Surface Alkoxylation of Silicas by Mild Reactions with Alcohols

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The surface alkoxylation reaction of silicas was investigated under mild reaction conditions with some low-molecular-weight saturated aliphatic alcohols. Silica gels and porous silica glass were treated with liquid alcohols using a Soxhlet extractor below their boiling points. The number of formed alkoxyl groups was examined by both thermal analyses and infrared spectra. It was shown that some of the surface hydroxyl groups were easily esterified to alkoxyl groups, even by contact with the alcohols under mild reaction conditions. The degree of alkoxylation was higher for the silica gels than for porous silica glass. The adsorption isotherms of methanol vapor at room temperature were measured on silica gel samples which were previously activated at various temperatures. The adsorption equilibrium strongly depends on the pretreated temperature. The surface methoxylation reaction took place not only on the surface hydroxyl groups, but also on the siloxane bridges, even at room temperature.

The surface hydroxyl groups of silicas play an important role in determining various surface properties, such as the adsorption, surface acidity and wetting properties. It is known that these hydroxyl groups react with various chemical reagents. Many chemical reactions are applied not only for estimating the surface hydroxyl content, but also for surface treatments of particles.[1,2] On the other hand, the surface state of silicas depends on their past history, and is easily changed by the atmospheric conditions surrounding the particles. For example, water molecules adsorbed from the atmosphere on a dehydroxylated surface react, causing a rehydroxylation of the surface.

The surface alkoxylation reaction with alcohols is one of the typical reactions of the surface hydroxyl groups, and has been investigated as a surface treatment which can shift a hydrophilic surface to become hydrophobic. It was reported that the surface hydroxyl groups are almost completely esterified to alkoxyl groups by reactions under the critical points of alcohols.[3] However, it is expected that they are partly esterified to alkoxyl groups, even by mild reactions, under ordinary temperature and pressure. This is not often ignored in considering the surface properties of the particles in connection with their past history.

In the present work, alkoxylation reactions of silica surfaces were investigated by contact with various alcohols under mild reaction conditions. The reactions were carried out by contact with the liquid alcohols, and by adsorption of methanol vapor. The number of formed alkoxyl groups is reported for reactions with liquid alcohols. The adsorption mechanism of methanol vapor on a thermally treated surface is discussed.

Experimental

Contact with Liquid Alcohols. Two pure amorphous silica gels and a porous silica glass were used in this experiment. Silica gels were bulky "silicic acid" (100 mesh) obtained from Mallinckrodt Co. and "silica 60" (70—230 mesh) obtained from Katayama Chem. Co. Porous Vycor glass was obtained from Corning Co. (Corning code #7930) and divided into small particles, the diameter of which was about 2 mm. The materials were washed with concd HNO_3 in order to remove any adsorbed impurities on the surface. The remaining acid was thoroughly rinsed using redistilled water. In order to develop hydroxyl groups fully on the surface, the washed particles had been kept in redistilled water for one week. They were then predried at 120 °C for 48 h. The specific surface areas of the samples measured by N_2 adsorption using the BET method were 578 (silicic acid), 244 (silica 60), and 135 (Vycor glass) $m^2\,g^{-1}$, respectively.

After the sample particles had been dried at 150 °C for 24 h, they were treated with the condensed liquid alcohols by using the Soxhelt extractor for 24 h. This apparatus was used not only for the mild rection conditions, but also for operational simplicity. The water produced by the alkoxylation reaction could be removed out more rapidly than by simple contact. Special-grade alcohols, from methanol to 1-hexanol, were distilled and dried using a molecular sieve 3A before use. After contact with an alcohol, the sample particles were dried at about 20 °C above the boiling point of the alcohol under atmospheric pressure.

TG and DTA analyses were carried out using a Rigaku TG-DSC balance. After the physisorbed water and the remaining alcohols were fully desorbed at 180 °C, 0.1 g of the sample was heated up to 1200 °C in air at a heating rate of 10 °C min^{-1}.

The infrared spectra were measured using the simple diffusive reflection method, employing a Nippon-Bunko DS-701G with a DR-21 reflection equipment. 0.01 g of the dried sample was mixed with 0.1 g of KBr powder in the reflection cell. All of the spectra were recorded in air at room temperature without outgassing the cell.

Adsorption of Methanol Vapor. Adsorption isotherms of methanol vapor were measured on Mallinckrodt Silicic acid. Before isotherm measurements, the sample particles were heated at various temperatures from 200 to 600 °C under 10^{-3} Pa until equilibrium at that temperature was attained. Spectroscopic-grade methanol was redistilled and dried using a molecular sieve (3A) previously dried at 380 °C.

The first adsorption isotherm was measured at 25 °C (±0.1 °C) by the gravimetric method with a quartz spring balance. Methanol vapor was gradually introduced up to a relative pressure of about 0.8. In order to obtain fully equilibrated isotherms, each experimental point was determined after the sample had been exposed to methanol vapor for at least 3 h. After the first isotherm had been determined, the sample was degassed at 70—80 °C under 10^{-3} Pa. The amount of irreversibly adsorbed methanol for this treatment (Γ_{irr}) was first measured and then the second adsorption isotherm was determined. Thermal analyses and IR spectra measurements were carried out for the sample after determining the second isotherms.

Results and Discussion

Alkoxylation by Contact with Liquid Alcohols. Table 1 shows the surface hydroxyl content of an untreated sample at various temperatures. The weight loss up to 1200 °C in the thermal analysis was converted to the number of hydroxyl groups by the stoichiometry of the reaction

$$2\text{Si-OH} \longrightarrow \text{Si-O-Si} + H_2O. \qquad (1)$$

The surface area of the sample was assumed to be constant below 600 °C. The decrease of the surface area with increasing temperature seems to be small in this temperature range, as previously reported.[4,5] The obtained results were close to the values previously reported.[1,4,6]

Table 1. Surface Hydroxyl Content of SiO_2 at Various Temperatures

Temp./°C	Surface hydroxyl content/nm^{-2}		
	Silica 60	Silicic acid	Vycor glass
200	6.38	5.09	13.5
300	6.25	4.99	12.9
400	5.15	4.52	10.8
500	3.52	3.67	8.04
600	2.26	2.60	5.22

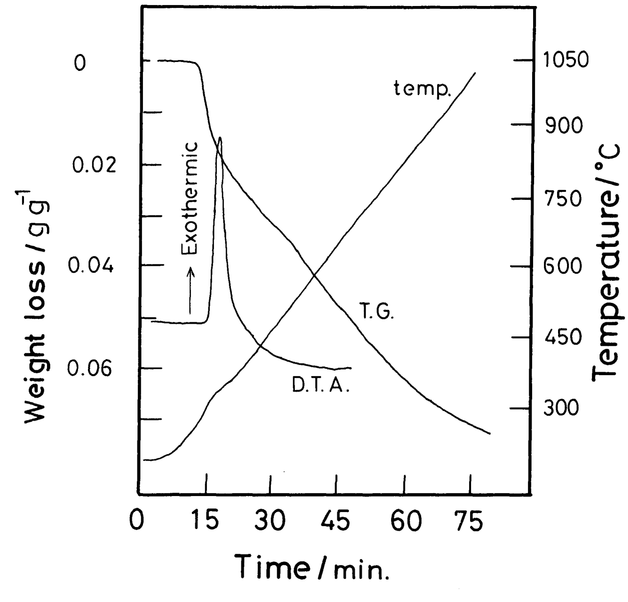


Fig. 1. TG and DTA profile for silicic acid treated by 1-propanol.

For those sample treated with the alcohols, DTA analyses showed exothermic peaks between 280 and 350 °C, as shown in Fig. 1. Also, a rapid decrease in the weight was shown at that temperature. These peaks were attributed to a thermal decomposition of the surface alkoxyl groups which were formed by the reaction

$$\text{Si-OH} + \text{R-OH} \longrightarrow \text{Si-OR} + H_2O. \qquad (2)$$

The number of the formed alkoxyl groups was estimated by the increase in the weight loss per unit surface area of the sample. ΔW_t was defined as the difference in the weight loss between the treated and untreated samples; $\Delta W_t = W_t(\text{treat.}) - \Delta W_t(\text{untreat.})$, where W_t is the weight loss in the TG analysis. ΔW_t is plotted against the molar weight of the alcohols (M) in Figs. 2—4. It can be seen that the amount of alkoxylation is higher for straight-chain alcohols than for branched-chain alcohols, and increases in the order *tert.-*<*sec.-*<*prim.-*. This agrees with the results regarding reactions under the conditions of higher temperatures and pressures.[3] Ballard et al. correlated this tendency to the effect of the cross-sectional area of the alkoxyl group.[7] They also reported that the number of the alkoxyl groups formed by the reaction with methanol was especially higher than that with the other straight-chain alcohols. The effective cross-sectional area of the methoxy groups is much lower than that of the higher

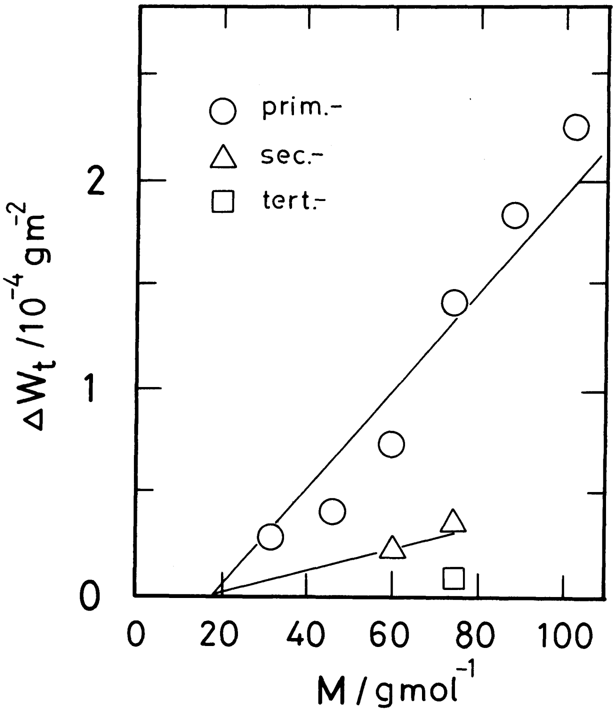


Fig. 2. Increase of the weight loss by TG analysis (ΔW_t) for silica 60 treated with various liquid alcohols.

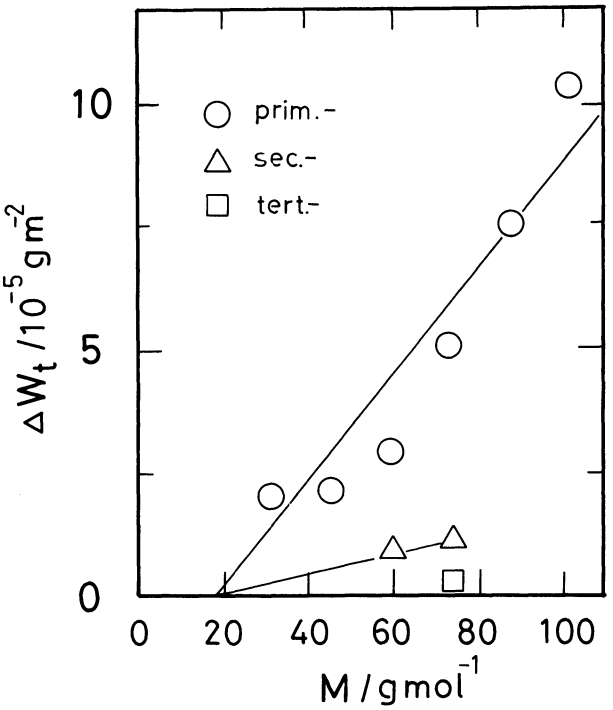


Fig. 3. Increase of the weight loss by TG analysis (ΔW_t) for silicic acid treated with various liquid alcohols.

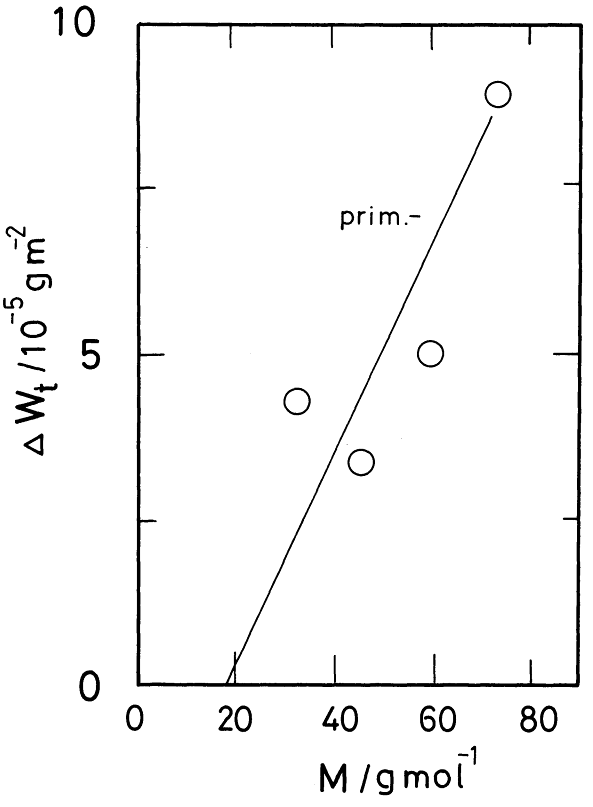


Fig. 4. Increase of the weight loss by TG analysis (ΔW_t) for porous Vycor glass treated with various liquid alcohols.

alcohols. Under the reaction condition that the water formed in the reaction is removed, a close-packed methoxy surface is achieved. A similar tendency is shown for those samples treated with methanol in our results.

Figures 2—4 show that ΔW_t is approximately proportional to the molar weight of the alcohols for the same structure. Under mild reaction conditions, the number of formed alkoxyl groups is expected to be small. When these samples are heated at high temperatures, it is assumed that the total weight loss in the TG analysis can be described by reactions (1) and (3), apparently

$$\text{Si-OR} + \text{Si-OH} \longrightarrow \text{Si-O-Si} + (\text{R-OH}), \tag{3}$$

where (R-OH) is actually decomposed to olefins, CO_2, H_2O, and so on. The weight loss in the TG analysis for the treated sample can be expressed by

$$W_t(\text{treat.}) = \frac{18 \times 10^{18}}{2L} n_{\text{OH(1)}} + \frac{10^{18}}{L} M n_{\text{R}}, \tag{4}$$

where $n_{\text{OH(1)}}$ is the number of surface hydroxyls (per 1 nm^2) decomposed according to Eq. 1, n_{R} the number of the alkoxyl groups, L Avogadro's constant, and M the molar weight of the alcohol. Assuming that the alkoxylation reaction occurs only on the surface hydroxyl groups, $n_{\text{OH(1)}}$ is expressed as

$$n_{\text{OH(1)}} = n_{\text{OH}} - 2n_{\text{R}}, \tag{5}$$

where n_{OH} is the total surface hydroxyl content of an untreated sample. Combining Eqs. 4 and 5 leads to

$$\begin{aligned} \Delta W_t &= W_t(\text{treat.}) - W_t(\text{untreat.}) \\ &= (10^{18}/L) n_{\text{R}} (M - 18). \end{aligned} \tag{6}$$

The linear relationship shown in Figs. 2—4 is expressed by Eq. 6. These results show that the number of formed alkoxyl groups is nearly constant for alcohols having the same structure.

The degree of alkoxylation was defined as the ratio of n_{R} to the total hydroxyl content of the untreated sample, n_{OH}. n_{R} was calculated by the slopes of Figs. 2—4, and is listed as the degree of alkoxylation in Table 2. These results suggest that the number of the alkoxyl groups formed by mild contact with liquid alcohols can not be neglected when considering the surface properties. It can also be seen that the degree of alkoxylation is lower

Table 2. Degree of Alkoxylation for Surface Hydroxyl Groups of SiO_2 by Contact with Liquid Alcohols

Alcohol structure	Degree of alkoxylation/%		
	Silica 60	Silicic acid	Vycor glass
Prim.-	24	14	6.9
Sec.-	10	4.5	

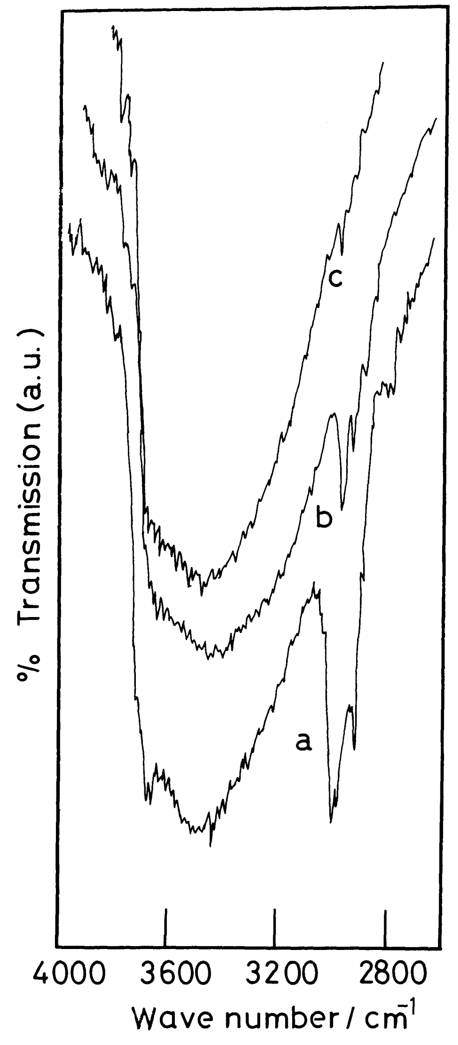


Fig. 5. Infrared spectra of SiO_2 (silicic acid) surface after treatd with liquid butyl alcohols: (1) 1-butanol; (b) 2-butanol; (c) *t*-butyl alcohol.

Table 3. Characteristic Absorption Frequencies of Each Alkoxyl Group on Silicic Acid

Alcohol	Wavenumber/cm^{-1}
Methanol	2993, 2950, 2846
Ethanol	2979, 2936, 2907
1-Propanol	2971, 2940, 2886
2-Propanol	2971, 2936
1-Butanol	2969, 2943, 2879
2-Butanol	2971, 2931
t-Butyl alcohol	2974
1-Pentanol	3003, 2979, 2914
1-Hexanol	2993, 2971, 2907

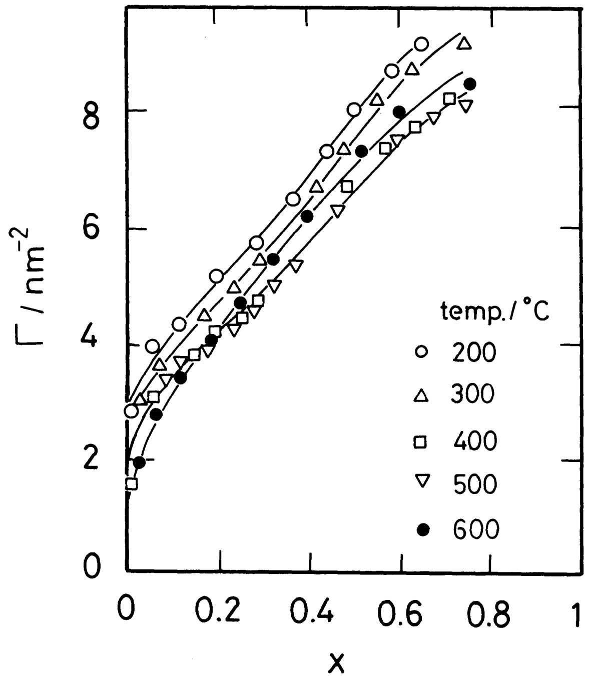


Fig. 6. First adsorption isotherms of methanol vapor on silicic acid at 25 °C. Number of adsorbed methanol (Γ) vs. relative pressure (x).

for Vycor glass than for silica gels. Porous glass has fewer surface hydroxyl groups that are active for the mild alkoxylation reaction.

Figure 5 shows the reflection infrared spectra of those samples treated with butyl alcohols. Since the spectra were measured without outgassing the cell, broad absorption bands due to adsorbed water were observed. However, the distinct absorption bands in the range 3000—2800 cm^{-1} are ascribed to stretching vibrations of the alkoxyl groups. These bands were not observed for untreated samples. The characteristic band profile is shown for each alkoxyl group. The intensity of the band increases with increasing number of alkoxyl groups. The absorption frequencies of the alkoxyl groups on silicic acid are summarized in Table 3. The observed frequencies due to the methoxy groups are somewhat lower than the values measured under the drying conditions.[8,9] It appears that the absorption frequencies of the alkoxyl groups are weakly affected by the adsorbed water.

Adsorption of Methanol Vapor. It has been reported that methanol is irreversibly adsorbed on a silica surface by two mechanisms.[8,10] One is chemisorption with forming the methoxy groups, and the other is adsorption by means of hydrogen bonds. The amount of irreversibly adsorbed methanol depends on the pretreatment conditions of the sample. Figure 6 shows the first adsorption isotherms of methanol vapor. It is seen that the adsorption equilibrium in the first measurement is affected by the pretreatment temperature. The number of adsorbed methanols decreases with increasing the pretreatment temperature, as in the case of water vapor adsorption.[11] On the contrary, Fig. 7 shows a congruency of the second isotherms for different pretreatment temperatures. The adsorption in the second measurement is due to the same mechanism for samples treated at different temperatures. These results

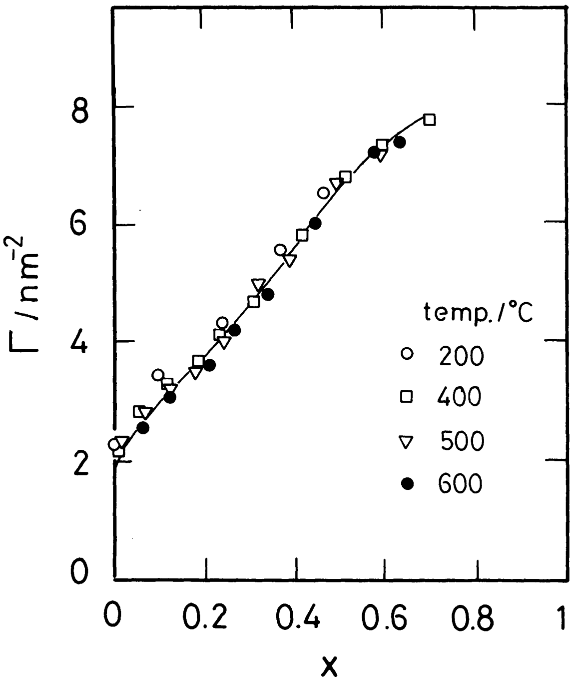


Fig. 7. Second adsorption isotherm of methanol vapor on Silicic acid at 25 °C. Number of adsorbed methanol (Γ) vs. relative pressure (x).

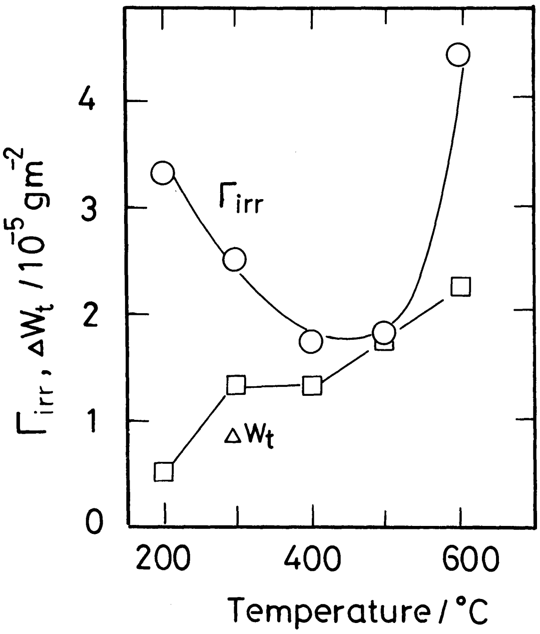


Fig. 8. Amount of methoxylation (ΔW_t) and amount of irreversibly adsorbed methanol (Γ_{irr}) on Silicic acid.

show that the adsorption in the first measurement involves both reversibly and irreversibly adsorbed methanol, whereas the second isotherm expresses the amount of reversibly adsorbed methanol. In addition, a methoxylation reaction was completed in the first measurement.

The monolayer capacity, which is calculated by the BET equation, is listed in Table 4. $\Gamma_m^{(1)}$ and $\Gamma_m^{(2)}$ are the monolayer capacities for the first and second isotherms, respectively. In Table 4, the total quantity of irreversibly adsorbed methanol (Γ_{irr}) is also listed. For all pretreatment temperatures, $\Gamma_m^{(2)}$ is almost constant and smaller than $\Gamma_m^{(1)}$. $\Gamma_m^{(1)}$ decreases with increasing the pretreatment temperature, except for the case treated at 600 °C. It can also be seen that the difference between $\Gamma_m^{(1)}$ and $\Gamma_m^{(2)}$ is roughly equal to Γ_{irr}. The decrease in $\Gamma_m^{(1)}$ shows the dependence of irreversible adsorption on the pretreatment temperature.

The amount of irreversibly adsorbed methanol is plotted against the pretreatment temperature in Fig. 8. Γ_{irr} involves both the methoxylated amount (ΔW_t) and the amount adsorbed by hydrogen-bond formation, Γ_h. Γ_h is listed in Table 4. ΔW_t was determined as the difference of the weight loss between the sample after the adsorption measurement and the untreated sample. The weight loss of the untreated sample was measured from the pretreatment temperature to 1200 °C. It is seen that the higher is the pretreatment temperature, the more methoxy groups are formed.

Thermal treatments of a solid sample influences not only the chemical state of the surface, but also the pore structure. The microporosity of Silicic acid was examined by Endo et al.[5,12] They applied the α_s method to adsorption isotherms of argon, and showed that silicic acid has microporosity. According to their results, the micropore volume of the untreated sample is about 0.05 $cm^3\,g^{-1}$. These micropores are filled with adsorbate molecules by a pore-filling mechanism at low pressures. The micropore volume decreases with increasing the thermal treatment temperature, and becomes almost zero by a treatment at 1000 °C. However, it remains 0.048 $cm^3\,g^{-1}$, even upon a treatment at 600 °C. The decrease of the micropore volume in our experiments is small and does not greatly affect the

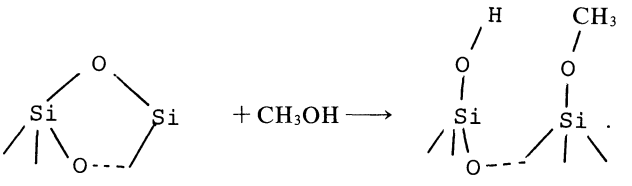
Table 4. Monolayer Capacity and Number of Irreversibly Adsorbed Methanol

Treatment temp./°C	$\Gamma_m^{(1)}$ / nm^{-2}	$\Gamma_m^{(2)}$ / nm^{-2}	$(\Gamma_m^{(1)}-\Gamma_m^{(2)})$ / nm^{-2}	Γ_{irr} / nm^{-2}	Γ_h / nm^{-2}
200	4.20	3.32	0.88	0.61	0.52
300	3.91	3.28	0.63	0.46	0.22
400	3.45	3.17	0.28	0.32	0.08
500	3.46	3.15	0.31	0.33	0.002
600	3.94	3.20	0.74	0.82	0.41

adsorption property. Thus, the temperature dependence of irreversible adsorption is mainly caused by a change in the chemical state of the surface.

The hydroxyl groups on silica surfaces interact with each other by means of weak hydrogen bonds at room temperature.[8,13] These groups are eliminated to form the siloxane bridges by thermal treatments. As the surface concentration of the hydroxyl groups decreases, they become isolated without any interaction. These isolated (free) hydroxyls are expected to be alkoxylated more easily than the hydroxyls interacting with each other. The proportion of isolated hydroxyl groups increases remarkably with increasing the treatment temperature in the range below 400—500 °C.[6,8] In this temperature range, the quantity of formed siloxane bridges is small, as is expected from the results given in Table 1. On the other hand, the number of methanols adsorbed by hydrogen bonds decreases with decreasing the number of hydroxyl groups. This is confirmed by the decrease of Γ_h below 500 °C, as shown in Table 4. The above considerations suggest that the methoxylation reaction takes place mainly on isolated hydroxyl groups on a surface pretreated below 500 °C.

In the case of a pretreatment at 600 °C, the obtained results show a different behavior from those undergoing a lower temperature treatment. In Fig. 6, the first adsorption isotherm on the 600 °C treated sample is lower than others at low pressures, but increases more sharply at high pressures. Also, increases of Γ_{irr} and Γ_h are shown in Table 4. These results suggest that the adsorption mechanism in the first measurement on the 600 °C treated sample is quite different from that on samples treated at lower temperatures. By treating 600 °C, the number of hydroxyl groups decreases by about half that of an untreated sample; the quantity of the formed siloxane bridges cannot be neglected. Borello et al. have reported that siloxane bridges on an Aerosil surface, which were formed by the treatment at temperatures between 400 and 700 °C, are reactive for methoxylation reaction.[8] The siloxane bridges are methoxylated according to the reaction



(7)

This reaction shows that hydroxyl groups are reformed by opening the siloxane bridges in addition to the methoxy groups. The number of hydroxyl groups is increased by reaction (7), and becomes greater than that on the surface just after a treatment at 600 °C. This effect causes an increase of Γ_h, as shown in Table 4. Thus, the methoxylation reaction takes place mainly on the siloxane bridges on a surface pretreated at 600 °C. This reaction occurs at high pressures ($x>0.2$), as is expected from Fig. 6. It seems that reaction (7) is induced by capillary condensation of methanol vapor.

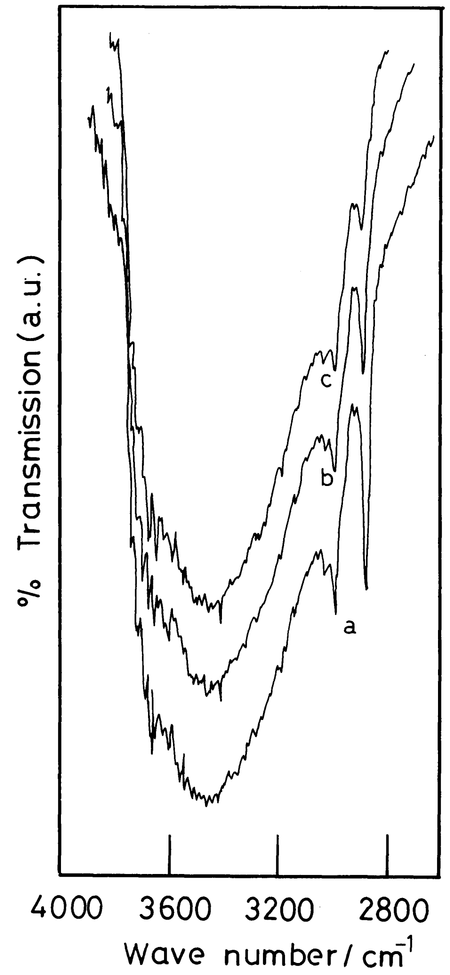


Fig. 9. Infrared spectra of SiO_2 (silicic acid) surface after adsorption of methanol vapor. Pretreatment temperature; (a) 600 °C; (b) 400 °C; (c) 200 °C.

Figure 9 shows the reflection IR spectra of the sample after the second isotherm measurements. The profile of the spectra agrees with that of samples treated by the Soxhlet extractor method. The intensity of the absorption bands due to C–H stretching in the methoxy groups increases as the pretreatment temperature increases. This agrees with the dependence of ΔW_t on the pretreatment temperature.

Conclusions

A part of the surface hydroxyl groups of silicas is easily esterified to alkoxyl groups, even under mild reactions, such as contact with the liquid alcohols and adsorption of alcohol vapor at room temperature.

For silica surfaces on which the hydroxyl groups are fully developed, the number of the alkoxyl groups formed by contact with liquid alcohols is nearly constant for alcohols of the same structure. The degree of alkoxylation of the surface hydroxyl groups is higher for silica gels than for porous silica glass.

The adsorption equilibrium of methanol vapor strongly depends on the pretreatment conditions of the surface. The number of formed methoxy groups increases with increasing the pretreatment temperature. The methoxylation reaction takes place mainly regarding the isolated hydroxyl groups on a surface pretreated below 500 °C. On a surface pretreated at 600 °C, it takes place on the siloxane bridges.

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