[October, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2613—2617 (1975) 2613

Studies of Surface Modification of Solids. III. Reaction of Silica with Trifluoroethanol

Kazuo Tsutsumi, Haruo Emori, and Hiroshi Takahashi
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

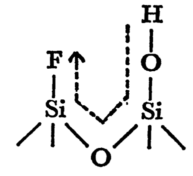
(Received August 19, 1974)

The esterification of silica was performed by reactions with 2,2,2-trifluoroethanol vapor and ethanol vapor with and without basic catalysts, such as ammonia and pyridine. The esterification with ethanol was referred to as the control. The extents of the esterifications were observed by means of infrared spectroscopy. The reactivity of the silica with trifluoroethanol was higher than that with ethanol. This is presumably because trifluoroethanol is more acidic than ethanol. The esterification was accelerated by the addition of ammonia as a base catalyst. For example, in the reaction of the silica with trifluoroethanol of 10.7 Torr at 30 °C for 3 hr, 35% of the surface silanols were esterified without any catalyst, while with the ammonia (0.2 Torr) catalyst, 98% of them was esterified. This suggests that the extraction of the proton from the hydroxyl groups of alcohol by NH_3 contributes to the esterification. The addition of pyridine influenced the reaction rate as well, but the esterification itself was disturbed by the addition of excess pyridine, because pyridine was adsorbed strongly on the surface silanol and its heterocyclic ring prevented the alcohols from adsorption. It is supposed that the physical adsorption of trifluoroethanol on the surface silanol is necessary in the first stage of the esterification. The esterified silica became hydrophobic, and it was hydrolyzed in the presence of water.

The surfaces of such metal oxides as silica and alumina are covered with hydroxyl groups, which are known to influence the adsorption properties of the surface.1) As is well known, the hydrophilicity of silica surface originates from the silanol groups and is lost upon the esterification of the silanol groups with alcohol:2)

$$\geqslant\text{Si-OH} + \text{ROH} \longrightarrow \geqslant\text{Si-O-R} + \text{H}_2\text{O} \qquad (1)$$

Hair *et al.* showed that silica treated with an ammonium fluoride solution had, in part, surface fluorine instead of silanol, and that its surface became hydrophobic. The activity of the Brönsted acid of the surface silanol was enhanced by the electronegativity of an adjacent fluorine atom, and the silica was endowed with a high catalytic activity for the cracking of cumene:3)



In this study, the adsorption and the reaction of 2,2,2-trifluoroethanol on the silica surface were investigated by means of infrared spectroscopy. The silica used in this experiment was preheated in an electric furnace at a high temperature in advance of the esterification. By this treatment, variously reactive OH groups other than the so-called "free OH groups" or "isolated OH groups" were removed from the surface.

The rate of the reaction of 2,2,2-trifluoroethanol vapor with silica in the presence of a catalyst vapor was investigated. The reactivity of the chlorinated silica was also studied. The esterification with ethanol was also referred to.

Experimental

Aerosil-380 (Japan Aerosil Co., Ltd.) was used as the sample of silica. It was heated at 800 °C in an electric furnace under air prior to use. By this thermal pretreatment, all the molecular water and mutually-hydrogen-bonded hydroxyl groups were removde from the silica surface. In consequence, the silica surface was covered only with the isolated silanol groups and the siloxane-type groups. The trifluoroethanol, ethanol, and water were purified by repeated vacuum distillation.

The spectroscopic work was performed in a quartz cell fitted with NaCl windows4), the cell was set in a Hitachi-EPI G3-type infrared spectrometer. The silica sample was pressed into an orbicular wafer about 10 mg/cm^2 thick. The sample was then set in a cell and heated *in vacuo* to any desired temperature. After the cell has then been cooled to room temperature under *vacuo*, the spectrum was observed. The silica was evacuated at 30 °C under 10^{-5} Torr in the cell prior to any reaction. The adsorption and the reaction studies were carried out in the same cell at various temperatures and pressures. In order to obtain the adsorption isotherm, the gaseous reactant was introduced into the cell at various pressures, and the extinction of the isolated silanols was measured at various stages during the adsorption and the reaction.

The hydroxyl group of surface silanol was exchanged also with chlorine by the use of thionyl chloride ($SOCl_2$).5) The silica wafer pretreated in the electric furnace at 800 °C was put into $SOCl_2$ and refluxed for a total period of 14 days. The chlorinated silica was transferred quickly into the cell of the spectrometer so as not to be hydrolyzed, and then evacuated at 30 °C prior to the reaction with the reagent:

$$\geqslant\text{Si-OH} + \text{SOCl}_2 \longrightarrow \geqslant\text{Si-Cl} + \text{HCl} + \text{SO}_2 \qquad (2)$$

Results and Discussion

Isolated OH Groups of Silica. The heat treatment of silica at 800 °C in the electric furnace resulted in the change of the spectra shown in Fig. 1.

The absorption bands of water molecules (3500 cm^{-1}) and hydrogen-bonded hydroxyl group (3650 cm^{-1}) disappeared, and only the band of the isolated hydroxyl groups (3750 cm^{-1}) remained. The silica surface was ultimately covered with the isolated silanol and the siloxane linkages.

In the infrared spectra of silica after the reaction with trifluoroethanol, the OH stretching vibration of the silanol groups decreased and the CH_2 stretching (3000—2800 cm^{-1}), the CH_2 bending (1470 cm^{-1}), the CH_2 twisting (1440 cm^{-1}), the overtone of the CF_3

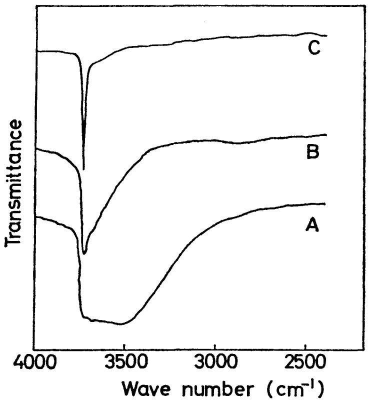


Fig. 1. Infraed spectra of silica after various treatments.
A: evacuation at 30 °C
B: evacuation at 400 °C
C: evacuation at 30 °C after heat treatment in electric furnace at 800 °C

asymmetric deformation (1360 cm^{-1}), and the CF_3 asymmetric stretching (1310 cm^{-1}) vibrations appeared (*cf.* Fig. 2).[6] The spectra indicate that the esterification occurs on the silanol according to the following equation:

$$\geqslant\text{Si-OH} + CF_3CH_2OH \longrightarrow \geqslant\text{Si-O-CH}_2\text{-CF}_3 + H_2O \qquad (3)$$

The 3750 cm^{-1} band remained after the esterification. The complete esterification of all the silanols could not be attained.

The rate of the esterification of the silica with trifluoroethanol was analyzed by measuring the diminishing rate of the absorbance of the 3750 cm^{-1} band due to the isolated silanol. Since the physically absorbed alcohol has previously been desorbed by the evacuation, the diminishing rate of the 3750 cm^{-1} band corresponded to the rate of the reaction. The degree of coverage (θ) by physical adsorption at the reaction temperatures was measured by taking the spectra of the silica with the residual gas present in the cell, while the reaction was still going on. One example of the determination of the surface coverage (θ) from the infrared spectra is given in Fig. 3 for illustration. From this figure, the surface coverage (θ) of ethanol to the silanol group under the conditions of an ethanol pressure of 20 Torr at 30 °C was determined. In this figure, θ is the ratio of $\overline{OB}$ to $\overline{AB}$. The $\overline{OB}$ absorbance at the reaction time of 18 min was interpolated from the values of the absorbances at the reaction times of 10 min and 20 min respectively.

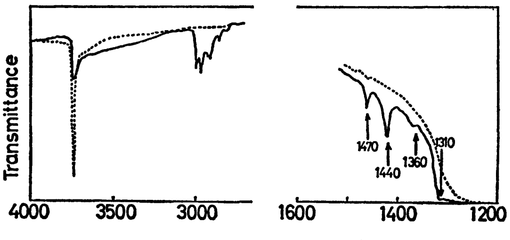


Fig. 2. Esterification of silica with trifluoroethanol (25.0 Torr).
Reaction period: 8 hr, Reaction temperature: 60 °C. Solid line: infrared spectrum after the esterification and the successive evacuation of the residual vapor of trifluoroethanol. Broken line: infrared spectrum of original silica.

The absorbance $\overline{AB}$ was obtained by deducting $\overline{OA}$ from $\overline{OB}$. By the same manner, the values of the surface coverage of trifluoroethanol under the various conditions were determined.[7] The ratio of the extinction with the residual gas present to the interpolated value gives the fraction of hydroxyl groups not covered by physically absorbed molecules, *i.e.*, $1-\theta$. In this case, it was supposed that the fraction was independent of the degree of esterification. By the calculations of this method, the reactivity of the silica with trifluoroethanol or ethanol was investigated. The rate of the esterification with trifluoroethanol is faster than that with ethanol (*cf.* Fig. 7, Curves A and B). The hydroxylic proton of alcohol takes part in the esterification reaction, and the rate of the reaction must be controlled by the ease of the proton release. Because of the inductive effect of the electronegative fluorine atoms bonded directly to the α-carbon, trifluoroethanol releases the proton more easily than ethanol. From this point of view, the difference in the reactivities of the two alcohols seems reasonable.

Heat of Adsorption. In view of the fact that the reaction of the silica with trifluoroethanol goes on slowly at high temperatures, the esterification may be considered to take place when there is physically adsorbed alcohol on the surface silanol. As is shown in Fig. 4, the quantity of physically adsorbed alcohol

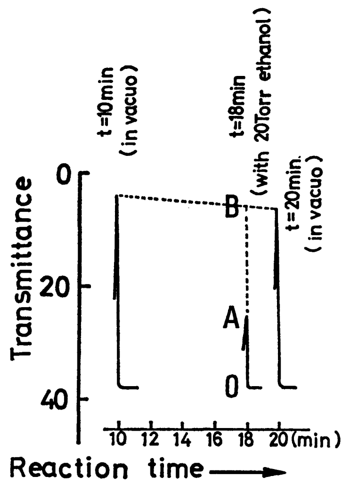


Fig. 3. Change of 3750 cm^{-1} -OH band of silica taken during the course of reaction at 30 °C, illustrating spectra used for determining the fraction of freely vibrating hydroxyl groups covered by physically adsorbed ethanol.

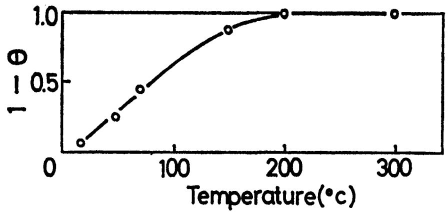


Fig. 4. Change of surface coverage of trifluoroethanol with temperature (trifluoroethanol pressure: 17.0 Torr).

Table 1. Isosteric heats of adsorption of trifluoroethanol on silica

Surface coverage (θ)	ΔH (kcal/mol)
0.1	8.0
0.2	7.0
0.3	6.4
0.4	6.8

on the surface silanol decreases with the rise in the temperature. By determining spectroscopically the amount of coverage on the freely-vibrating OH groups of the silica, it is possible to obtain the isotherms for the adsorption on these groups, independent of the adsorption at any other sites. The fraction of coverage (θ) was thus decided at various temperatures and pressures, from which the isosteric heats of the physical adsorption of trifluoroethanol on the free hydroxyl groups of the silica were derived. Some typical adsorption isotherms determined at various temperatures are given in Fig. 5. The slope of the plot relating log P to $1/T$ is proportional to the isosteric heat of adsorption, according to Clausius-Clapeyron's equation. Same typical plots are given in Fig. 6. The heats calculated from these plots are given in Table 1.

Esterification Catalyzed by Ammonia. An acid or base catalyst is normally used in the esterification.[8] Therefore, the catalytic effects of NH_3 and pyridine on the esterification were examined. In the presence of NH_3, the rate of the esterification with trifluoroethanol increased remarkably (*cf.* Fig. 7, Curves B and E). The reaction of the silica with ethanol in place of trifluoroethanol was found to be accelerated by the NH_3 catalyst (Fig. 7, Curves A and C).

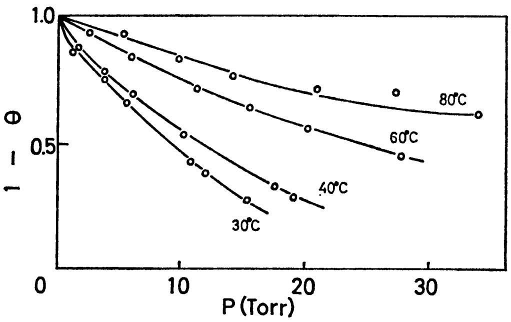


Fig. 5. Adsorption isotherms of trifluoroethanol interacted with the free hydroxyl groups on silica.

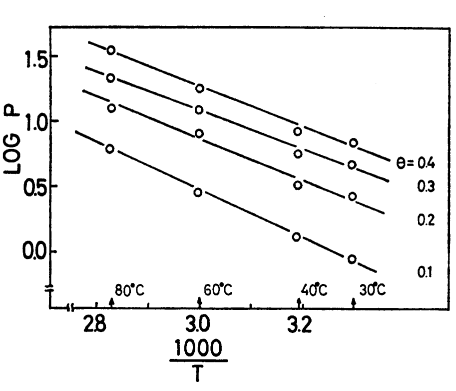


Fig. 6. Examples of the relations between log P and $1/T$ for the adsorption isotherms of trifluoroethanol on Aerosil-380.

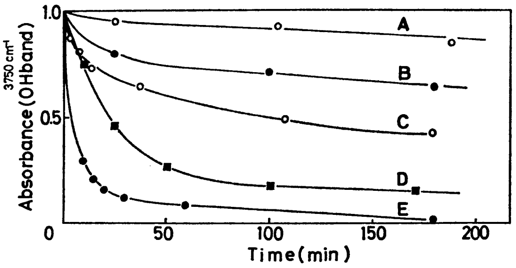
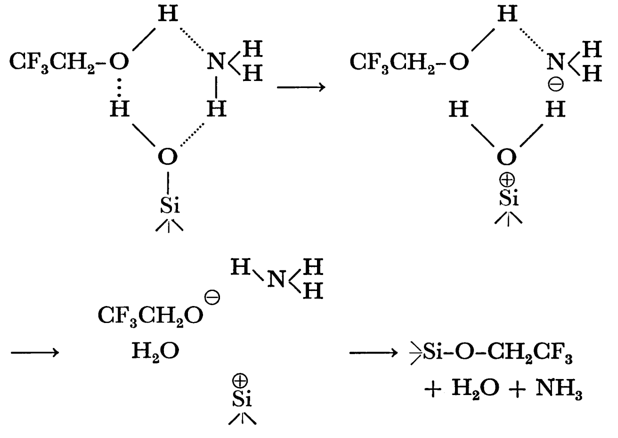


Fig. 7. Esterification rate at 30 °C under various conditions.

A: ethanol [7.0 Torr]
B: trifluoroethanol [11.3 Torr]
C: ethanol [7.8 Torr] and ammonia [0.2 Torr]
D: trifluornethanol [11.2 Torr] and pyridine [0.3 Torr]
E: trifluoroethanol [10.8 Torr] and ammonia [0.2 Torr]

The mechanism of the esterification catalyzed by NH_3 can be explained as follows. In the first stage, the alcohol molecule is adsorbed on the silanol, and then ammonia containing lone-pair electrons forms a hydrogen bond with the hydroxylic proton of alcohol. On the basis of the hypothesis, the model of the adsorption of these molecules may be written as in the picture below. The reaction is completed by the formation of the ester and water. Since the ability of NH_3 to draw out the hydroxylic proton of alcohol is proportional to the acidity of alcohol, the catalytic action of NH_3 on the esterification with trifluoroethanol is more effective than on that with ethanol. No reaction between trifluoroethanol and NH_3 occurred without the silica. It is certain that NH_3 adsorbs directly on the isolated silanol. This problem will be discussed in the next paragraph.



Esterification Catalyzed by Pyridine. When pyridine was used as the catalyst, the esterification of the silica with trifluoroethanol was accelerated (*cf.* Fig. 7, Curves B and D). Since pyridine could not be completely desorbed by the evacuation at 30 °C, the effect on the esterification rate of the fraction of hydroxyl groups covered by the strongly adsorbed pyridine (θ=0.07) was considered in Curve D of Fig. 7. However, the catalytic effect of pyridine was not so remarkable as that of NH_3. It is noticeable that an excess of

Table 2. Heats of adsorption on silica

Absorbate	$\Delta H^{a)}$ (kcal/mol)	$\Delta H^{b)}$ (kcal/mol)$^{c)}$
Trifluoroethanol	$7.1\pm0.9^{a)}$	6.2
Ammonia	$8.9\pm0.2^{b)}$	9.8
Pyridine	$10.8\pm1.0^{b)}$	10.6

a) Obtained from Table 1. b) After Hertl and Hair.[7]
c) Calculated from frequency shift by using Eq. (4).

pyridine lowers the esterification rate. This means that pyridine strongly adsorbed on the isolated silanol retards the adsorption of alcohol on it.

In Table 2, the heats of the adsorption of trifluoroethanol, NH_3, and pyridine on the isolated silanol are shown. The heat of adsorption ($\Delta H^{a)}$) is obtained by measuring the isosteric heat of adsorption in the freely vibrating hydroxyl group.[8] In the case of trifluoroethanol, the heat of adsorption ($\Delta H^{a)}$) was calculated from the data of the adsorption isotherm, as is shown in Figs. 5 and 6 by using Clausius-Clapeyron's equation. When physical adsorption takes place on the surface of the silica, it is observed that the band in the infrared spectrum attributable to the freely vibrating hydroxyl group is perturbed to lower frequencies. The heat of adsorption ($\Delta H^{b)}$) is a function of the frequency shift.
This was given by this equation:[9]

$$\Delta H^{b)} = 0.455\ (\Delta\nu\ \mathrm{cm^{-1}})^{1/2} - 2.3. \qquad (4)$$

In this equation, $\Delta\nu$ means the frequency shift of the OH stretching vibration. As is shown in Table 2, the strength of the adsorption of these molecules on the isolates silanol is in the order of: pyridine>ammonia>trifluoroethanol. The hydrogen bonding between the hydroxylic proton of the silanol and pyridine is very strong. A test showed that pyridine completely covered the surface silanols at the pressure of 4 Torr, for instance, whereas ammonia could not cover all the silanols even at 80 Torr. The infrared spectrum of the ammonia adsorbed on the silica is shown in Fig. 8. The disappearance of the isolated hydroxyl bands (3750 cm^{-1}) is accompanied by the appearance of two new bands, at 3400 and 3320 cm^{-1}. These two bands can be attributed to the asymmetric and symmetric N–H stretching vibrations. The OH vibration is shifted by about 700 cm^{-1} and is observed as a very broad absorption band at about 3050 cm^{-1}. Since the intensity of the absorption band at 3750 cm^{-1} can be restored by the evacuation at 30 °C, ammonia seems to be adsorbed physically on the surface silanol.

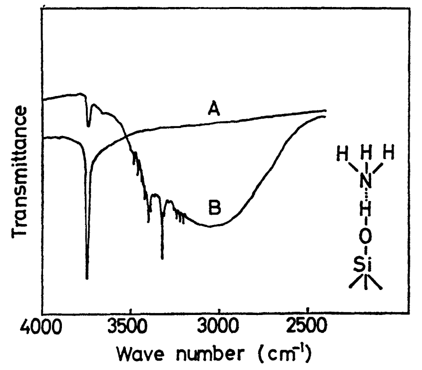


Fig. 8. Infrared spectrum of adsorbed ammonia.
A: Silica
B: Silica with ammonia (82.0 Torr)

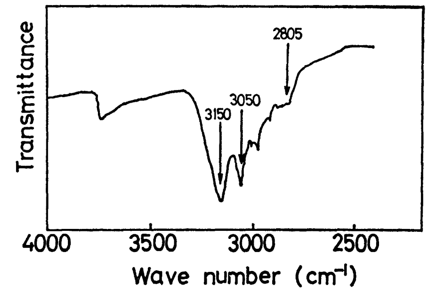
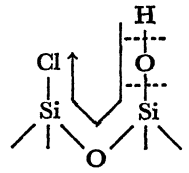


Fig. 9. Infrared spectrum of the chlorinated silica after the treatments of the esteification with trifluoroethanol in the presence of ammonia at 30 °C. (Indicated bands are assigned to ammonium chloride)

The pyridine adsorbed on the silanol could not be removed entirely by evacuation at room temperature. When the isolated silanols are completely covered by pyridine, the esterification of the silica with trifluoroethanol is unfavorable because of the steric hindrance of the heterocyclic ring of pyridine.

Esterification of the Chlorinated Silica. The chlorination of silica was evidenced by the appearance of the infrared absorption band due to NH_4Cl molecules when the $SOCl_2$-treated silica was exposed to ammonia (*cf.* Fig. 9).[10] However, no infrared absorption bands attributable to Si–Cl bands were recognized. The reaction of the chlorinated silica with trifluoroethanol formed so few esters that they could not be observed by infrared spectroscopy. This might be because of the strengthening of the acidity of the residual silanol after about 60% of the surface OH groups has been replaced by chlorine atoms.



As a consequence, it became difficult to split the silicon atom from the oxygen which is necessary for the esterification. In the presence of NH_3 (0.8 Torr) as the catalyst, the esterification of the chlorinated silica with trifluoroethanol of 33.1 Torr at 30 °C for 25 min reached 80% of the surface OH groups.

Hydrolysis and Pyrolysis of the Esterified Silica. The nature of the silica surface was modified by treatment with trifluoroethanol and became very hydrophobic. For instance, when the modified silica wafer was immersed in water, it first floated on the surface of the water. However, the wafer floating on the water surface then began to sink very slowly. The change in the affinity of the esterified silica with water may be elucidated by the hydrolysis of the ester. As the ester (Si–O–CH_2–CF_2) possesses an oxygen atom between the silicon and the carbon atoms, it has a tendency to be hydrolyzed. The absorption of the OH stretching vibration of trifluoroethanol and that of the water molecules appeared in the infrared spectrum of the esterified silica in the presence of water vapor. The spectrum obtained after the evacuation showed an increase in the isolated hydroxyl groups and a decrease in the $-CH_2-CF_3$ groups. When the esterified silica was placed in water vapor of 15 Torr at 30 °C for one hr, it was found that 26% of the ester was hydrolyzed. Moreover, samples which had been kept in water for one day were completely hydrolyzed. At the same time, the siloxane linkages were opened.

$$\geqslant Si\text{-}O\text{-}CH_2CF_3 + H_2O \longrightarrow \geqslant Si\text{-}OH + CF_3CH_2OH \tag{5}$$

The surface species of the esterified silica were stable up to about 200 °C. However, they were decomposed by evacuation above 300 °C.

References

1) H. P. Boehm, *Adv. Catal.*, **16**, 179 (1966). H. Utsugi *et al.*, *Nippon Kagaku Kaishi*, **1972**, 1007.

2) K. Tsutsumi and H. Takahashi, *ibid.*, **1972**, 1800. H. Utsugi *et al.*, *ibid.*, **1972**, 1557.

3) I. D. Chapman and M. L. Hair, *J. Catal.*, **2**, 145 (1963).

4) K. Tsutsumi, T. Ida, and H. Takahashi, This Bulletin, to be published.

5) M. Forman, *Trans. Faraday Soc.*, **57**, 2000 (1961).

6) A. J. Barnes, H. E. Hallam, and D. Jones, *Proc. Roy. Soc., Ser. A*, **335**, 97 (1973).

7) W. Hertl, *J. Phys. Chem.*, **72**, 1248 (1968).

8) R. C. Azrak and C. L. Angell, *ibid.*, **77**, 3048 (1973).

9) W. Hertl and M. L. Hair, *ibid.*, **72**, 4676 (1968).

10) R. S. McDonald, *ibid.*, **62**, 1168 (1958).