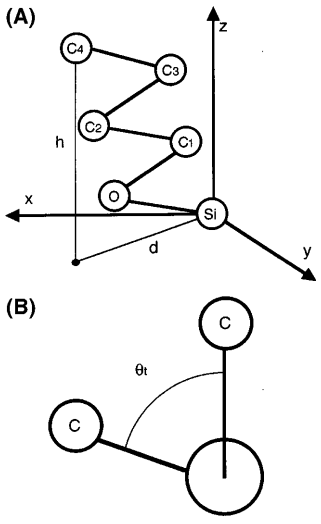

Fig. 6 Schematic illustrations of the modifier model used for the molecular dynamics simulation. **A** structure of the *n*-butoxy group attached to the silica surface; *h* is the height of the terminal methyl group from the silica surface and *d* is the distance between a silicon atom and the projection position of the terminal methyl group for the silica surface. **B** Torsion angle of a butoxy chain indicating the dihedral angle, θ_τ

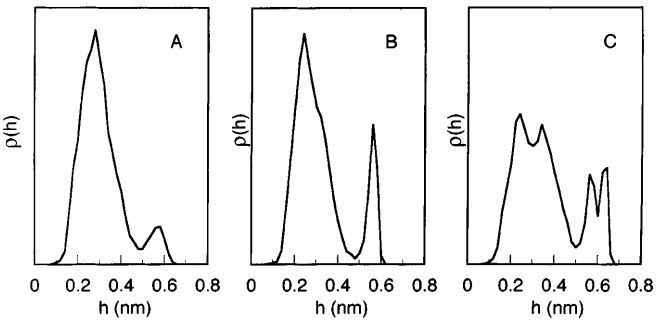

Fig. 7 Distribution of *h*: density **A** 0.31, **B** 0.63, **C** 0.94 –OR/nm^2

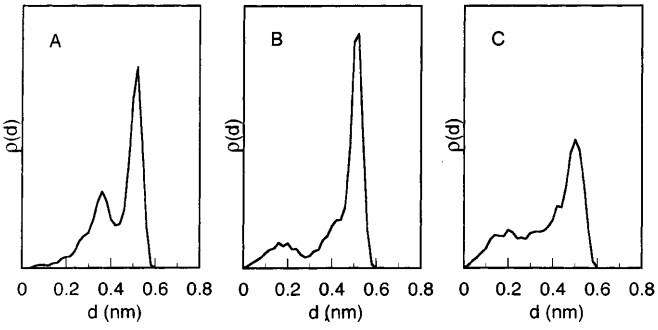

Fig. 8 Distribution of *d*: density **A** 0.31, **B** 0.63, **C** 0.94 –OR/nm^2

D value and at a high density of the butoxy group. The difference would be affected by the bulkiness of the modifier [21]. These results indicate that the steric structure of the *n*-butoxy groups which cover the surface is effective in obtaining a hydrophobic surface.

Variation of conformation in the *n*-butoxy group observed by MD simulations

MD simulations produced detailed information on the dynamic conformation of alkoxy chains. Three modified surface models, designated as A, B and C, each having different numbers of surface alkoxy groups, are shown in Table 2. The simulation was started in the state of all-trans alkyl chains, the structures of which were optimized. To analyze the properties of the steric structure of the butoxy groups, the two variables shown in Fig. 6A were used: *h*, which is the height of the terminal CH_3 groups from the silica surface, and *d*, which represents the distance from the silicon atom attached to a butoxy group to the projection of its terminal CH_3 on the surface. Distributions of *h* and *d* are shown in Figs. 7 and 8, respectively. The terminal CH_3 group position reflects the adsorptive structure of the butoxy groups such as standing up or lying down on the surface.

The height and distance distributions of model A exhibit sharp peaks at about 0.28 nm (Fig. 7A) and 0.54 nm (Fig. 8A), respectively. Small *h* values and large *d* values suggest that the butoxy groups lie parallel to the silica surface to take a low surface energy. In the case of model B, as shown in Figs. 7B and 8B, these same tendencies were recognized; therefore, the *n*-butoxy groups are considered to be lying in the medium density of the modifier groups. However, it was seen that the area having small *h* values slightly decreased and the area of large *h* values increased compared with the results of model A. The small *d* value at about 0.18 nm also increased slightly; therefore, a few butoxy groups are considered to stand perpendicular to the surface in model B, and almost all the butoxy groups lie parallel to the surface as in model A. Model C displayed a different shape from the other two models. A decreasing main peak in the distribution curve shows the structural change of the butoxy groups. This high-density model has many butoxy groups standing up: the groups cannot lie on the surface because of crowding.

The other conformational observation was required to confirm such structural changes of the butoxy groups. The conformation scheme showing the trans-gauche isomeric rotation of the C_2-C_3 or C_1-O axis is shown in Fig. 6B. Statistical data of the C_1-O and C_2-C_3 rotational angles reveal the conformational torsion of each segment. The distributions of the rotational angles of the no. 3 (C_2-C_3) and no. 1 (C_1-O) axes in model A are shown in Fig. 9. The torsion angle is the dihedral angle of four connected atoms; therefore, 180° is the complete

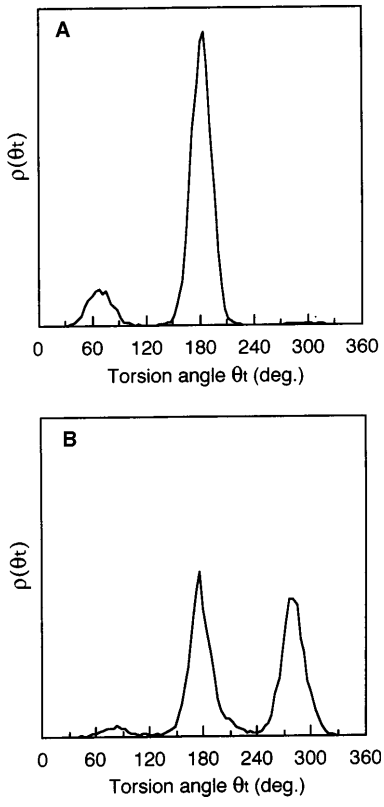

Fig. 9 Torsion angles of a butoxy chain at 1.09 $-OR/nm^2$. **A** C_2-C_3, **B** C_1-O

trans conformation state. The C_1-O torsion distribution was broad, and the right distribution exhibited a gauche structure; therefore, the C_1-O bond rotates frequently, while the C-C bond rotation is difficult in the butoxy group configuration, because the trans form is superior to the gauche form in the crowded distributions. From the previous results of *h* and *d*, the structure of the *n*-butoxy group on the surface was mainly caused by C_1-O bond rotation.

Mobility of the methyl groups in the *n*-butoxy group observed by MD simulations

MD simulations also resulted in the understanding of the mobility of the butoxy groups. The time dependence of the average mean squared displacements of individual terminal groups over the all chains in simulation were most available to understand the mobility of hydrocarbon chains. The mobility of the methyl groups at each density is shown in Fig. 10. At 0.31 $-OR/nm^2$, the high mobility of the methyl groups indicates that the alkyl chains are more flexible than those in the models at high density; however, the mobility decreased at concentrations above 0.5 $-OR/nm^2$. Such information concerning

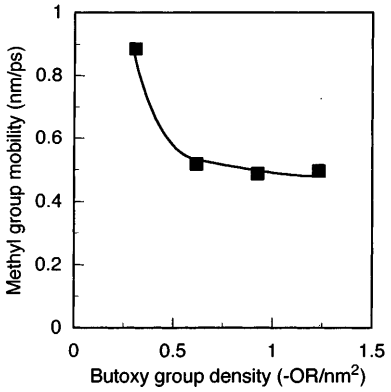

Fig. 10 Mobility of terminal methyl groups as a function of *n*-butoxy group density

the mobility of the butoxy groups is in accord with the results obtained by fractal dimension analysis.

Relationship between experiment and simulation

The fractal dimension analysis demonstrated that the behavior of the variation of *D* changed after and before 0.40 $-OR/nm^2$ *n*-butoxy group density. This result suggested that *n*-butoxy groups lying parallel to the surface become unable to move freely due to their concentration. From MD simulations, the methyl group mobility at a density of 0.31 $-OR/nm^2$ was more mobile than that at 0.62 $-OR/nm^2$. The experimental value of about 0.40 $-OR/nm^2$ obtained from the analysis of the fractal dimension is between the simulation values of 0.31 and 0.62 $-OR/nm^2$; therefore, the simulated results for the mobility change of the *n*-butoxy group were consistent with the experimental result.

On the other hand, in MD simulations, a structural difference of *n*-butoxy groups was observed between model B (0.62 $-OR/nm^2$) and model C (0.92 $-OR/nm^2$). The surface property change from hydrophilic to hydrophobic for the n-modified sample occurs at 0.84 $-OR/nm^{-2}$, which was obtained using a preferential dispersion test. This value is in the range 0.62–0.92 $-OR/nm^2$ of the MD simulation results; therefore, it is proved that the molecular ordered structure is closely related to surface wettability.

The comparisons between experimental and simulated results lead to the following considerations about the n-modified surface. The steric hindrance of the *n*-butoxy groups occurs at about 0.40 $-OR/nm^2$, when the *n*-butoxy groups stand perpendicular to the surface. Furthermore, the C-C bond in the *n*-butoxy groups takes a trans conformation, and the C_1-O bond rotates to the minimum energy with increasing surface density. As a result, *D* increases in a different manner in the initial increasing region. It is further shown that the

variation of surface structure is closely related with the change at about 0.84 $-OR/nm^2$ to hydrophobic from hydrophilic on the n-modified sample surface.

Conclusions

Silica powder was modified with *n*- and *t*-butyl alcohol. Two series of silica surfaces with various concentrations were characterized by fractal dimension analysis. Various experimental phenomena caused by the structural changes of modification groups have been confirmed statistically by MD simulations. The following results were obtained from this study.

1. The properties of the modified surface depend on the structure of the modifier introduced and on the surface of the original structure. Such covering structure of the modifiers is influenced by the number and the structure of the modifiers.
2. The n-modified surface changes with increasing surface density of the modifier to some complicated structure, and the mobility of the *n*-butoxy groups changes greatly at about 0.40 $-OR/nm^2$.
3. Result 2 is confirmed from MD simulations.
4. The n-modified surface structure variation with modifier crowding is mainly due to C-O and Si-O bond rotation rather than the C-C bond rotation of the butoxy groups.
5. The change in the wettability of the modified surface is influenced by the surface density of the modifier, the covering structure and the bulkiness.

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