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Interaction between Water and Hydroxylated Surface of Silica-Alumina

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The interaction between water and the fully-hydroxylated surfaces of silica,alumina and silica-alumina has been investigated by measuring the physisorption isotherms of water at three temperatures and by computing the isosteric heat of adsorption and the site energy distribution therefrom. The number of adsorption site evaluated on the surfaces of each of the two component oxides decreases exponentially with the increase in the site energy, whereas that of the silica-alumina samples gives a peak at a relatively high energy region, suggesting the presence of strong water-physisorption sites characteristic to silica-alumina. These results can be elucidated on the basis exponentially of the postulation that new sites having protonic acid character appear when the two component oxides contact with each other, as described previously. Furthermore, it is found that the strength of such new sites for physisorption of water increases with decreasing content of alumina in silica-alumina.

Silica-alumina is one of the solid-acid catalysts; its interactions with basic molecules such as ammonia[1-6] and amines[7,8] are widely studied, while the quantitative investigations on the interactions with water are very few, though the fact that the Lewis acid sites on silica-alumina can transfer to the Brönsted acid sites by adsorbing water molecules is well known.[1,9]

In the preceding paper,[10] the present authors described a finding that the number of sites for the physisorption of water on silica-alumina is more than the number calculated from the simple addition of the values obtained on each component oxide. This result was explained by postulating the appearance of new sites for water physisorption in the vicinity of the contact region of the two component oxides. The postulation predicts the new sites thus formed to have the character of protonic acid sites. The measurements of the infrared spectrum of *n*-butylamine adsorbed on the same samples of silica-alumina substantiated the appearance of strong protonic acid sites which are absent on the surfaces of the individual oxides, the strength of which increases with decreasing amount of alumina in silica-alumina.[11] Here, it must be interesting to study the energetic aspect of the interaction between water molecules and the new sites produced on silica-alumina.

On working the thermodynamics of water physisorption on the surfaces of a metal oxide, however, difficulties arise in the preparation of the surface. The present authors have intended to study the surface properties of metal oxides in relation to the amount of chemisorbed species such as CO_2 and hydroxyl groups.[12-14] During the course of this study, it has become clear that the surface of metal oxides usually adsorbs water at a time physically and chemically at room temperature, the desorbability of the chemisorbed water being dependent upon the nature of the oxides.[12] Furthermore, the rate of chemisorption of water on silica was found to be considerably smaller than that on the other oxides.[10]

The purpose of this work is therefore to prepare with special precautions the fully hydroxylated surfaces of silica-alumina, and then to study the energetics of the interaction of water with them by measuring the physisorption isotherms of water and by evaluating the differential heat of adsorption and the site energy distribution.

Experimental

Materials. The samples used in this study were the same as those used in the previous works.[10,11] Pure silica (S) was prepared by the hydrolysis of ethylsilicate in water. Pure alumina (A) was produced by hydrolysing aluminum isopropoxide in 2-propanol-water mixture. By mixing the two kinds of pure samples in aqueous gel state in an agate ball mill for 30 min, three kinds of silica-alumina samples containing 25, 50, and 75 wt% of alumina (SA-25, SA-50, and SA-75) were prepared. These gels were all washed with distilled water, dried at 100 °C for 20 hr, and calcined at 500 °C for 10 hr in air.

The specific surface area of the samples was determined by means of the BET method using the nitrogen adsorption at the temperature of liquid nitrogen, where the cross-sectional area of a nitrogen molecule was assumed to be 16.2 Å^2. The surface areas of the samples treated at 600 °C for 4 hr in a vacuum of 10^{-5} Torr were found to be 640, 189, 423, 427, 317 m^2/g for samples S, A, SA-25, SA-50, and SA-75, respectively.

Water Adsorption Isotherm. Water adsorption isotherms were measured volumetrically by using a conventional apparatus equipped with an oil manometer which serves to read sensitively the equilibrium pressure. In order to study the thermodynamics of water physisorption, it is necessary to prepare the completely-hydrated surfaces of the samples. For this purpose, the water adsorption procedure was performed in the following way. After degassing a sample at 600 °C for 4 hr, the first adsorption isotherm of water was measured at 25 °C. Next, the sample was exposed to the saturated water vapor at 25 °C for 12 hr in order to prepare the fully-hydroxylated surface, because the rate of surface hydroxylation of silica has been found to be considerably slow in a relatively low pressure of water.[10] Since the temperature at which surface hydroxyl groups start to be removed depends on the nature of oxides,[10,12] it will be delicate to establish the exact condition under which the physisorbed water is removed completely and all the surface hydroxyl groups are left. Here, in order to obtain a surface state reproducible and approximate to that described just above, the sample was subjected to the following treatment. The fully-hydroxylated surface was degassed at 30 °C for 4 hr in a vacuum of 10^{-5} Torr in order to remove physisorbed water, and then the second adsorption isotherm was measured at the same temperature as before. The degassing of the sample under the above condition and the measurement of adsorption isotherm at different temperatures (10, 18, and 25 °C) were further repeated on the same sample taken. The equilibrium for the second adsorption was attained 30 min after each dose of water vapor. When the second adsorption measurement was carried out repeatedly at the same temperature after degassing the sample, the isotherms obtained were in good agreement with each other, which substantiates the reproducibility of the fully-hydroxylated surfaces of the samples and consequently the reliability of the thermodynamical data of physisorbed water calculated therefrom.

Results and Discussion

The first and second adsorption isotherms obtained on pure alumina are given in Fig. 1. The first adsorption isotherm involves the amounts of both physisorbed and chemisorbed water, while the second adsorption isotherm involves only physisorbed water; the difference between them should consequently be the amount of chemisorbed water.[12,14] Figure 2 shows the adsorption isotherms of water on silica. It can be seen from Fig. 2 that the shape of the adsorption isotherms on silica is quite different from that on alumina; the amount of adsorbed water in the second adsorption on silica is greater than that in the first one, contrary to the case of alumina. This queer phenomenon is considered to be due to a slow rate of rehydroxylation of the silica surfaces, as discussed in the previous paper.[10]

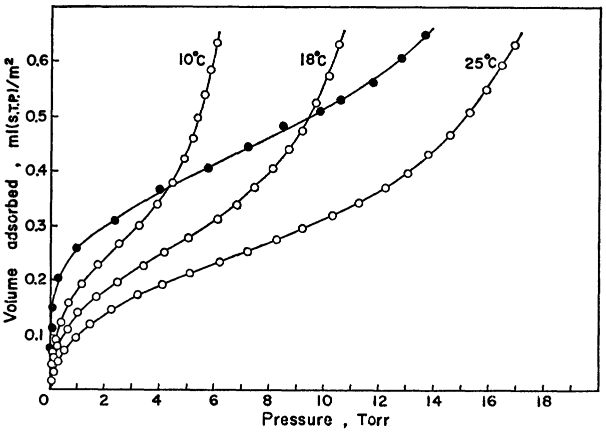


Fig. 1. Adsorption isotherms of water on alumina: ●, first adsorption at 25°C; ○, second adsorption on hydroxylated surface at 10, 18, and 25°C.

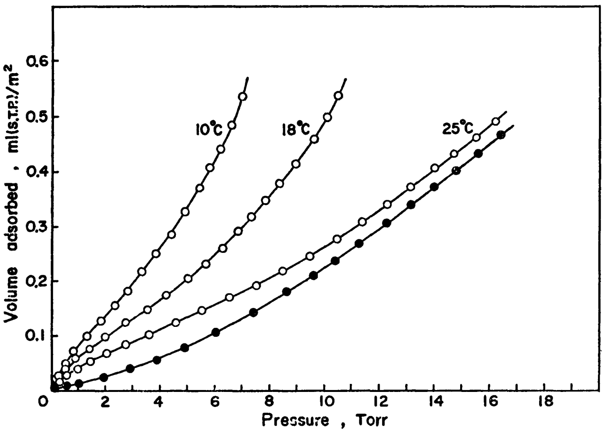


Fig. 2. Adsorption isotherms of water on silica: ●, first adsorption at 25°C; ○, second adsorption on hydroxylated surface at 10, 18, and 25°C.

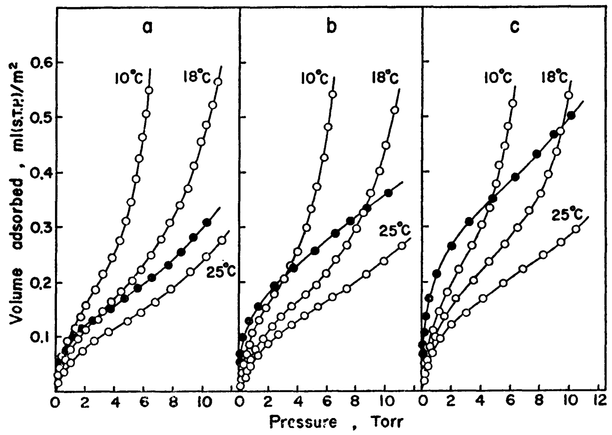


Fig. 3. Adsorption isotherms of water on silica-alumina: (a) SA-25, (b) SA-50, (c) SA-75; ●, first adsorption at 25°C; ○, second adsorption on hydroxylated surface at 10, 18, and 25°C.

The adsorption isotherms of water on the silica-alumina samples (SA-25, SA-50, and SA-75) are illustrated in Fig. 3. The sample SA-25 containing the least amount of alumina gives apparently the same type of isotherms as that of pure alumina, while the isotherms on the other samples are slightly modified from those of the sample SA-25. In addition, the difference between the first and the second adsorption isotherms seems to increase with the increase in alumina content.

From the physisorption isotherms obtained at different temperatures, the isosteric heat of adsorption, q_{st}, can be computed by using the Clausius-Clapeyron equation:

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{q_{st}}{RT^2} \qquad (1)$$

The isosteric heat q_{st} is the heat of adsorption at a constant amount of adsorption, being greater by RT than the differential heat of adsorption. Integrating the Eq. (1), we can obtain the equation (2):

$$\ln P = -\frac{q_{st}}{RT} + C \qquad (2)$$

The value q_{st} can be determined from the slope of the linear plot of $\ln P$ *vs.* $1/T$. The value q_{st} thus obtained is represented in Fig. 4 as a function of the surface coverage θ, the latter being referred to the monolayer capacity of water calculated by applying the BET method to the second adsorption isotherm. Figure 4 shows that the q_{st} values obtained on all the samples tested decrease almost exponentially with coverage, which gives an evidence for the surface heterogeneity of hydroxylated surfaces for water physisorption, and that the strength of the sites depends on the nature of the substrates, being greater on aluminol than on silanol. On the surfaces of the silica-alumina samples, the interaction energies lie between those of the two pure oxides, but not additive. The isosteric heats on the surface of SA-25 are relatively larger than the others.

The differential entropy, $\bar{S}_s$, of adsorbed water can

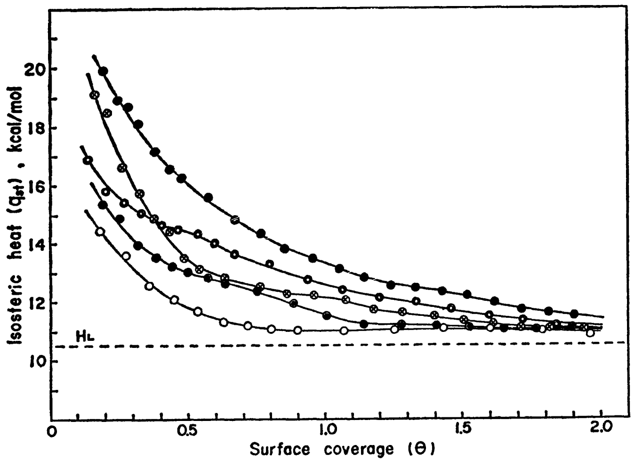


Fig. 4. Isosteric heat of adsorption of water physisorbed on silica, alumina, and silica-alumina: ○, S; ●, A; ◎, SA-25; ⊙, SA-50; ⊗, SA-75. Broken line indicates the heat of liquefaction of water at 25°C.

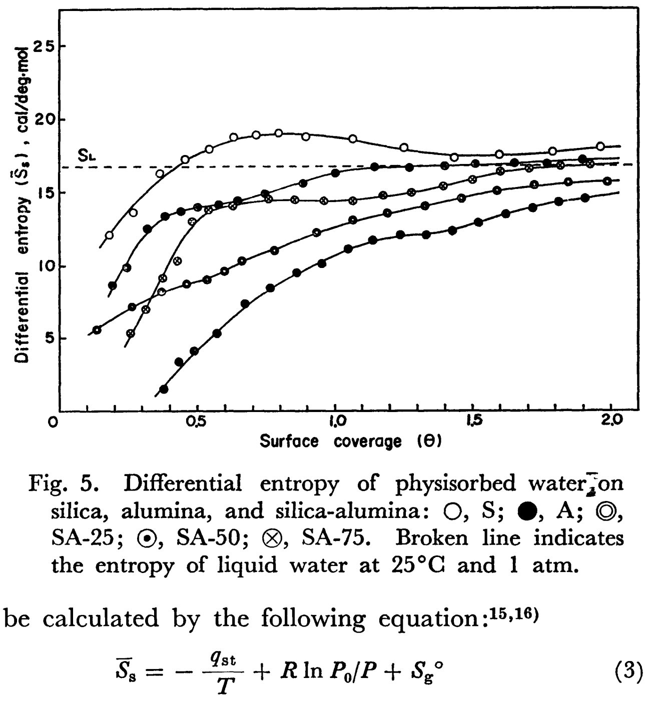


Fig. 5. Differential entropy of physisorbed water on silica, alumina, and silica-alumina: ○, S; ●, A; ◎, SA-25; ⊙, SA-50; ⊗, SA-75. Broken line indicates the entropy of liquid water at 25°C and 1 atm.

be calculated by the following equation:[15,16)]

$$\bar{S}_s = -\frac{q_{st}}{T} + R\ln P_0/P + S_g{}^\circ \qquad (3)$$

Here, P_0 is the standard pressure, P the equilibrium pressure, and $S_g{}^\circ$ the standard entropy of water vapor (45.11 cal/deg·mol at 25 °C and 1 atm). Figure 5 shows the plots of the differential entropy against the coverage. It can be seen from Fig. 5 that water molecules are adsorbed more strongly on surface hydroxyl groups of alumina with less mobility than on those of silica. The entropy of water adsorbed on the surfaces of silica-alumina lies between those on the two single oxides.

Assuming that the number of adsorbed molecules expresses the number of sites, the site energy distribution can be estimated from the relation:[17)]

$$g(\varepsilon) = \frac{\mathrm{d}N}{\mathrm{d}(H_d)} \qquad (4)$$

Here, N is the number of adsorption sites, and H_d the differential heat of adsorption. Practically, the distribution can be calculated by the graphical differentiation of the plot of q_{st} *vs.* adsorbed amount. The site energy distribution curve thus obtained is represented in Fig. 6. Figure 6 shows that the number of adsorption sites with higher energies is much more on alumina than on silica, and that both curves decrease monotonously. On the other hand, the distribution curves on the silica-alumina samples reveal a marked peak at a higher energy region, which is not observed on the surfaces of each of the individual oxides. Furthermore, it is to be noted that the peak appears at the higher energy of adsorption on the silica-alumina samples containing the less amount of alumina: at 14, 12, and 11.5 kcal/mol for SA-25, SA-50, and SA-75, respectively. The appearance of these peaks may probably be associated with the new adsorption sites characteristic of the silica-alumina samples.

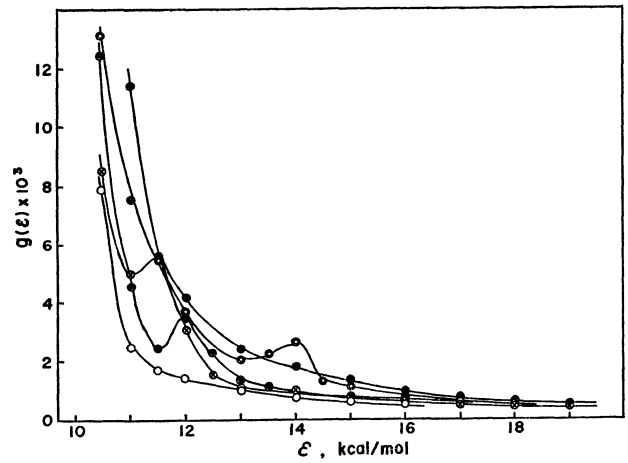
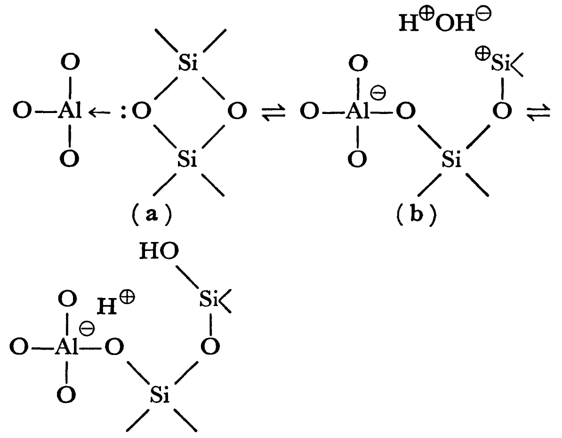


Fig. 6. Site energy distribution for the physisorption of water on silica, alumina, and silica-alumina: ○, S; ●, A; ◎, SA-25; ⊙, SA-50; ⊗, SA-75.

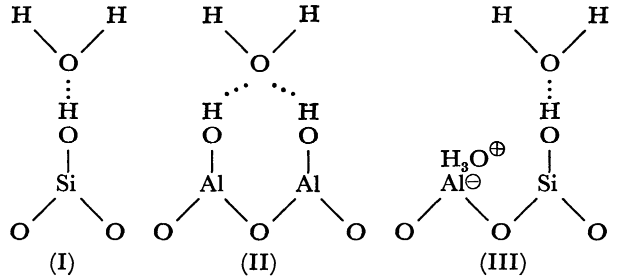
It has been known that there exist aprotonic acid sites on the surfaces of silica-alumina degassed at relatively higher temperatures, which can convert to protonic acid sites when exposed to water vapor.[1,9)] In the preceding work,[11)] it has been found that the infrared spectra of *n*-butylamine adsorbed on the present samples of silica-alumina have the band at 1540—1520 cm^{-1}, which is assigned to the symmetrical $NH_3{}^+$ bending vibration, and that the strength of this band decreases and at the same time the frequencies of the band shift to 1520—1503 cm^{-1} by pumping off the sample disk at elevated temperatures; these findings have never been observed on pure silica or alumina. The infrared studies have also led to another conclusion that the strength of the protonic acid sites increases with the decrease in the amount of alumina in silica-alumina. Similar conclusions obtained on the adsorption sites for *n*-butylamine as found by the infrared studies and for water as found by the present investigation seem to be explainable from the same stand point in the following way.

In the previous paper,[10)] the formation of the additional physisorption sites for water on silica-alumina, which are absent on the surfaces of each of the component oxides, has been expressed schematically as follows:



When the surfaces of both alumina and silica contact with each other, aluminum atom will attract the lone pair electrons on the oxygen atoms of silica owing to a strong electron-accepting ability of aluminum atoms (a); this will result in the splitting of Si–O–Si bonds and the formation of Al–O–Si bonds (b). When such surfaces are exposed to water vapor, a water molecule will be chemisorbed through the dissociation (c) to form a proton attached to an aluminum atom and a hydroxyl group bonded to a silicon atom. According to this proposition, a new type of sites formed should have the character of the Brönsted acid. It may be valid to consider that such an acidic site formed on silica-alumina acts as a stronger adsorption site for water compared to surface hydroxyl groups on each component oxide. Thus, the distribution curves on silica-alumina in Fig. 6 can be interpreted to reveal the overlapped effects of both the water adsorption to hydroxyl groups on heterogeneous surfaces through hydrogen bonding and that onto protonic sites, which appear to be relatively uniform in energy, through hydration.

In conclusion, three kinds of adsorbed water may thus be present in the first physisorption layer of water on silica-alumina:



The physisorption mode on silica (I) is possibly due to the fact that the population of surface hydroxyl groups is fairly small (less than 5 OH's/100 Å^2),[18,19] the ratio of H_2O : OH being nearly equal to 1 : 1 as indicated in the previous work,[10] and that the interaction energy is rather smaller and moreover the mobility of the physisorbed water is higher as indicated in the present work.

On the surface of alumina, however, the situation may be different from the case of silica: a water molecule will be physisorbed on two hydroxyl groups (II). This can be led from the fact that the hydroxyl groups of about 14 OH's/100 Å^2 are present on the surface of alumina, the ratio of H_2O : OH being about 1 : 2;[10] this physisorption mode may also be supported by larger adsorption energies (Fig. 4) and smaller entropies of adsorbed water (Fig. 5), compared to those on silica or silica-alumina.

The additional physisorption mode of water (III) will appear on the new sites, which should be produced in the vicinity of the contact region of the two component oxides according to the present preparation method of the samples. The physisorption of water on such new sites, indeed, implies the hydration of proton on the surfaces. The heat of hydration of proton in solution is well known to be very large (258 kcal/g·ion).[20] Abnormally large heats of adsorption of water observed on the surfaces of silica-alumina can thus be interpreted by the hydration of proton sites which also act as the strong Brönsted acid sites. However, the fact that the strength of the site energy is greater on silica-alumina samples containing smaller amount of alumina remains to be solved.

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