

Vapor Phase Fluorination of Silica Surface with Chlorofluoromethanes and CF₄

Susumu OKAZAKI* and Akito KUROSAKI

Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Nakanarusawa, Hitachi, Ibaraki 316
(Received November 22, 1986)

For a surface modification, fluorinations of silica samples including a quartz fiber and a commercial glass fiber, were carried out at around 500 °C in a conventional flow reactor. The surface compositions before and after the fluorination were determined by XPS analyses. Among chlorofluoromethanes and CF₄, CCl₃F was the most effective for fluorination. Surface OH groups were completely removed or replaced by the fluorination. Adsorptions of water vapor, hexane, hexafluoropropene, and octafluorocyclobutane showed that the silica surface became more hydro- and lipophobic after the fluorination. On the contrary, the chlorofluoro-methane-treated surface exhibited a higher affinity to the perfluorocarbons compared to the untreated surface.

In general, a SiO₂ surface has been fluorinated in the liquid phase with an aqueous solution of HF,¹⁾ NH₄F,²⁾ or NH₄HF₂.³⁾ Recently, it was found that a SiO₂ surface may be more conveniently fluorinated by a vapor phase treatment at high temperatures (e.g., 1500 °C) with volatile fluorine compounds such as CF₄,⁴⁾ SF₄,⁵⁾ NF₃,⁶⁾ and CCl₂F₂.⁷⁾ The vapor phase treatment was reported to be especially effective for the removal of surface OH groups which cause a loss of photoactivity when SiO₂ is used as an optical fiber.⁸⁾ The treatment process, however, is still undesirable since the fluorine compounds cited above are expensive and/or unstable in moist air except for CCl₂F₂; also, the treatment temperature is too high. Thus, it is preferable to perform a vapor phase treatment or fluorination by using less expensive and more stable fluorides such as chlorofluorocarbons (flon) at lower temperatures.

It was previously found that some chlorofluoromethanes are effective for the vapor-phase fluorination of Al₂O₃ at temperatures lower than 500 °C.⁹⁾ In addition, a certain flon, CClF₃, was also effective for the surface fluorination of mordenite (SiO₂/Al₂O₃ molar ratio=19) at about 450 °C.¹⁰⁾ Hence, it is possible that some flons are available for the vapor phase fluorination of a SiO₂ surface. However, the reaction conditions must be carefully selected because of the large possibility of SiF₄ formation in such a fluorination of SiO₂.

Thus, in this study the most suitable flon and the optimal treatment conditions to promote the surface fluorination of SiO₂ with flon were sought first. Then, changes in the surface composition and property were examined, since they have only been slightly clarified in previous studies.^{4–7)} As for surface properties changes in the adsorptive activity for water vapor and hexane are examined to determine the effect of the fluorination on the affinity of a SiO₂ surface to a polar or nonpolar compound. In addition, such perfluorocompounds as hexafluoropropene and octafluorocyclobutane were selected as adsorbents since they are known to be inert, in general, in interactions with other molecules.

During this study, an emphasis was placed on comparing the effects of a flon-treatment with that of the

most widely adopted HF acid-treatment in order to increase the effectiveness of the vapor-phase treatment using flon.

Experimental

Materials. A commercial fine silica powder, Aerosil 200 (Nippon Aerosil Co.) was used as the main silica sample (SA) after heat treatments at temperatures higher than 1000 °C. In addition, a quartz fiber supplied by Gaschro Kogyo Co., and a commercial glass fiber supplied by Nittobo Co. (E Glass, SiO₂ 52–56%; Al₂O₃ 12–16%; CaO 15–25%; MgO 0–6%; B₂O₃ 8–13%; Na₂O+K₂O 0–1%) were used for comparisons of the reactivity with that of SA.

Various chlorofluoromethanes, CF₄, hexafluoropropene, and octafluorocyclobutane, all of which were of purities higher than 99%, supplied by Mitsui-Dupont Fluorochemical Co., were directly used without further purification.

Fluorination Procedure. Fluorinations were carried out in a closed system by circulating gaseous chlorofluoromethane through a sample bed at 450–550 °C. The replacement of OH groups with fluoride ions was also carried out by soaking SA in dilute hydrofluoric acid (0.1 or 1.0 wt%) at room temperature for 30 min.

Structure and Surface Composition. The structure of silica before and after fluorination with flon or diluted hydrofluoric acid was determined from the powder diffraction patterns obtained with a Rigaku Geigerflex X-ray diffractometer by using Cu K α radiation. The structural change was also examined using a scanning electron microanalyzer (SEM).

The compositions in the surface layer were determined by IR and XPS. The XPS was measured with Mg K α radiation. The base pressure of the spectrometer was usually below 10^{–7} Torr (1 Torr=133.322 Pa) during the experiments. The compositions were calculated from the areas of the spectral peaks (i.e., the maximum in the counting rate) on the basis of the photo ionization cross section at 1245 eV in units of the Cls cross section of 22200 barns.¹¹⁾ The behavior of the surface OH groups was examined by IR spectroscopy using a self-supporting disc.

Determination of Surface Properties. Surface areas were determined by applying the BET equation for the adsorption isotherm of N₂ at –196 °C. The effect of the flon-treatment on the surface properties of silica was examined by the adsorptions of water vapor, hexane, hexafluoropropene, and octafluorocyclobutane at 50 °C.

Table 1. Surface Fluorination of SiO₂

Sample	Treatment condition ^{a)}		Content/atom%		F1s peak position ^{b)/eV}
	Pressure/Torr	Time/min	F	Cl	
SiO ₂ (1000)-CCl ₄	54	30	0	1.2	—
SiO ₂ (1000)-CCl ₃ F	54	30	4.2	0	688.7
SiO ₂ (1000)-CCl ₂ F ₂	54	30	2.5	0	688.5
SiO ₂ (1000)-CClF ₃	54	30	0.8	0	688.6
SiO ₂ (1000)-CF ₄	54	30	0	0	—
SiO ₂ (1000)-CF ₄	200	120	2.4	0	688.5
SiO ₂ (1000)-CHF ₃	54	30	0.4	0	688.0
SiO ₂ (1000)-HF acid ^{c)}	—	30	8.1	0	688.7

a) The treatment temperature was kept constant at 550°C. b) The binding energy values were measured by referring to the Cls value of the contaminant carbon (285 eV). c) The SiO₂ sample was treated with 0.1 wt% HF soln. at room temperature, and then dried at 120°C, followed by evacuation at 500°C for 1 h.

Table 2. Surface Fluorination of SiO₂

Sample	Treatment condition ^{a)}		Content/atom%		F1s peak position ^{b)/eV}
	Pressure/Torr	Time/min	F	Cl	
SiO ₂ (1000)-CCl ₃ F	54	30	4.2	0	688.7
SiO ₂ (1100)-CCl ₃ F	54	30	3.0	0	688.3
SiO ₂ (1150)-CCl ₃ F	54	30	3.2	0	688.8
Quartz fiber-CCl ₃ F	103	30	5.4	0	689.1
Quartz fiber-CCl ₂ F ₂	105	30	Trace	0	—
E-Glass fiber-CCl ₃ F	107	30	13.2	0	686.9

a) The treatment temperature was kept constant at 550°C. b) The binding energy values were measured by referring to the Cls value of the contaminant carbon (285 eV).

Results and Discussion

Reactivities of Various Flons and Diluted HF Acid Toward Silica Surface. As shown in Table 1, CCl₃F exhibited the highest fluorination activity among various flons. The order of the fluorination activities of these flons the opposite to that of the C-Cl¹²⁾ or C-F¹³⁾ bond strength of the flon molecules. Thus, the ease of the C-Cl¹²⁾ or C-F¹³⁾ bond splitting seems to determine the surface fluorination activities of flon.

Since the CCl₃F having the weakest C-Cl or C-F bond was found to be the most active as a fluorinating reagent, it was used for the surface fluorination of SiO₂ in the succeeding study.

Comparison of Reactivities of Various SiO₂ Materials. As shown in Table 2, a quartz fiber sample was fluorinated more readily than SA. A commercial glass fiber sample was fluorinated much more markedly. In this case, however, the F1s peak position (686.9 eV) for the fluorinated sample was remarkably different from that for a simple or pure silica sample, such as the quartz and SA. It rather coincided to that for the CCl₃F-treated Al₂O₃ (686.8 eV). Therefore, the F component introduced by the CCl₃F-treatment was presumed to be bound not to Si, but the Al atom on the treated glass fiber. Evidence suggested that heat treated SiO₂ is less active than Al₂O₃ in the reaction toward the flon. Nevertheless, it is noteworthy that SA was considerably fluorinated with a relatively stable compound CCl₃F, even after heat-treatment at a high tempera-

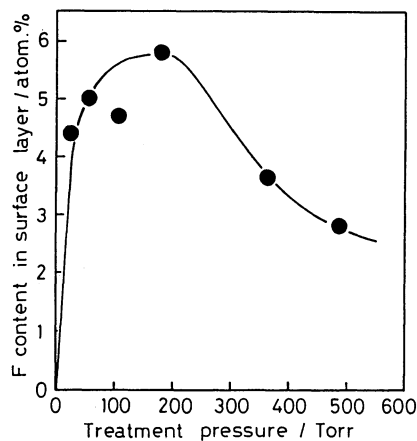


Fig. 1. Effect of the CCl₃F-treatment pressure on the F content in surface layer. Treatment temperature: 550°C; Treatment time: 2 h.

ture, such as 1150°C.

Effect of CCl₃F-Treatment Conditions. As Fig. 1 shows, there was an optimal CCl₃F pressure to increase the F content of the treated silica. The infrared spectra, which were taken for the gaseous components obtained by 54, 200, and 500 Torr treatment, indicated a peak at 1010–1022 cm⁻¹ assignable to a Si-F bond¹²⁾ only for the product obtained at 500 Torr. This finding suggested that excessive fluorination, or formation of SiF₄, may be avoided when fluorination is gently carried out by using a flon of lower pressure or concentration.

The treatment temperature was more effective on the surface fluorination than the treatment gas pressure. Thus, the F content in the surface layer increased linearly with temperature up to 550 °C (Fig. 2).

Changes of Surface Area and Structure. The specific surface area somewhat decreased with an increase in the F content of the CCl_3F -treated SA. The decrease in the surface area, however, was not so remarkable as in the case of the diluted HF acid treatment (shown in Fig. 3).

The XRD and SEM analyses revealed that SA was still amorphous, even after treatment with the CCl_3F or the diluted HF acid.

Surface Constitution Examined by IR Spectra. The IR spectrum of SA exhibited a sharp and slightly asymmetric peak at 3734 cm^{-1} (Fig. 4). This peak, assignable to the isolated OH groups,¹⁴⁾ was still observed even after heat-treatment at high temperatures, such as 1000 °C. This was also observed for a sample treated with dilute HF acid. On the other hand, this peak due to the isolated OH groups was not found in all for the SA samples which were treated with CCl_3F at 500 °C. The complete removal of surface OH groups is considered to be due to the replacements of the OH groups with F atoms. In fact, a

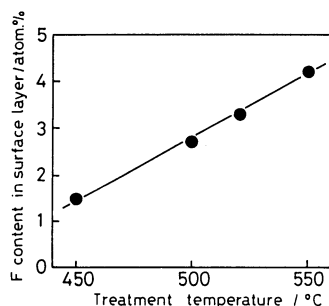


Fig. 2. Effect of the CCl_3F -treatment temperature on the F content in surface layer. Treatment pressure: 54 Torr; treatment time: 0.5 h.

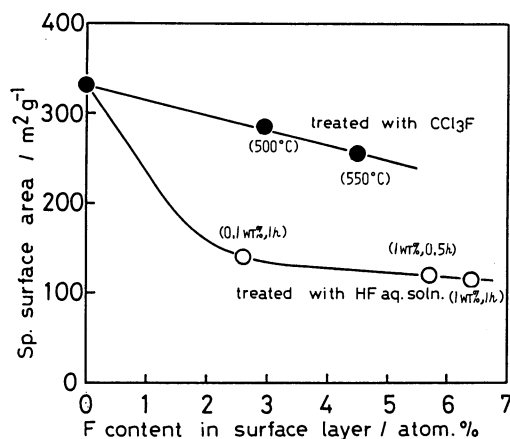


Fig. 3. The variation of specific surface area with F content in surface area. The CCl_3F -treatment was carried out at 54 Torr and 500 or 550 °C. The acid treatment was carried out at room temperature for 0.5 or 1 h with the diluted HF.

shoulder due to a Si-F bond appeared at 940 cm^{-1} ,¹⁵⁾ in accordance with the disappearance of the peak due to the OH groups.

Unlike the Si-F bond in SiF_4 molecule, the bond formed on the silica sample was fairly stable towards moisture. Thus, the band due to the Si-F bond of the treated SiO_2 did not disappear after contact with water vapor (10 Torr) at room temperature for 1 h, and even after further contact with that (15 Torr) at 120 °C (Fig. 5). The band attributable to the free silanol groups at 3734 cm^{-1} ¹⁵⁾ reformed with difficulty after contact with water vapor (15 Torr) for a long time, such as 15 h.

Changes in Adsorptive Activities for Various Gases. For Water Vapor. As is exhibited in Fig. 6(A), the adsorptive activity of silica for water vapor was remarkably enhanced by a treatment with dilute HF acid. On the other hand, the activity was somewhat decreased by the CCl_3F -treatment at 450 °C. Furthermore, the activity was entirely removed by a treatment at 500 °C.

Water vapor is considered to be adsorbed on the silica surface through hydrogen bonding,¹⁵⁾ and the amount of physically adsorbed water should be related to the number of the surface OH groups. During a treatment with dilute HF acid, the surface siloxane may be hydrolyzed. The hydrolysis should increase the amount of surface OH groups on silica surface, although a part of the OH groups may be replaced by

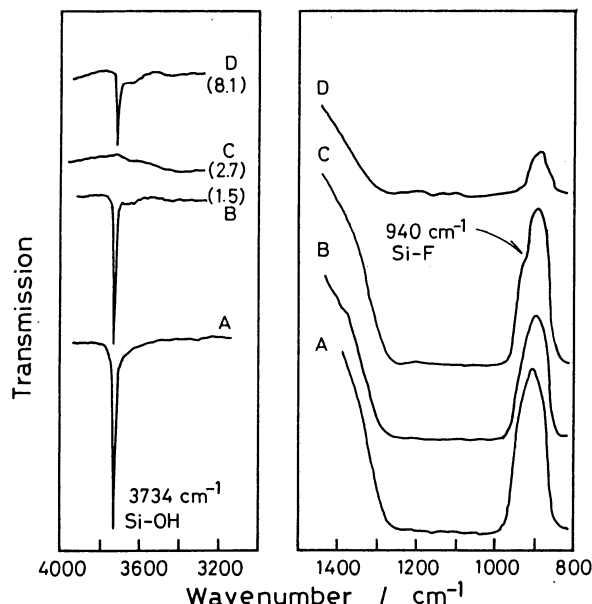


Fig. 4. IR spectra of SiO_2 treated with CCl_3F or diluted HF. A: Background or the untreated sample after evacuation at 500 °C for 2 h; B, C: for the samples treated with CCl_3F (54 Torr) at 450 and 550 °C for 0.5 h, respectively; D: for the sample treated with 0.1 wt% HF solution at room temperature for 0.5 h, and then dried at 120 °C, followed by evacuation at 500 °C for 1 h. The numbers in parentheses indicate the F content of respective samples.

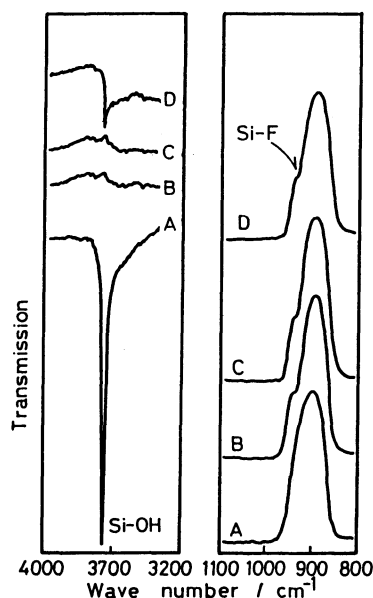


Fig. 5. Effect of contact with water vapor on IR spectra. A: Background or the untreated SiO_2 sample after evacuation at 550°C for 2 h; B: for the sample treated with CCl_3F (200 Torr) at 550°C for 0.5 h; C: further contact of B with water vapor (15 Torr) at 120°C for 1 h; D: further contact of C with water vapor (15 Torr) at room temperature for 15 h.

F^- ion in the acid solution. The net increase in the amount of the surface OH groups should contribute to the enhancement of the adsorptive activity for water vapor.

While, in the case of the CCl_3F -treatment, the amount of the surface OH groups may be reduced in accordance with the progress of the surface fluorination, especially the surface OH group may be fully replaced by a F atom in a treatment at higher temperatures as has been revealed by the IR study for the treated silica (Fig. 4). A silica surface which is sufficiently covered by F atoms may be hydrophobic owing to the low surface energy ascribable to the F atoms. In fact, an SA sample treated with CCl_3F at 550°C remained floating on water for about 1 week at room temperature; nevertheless, the untreated or the diluted HF acid-treated SA sank into water as soon as it was placed on the water surface.

For Hexane Vapor. As shown in Fig. 6(B), the adsorptive activity of silica for gaseous hexane decreased slightly with a CCl_3F -treatment at 500°C . It was further decreased by a treatment at a higher temperature, 550°C . A decrease in the adsorptive activity for hexane was also observed for the dilute HF acid-treated sample in the adsorption at a pressure higher than 20 Torr.

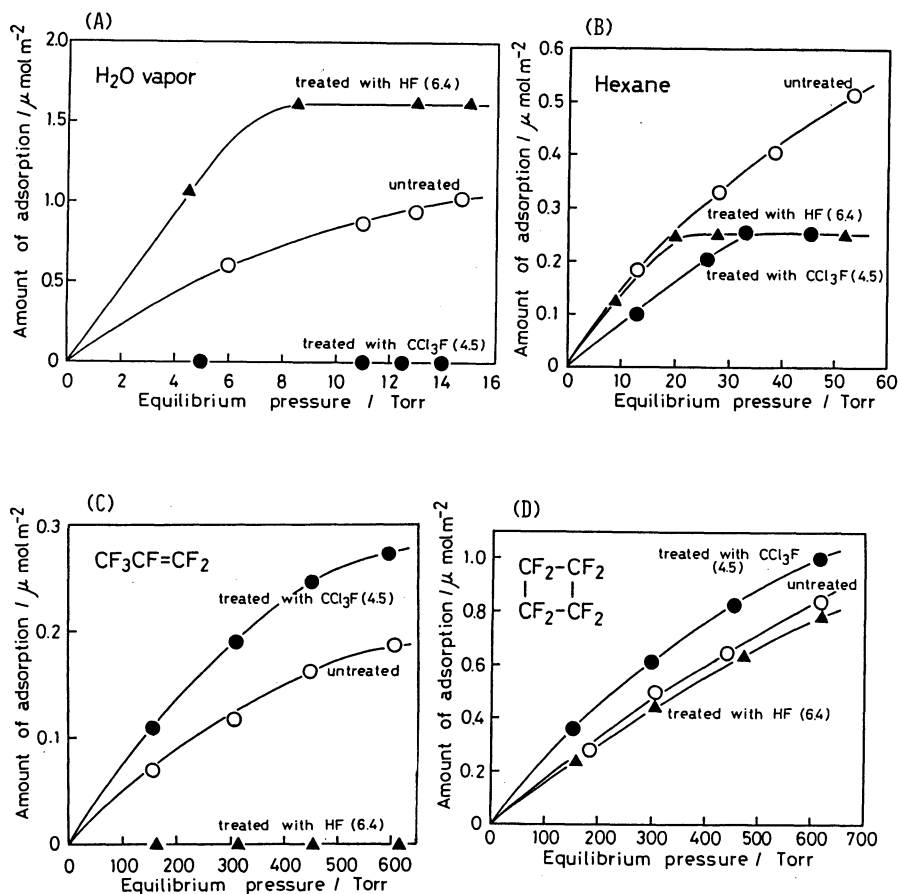


Fig. 6. Effect of the surface fluorination on the adsorptive activities for various compounds. All the adsorptions were carried out at 50°C , and the numbers in parentheses indicate the F content of respective samples.

The results for the CCl_3F -treated silica seem to be in conflict with the current view that hydrophobic solids should exhibit an affinity for nonpolar or lipophilic compounds. The evidence that the CCl_3F -treated silica is concurrently hydrophobic and lipophobic is considered to be a result of the extremely low surface energy of the solid surface which is well-covered by F atoms. Similar characteristics are also revealed in the oil- and water-repellency of some polyfluoro or perfluoro compounds used as a special fiber treatment agent.¹⁶⁾

For Perfluorocompounds. Finally, the results of the adsorptions of hexafluoropropene and octafluorocyclobutane are displayed in Figs. 6(C) and (D). In contrast to the adsorptive activities for water and for hexane, those for the perfluorocarbons were fairly increased by the CCl_3F -treatment. These increases in the adsorptive activities may have resulted from an affinity of the F atoms in the perfluoro-compounds to the atoms of the same kind on the well-fluorinated silica surface. However, the essence and the details of the interaction between the adsorbent and the adsorbates are not clear at the present stage of this study.

In contrast with the CCl_3F -treated surface, a silica surface treated with dilute HF acid was entirely inactive for the adsorption of hexafluoropropene, possibly due to the highly polar character of the acid-treated surface. The decrease in the adsorptive activity of silica was also observed for the adsorption of octafluorocyclobutane (bp -5°C), which is more condensable than hexafluoropropene (bp -29.4°C), although the decrease was not so remarkable as that observed for the hexafluoropropene adsorption.

Conclusion

The results of this study are as follows:

- (1) Flon-treatments are available for the vapor phase fluorination of a SiO_2 surface at around 500°C .
- (2) Among various chlorofluoromethanes and CF_4 , CCl_3F having the weakest C-Cl and/or C-F bonds is especially suitable for the surface fluorination.
- (3) Complete removal of surface OH groups on SiO_2 by the CCl_3F -treatment is accomplished at 500°C . This temperature is much lower than that of another

treatment (e.g. 1500°C) with volatile fluorides (such as Cl_2 , SF_6 , and NF_3), which was reported to be carried out in order to remove surface OH groups.

- (4) The formation of SiF_4 can be suppressed by decreasing the pressure or concentration of CCl_3F in a reactor.

- (5) A silica surface becomes more hydro- and lipophobic with the CCl_3F -treatment. On the other hand, the affinity of a SiO_2 surface to perfluorocompounds is increased by a CCl_3F -treatment.

This work was supported by a Grant-in-Aid for Scientific Research No. 60550562 from the Ministry of Education, Science and Culture.

References

- 1) S. Okazaki, A. Kurosaki, and S. Suzuki, *Bull. Chem. Soc. Jpn.*, **57**, 1046 (1984); W. N. Webb, *Ind. Eng. Chem.*, **49**, 261 (1957).
- 2) H. J. Reitsman and C. Boelhower, *J. Catal.*, **33**, 39 (1974). P. O. Sochart, S. A. Selim, J. P. Damon, and P. G. Rouxhet, *J. Colloid Interface Sci.*, **70**, 209 (1979).
- 3) V. C. F. Holm and A. Clark, *Ind. Eng. Chem., Proc. Res. Dev.*, **2**, 38 (1963).
- 4) T. Abiru, N. Matsuhiro, T. Ohashi, K. Kosaka, and O. Fukuda, *Denkitsu-shingakkai-sokai*, 1984, Abst. 1148, pp. 4—202.
- 5) M. Robinson, *Mat. Res. Bull.*, **15**, 735 (1980).
- 6) T. Nakai, Y. Mimura, H. Tokiwa, and O. Shinbori, *Denkitsu-shingakkai-sokai*, 1985, Abst. 1156, pp. 4—480.
- 7) H. Kanamori, N. Yoshioka, and G. Tanaka, *Denkitsu-shingakkai-sokai*, **1983**, Abst. 1096, pp. 4—182.
- 8) Y. Sugahara and M. Takeda, *Boeigijutsu*, **1982**, 23.
- 9) A. Kurosaki and S. Okazaki, *Chem. Lett.*, **1983**, 1741.
- 10) S. Okazaki and H. Jouhouji, *Bull. Chem. Soc. Jpn.*, **59**, 1931 (1986).
- 11) J. H. Scofield, *J. Electron Spectros. Relat. Phenomena*, **8**, 129 (1976).
- 12) R. Foon and K. B. Tait, *J. Chem. Soc., Faraday Trans. 1*, **68**, 104, 1121 (1972).
- 13) G. Glockner, *J. Phys. Chem.*, **63**, 827 (1959).
- 14) T. E. Elmer, I. D. Chapman, and M. E. Nordberg, *J. Phys. Chem.*, **1963**, 2219.
- 15) M. L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker Inc., New York (1967), p. 79.
- 16) N. Ishikawa and Y. Kobayashi, "Fusso no Kagaku," Kodansha, Tokyo (1977), p. 194.