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Effect of steric hindrance on surface wettability of fine silica powder  
modified by *n*- or *t*-butyl alcohol

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## Abstract

Fumed silica is an important industrial material, which is widely used in medical, cosmetic, and electronic products. One important industrial application of the fumed silica powder is using it as fillers, which are key materials for reinforcing the high-performance / high-functional industrial products. However, the use of fumed silica as filler is limited to micrometer or millimeter sized particles, because nanometer sized silica particles tend to aggregate. In this study, the surface of fine silica powder is modified with *n*- and *t*-butyl alcohols, which exhibit different steric hindrance effects. The surface wettability of each modified silica powders is determined in two ways: macroscopic and microscopic wettability. Macroscopic wettability refers to preference dispersion test and microscopic wettability refers to evaluation of the molecular level by Fourier transform infrared spectroscopy (FT-IR). The modification ratio of each sample is confirmed by thermogravimetry-differential thermal analysis (TG-DTA), and the hydrophobicity of these modified silica powders is evaluated by the preference dispersion test. Molecular level evaluation of surface wettability by FT-IR confirms an obvious structural difference due to the steric hindrance of the *n*- and *t*-butoxy groups on the surface of silica. In addition, a correlation between macroscopic and microscopic evaluation results for the surface wettability of modified silica powders is confirmed.

**Keywords:** Silica, surface modification, FT-IR, preference dispersion, butyl alcohol

## 1. Introduction

Fumed silica is a unique industrial material, thanks to its extremely small particle size, large surface area, and high purity [1]. Fumed silica is widely used in medical products as glidant [2], in cosmetics as sun protection agent [3], in electronics as chemical-mechanic planarization (CMP) [4,5], in paints and printing inks as thickening agent [6-8], an anticaking agent in the processing of dry materials, and in thermal insulators in high temperatures as high as 1000 °C. Another important industrial use of the fumed silica powder is using it as filler. Silica fillers are key materials for reinforcing the high-performance / high-functional industrial products [9,10] and recently high performance fillers, which can answer divers industrial requirements are desired. Nanosized silica fillers show an advantage over their micrometer or millimeter sized counterparts thanks to their high surface area, which leads to better reactivity and adhesion between filler and matrix particles. However, nanosized silica particles usually suffer from aggregation [11-13], which is nanosized particles tend to stick to each other due to the high surface area. Therefore, the development of monodisperse silica nanoparticles, which hardly aggregate is of great importance for both industrial and academic applications.

Another factor that causes aggregation in silica particles is hydroxyl groups (-

OH), which are present on the surface of fumed silica particles [1]. These hydroxyl groups can be in the form of isolated hydroxyl groups, hydrogen-bonded hydroxyl groups, geminal hydroxyl groups, and siloxane groups, which usually facilitate the aggregation of silica particles. Therefore, the surface of silica particles is usually modified by various functional groups like alcohol [14,15], silane coupling agent [16-18], and silicone oil [19,20] in order to prevent them from aggregation. Determining the amount of modification is also important and evaluation methods like measuring the weight loss by thermogravimetric and differential thermal analysis (TG-DTA) [11,15], examining the wettability by preferential dispersion test [15], measuring total organic carbon content [1], and measuring the contact angle between the silica surface and water [21,22] have been reported. However, to the best of our knowledge a systematic study, which investigates the interaction of water molecules and modifiers present on the surface of silica particles is lacking. Molecular level understanding of the surface structure of modified silica particles is also important for improving the performance of silica nanoparticles, i.e., the wettability of a fumed silica surface is dependent on the molecular structure of the functional species on the surface of silica particles [23].

Fourier Transform infrared spectroscopy (FT-IR) has been widely used for observation of fumed silica surfaces and the states of their hydroxyl groups [24]. However,

a comparison between macroscopic and microscopic results will help to obtain a better view of the surface wettability of modified fumed silica surfaces. In the present study, the wettability of fumed silica surfaces modified by two different structures of butyl alcohols is measured. Here, preference dispersion test in water is used as macroscopic wettability evaluation method, and water vapor adsorption test determined by FT-IR is used as microscopic wettability evaluation method, and a mechanism for the formation of a water film on the surface of silica is proposed in molecular level.

## **2. Experimental**

### **2.1 Materials**

Fumed silica powder (Aerosil 200, A200) is provided by Nippon Aerosil Co., Ltd. A200 is non-porous and its surface is smooth, it is adequate material to investigate their surface structures macroscopically and microscopically. The specific surface area (200 m<sup>2</sup>/g) is measured using the Brunauer-Emmett-Teller (BET) method by nitrogen adsorption isotherms [25]. *n*- and *t*-butyl alcohols (special chemical grade, Kanto Chemical Co., Inc.) are used as modifying agents, and *n*-hexane is used as solvent.

## 2.2 Surface modification

Surface modification of the fumed silica is carried out using the autoclave [26, 27]. 2.0 g of A200 sample is dispersed in *n*-hexane containing 0–1.4 ml/g of either *n*- or *t*-butyl alcohol. The samples are dispersed in *n*-hexane and placed in the autoclave system. Autoclave system is purged by N<sub>2</sub> gas for 5 min to completely remove the air. Finally, the system is heated at 260°C for 1 h at 30 bar.

## 2.3 Evaluation of the Surface Structure

The proportion of butoxy groups introduced onto the silica particles is determined by thermogravimetry-differential thermal analysis (TG-DTA; TG/DTA300 SSC 5200H, Seiko Instrument, Inc.). Measurements are conducted in air flow of 250 ml/min at up to 500 °C with a heating ramp of 20 °C/min. The modification ratio of butoxy group  $\theta$  (%) on the silica surface is calculated using the following equation:

$$\theta(\%) = \frac{(\Delta G/y_3 - w) \times N_A}{mw \times S \times N_{OH}} \times 100 \quad (1)$$

where  $\Delta G$  is the weight loss of the modified sample measured by TG-DTA,  $y_3$  is the initial weight of the modified sample,  $w$  is the weight loss of surface silanol groups from unmodified silica,  $mw$  is the molar weight of the species used for modification,  $S$  is the BET specific surface area calculated from the nitrogen adsorption isotherm,  $N_A$  is

Avogadro's number, and  $N_{\text{OH}}$  is the surface silanol density (-OH/m<sup>2</sup>) [11, 28].

The extent of silica surface modification is also observed using FT-IR (IR 5300, Jasco Corporation; operated at a resolution of 2 cm<sup>-1</sup> and with 16 scans per spectrum). The modified samples are molded and placed into a sample cell. The system is depressurized to 10<sup>-1</sup> Pa, and the sample is pretreated by degassing at 160°C. FT-IR spectra are quantitatively analyzed. Absorbance at 1864 cm<sup>-1</sup> is used as the standard peak because it is reported to be proportional to the thickness of the sample pellet [29]. The absorbance of the modifiers is examined in the range of 2800–3000 cm<sup>-1</sup>.

#### **2.4 Determination of the amount of water vapor adsorption by FT-IR**

The microscopic wettability of modified silica is determined by measuring water vapor adsorption using FT-IR [30]. 0.02 g of modified silica pellet is prepared with a diameter of 13 mm at 0.7 kPa using die set for compaction. The pellet is placed in a sample cell, and the system is evacuated for 4 h at 160 °C. The sample chamber is cooled to room temperature and the IR spectrum is obtained. Subsequently, water vapor is introduced into the sample chamber until the relative pressure is about 0.1. After adsorption reached equilibrium, the FT-IR spectrum is recorded. These steps are repeated with increasing vapor pressure until the maximum relative pressure is reached. The

amount of water vapor ( $S_{OH}$ ) is calculated from the areas of the silanol peaks as follows:

$$S_{OH} = \frac{S_A - S_{CH}}{I(1864 \text{ cm}^{-1}) - I(2450 \text{ cm}^{-1})} \quad (2)$$

where  $S_A$  is the area of the peaks in the 2450–4000  $\text{cm}^{-1}$  region,  $S_{CH}$  is the area of the peaks in the 2750–3000  $\text{cm}^{-1}$  region which indicated the C-H stretching region, and  $I(1864 \text{ cm}^{-1})$  and  $I(2450 \text{ cm}^{-1})$  are the absorbance at the respective wavelengths.

## 2.5 Preference dispersion test

The macroscopic wettability of the modified silica samples is determined by a preference dispersion test. Fumed silica sample is dried at 160 °C for 4 h. The sample is then stirred in distilled water, and the wettability is determined by visual observation it is noted that hydrophilic samples are dispersed in the water, while hydrophobic samples are floated on the water surface. The samples are slowly placed in a thermostatic tank at 30 °C, and observed for 6 h with an additional dispersion every 30 minutes [15, 31].

## 3. Results and Discussion

### 3.1 Characteristics of modified fumed silica surface

Degree of surface modification ratio,  $\theta\%$ , as a function of alcohol content is shown in Fig. 1. Here, the modification ratio is the fraction of modified hydroxyl groups,

relative to the total hydroxyl groups on the surface of unmodified silica. It is shown that modification ratio increases more drastically for *n*-modified silica when butyl alcohol content increases, as compared to *t*-modified silica. The modification ratios of *n*- and *t*-silica are 30% and 20% when 0.1 ml/g of *n*- and *t*-butyl alcohol are used, respectively. As the alcohol concentration increases to >0.1 ml/g, the modification ratio increases at a slower rate than that at lower concentrations. Decrease of modification rate at butyl alcohol concentrations higher than 0.1 ml/g is due to the steric hindrance of those modification agents that are already present on the surface of silica particles. The highest modification ratios obtained for *n*- is 49% and *t*-silica is 39%, when the adding amount of alcohols are 0.5 ml and 1.5ml, respectively.

The surface modification by butyl alcohols proceeds via a dehydration reaction between hydroxyl groups on the silica surface and R-OH groups in the alcohol. As a result, Si-OH is replaced by Si-O-R, where R is either *n*- or *t*-butoxy groups. The differences in the modification ratios of *n*- and *t*- modified silica are attributed to the chemical structure of the butyl alcohols. The *n*-butoxy group is relatively narrow and their conformation is changeable (flexible), while the *t*-butoxy group is very bulky and their conformation is hardly changeable (rigid). Therefore, difference in the nature of chains between *n*-butoxy and *t*-butoxy isomers is the main reason of the difference in modification ratio. Effect of

structural differences are confirmed by calculating the area of each butoxy group occupied on the silica surface [32, 33]. Results are summarized in Table 1.

The theoretical occupation area of each butoxy groups,  $\sigma_1$ , is calculated from Van der Waals radii and Bond lengths.  $\sigma_2$  is occupation area of each type of butoxy group calculated based on the TG-DTA results by assuming 100% surface coverage of hydroxyl groups on silica surface at the maximum modification ratios (*n*-butoxy = 49% and *t*-butoxy = 39%).  $\sigma_3$  is occupation area of each type of butoxy group calculated from TG-DTA results assuming 100% surface coverage at the turning points of the modification ratios (turning point of *n*-butoxy and *t*-butoxy occur when modification ratio is 30% and 20%, respectively). The  $\sigma_1$  value of the *n*-butoxy groups varies in a range instead of one specific value, because of conformational changes. The lower limit ( $\sigma_1 = 0.3 \text{ nm}^2$ ) assumes that the *n*-butoxy groups are well oriented vertically on the silica surface, and the upper limit ( $1.7 \text{ nm}^2$ ) corresponds to the *n*-butoxy chains lying parallel to the silica surface. At the maximum modification ratio, the occupancy area for *n*-modified silica is calculated to be  $\sigma_2 = 0.7 \text{ nm}^2$ , while the theoretical minimum occupancy area of *n*-butoxy group ( $\sigma_1$ ) is  $0.3 \text{ nm}^2$ . At turning point the calculated occupancy area of *n*-modified silica is  $1.2 \text{ nm}^2$ , which is smaller than the theoretical maximum,  $1.7 \text{ nm}^2$ . In contrast, experimentally determined occupancy area for the *t*-butoxy group ( $\sigma_2 = 0.9 \text{ nm}^2$ ) is larger

than the theoretical value at the turning point,  $\sigma_1 = 0.6 \text{ nm}^2$ .

When the density of *n*-butoxy modifiers on the surface of silica is high, *n*-butoxy chains tend to be oriented perpendicular to the silica surface, which reduces the average occupancy area close to the theoretical minimum,  $0.3 \text{ nm}^2$ . In case of lower densities, *n*-butoxy chains will lay parallel to the surface of silica occupying an area close to the theoretical area,  $1.7 \text{ nm}^2$ . At the maximum modification ratio of *n*-modified silica with modification ratio of 49%, the average occupancy area of the *n*-butoxy groups is estimated to be  $0.3 \text{ nm}^2$ . This is not plausible because this theoretical value does not include steric hindrance. The occupancy area of  $1.2 \text{ nm}^2$  calculated at the turning point of *n*-modified silica with modification ratio of 30%, is more reasonable, as there is not enough space for all chains to lay parallel to the silica surface. Based on these results, *n*-butoxy groups experience significant steric hindrance at a modification ratio of 30%, above which the *n*-butoxy groups begin to be oriented perpendicular to the silica surface.

In addition to silanol groups, unmodified silica surfaces contain siloxane groups [1]. Hence, some sites are inaccessible to *t*-butoxy groups. The *t*-butoxy groups are significantly more bulky and less flexible than *n*-butyl chains, therefore they experience greater steric hindrance and  $\sigma_2 = 0.9 \text{ nm}^2$  is a reasonable occupancy area for the *t*-butoxy groups.

Fig. 2 shows the FT-IR spectrum of each type of hydroxyl group on silica surface. There are two types of hydroxyl groups on the surface of fumed silica particles: (1) free hydroxyl groups and (2) H-bonded hydroxyl groups [34]. Free hydroxyl groups can exist in two types of isolated and geminal types. Moreover, H-bonded hydroxyl groups can possess terminal H bonded and non-terminal H bonded hydroxyl groups. The spectral peak of the free hydroxyl groups occurs at  $3747\text{ cm}^{-1}$ , H-bonded hydroxyl groups at  $3740\text{--}3000\text{ cm}^{-1}$ , and terminal H-bonded hydroxyl groups at either  $3720$  or  $3725\text{ cm}^{-1}$  [35,36]. The IR spectra of the butoxy groups on the modified silica surfaces occur at  $3000\text{--}2800\text{ cm}^{-1}$  as a result of C-H stretching. Since the distance of H-bonded hydroxyl groups are short from their neighboring hydroxyl groups, it is reported that the H-bond interactions of terminal hydroxyl groups are weak, and therefore their IR peaks are shifted to either  $3720$  or  $3725\text{ cm}^{-1}$  [34].

Fig. 3 shows the FT-IR spectra of *n*- and *t*-modified silica at various modification ratios. The peak area of the free hydroxyl groups at  $3747\text{ cm}^{-1}$  decreases significantly with increasing modification ratio, and almost disappeared at the maximum modification ratios, 49% of *n*-silica and 39% of *t*-silica. The peaks at  $2800\text{--}3000\text{ cm}^{-1}$ , ascribed to alkyl chains, increase with increasing modification ratio. A similar trend is confirmed for both *n*- and *t*-modified silica particles; the increasing modification ratios

are in good agreement with results in Fig. 1.

### **3.2 Macroscopic wettability evaluated by preference dispersion test**

Preference dispersion test results which observed after 3h are shown in Fig. 4, and the photograph of the example samples shows Fig. 5. The *n*-modified silica samples with modification ratio of <30% are well dispersed in water, which means they are hydrophilic. *n*-modified silica samples with modification ratio of 30–32% are partially hydrophobic, and samples with modification ratio of >32% are completely hydrophobic. In contrast, *t*-modified silica sample is hydrophilic when modification ratio is < 25%, partially hydrophobic when modification ratio is 25%–26.5%, and completely hydrophobic when modification ratio is >26.5%. A comparison between Fig. 1 and Fig.4 shows that for *t*-modified silica the modification ratio and hydrophilic/hydrophobic turning points differ, while they are consistent for *n*-modified silica.

It is noted that *n*-modified silica with modification ratio of 30% and 32% are partially hydrophobic at first, however they become hydrophilic after being dispersed in water for 6 h, inferring that the surface of *n*-modified silica with modification ratio of 30–32% are hydrolyzed in water due to the accessibility of the Si-O-*n*Bu linkage because of the flexibility of *n*-butyl chains. Bulky *t*-butoxy groups, in contrast, remain stable even

after 6 hours because the Si-O-*t*Bu linkage is inaccessible by the surrounding water molecules.

### **3.3 Amount of water vapor adsorption on unmodified silica observed by FT-IR**

The water vapor adsorption isotherm and FT-IR spectra of unmodified silica under different relative vapor pressures are shown in Fig. 6. As shown in Fig. 6 a), at  $P/P_0 = 0.7$  a single water molecule is adsorbed onto each surface hydroxyl group [34]. At  $P/P_0 = 0.8$ , two water molecules are adsorbed on each hydroxyl group [34], suggesting that the surface hydroxyl groups are saturated with water molecules. However, free hydroxyl groups are still present on the surface of silica at  $P/P_0 = 0.8$ . The free hydroxyl peak at  $3747\text{ cm}^{-1}$  decreases with increasing relative pressure and a slight shift to lower wavenumber is observed at  $3720$  and  $3725\text{ cm}^{-1}$ , as shown in Fig. 6 b). These results demonstrate that water molecules are not uniformly adsorbed on the silica surface. Instead, they are partially adsorbed onto the H-bonded hydroxyl groups and formed a two-dimensional layer on the silica surface, as schematically illustrated in Fig. 7.

The water adsorption mechanisms on silica surfaces have been reported by Fuji [37]. The adsorption mechanism at low humidity and high humidity is shown in Fig. 7. As shown in Fig. 7(a), at low humidity water molecules undergo localized adsorption. As

humidity increases, more water molecules are adsorbed in a cooperative process, Fig. 7(b), at high humidity water molecules from the two-dimensional layer, Fig.7(c), resulting in greater water adsorption. The continuous formation of two-dimensional water layer followed by additional water adsorption result in the formation of multiple layers of water molecules on the surface of silica particles. The amount of water adsorption increases rapidly with high relative pressure. Finally, the formation of a continuous two-dimensional layer of water molecules affects the wettability of the silica surface. This water adsorption mechanisms has not been revealed by microscopic observation. Based on the Fig. 6, the formation of the two-dimensional layer and a continuous two-dimensional layer of water molecules were revealed by water vapor adsorption test on silica surface microscopically.

### **3.4 Microscopic wettability evaluated by the amount of water vapor adsorption by**

#### **FT-IR**

##### **3.4.1 Observation of water adsorption behavior on modified silica surface**

The observed water adsorption behavior of modified silica surfaces is explained based on the adsorption mechanisms of unmodified silica surfaces [37] as explained in the following. Based on the results of preference dispersion, *n*-modified silica with

modification ratio of 19% and *t*-modified silica with modification ratio of 20% are chosen as representative hydrophilic samples. In addition, *n*-modified silica with modification ratio of 49% and *t*-modified silica with modification ratio of 39% are chosen as representative hydrophobic samples. The water vapor adsorption of these modified silica particles is examined by FT-IR.

Fig. 8 shows the FT-IR spectra of hydrophilic *n*-modified silica with modification ratio of 19% and *t*-modified silica with modification ratio of 20% at different relative vapor pressures. In these modified silicas, the peak intensity of free hydroxyl group at  $3747\text{ cm}^{-1}$  decreases with increasing the relative pressure. However, the rate of peak area decrease is slower than that of the unmodified silica. In addition, similar peak shifts to lower wavenumber are observed in the  $3740\text{--}3680\text{ cm}^{-1}$  plateau.

The decrease in free hydroxyl groups is more significant for the *t*-modified silica with modification ratio of 20% sample than that of *n*-modified silica with modification ratio of 19% sample because: On one hand, *n*-butoxy groups lie flat on the silica surface, corresponding to  $\sim 0.5$  butoxy groups/nm<sup>2</sup>, and shielding free hydroxyl groups from water molecules [15]. On the other hand, *t*-butoxy groups are conformationally stable. Therefore, some of the remaining hydroxyl groups are protected from modification by steric hindrance of *t*-butoxy groups. The presence of the butoxy

groups hinders the formation of a continuous two-dimensional water layer, resulting in smaller peak reductions ( $3747\text{ cm}^{-1}$ ) and slighter shift ( $3740\text{--}3680\text{ cm}^{-1}$ ) compared to those of unmodified silica.

Fig. 9 shows the FT-IR spectra of the hydrophobic *n*-modified silica with modification ratio of 49% and *t*-modified silica with modification ratio of 39% samples at different relative vapor pressures. In these samples, all of the free hydroxyl groups are modified, and therefore do not appear in the FT-IR spectra. Two samples exhibit similar trends during water adsorption. The peak area of H-bonded hydroxyl group at  $3740\text{--}3000\text{ cm}^{-1}$  increases with increasing relative pressure. Although the surfaces of these samples are hydrophobic, the proportion of H-bonded hydroxyl groups increases because water molecules preferentially adsorb on these hydroxyl groups, resulting in the formation of a two-dimensional layer of water on the surface of silica particles. This result is in good agreement with those of unmodified and hydrophilic modified silica particles. Therefore, water molecules can adsorb onto H-bonded hydroxyl groups regardless of the surface status, although the accessibility of these hydroxyl groups is affected by surface modifications.

#### **3. 4. 2 Calculation of the amount of adsorbed hydroxyl groups from peak area of FT-**

## IR

Water vapor adsorption is estimated from the peak area of the hydroxyl group.

The relationship between the relative pressure and the O-H stretching peak area of H-bonded hydroxyl groups ( $4000\text{--}2450\text{ cm}^{-1}$ ,  $S_{\text{OH}}$ ) for *n*- and *t*-modified silica samples are shown in Fig. 10 a) and 10 b), respectively.  $S_{\text{OH}}$  is calculated by equation (2). Although the absorption peak of the free hydroxyl groups ( $3747\text{ cm}^{-1}$ ) is included within this spectral range, it can be ignored since its contribution is negligible compared to that of H-bonded hydroxyl groups. As shown in Fig. 10 a), the *n*-modified silica with modification ratio of 19% sample exhibit a similar trend to that of unmodified silica shown in Fig. 10 b), although the peak area in the spectrum of the former is smaller throughout the range of relative pressure test. The trends in the *n*-modified silica with modification ratio of 32% and 36% are similar for  $P/P_0 \leq 0.5$ , and changes are more sluggish than those of *n*-modified silica with modification ratio of 19%. For the *n*-modified silica with modification ratio of 32%, a significant increase in peak area is observed at  $P/P_0 \geq 0.5$ . The peak area for the *n*-modified silica with modification ratio of 36% increases more linearly with increasing the relative pressure.

As shown in Fig. 10 b), the unmodified silica shows the largest peak area of the samples and its hydroxyl group peak area gradually increases with increasing relative

pressure. The *t*-modified silica with modification ratio of 20% and 39% samples show similar trends and almost identical peak areas at  $P/P_0 \leq 0.5$ . The *t*-modified silica with modification ratio of 20% sample is hydrophilic, while *t*-modified silica with modification ratio of 39% sample is hydrophobic as confirmed by preference dispersion test. For *t*-modified silica with modification ratio of 20%, a significant increase in adsorption is observed at  $P/P_0 \geq 0.5$ , attributed to the shielding of free hydroxyl groups by *n*-butyl chains on the surface of *n*-modified silica with modification ratio of 19%.

At high relative pressures, water molecules are more strongly adsorbed on the H-bonded hydroxyl groups than the free hydroxyl groups. Therefore, the hydroxyl group peak area of unmodified silica gradually increases. In contrast, only a small fraction of free hydroxyl groups remains on *t*-modified silica with modification ratio of 39% because of its hydrophobicity. However, the water vapor adsorption of the H-bonded hydroxyl groups on the *t*-modified silica with modification ratio of 39% gradually increases. Although the surface of the *t*-modified silica with modification ratio of 20% is hydrophilic, water molecules are preferentially adsorbed on the H-bonded hydroxyl groups at low relative pressures. This proves that the initial water adsorption process at low relative pressure is similar for both *n*- and *t*-modified silica surfaces.

As already shown in Fig. 1, the steric hindrance effect of the *t*-butyl groups are

evident in the *t*-modified silica with modification ratio of 20% sample. At this modification ratio, a large amount of *t*-butoxy groups are supposed to be present on the surface of silica. However, its surface remains hydrophilic because of the presence of free hydroxyl groups. That is why a rapid increase in water adsorption is observed for the *t*-modified silica with modification ratio of 20% at  $P/P_0 \geq 0.5$ . In contrast, the *t*-modified silica with modification ratio of 39% is hydrophobic and only a small amount of free hydroxyl groups are expected to exist on its surface. Hence, the rapid increase in adsorption at  $P/P_0 \geq 0.5$  is not observed in the *t*-modified silica with modification ratio of 39%.

#### **4. Conclusions**

Fumed silica surfaces were modified with either *n*- or *t*-butyl alcohols at various concentrations. Changes in surface wettability were observed macroscopically by water preference dispersion tests and microscopically by the water vapor adsorption test determined by FT-IR. Following results were obtained.

1. Macroscopic water preference dispersion test confirmed that butyl alcohols with different molecular structures effectively modified the surface of silica particles with different hydrophobicity. Silica modified by bulky, rigid, *t*-butoxy groups was more

hydrophobic than *n*-butyl-modified silica.

2. Microscopic water vapor adsorption test by FT-IR confirmed that, water molecules preferentially adsorbed onto H-bonded hydroxyl groups during the initial stage of adsorption. Therefore, the hydrophobic effects of different structural surfaces became more distinct at  $P/P_0 \geq 0.5$ .
3. The hydrophilic/hydrophobic turning points of the *n*- and *t*-silica were in accordance with the observation results by the preference dispersion test and by the water vapor adsorption test. Furthermore, macroscopic and microscopic observation results were correlated.

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Table 1. Occupancy areas of *t*- and *n*-butoxy groups on silica surface.  $\sigma_1$ , is calculated from Van der Waals radii and Bond lengths;  $\sigma_2$  is calculated based on the surface coverage of hydroxyl groups on silica surface at *n*-butoxy = 49% and *t*-butoxy = 39%.  $\sigma_3$  is calculated from surface coverage at turning point of *n*-butoxy and *t*-butoxy occur when modification ratio is 30% and 20%, respectively.

Occupancy area	<i>n</i> -butoxy groups [nm <sup>2</sup> ]	<i>t</i> -butoxy groups [nm <sup>2</sup> ]
$\sigma_1$	0.3–1.7	0.6
$\sigma_2$	0.7	0.9
$\sigma_3$	1.2	1.4



## Figure captions

Fig. 1 Change in modification ratio of *n*-silica and *t*-silica as a function of amount butyl alcohol contents.

Fig. 2 FT-IR spectrum of each type of hydroxyl group on silica surface.

Fig. 3 FT-IR spectra of various modification ratio of *n*- and *t*- silica.

Fig. 4 Results of the preference dispersion test for *n*-silica and *t*-silica observed after 3h.

Fig. 5 Photograph of the hydrophilic and hydrophobic samples of the preference dispersion test.

Fig. 6 a) The water vapor adsorption isotherm and b) FT-IR spectra of unmodified silica under different relative vapor pressures.

Fig. 7 Adsorption mechanisms of water on silica particle surface.

Fig. 8 FT-IR spectra of modified silica at each relative pressure during the water vapor process obtained from modification ratio of 19 % of *n*-silica and 20 % of *t*-silica.

Fig. 9 FT-IR spectra of modified silica at each relative pressure during the water vapor process obtained from modification ratio of 49 % of *n*-silica and 39 % of *t*-silica.

Fig. 10 Relationships between relative pressure and spectrum area of -OH stretching for modification ratio of a) 19%, 32%, and 36% of *n*-silica b) 20%, and 39% of *t*-silica, and unmodified silica.