The Adsorption of Water on SiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$. The Relation between the Amounts of Physisorbed and Chemisorbed Water

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The specific surface area, the water content, and the water adsorption isotherm have been measured in order to investigate the interaction between the surfaces of SiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$ and water molecules. Al_2O_3 gives II-type adsorption isotherms and the amount of adsorbed water on it increases with a rise in the temperature of pretreatment, whereas SiO_2 gives isotherms approximate to the III-type and the amount of adsorbed water is larger when treated at lower temperatures. With $SiO_2 \cdot Al_2O_3$, it was found that the type of isotherms and the effect of the pretreatment temperature are similar to those of Al_2O_3, and that the amount of adsorption increases with an increase in the Al_2O_3 content. By analysing the adsorption data, the ratio of the amount of physisorbed water in the first layer to the amount of the underlying chemisorbed water was calculated. As a result, it was found that the H_2O:OH ratio is 1:2 on the surface of Al_2O_3, whereas it is 1:1 on the surface of SiO_2. The analysis of the isotherms on $SiO_2 \cdot Al_2O_3$ showed that the adsorption property of water on them is not additive: *e.g.*, the amount of adsorbed water on $SiO_2 \cdot Al_2O_3$ is larger than the sum of the water adsorbed on each component. Thus, it has been concluded that, on the surface of SiO_2 in contact with Al_2O_3, the surface hydroxylation proceeds more rapidly than on the surface of pure SiO_2.

Silica-alumina ($SiO_2 \cdot Al_2O_3$) is a catalyst widely used for such reactions as cracking and isomerization, and its surface properties have been studied extensively. Among these, the relation between the surface acidity and the catalytic activity[1–4] has been the most important property; it has been studied by using such basic substances as ammonia,[5–7] amine,[8] and pyridine[9,10] as adsorbates. Recently, it has become clear that the surface hydroxyl groups are present on the surfaces of most metal oxides placed in the usual atmosphere, that they affect their surface properties, and that they also play important roles in catalytic actions.[11,12] Finch and Clark[12] have reported that more than 0.45% water is necessary for the isomerization reaction of 1-butene by using $SiO_2 \cdot Al_2O_3$ as a catalyst; in this case, water acts cooperatively with a complex for polymerization.

In the preceding papers the ratio of the number of physisorbed water molecules to the amount of the underlying chemisorbed water (surface hydroxyl groups) has been investigated; it was found to be 1:2 (H_2O:OH) for TiO_2 (rutile) and α-Fe_2O_3[13] and 1:1 for ZnO[14] in the monolayer coverage of physisorbed water. On the surface of the $SiO_2 \cdot Al_2O_3$ catalyst there should be two kinds of surface hydroxyl groups, silanol and aluminol, differing in properties. It has been reported that the remaining surface hydroxyl groups of $SiO_2 \cdot Al_2O_3$ after the treatment at higher temperatures were those on SiO_2.[15] There have been many discussions of the nature of acidic sites on $SiO_2 \cdot Al_2O_3$,[16] but the water adsorption property, which should affect the surface acidity, has not yet been investigated in detail. The purpose of this work is to investigate the water adsorption property on SiO_2, Al_2O_3, and three kinds of $SiO_2 \cdot Al_2O_3$, all differing in composition in order to ascertain the relation between the amounts of physisorbed and chemisorbed water on them, and to clarify the details of the interaction between oxide surfaces and water molecules.

Experimental

Materials. Pure SiO_2 gel (S) was produced by the hydrolysis of ethyl-silicate with water at 100°C, the latter being purified by double distillation from a commercial, guaranteed reagent. Al_2O_3 gel (A) was prepared by the following process. Metallic aluminum was treated with a 5% NaOH solution to remove the surface impurity, and then washed with water, absolute ethanol, and ether. The 25 g of metallic aluminum thus treated were permitted to react with 300 m*l* of pure isopropanol in a reflux flask, in the presence of 1 g of mercuric chloride as a catalyst. The aluminum isopropoxide thus formed[17] was distilled under a reduced pressure of 2.5 Torr (108—108.5°C). An Al_2O_3 gel sample was obtained by the hydrolysis of this aluminum isopropoxide in a mixed solution of isopropanol and water (3:1). Three kinds of $SiO_2 \cdot Al_2O_3$ were obtained by mixing SiO_2 (S) and Al_2O_3 (A) samples of different compositions. SA-25, SA-50, and SA-75 contain Al_2O_3 gel of 25, 50, and 75wt.% respec-

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tively. The mixing of SiO_2 and Al_2O_3 gels was carried out in an agate-ball mill. Finally, the pure and mixed gels thus obtained were washed sufficiently with distilled water, dried at 100°C, and calcined at 500°C for 10 hr in air.

Specific Surface Area. The specific surface area of the samples pretreated at 600°C for 4 hr under the reduced pressure of 10^{-5} Torr was measured by applying the BET theory[18] to the nitrogen adsorption data at −196°C. The conditions of the pretreatment were the same as those for the water adsorption measurement. The molecular area of nitrogen was assumed to be 16.2 Å². The values obtained on the S, A, SA-25, SA-50, and SA-75 samples were 640, 189, 423, 427, and 317 m²/g respectively.

Water Content. The water content of the samples was measured by the successive-ignition-loss method.[19] The samples were treated in the same apparatus as was used for the adsorption measurement for 4 hr at various temperatures, from room temperature to 1100°C; the vapor evolved was determined volumetrically at each step. From these data, the water content remaining on the surface could be obtained as a function of the pretreatment temperature. In this calculation the water content at 1100°C was assumed to be zero, as the amount of water vapor expelled at 1100°C was negligibly small.

Water-adsorption Isotherm. The sample was at first treated at 600°C for 4 hr under the reduced pressure of 10^{-5} Torr. The measurement of the water adsorption isotherm was carried out volumetrically at 20°C, by using an oil manometer to read the equilibrium pressure. After the first adsorption isotherm had been determined, the sample was again treated at 30°C for 4 hr at 10^{-5} Torr, and then the second adsorption isotherm was measured at the same temperature as before. The same adsorption measurements were repeated subsequently for one sampling after the sample had been treated at various temperatures, from 100 to 500°C.

Results

The water content of the samples is shown in Fig. 1 as a function of the pretreatment temperature. It indicates the amount of water bonded to the surface treated at the given temperatures, expressed in the number of hydroxyl groups per 100 Å². At lower temperatures there is a large possibility that it includes the amount of physisorbed water. It can be seen from Fig. 1 that the water content of pure Al_2O_3 is the most, and that the value of SiO_2 is the least. With $SiO_2 \cdot Al_2O_3$, the greater the portion of Al_2O_3, the more the water content. Furthermore, the water-content curve of pure SiO_2 is characteristic in that it decreases almost linearly with the rise in the temperature.

The water-adsorption isotherms of five samples are given in Figs. 2—4. In the case of Al_2O_3, the adsorption isotherms belong to the II-type of Brunauer's classification;[20] the amount of adsorbed water is the largest in the measurement after 600°C treatment, and the smallest in the measurement after 30°C treatment. When the pretreatment temperature rises from 30

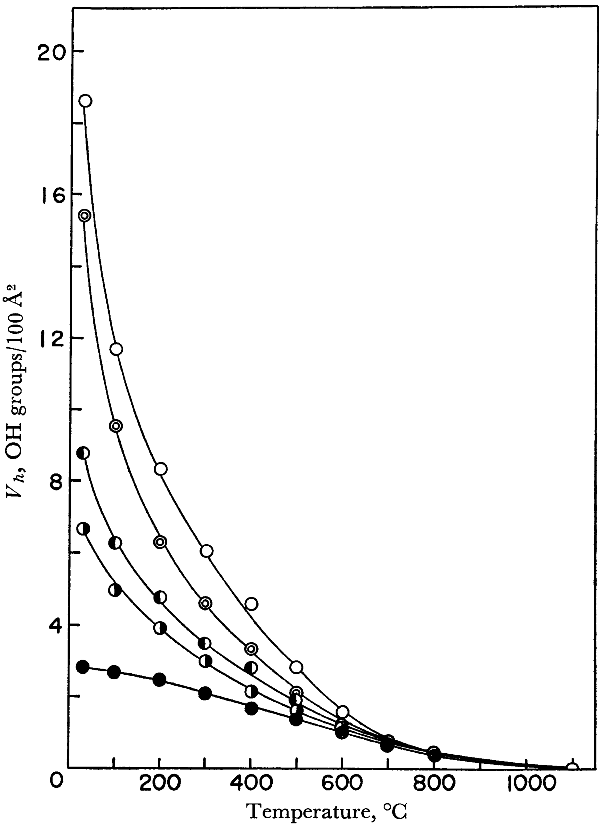

Fig. 1. Water content of SiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$: ●, S; ○, A; ◑, SA-25; ◐, SA-50; ◎, SA-75.

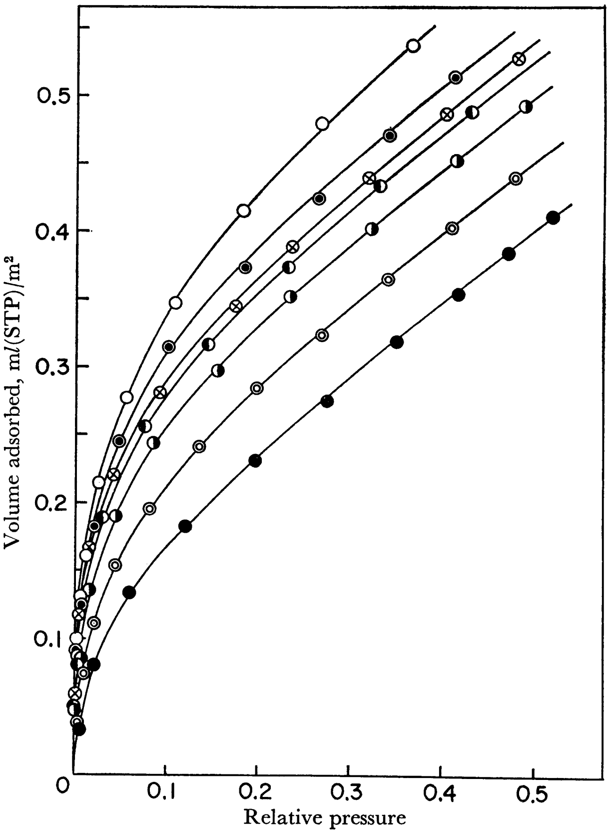

Fig. 2. Water-adsorption isotherm on Al_2O_3 at 20°C, pretreated at 600°C, ○; 30°C, ●; 100°C, ◎; 200°C, ◑; 300°C, ◐; 400°C, ⊗; 500°C, ◉.

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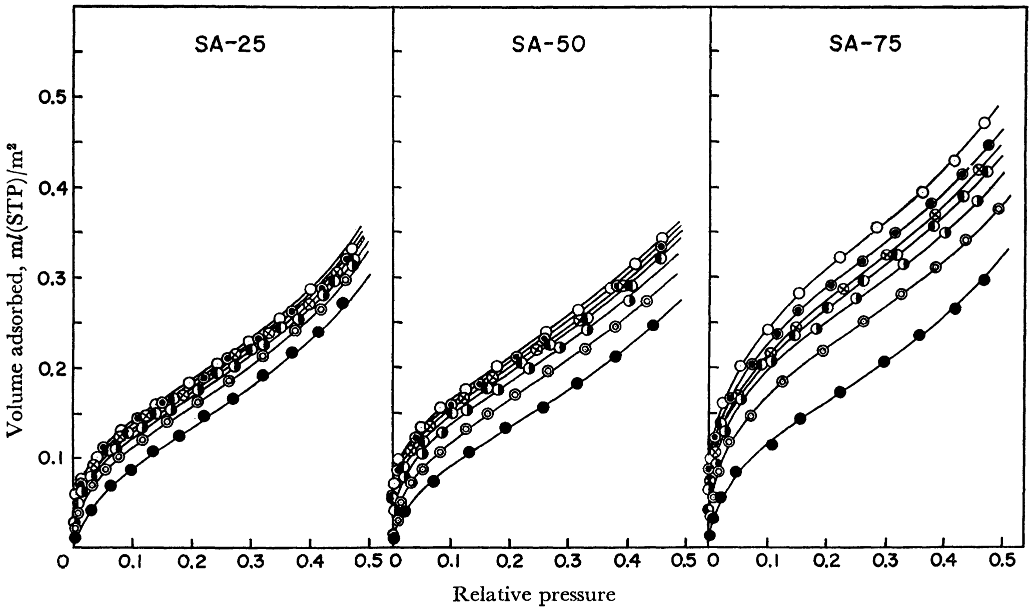

Fig. 3. Water-adsorption isotherm on $SiO_2 \cdot Al_2O_3$ at 20°C, pretreated at 600°C, ○; 30°C, ●; 100°C, ◎; 200°C, ◑; 300°C, ◐; 400°C, ⊗; 500°C, ◉.

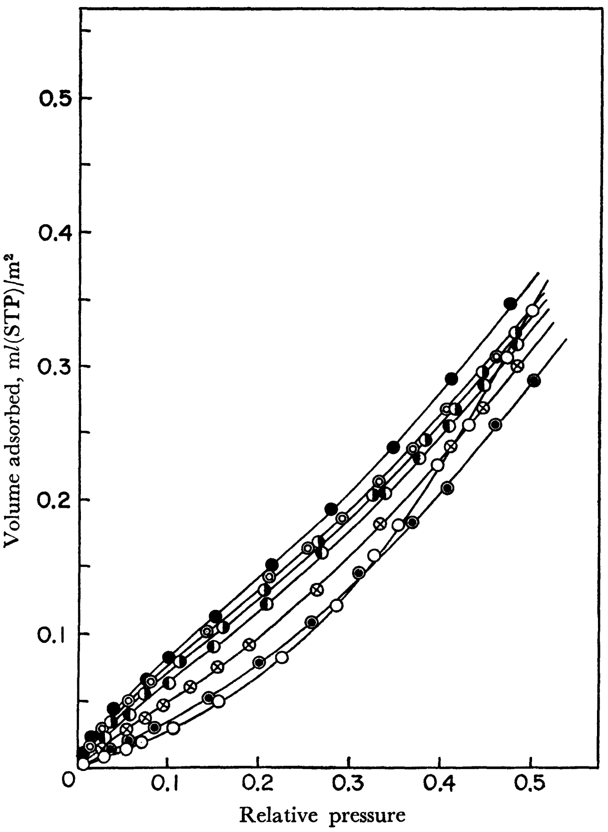

Fig. 4. Water-adsorption isotherm on SiO_2 at 20°C, pretreated at 600°C, ○; 30°C, ●; 100°C, ◎; 200°C, ◑; 300°C, ◐; 400°C, ⊗; 500°C, ◉.

to 500°C, the amount of adsorbed water increases and approaches the value of the 600°-treated sample. Moreover, Fig. 2 shows that the sample of Al_2O_3 chemisorbs water considerably. The same situation appears in the case of $SiO_2 \cdot Al_2O_3$ (Fig. 3), and the amount of adsorbed water increases with an increase in the content of Al_2O_3.

The water-adsorption isotherms on pure SiO_2 are given in Fig. 4; they are quite different from those on pure Al_2O_3 and $SiO_2 \cdot Al_2O_3$. First, the results generally show that the higher the pretreatment temperature, the less the amount of adsorbed water. Second, the shape of the isotherms on the sample pretreated at lower temperatures is of the II-type, whereas it seems to approach the III-type when the pretreatment temperature rises. Young[21] has reported that, on a flame silica, the water-adsorption isotherms were of the III-type and that the amount of adsorbed water decreased with the rise in the pretreatment temperature to 450°C. Most metal oxides chemisorb water molecules, even at the lowest equilibrium pressure, to form surface hydroxyl groups, and further physisorb water molecules on them through hydrogen bonding, resulting in II-type isotherms, as is shown in Figs. 2 and 3. On the contrary, the surface of pure SiO_2 adsorbs more water when the pretreatment temperature is lower and, accordingly, when the remaining surface hydroxyl groups are larger in number, as may be seen from Figs. 1 and 4. Moreover, the amount of adsorbed water on the 600°C-treated sample is quite small at lower pressures, but it increases more sharply at higher pressures compared to the cases of the other samples, as is shown in Fig. 4. These results suggest that the rate of the surface hydroxylation of SiO_2 is slower than in the cases of Al_2O_3 and other metal oxides and that, therefore, the physisorption only occurs during the water-adsorption measurement. Our experience has shown that, in the first adsorption-isotherm measurement on SiO_2 (after 600°C treatment), the time required for the attainment of the equilibrium pressure was within 20 min in the low-pressure range, but was prolonged in the higher-pressure range,

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[21] G. J. Young, *J. Colloid Sci.*, **13**, 67 (1958).

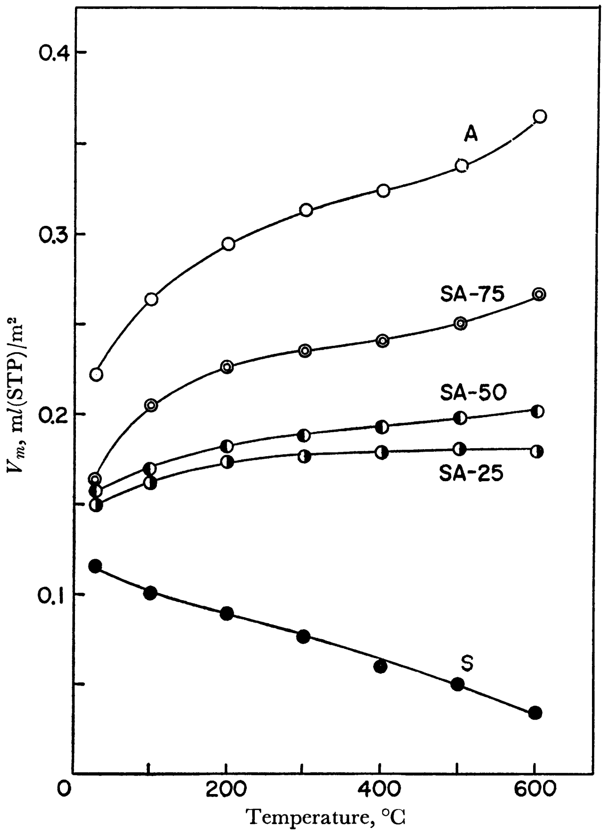

Fig. 5. Dependence of V_m value on pretreatment temperature.

taking more than a few hours. In the second adsorption measurement, however, the equilibrium was attained within 30 min over the whole range of pressure. The results of Hockey and Pethica[22] and those of Egorova *et al.*[23] agree with the present findings, supporting of the idea that, on the surface of SiO_2, the rate of surface hydroxylation is so slow that the surface can only be hydroxylated at higher relative pressures.

By applying the BET method[18] to the adsorption isotherms, the monolayer capacity, V_m, of water was calculated and plotted against the pretreatment temperature (Fig. 5). The V_m value on Al_2O_3 increases with a rise in the temperature of pretreatment. In a previous paper, the same plot was taken on ZnO, TiO_2, and α-Fe_2O_3.[24] In the cases of ZnO and TiO_2, the temperature at which the steep increase in V_m starts was distinct; this was explained in terms of the commencement of the removal of chemisorbed water by the pretreatment and the reversible rehydroxylation on exposing the surface to water vapor. Also, in the present case additional chemisorption on Al_2O_3 is considered to occur, though the temperature showing the commencement of the steep increase in V_m is not clear similarly to the case of α-Fe_2O_3. The removal of chemisorbed water may occur at least at 150°C, as is to be expected from Fig. 1. On the other hand, the V_m value of SiO_2 decreases almost linearly with the rise in the pretreatment temperature; this is parallel to the decrease in water content shown in Fig. 1. This suggests that, on the surface of SiO_2, the physisorption of water only occurs on the surface hydroxyl groups during the adsorption measurement. With $SiO_2 \cdot Al_2O_3$, the V_m value increases similarly to that of pure Al_2O_3, but the increase in V_m becomes slower when the content of SiO_2 is greater, as is shown in Fig. 5.

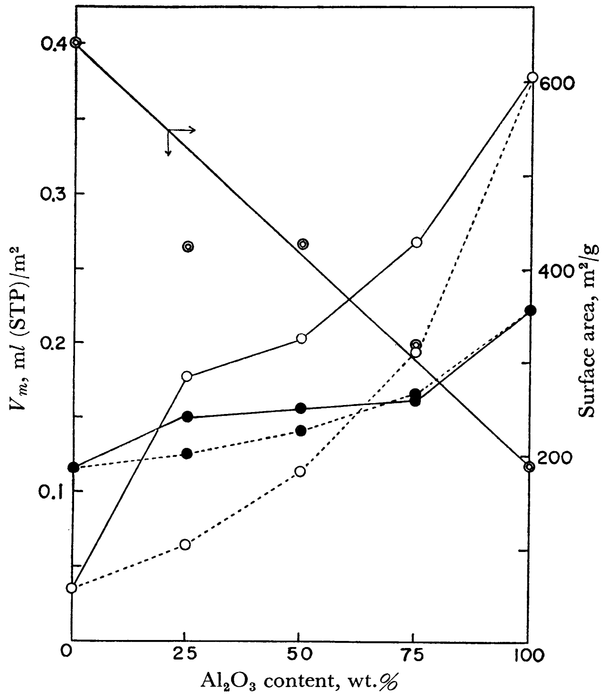

Fig. 6. Dependence of V_m value and specific surface area on Al_2O_3 content: pretreated at 600°C, ○; 30°C, ●.

In order to ascertain the dependence of V_m on the composition, V_m is replotted against the Al_2O_3 content in Fig. 6. This plot can be taken for each pretreatment temperature, but in Fig. 6 only two limiting cases are represented (600° and 30°C treatments). The other plots at the intermediate temperatures can be inserted in a regular order between them. The specific surface area of the sample is also plotted in Fig. 6. As may be seen from Fig. 6, the surface areas of $SiO_2 \cdot Al_2O_3$ are almost all on the straight line connecting the values of SiO_2 (640 m^2/g) and Al_2O_3 (189 m^2/g); the one exception is the SA-25 sample, which gives a fairly smaller value than would be expected from the composition. If the surface area of $SiO_2 \cdot Al_2O_3$ is composed of the sum of each component, the portion of the surface of Al_2O_3 in $SiO_2 \cdot Al_2O_3$, $S_{(A)}/S_{(SA)}$, is about 9, 23, and 47% for SA-25, SA-50, and SA-75 respectively. Furthermore, if the water adsorption occurs additively on the surfaces of $SiO_2 \cdot Al_2O_3$, the V_m value will change as shown by the dotted curves. The experimental results on $SiO_2 \cdot Al_2O_3$, especially on SA-25, deviate greatly from these synthetic curves, indicating that the water adsorption does not occur additively on the surface of $SiO_2 \cdot Al_2O_3$. It has been established that $SiO_2 \cdot Al_2O_3$ of a composition of 13—25 wt.% Al_2O_3

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[22] J. A. Hockey and B. A. Pethica, *Trans. Faraday Soc.*, **57**, 2247 (1961).

[23] T. S. Egorova, Yu. A. Zarif'yants, V. F. Kiselev, K. G. Krasil'nikov, and V. V. Murina, *Zh. Fiz. Khim.*, **36**, 1458 (1962).

[24] T. Morimoto, M. Nagao, and F. Tokuda, This Bulletin, **41**, 1533 (1968).

Table 1. Relation between the amounts of physisorbed and chemisorbed water on SiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$ (SA-50)

Sample	Treat. temp., °C	V_m, m*l*(STP)/m²	V_p, H_2O molecules/100Å²	V_c,	V_h,	V_c+V_h,	$\frac{V_p}{V_c+V_h}$, H_2O/OH
				OH groups/100Å²			
SiO_2	30	0.116	3.12	—	2.78	—	—
	100	0.100	2.69	—	2.72	2.72	0.99
	200	0.089	2.40	—	2.50	2.50	0.96
	300	0.077	2.07	—	2.10	2.10	0.99
	400	0.060	1.62	—	1.69	1.69	0.96
	500	0.051	1.37	—	1.40	1.40	0.98
	600	0.035	0.94	—	1.03	1.03	0.91
Al_2O_3	30	0.223	6.00	—	18.66	—	—
	100	0.264	6.00	2.20	11.92	13.92	0.43
	200	0.295	6.00	3.87	8.28	12.15	0.49
	300	0.314	6.00	4.89	6.04	10.93	0.55
	400	0.324	6.00	5.43	4.58	10.01	0.60
	500	0.336	6.00	6.08	2.80	8.88	0.68
	600	0.378	6.00	8.34	1.60	9.94	0.60
SA-50	30	0.157	4.23	—	8.78	—	—
	100	0.169	4.23	0.64	6.26	6.90	0.61
	200	0.182	4.23	1.34	4.76	6.10	0.69
	300	0.188	4.23	1.66	3.50	5.16	0.82
	400	0.193	4.23	1.93	2.82	4.75	0.89
	500	0.198	4.23	2.20	1.99	4.19	1.01
	600	0.203	4.23	2.47	1.17	3.64	1.16

has a large catalytic activity.[6,25] The present results seem to show a characteristic activity of SA-25 in the adsorption of water.

Discussion

On the basis of these experimental results, the relation between the amounts of physisorbed and chemisorbed water on pure SiO_2 and Al_2O_3 was first obtained as is shown in Table 1. V_m is the monolayer capacity obtained from the water-adsorption isotherm. This may be considered to include only physisorbed water in the case of SiO_2, as has been discussed above. V_p is the amount of physisorbed water, expressed in the number of water molecules per 100 Å². For the same reason, the amount of chemisorbed water, V_c, on SiO_2 is zero in the initial stage of the adsorption process. V_h is the water content; it indicates the amount of water chemisorbed before the adsorption measurement, expressed in the number of hydroxyl groups per 100 Å². Thus, the value of V_h is equal to the total amount of chemisorbed water in the case of SiO_2. It may be seen from Table 1 that the ratio of V_p to V_h is approximate to 1 on every surface of SiO_2 treated at different temperatures. This finding indicates that the initial physisorption of water occurs only on silanol groups in the ratio of 1:1. The surface density of silanol groups is 2.78 OH groups/100 Å² at most; this is reasonable compared with the maximum value calculated by Schneider[26] on the surface of amorphous SiO_2 (5.0 OH groups/100 Å²), although it is considerably smaller than the number of surface hydroxyl groups on Al_2O_3 and the other metal oxides.[13] Several authors have also found that the number of the surface hydroxyl groups on SiO_2 is small.[21,22,27] These silanol groups are, therefore, believed to be scattered and isolated on the surface of SiO_2, on which each water molecule is bonded through hydrogen bonding in the ratio of 1:1. On the surface of ZnO a similar ratio has also been found,[14] but there the mechanism of water adsorption seems to be different from the present case.

The V_m value on Al_2O_3 treated at various temperatures is composed of both physisorbed and chemisorbed water, as has been described above, but the second adsorption isotherm obtained after the treatment at 30°C contains only physisorbed water, for the reason discussed in previous papers.[13,24] Therefore, in the case of Al_2O_3, the V_m value obtained from the second adsorption isotherm (after the 30°C treatment) was taken as the amount of physisorbed water, V_p, and the difference between V_m and V_p, as the amount of the chemisorbed water, V_c.[28] The sum of V_c and V_h is, accordingly, the total amount of the chemisorbed water after the adsorption measurement. Thus, in the case of Al_2O_3, the $V_p:(V_c+V_h)$ ratio should be the true ratio of the amounts of physisorbed and chemisorbed water in the first layer of physisorption; it is found to be approximately 1 : 2, as is shown in Table 1. This suggests that, on the surface of Al_2O_3, one water molecule is physisorbed onto two surface hydroxyl groups, as in the cases of TiO_2 (rutile) and α-Fe_2O_3.[13] In addition, when the pretreatment temperature of Al_2O_3 rises over 200°C, V_h decreases, V_c

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[25] A. Clark and V. C. F. Holm, *J. Catal.*, **2**, 16, 21 (1963).

[26] M. Schneider, Ph. D. Thesis, University of Heidelberg, Germany (1962); H. P. Boehm, *Advan. Catal.*, **16**, 179 (1966).

[27] G. J. Young and T. P. Bursh, *J. Colloid Sci.*, **15**, 361 (1960).

[28] J. J. Jurinak, *ibid.*, **19**, 477 (1964).

TABLE 2. RELATION BETWEEN THE AMOUNTS OF PHYSISORBED AND CHEMISORBED WATER ON $SiO_2 \cdot Al_2O_3$ (SA-50)

Treat. temp., °C	$V_{m(SA)}$, ml(STP) /m²	$V_{m(A)}$, ml (STP) /0.23 m²	$V_{p(A)}$, H_2O molecules/23 Å²	$V_{c(A)}$,	$V_{h(A)}$,	$V_{c(A)}+V_{h(A)}$,	$\frac{V_{p(A)}}{V_{c(A)}+V_{h(A)}}$, H_2O/OH
				OH groups/23 Å²			
30	0.157	0.068	1.83	—	6.64	—	—
100	0.169	0.092	1.83	1.30	4.17	5.47	0.33
200	0.182	0.114	1.83	2.45	2.83	5.28	0.35
300	0.188	0.129	1.83	3.27	1.88	5.15	0.36
400	0.193	0.147	1.83	4.24	1.52	5.76	0.32
500	0.198	0.159	1.83	4.89	0.91	5.80	0.32
600	0.203	0.177	1.83	5.82	0.38	6.20	0.30

increases, and the sum of V_h and V_c is almost constant; this suggests that the rehydroxylation of the dehydroxylated sites occurs reversibly on the surface of Al_2O_3 upon exposure to water vapor.

In the case of $SiO_2 \cdot Al_2O_3$, the meaning of the H_2O:OH ratio is fairly obscure, since water molecules can be adsorbed differently on the two kinds of surfaces. The SA-50 data listed in Table 1 are temporarily-calculated values, the mean value of the values on the two kinds of surfaces, which are obtained by the same method as was used in the case of pure Al_2O_3. In this calculation it is assumed that the physisorption only occurs on the 30°-treated surface of SA-50, and that V_p is constant on every surface treated at different temperatures. The H_2O:OH ratio of SA-50 thus calculated increases remarkably with the rise in the pretreatment temperature, though the values of pure SiO_2 and Al_2O_3 are almost invariable. This tendency becomes smaller in the order: SA-25 (0.72—1.53), SA-50 (0.61—1.16), SA-75 (0.36—0.63); the larger the portion of SiO_2, the greater the effect. Certainly, this effect results from the fact that, when the surface treated at higher temperatures is exposed to water vapor, the rehydroxylation occurs reversibly and rapidly on the dehydroxylated sites of both SiO_2 and Al_2O_3 in $SiO_2 \cdot Al_2O_3$, as in the case of pure Al_2O_3, in spite of the fact that the rehydroxylation is difficult on SiO_2. Since the physisorption of water initially occurs on the surface hydroxyl groups, the amount of physisorbed water on $SiO_2 \cdot Al_2O_3$ is also expected to decrease, as in the case of pure SiO_2, when the pretreatment temperature rises. Thus, in calculation of SA-50 shown in Table 1, V_p was overestimated and, accordingly, V_c+V_h was underestimated, resulting in the increase in the H_2O:OH ratio at higher pretreatment temperatures.

Another calculation was made on the SA-50 sample as an example (Table 2), assuming that the surface of SiO_2 in $SiO_2 \cdot Al_2O_3$ only physisorbs only water molecules. On this sample, the portion of the surfaces occupied by Al_2O_3 is 23%. By subtracting the amount of physisorbed water on 77 Å² of pure SiO_2 from the V_m value of SA-50, we can obtain the sum of the amounts of physisorbed and chemisorbed water, $V_{m(A)}$, on 23 Å² of Al_2O_3. By means of the same method as was used in the case of Al_2O_3, $V_{m(A)}$ can be separated into the amounts of chemisorbed ($V_{c(A)}$) and physisorbed water ($V_{p(A)}$); assuming that the $V_{m(A)}$ value obtained after the 30°C treatment is composed of only the amount of physisorbed water, as in the case of pure Al_2O_3, the $V_{p(A)}$ value of 1.83 water molecules per 23 Å² for SA-50 is obtained. On the measurements after the pretreatment at higher temperatures, the chemisorption of water also occurs; its amount can be determined by subtracting $V_{p(A)}$ from $V_{m(A)}$. On the other hand, the water content of SA-50 illustrated in Fig. 1 should be composed of those on SiO_2 and Al_2O_3. On the basis of the above assumption that the surface of SiO_2 does not chemisorb water molecules, the water content of Al_2O_3, $V_{h(A)}$, can be calculated. Thus, the ratio of the amount of physisorbed water ($V_{p(A)}$) to the total amount of chemisorbed water ($V_{c(A)}+V_{h(A)}$) can be given as 0.30—0.36 for every measurement, whatever the treatment temperature may be, as is shown in Table 2. Similar results were obtained on the SA-25 (0.21—0.31) and SA-75 (0.24—0.34) samples; they are all considerably smaller than that on pure Al_2O_3 (0.5).

Such small values seem to be quite difficult to accept if we take into account the surface hydrophilicity of pure Al_2O_3. These unlikely small values probably arise from the assumptions that the water chemisorption does not occur on the surface of SiO_2 and that, consequently, all the chemisorption of water on $SiO_2 \cdot Al_2O_3$ in the adsorption process is to be attributed to the surface of Al_2O_3 in $SiO_2 \cdot Al_2O_3$. Rather, it may be reasonable

TABLE 3. AMOUNT OF CHEMISORBED WATER ON SiO_2 IN $SiO_2 \cdot Al_2O_3$

Treat. temp., °C	SA-25			SA-50			SA-75		
	$V_{c(A)}$,	$V_{m(S)}$,	$V_{c(S)}$,	$V_{c(A)}$,	$V_{m(S)}$,	$V_{c(S)}$,	$V_{c(A)}$,	$V_{m(S)}$,	$V_{c(S)}$,
	OH groups/100 Å²			OH groups/100 Å²			OH groups/100 Å²		
100	16.44	1.41	0.47	5.65	1.03	0.34	6.02	3.40	1.13
200	29.67	2.55	0.85	10.65	2.03	0.68	9.19	4.72	1.57
300	36.78	3.15	1.05	14.22	2.79	0.93	10.98	5.40	1.80
400	48.33	4.24	1.41	18.43	3.88	1.29	12.57	6.34	2.11
500	54.00	4.74	1.58	21.26	4.53	1.51	14.15	7.15	2.38
600	60.89	5.37	1.79	25.30	5.06	1.69	17.17	7.83	2.61

TABLE 4. COMPARISON OF V_h VALUES OF $SiO_2 \cdot Al_2O_3$ (OH GROUPS/100 Å^2)

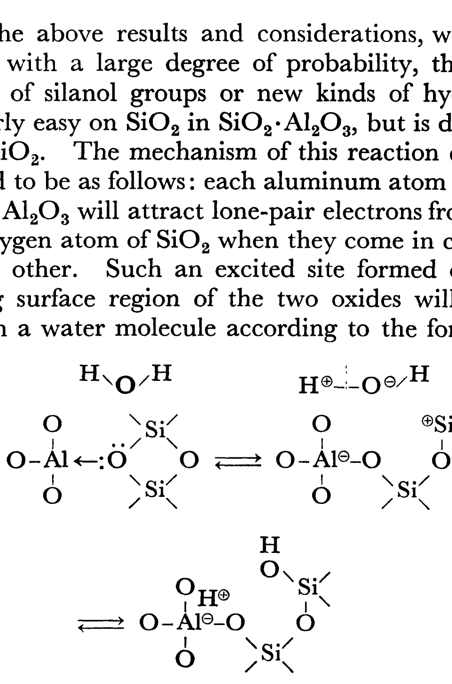
Temp., °C	S	SA-25		SA-50		SA-75		A
	exp.	calcd	exp.	calcd	exp.	calcd	exp.	exp.
30	2.78	4.21	6.67	6.43	8.78	10.24	16.46	18.66
100	2.72	3.53	4.91	4.79	6.26	6.95	9.64	11.72
200	2.50	3.02	3.94	3.83	4.76	5.22	6.32	8.28
300	2.10	2.45	3.02	3.01	3.50	3.95	4.68	6.04
400	1.69	1.95	2.16	2.35	2.82	3.05	3.34	4.58
500	1.40	1.53	1.61	1.72	1.99	2.06	2.04	2.80
600	1.03	1.08	1.03	1.16	1.17	1.30	1.06	1.60

to suppose that water molecules can be chemisorbed also on the surface of SiO_2 in $SiO_2 \cdot Al_2O_3$. In the calculation in Table 2, the number of the silanol groups thus probably formed is included in $V_{c(A)}$; this results in the overestimation of $V_{c(A)}$ and, accordingly, the underestimation of $V_{p(A)}$: $(V_{c(A)}+V_{h(A)})$. The overestimation of $V_{c(A)}$ can be understood more clearly by recalculating the data per 100 Å^2 from those per 23 Å^2, as in Table 3. The number of surface aluminum atoms of α-Al_2O_3 is estimated crystallographically to be 10.20 aluminum atoms per 100 Å^2 on the (0001) plane of α-Al_2O_3. Peri and Hannan[29] assumed the value of 12.5 OH groups/100 Å^2 as the surface density of hydroxyl groups on the fully hydroxylated surface of γ-Al_2O_3. The surface density of aluminum atoms and, accordingly, the maximum number of surface aluminol groups on the $SiO_2 \cdot Al_2O_3$ samples tested here can be expected to be almost the same as has been cited above. The V_c values on pure Al_2O_3 in Table 1 are, therefore, reasonable, but the $V_{c(A)}$ values are extraordinarily large, as is shown in Table 3; this proves that $V_{c(A)}$ has been overestimated.

Next, let us estimate the amount of chemisorbed water on SiO_2 in $SiO_2 \cdot Al_2O_3$, as has just been suggested. On the basis of the value of $V_{c(A)}$ in Table 3 and that of V_c of pure Al_2O_3 in Table 1, the excess amount of chemisorbed water per 23 Å^2 can be calculated; this water is transferred to the surface of 77 Å^2 of SiO_2. Here, the amount of water chemisorbed on Al_2O_3 in $SiO_2 \cdot Al_2O_3$ is assumed to be the same as that chemisorbed on pure Al_2O_3. The $V_{m(S)}$ value thus obtained is given in Table 3, expressed in the number of hydroxyl groups per 100 Å^2. When the chemisorption of water occurs on SiO_2 to form the silanol groups, additional physisorption will also occur on them. Accordingly, assuming that the physisorption on SiO_2 in $SiO_2 \cdot Al_2O_3$ would occur in the ratio of 1:1 (H_2O:OH), as in the case of pure SiO_2, one third of the $V_{m(S)}$ value is the amount of chemisorbed water. The $V_{c(S)}$ value thus obtained is 2.61 OH groups/100 Å^2 at most, as is shown in Table 3; this is comparable with the V_h value on SiO_2 and indicates the number of silanol groups retained before the water-adsorption measurement. $V_{c(S)}$ is the mean value on the unit surface area of SiO_2 in $SiO_2 \cdot Al_2O_3$, but the silanol groups newly formed during the adsorption process are probably concentrated in the contacting surface region of SiO_2 and Al_2O_3.

Finally, assuming that the V_h value of each oxide in $SiO_2 \cdot Al_2O_3$ is the same as that of single oxide, and taking into account the surface areas occupied by the two components, we can calculate the V_h values of $SiO_2 \cdot Al_2O_3$ and compare them with the experimental data read from Fig. 1 (Table 4). It may be seen from Table 4 that the experimental V_h value is always larger than the calculated one, but that the former approaches the latter as the sample is pretreated at higher temperatures. In other words, the water content is not additive and the partial chemisorption of water occurs on $SiO_2 \cdot Al_2O_3$ before the adsorption measurement.

From the above results and considerations, we may conclude, with a large degree of probability, that the formation of silanol groups or new kinds of hydrated sites is fairly easy on SiO_2 in $SiO_2 \cdot Al_2O_3$, but is difficult on pure SiO_2. The mechanism of this reaction can be considered to be as follows: each aluminum atom on the surface of Al_2O_3 will attract lone-pair electrons from the surface oxygen atom of SiO_2 when they come in contact with each other. Such an excited site formed on the contacting surface region of the two oxides will react easily with a water molecule according to the formula:



In this process, the water molecule can be adsorbed *via* dissociation; on the surface of SiO_2 a silanol group is formed, and on the surface of Al_2O_3, H^+ is adsorbed on the negative site of the aluminum atom.

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[29] J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, **64**, 1526 (1960).