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The Alkoxylation of Aerosil Silica with C_1–C_4 Alcohols

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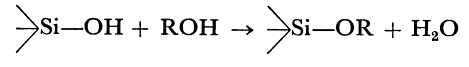
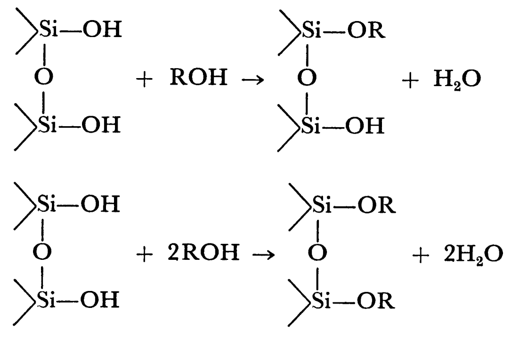
The Aerosil surface was treated with C_1–C_4 alcohols under both high-pressure and low-pressure conditions. The high-pressure treatment was carried out at various temperatures up to 250 °C using an autoclave, while the low-pressure treatment was done at 280 °C under vapor pressure at room temperature. The surface changes were followed by IR spectroscopy, and the carbon content was determined. The degrees of alkoxylation (OR groups/100 Å^2) of the Aerosils treated sufficiently under low pressures were 1.3—1.6, approximately equal to the amount of OH isolated before the treatment, while the values under high pressures reached 2.3—3.4, equal or near to the amount of the total OH. The values for methoxylation were particularly higher, while those for *t*-butoxylation were quite low. These results, in addition to the observation of the IR spectra, indicate that the isolated OH groups are predominantly esterified under low pressures, while under high pressures the vicinal OH groups are esterified as well, and the opening of the siloxane bonds occurs easily in the case of methoxylation. The stability of the alkyl groups on the Aerosil against heating decreased in the order of: primary > secondary > tertiary.

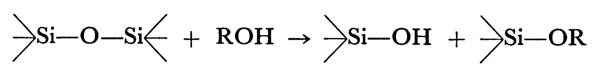
It is well known that a silica gel surface is alkoxylated with alcohols and that the resulting surface is hydrophobic. It is considered[1–3] that the alkoxylation occurs through the esterification of surface hydroxyl groups and the opening of surface siloxane bonds. The surface hydroxyls consist of the isolated OH, the single OH, the vicinal OH, and the hydrogen-bonded OH.


(1)

Isolated


(2)

Vicinal


Siloxane (3)

The reaction has been studied by several workers[1–17] under both high- and low-pressure conditions; however, the investigations under the two conditions have been carried out separately by different workers. Regarding a comparison in the alkoxylations under the two conditions, only Stöber *et al.*[4] have reported comparatively the degrees of alkoxylation under the two conditions. From the values, a satisfactory discussion is impossible because of the differences in the experimental conditions other than the pressure.

In the present study, including the differences in the alkoxylations under the two conditions, the effects of the kinds of alcohols and the experimental conditions on the reaction were systematically examined by means of C_1–C_4 alcohols. The conditions under which Reactions 1, 2, and 3 take place were discussed on the base of the results. In addition, the stability against the heating of the alkoxyl groups on the Aerosil surface was examined.

Aerosil-200 (Japan Aerosil Co., Ltd.) was chosen as the sample, because the Aerosil powder was adequate for the production of a transparent disc, and the same kinds of silica have been used by many workers. The reaction was mainly carried out under high pressures using an autoclave. Some runs were carried out under low pressures, though, that is, under vapor pressures of the alcohols at room temperature. The surface changes upon the treatments were followed by infrared spectroscopy, and the carbon content was determined.

Experimental

Materials. The Aerosil powder was pressed into discs 10 mm in diameter, each weighing about 10 mg, at a pressure of about 5 ton/cm^2. All the alcohols used were the purest commercially available reagents.

The surface area of the Aerosil was determined by means of the BET method, and the cross-sectional area of nitrogen was assumed to be 16.2 Å^2. The surface area of the disc before the treatment was 217 m^2/g, while those of the discs alkoxylated sufficiently were 176—188 m^2/g.

The content of the total hydroxyl groups of the Aerosil was determined from the weight loss induced by heating the Aerosil, previously dried to a constant weight at 110 °C, for 4 h at 1100 °C. The content of the isolated hydroxyl groups was determined from the chlorine content on the surface of Aerosil allowed to react with dichlorodimethylsilane, according to the procedures reported by Armistead *et al.*[18] The chlorine content was determined as follows: the chlorine on the Aerosil was extracted with a 0.1 M-NaOH solution, and then the amount of chlorine in the solution was titrated with a 0.0141 M-$Hg(NO_3)_2$ solution according to the procedures described in JIS-K0101 of the Industrial Analysis. The amount of the total OH groups and that of the isolated OH on the surface were 2.7 and 1.5 groups per 100Å^2 respectively. The former agreed with the value of 3.0±0.3 reported by the manufacturer of the Aerosil. The latter is considered to be reasonable by comparison with the following values obtained for the Aerosils: 1.4—1.5 by Hair *et al.*,[19] 1.4±0.1 by Armistead *et al.*,[20] 1.4±0.3 by Colin *et al.*,[21] and 1.4 by Tsutsumi *et al.*[12]

Alkoxylation Processes. The autoclave used was made of stainless steel and had a volume of about 30 ml. Several discs were placed in the upper part within the autoclave, supported with a holder and above the liquid phase of 15 ml of alcohol brought into the autoclave. Prior to use, some discs were heated for 3 h at constant temperatures over the range of 550 to 900 °C in the air. The autoclave was heated in an electric oven and was kept at a constant temperature. The reaction was carried out at temperatures over the range of 30—250 °C. The autoclave was quenched with running water immediately after it was taken out of the oven.

In the case of low-pressure treatment, the discs were allowed to stand in contact with alcohol vapor at 280 °C in a glass apparatus. Prior to use, the discs were out-gassed in the same apparatus for 3 h at 280 and 570 °C under a residual pressure of about 10^{-5} Torr.

Infrared Spectroscopy. The spectrometer used was a Hitachi EPI-G Spectrophotometer. The discs were taken out into the atmosphere after they had been out-gassed; then they were immediately subjected to the infrared measurement. The moisture in the atmosphere will have little effect on them, since the discs alkoxylated have hydrophobic surfaces.

Determination of the Alkoxyl Group Concentration on the surface. The carbon content of the discs was measured by the usual combustion method. The amount of the alkoxyl groups (mol/g) was calculated from the carbon content. The degree of alkoxylation, the surface concentration of alkoxyl groups per 100Å^2, was determined from the amount of the alkoxyl groups and the surface area of the disc. The relative amount of the alkoxyl groups was also determined by the spectroscopic method.

Results and Discussion

Effect of Reaction Temperature on the Alkoxylation. It took a few hours for the autoclave to be heated to 250 °C. In order to follow the change in the Aerosil surface during that period, the infrared spectra of the Aerosil were observed at several stages during the course of heating. Those for *n*-BuOH are illustrated in Fig. 1. The increase in the bands at 2800—3200 cm^{-1} due to butyl groups corresponding to the decrease in the band at 3750 cm^{-1} due to the isolated OH groups indicates that the isolated OH groups were esterified with *n*-BuOH.

The discs were treated with the alcohols in the autoclave for 20 h at the given temperatures. The infrared spectra of the resulting discs were then observed. The spectral changes with an increase in the reaction temperature were similar to those shown in Fig. 1. The changes were quantitatively followed by means of both the optical density for the 3750 cm^{-1} band and that for the 2960 or 2970 cm^{-1} band assigned to CH stretching. Figure 2 illustrates the results obtained for the Aerosils treated with MeOH and *n*-PrOH. In Fig. 2, the increase in the optical density of the 2960 or 2970 cm^{-1} band is attended by the decrease in that of the 3750 cm^{-1} band. This relation clearly indicates that the isolated OH groups are increasingly esterified with an increase in the reaction temperature.

Figure 3 shows the amounts of alkoxyl groups obtained from the carbon content as a function of the reaction temperature. The amounts of every alkoxyl group increased with an increase in the temperature, and each arrived at its highest value at 200—250 °C. This change corresponds to the change in the optical densities of the bands due to alkyl groups in Fig. 2. The Aerosil treated with methanol had the highest values among all the alkoxylated Aerosils throughout the temperature range, the values decreased in the

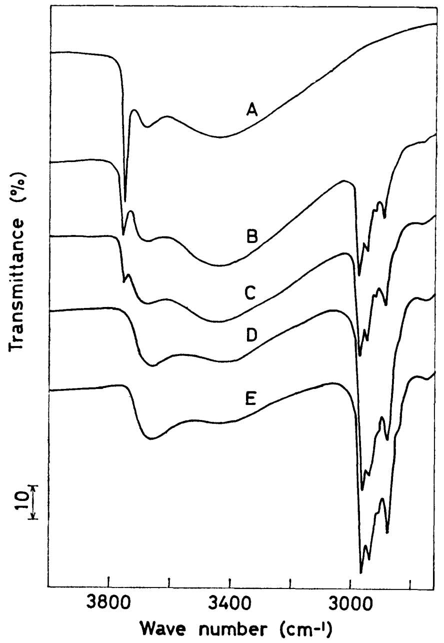


Fig. 1. Change of infrared spectra of Aerosil treated with 1-butanol during the course of reaction.
A: Original Aerosil, B: 100 °C, C: 160 °C, D: 200 °C, E: 240 °C (The numerical values indicate the temperatures at each stage during the course of heating up to 250 °C).

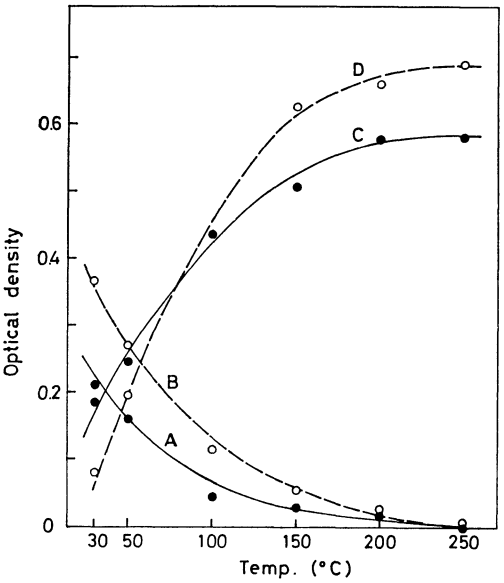


Fig. 2. Optical density for the isolated silanol band and that for the alkyl band as a function of reaction temperature.
A: OH band at 3750 cm^{-1} for the Aerosils treated with methanol, B: OH band at 3750 cm^{-1} for the Aerosils treated with 1-propanol, C: CH_3 band at 2960 cm^{-1} for the Aerosils corresponding to A, D: *n*-C_3H_7 band at 2970 cm^{-1} for the Aerosil corresponding to B.

order of: MeOH > EtOH > *n*-BuOH > *i*-BuOH > *s*-BuOH. The values for *n*-PrOH and *i*-PrOH are similar to those for *n*-BuOH and *i*-BuOH respectively; therefore, those values are omitted in Fig. 3.

It has previously been reported[1,9] that *t*-BuOH did not react easily with silica gel. It was found from the characteristic adsorption bands due to the *t*-butyl groups, however, that the alkoxylation was effectively carried out for 3 h at 200—240 °C. The bands were intense, but small in comparison with those due to the other alkyls, and the band at 3750 cm^{-1} still remained to a considerable extent.

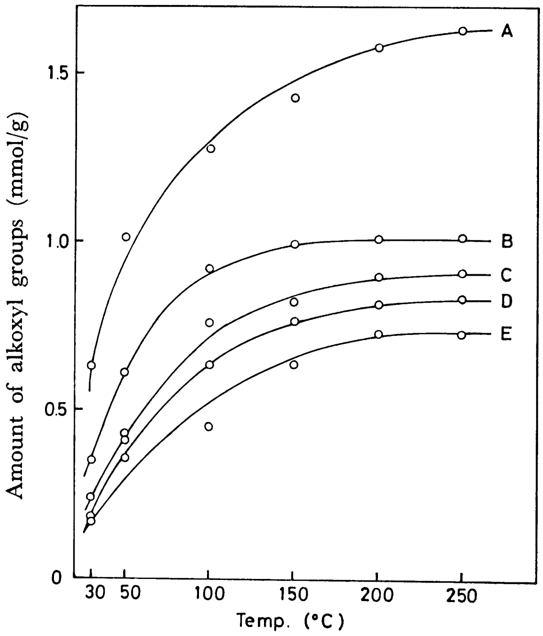


Fig. 3. Amount of alkoxyl groups as a function of reaction temperature.
A: Methoxyl, B: ethoxyl, C: butoxyl, D: isobutoxyl, E: secondary butoxyl.

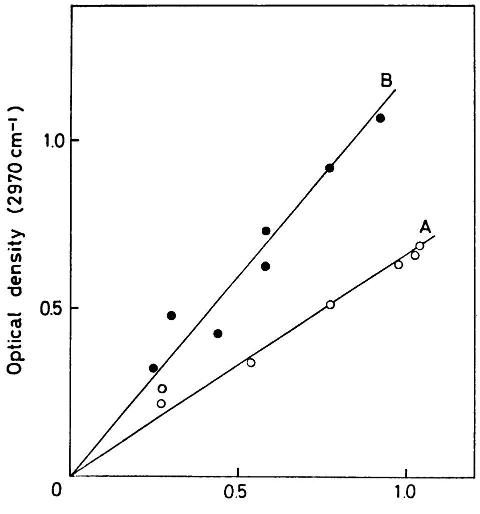


Fig. 4. Relation between amount of alkoxyl groups obtained from carbon content and optical density for the alkyl groups.
A: Ethoxyl, B: butoxyl.

The amounts of alkoxyl groups obtained by means of the carbon content were checked by means of the optical densities of the absorption bands due to the alkyl groups. Figure 4 illustrates the results for the ethoxyl and butoxyl groups. The two values bear a nearly linear relationship to each other.

Effect of Thermal Pretreatment on the Alkoxylation. The Aerosil discs were heated prior to the reaction at temperatures of 550, 700, 800, and 900 °C for 3 h in the air. The surface areas of the resulting discs corresponding to these temperatures, were 209, 167, 146, and 76 m^2/g respectively. The discs were treated with alcohols at 250 °C for 20 h in the autoclave immediately after the thermal pretreatment. Figure 5 shows the amounts of alkoxyl groups in the discs as a function of the thermal pretreatment temperature. The decrease in the amounts with the increase in the temperature must result from the decrease in both the surface area and the hydroxyl groups induced by the thermal pretreatment. The values for methoxyl were higher than those for the other alkoxyls at all pretreatment temperatures, as in the case of non-pretreatment. The infrared spectra of the Aerosils which were heated at 700, 800, and 900 °C prior to the reaction and then treated with methanol are shown in Fig. 6. The bands due to methyl groups decreased in intensity as the bands due to the isolated OH groups decreased with an increase in the pretreatment temperature.

Comparison of the Reactions under Low Pressures with Those under High Pressures. The infrared spectra of the Aerosils treated under low pressures were compared with those of the Aerosils treated under high pressures. The isolated hydroxyl band at 3750 cm^{-1} vanished almost entirely even upon the low-pressure treatment, not to mention the high-pressure treatment; however, the alkoxyl bands at 2800—3200 cm^{-1} ap-

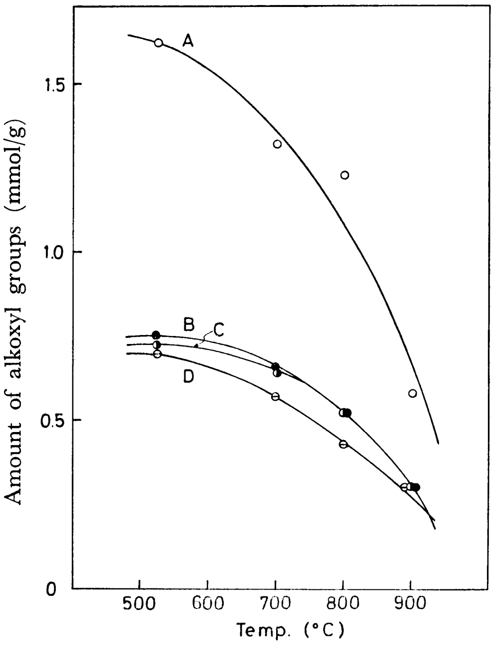


Fig. 5. Amount of alkoxyl groups as a function of thermal pretreatment temperature.
A: Methoxyl, B: ethoxyl, C: propoxyl, D: butoxyl.

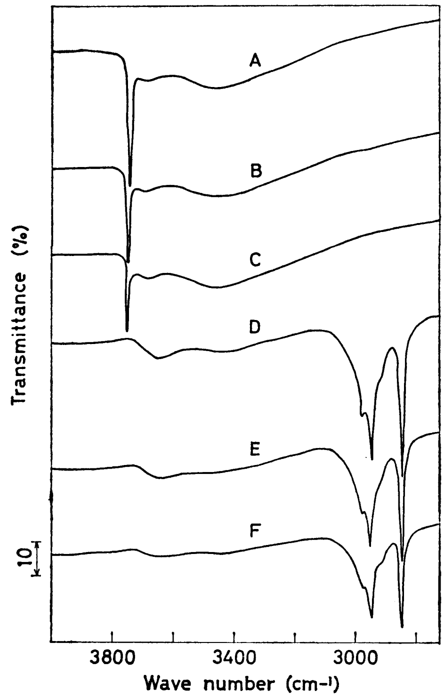


Fig. 6. Infrared spectra of the Aerosils treated with methanol after thermal pretreatment.
A: Aerosil heated for 3 h at 700 °C, B: Aerosil heated for 3 h at 800 °C, C: Aerosil heated for 3 h at 900 °C, D: Aerosil obtained by treatment of A, E: Aerosil obtained by treatment of B, F: Aerosil obtained by treatment of C.

peared with a stronger intensity in the case of the high-pressure treatment. The preliminary observations indicate that the isolated hydroxyl groups were almost completely esterified, even under low pressures, if sufficient time was available, while under high-pressures reactions other than the esterification of the isolated hydroxyl groups may have occurred simultaneously.

In order to obtain further information about the mode of the alkoxylation, the quantitative relations of the isolated OH and the alkoxyl groups on the Aerosils alkoxylated in varying degrees were examined by means of the optical densities of the two groups. The degrees of the alkoxylation were made to vary by a change in the reaction time under low-pressure conditions and by a change in the reaction temperature under high-pressure conditions. The optical densities for the methyl and propyl bands are plotted against those for the isolated OH band, in Fig. 7. The values bear a linear relationship to each other about the Aerosils with low optical densities of the alkyl bands; however, about those with higher optical densities upward deviations from the linearity were observed. These results show that the alkoxylation under low-pressure conditions is due only to the esterification of the isolated OH groups and support the above consideration that the alkoxylation under high-pressure conditions involves reactions other than esterification.

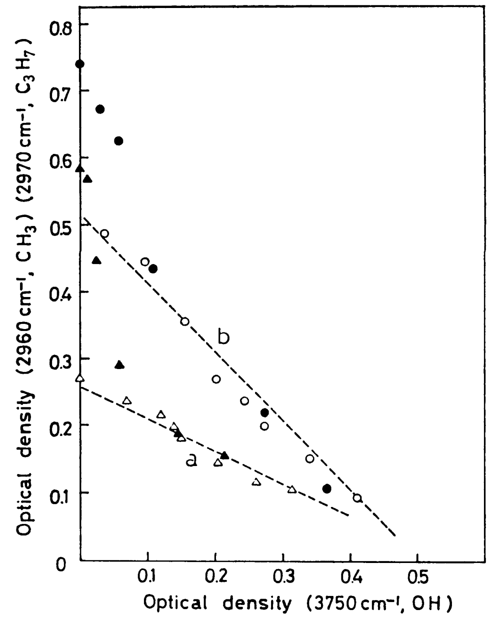


Fig. 7. Relation between optical density for the isolated silanol and that for the alkyl groups.
a △, ▲: Aerosil treated with methanol, b ○, ●: Aerosil treated with 1-propanol, △, ○: low-pressure treatment; ▲, ●: high-pressure treatment.

Comparison of the Degrees of Alkoxylation. Table 1 shows the degrees of alkoxylation for the completely alkoxylated Aerosils. The values in the case of the low-pressure treatment were lower than those in the case of the high-pressure treatment. The former were approximately equal to the surface concentration of the isolated OH groups, 1.5 groups/100 Å^2, although the values for methoxyl groups were a little higher. The latter were in the range of 2.3—3.4 groups/100 Å^2, except for the much higher value for methoxyl, and were equal or near to the surface concentration of the total OH groups, 3.0 groups/100 Å^2. These facts indicate that, under low pressures, the alcohols react in a 1 : 1 ratio with the isolated OH groups, while under high pressures they react in a 1 : 1 with the total OH groups. However, the branched-chain alcohols can not react with all the OH groups completely because of their larger cross-sectional molecular areas. The degree of alkoxylation in the case of the high-pressure treatment decreased in the following order:

Table 1. Degrees of alkoxylation
(Alkoxyl groups/100 Å^2)

Alcohols	Low-pressure		High-pressure	
	Thermal pretreatment at 280 °C	Thermal pretreatment at 570 °C	Non	Thermal pretreatment at 550 °C
MeOH	1.8	1.9	5.5	5.5
EtOH	1.6	1.8	3.4	2.5
n-PrOH	1.4	1.6	3.2	2.4
i-PrOH	1.4		2.7	
n-BuOH	1.3	1.7	3.2	2.4
i-BuOH	1.3		2.7	
s-BuOH	1.3		2.3	
t-BuOH	0.4		0.7	

MeOH> EtOH> *n*-BuOH> *i*-PrOH, *i*-BuOH> *s*-BuOH >*t*-BuOH. This order was the same as that of the amount of alkoxyl groups, since there was no considerable difference in the surface area of the alkoxylated Aerosils. Lambert *et al.*[16] have reported the same tendency for the pentanol isomers under low pressures. As they have explained, the steric factors must play an important part. That the degree of methoxylation was much larger than the concentration of the total OH groups indicates that, in addition to Reactions 1 and 2, Reaction 3 contributes in no small measure to the methoxylation. It has been concluded in a previous paper,[22] from the dissolution of silica gel in methanol methanol can easily open the siloxane bond at high temperatures and high pressures. The higher degree for the methoxylation is perhaps based on this function of methanol, in addition to the small cross sectional area of a methoxyl group.

The thermal pretreatment had an effect on the alkoxylation under low-pressure conditions, as is well known, but it was somewhat inhibitory of the alkoxylation under high-pressure conditions, as shown in Table 1. Only the methoxylation was not affected by the thermal pretreatment. In the runs under high pressures, the discs were heated in the air and then subjected to room temperature, if only for a moment, before they were sealed with an alcohol in the autoclave. During this procedure, not only the strained siloxane[2,22,23] but also the stable siloxane are caused by the dehydration of the vicinal OH groups. The stable siloxane can not easily be opened with methanol. The lowering of the degrees of alkoxylation by thermal pretreatment may be attributed to the alteration of the vicinal OH groups into the stable siloxane bonds.

Stability of Alkoxyl Groups on the Aerosil Surface against Heating. The Aerosils alkoxylated were heated at various temperatures in a vacuum of about 10^{-5} Torr, and their changes were observed by means of the infrared spectra. Morterra *et al.*[24] have observed the change about the methyl group, and Raymond *et al.*[15] have observed that about the butyl and secondary butyl groups; however, no systematic observation through various kinds of alkyls has yet been carried out. A remarkable removal of the alkyl groups occurred at the following temperatures for each alkyl group: Me: 650—750 °C, Et, *n*-Pr, *n*-Bu, *i*-Bu: 500—550 °C, *i*-Pr, *s*-Bu: 420—470 °C, *t*-Bu: about 400 °C. Methyl groups were particularly stable, and the infrared observations suggested that the removal reaction of the methyl groups is different from that of the other alkyl groups. It was found from the above results that the stability decreases in this order; primary> secondary> tertiary and that it is independent of the number of the carbon.

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