The Heat of Immersion of Aluminum Oxide in Water

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It has been reported by several authors[1-4] that various silicas show a maximum in the temperature range of 200 to 300°C in the curve of the heat of immersion in water vs. the outgassing temperature. Two theories have been proposed to explain this phenomenon. According to one theory, the hydroxyl groups on the surface of silica samples form hydrogen bonds with water molecules upon immersion. Most of the heat evolved upon immersion is thus due to the hydrogen bonding energy; the highest concentration of surface hydroxyl groups brings the maximum in the heat of immersion. At temperatures higher than 300°C condensation of the surface hydroxyl groups occurs, converting silanol groups to siloxanes, which are not rehydrated easily on immersion in water; consequently, the heat of immersion decreases. On the other hand, at lower temperatures the surface hydroxyl groups are partly covered by some amount of water molecules adsorbed physically, so that the heat becomes less.[1,2]

According to another theory, the condensation of surface hydroxyl groups proceeds with heat treatment, forming a siloxane surface which, on immersion in water, reproduces the hydroxyl groups by a reverse reaction. The immersion heat increases as the dehydration proceeds with the heat treatment. When the temperature of the treatment rises further, the siloxane surface formed is stabilized and becomes difficult to be rehydrated; therefore, the heat of immersion decreases.[3,4]

In these two explanations it may be seen that the existence and behavior of surface hydroxyl groups play an important role. Also, from the viewpoint of catalytic action, the behavior of the surface hydroxyl groups on metal oxide is important. The present investigation will deal with the behavior of the surface hydroxyl groups on alumina by measuring the heat of immersion in order to compare it with that of those groups on silica samples and to test the validity of the two explanations mentioned above in the case of alumina samples.

Experimental

Samples.—The samples studied were α- and γ-alumina. The former, made by the Showa Denko Co., was washed with 4 N hydrochloric acid and then with water until the value of the electrical conductance of the mother liquor became that of water, while the latter was prepared by calcining, at 550°C in air, gibbsite, which was supplied by

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[1] A. C. Makrides and N. Hackerman, *J. Phys. Chem.*, **63**, 594 (1959).

[2] M. M. Egorov, V. F. Kiselev, K. G. Krasilnikov and V. V. Murina, *J. Phys. Chem.* (*U. S. S. R.*), **33**, 65 (1959).

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

[4] J. W. Whalen, "Solid Surfaces and the Gas-Solid Interface," Ed. by L. E. Copeland et al., Am. Chem. Soc., Washington, D. C. (1961). p. 281.

the Showa Denko Co., and then washing it with water in a way similar to that used for the former. X-Ray investigations showed that the latter is amorphous, while the former gives the α-form. Just prior to the immersion measurement, the sample was outgassed in a glass ampoule for 4 hr. at a given temperature in a vacuum of 10^{-4} mmHg, and then sealed off. When the pretreatment was carried out above 500°C, silica ampoules were used.

Immersion Measurement. — The heat evolved upon the immersion of the sample in water was measured by a precision calorimeter equipped with a thermistor as a temperature-sensing element.[5,6] The galvanometer reading was calibrated by supplying a given electrical energy through a constantan wire of about 50 Ω. In the course of the measurements of the immersion heat, the slow heat evolution described by Guderjahn et al.[7] has never been detected; rather, the evolution of heat was extinguished in just a few minutes. All the measurements were carried out at 25 ± 0.01°C.

Surface Area Measurement.—The B. E. T. surface areas were measured by nitrogen adsorption. The surface area of α-alumina was constant (1.91 m^2/g.), independent of the outgassing temperatures employed here, while the area of γ-alumina was almost constant to 600°C and then decreased with the further rise in the outgassing temperature above 600°C, as Fig. 1 shows.

Water Content. — The water content of the samples was determined as follows: the water vapor generated by the heat treatment of the samples in an evacuated apparatus was gathered in a trap cooled at the boiling point of nitrogen, and then the volume of the vapor reevaporated at room temperature was measured volumetrically. In order to raise the sensitivity of the pressure reading, an oil manometer was used. The measurements were carried out at 100°C temperature intervals from 300 to 1100°C, keeping the sample at each temperature for 4 hr.

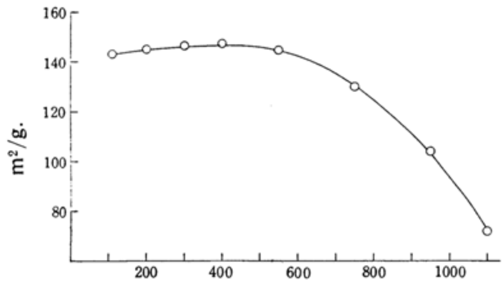

Fig. 1. Temperature variation of the specific area of γ-Al_2O_3.

Results and Discussion

The findings on the immersion heat of alumina in water are shown in Fig. 2. The heat of immersion of α-alumina, like that of γ-alumina, increases to a maximum value and then decreases as the outgassing temperature is raised. This phenomenon was also found in the case of silica, as has been mentioned above. It may be seen, however, that there are two remarkable differences between the immersion heat curve of silica and that of alumina. First, the absolute values of the heat of alumina are much greater than those

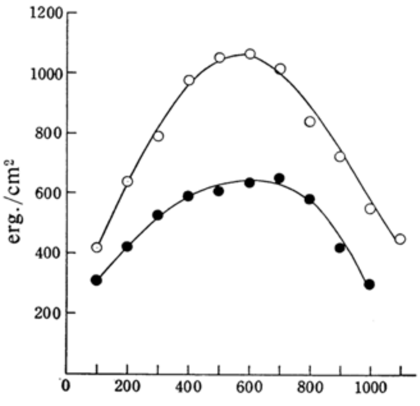

Fig. 2. Immersion heat vs. outgassing temperature curve of Al_2O_3.
○ α-Al_2O_3 ● γ-Al_2O_3

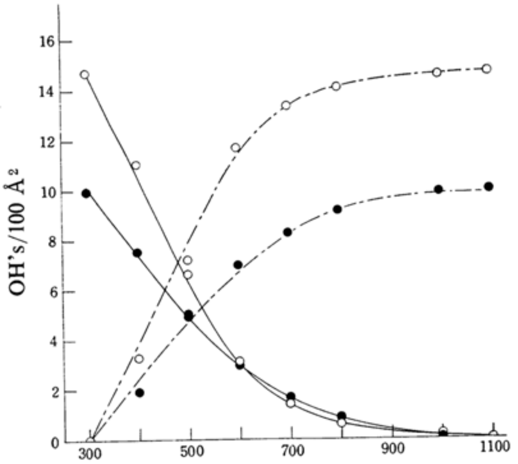

Fig. 3. Temperature variation of the dehydration amount and the water content of Al_2O_3.
○ α-Al_2O_3 ● γ-Al_2O_3
------ dehydration amount
—— water content

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[5] A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *J. Phys. Chem.*, 57, 649 (1953).

[6] T. Morimoto, M. Yamaguchi. T. Matsumoto and K. Juna, *Rep. Res. Lab. Surface Science, Okayama Univ.*, 2, 65 (1962).

[7] C. A. Guderjahn, D. A. Paynter, P. E. Berghausen and R. J. Good, *J. Phys. Chem.*, 63, 2066 (1959).

of silica, and, second, the outgassing temperature at which the heat of immersion of alumina showed a maximum is 600 to 650°C, much higher than that (200~300°C) in the case of silica. This latter fact suggests that the bonding energy of aluminol is remarkably large. Wade and Hackerman[8] could not find such a maximum on alumina since they treated alumina only to 450°C.

The amounts of dehydration and the water contents of alumina are given in Fig. 3. Since the degassed amounts of both α- and γ-alumina from 1000 to 1100°C were negligible, the water contents at various temperatures were calculated by assuming the value at 1100°C to be zero. Furthermore, assuming that the dehydrated water arises from the condensation of surface hydroxyl groups, the numerical value of these amounts was expressed in OH's/100Å^2. It may be seen from these curves that the water contents of alumina decrease steeply from 300 to 600°C, followed by a slow dehydration up to 1100°C.

Crystallographic data show that the surface layer of α-alumina consisting of the closest packing of oxygen ions contains 19 O^{2-}/100Å^2, as was calculated by Wade and Hackerman.[8] If all the oxide ions are hydrated normally, the same number of hydroxyl groups will be formed; this can be compared to 8 OH's/100Å^2 for the silica surface.[9] All the figures obtained as the water contents of alumina above 300°C are less than this value. Moreover, it is known that physically-adsorbed water molecules on solid surfaces can be removed by heating them up to 200~250°C.[1,10] In view of these circumstances, it is plausible to consider that the water vapor which was generated above 300°C had been bound chemically on the surface, forming surface hydroxyl groups. The water content of samples decreases linearly from 300 to 600°C, while, on the other hand, the immersion heat of the same samples increases linearly in the same temperature range. It may be considered from these observations that, on the samples treated in such a temperature range, the rehydration of dehydrated sites on the surface occurs easily on immersion in water, accompanied by the evolution of hydration energy. The appropriateness of this consideration seems to be supported by the following fact: in such a temperature range the increase in the immersion heat of α-alumina, in which the decrease in water content is more marked, is steeper than in the case of γ-alumina, in which the decrease in water content is less. In this range of outgassing temperature, surface hydroxyl groups, aluminoles, will be regenerated reversibly from dehydrated sites on immersion in water. Therefore, one can calculate the heat of hydration from the amount of dehydration and the immersion heat. Figure 4 shows the relation between the immersion heat and water contents in this temperature range. Regarding each of these curves as straight near the end, the heats of hydration on the surfaces of α- and γ-alumina can be calculated as 15.8 and 9.60 kcal./mol. water respectively. These values are several times greater than those obtained on the surface of silica samples[4] and are a little greater than the values known as the energy of hydrogen bonds.

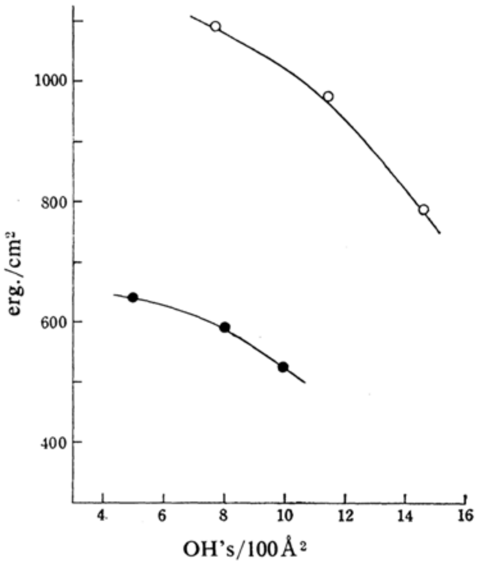

Fig. 4. Immersion heat vs. water content curve of Al_2O_3.

○ α-Al_2O_3 ● γ-Al_2O_3

When the outgassing temperature exceeds 600°C, the immersion heat begins to decrease, probably because of the stabilization of the dehydrated product, aluminoxane, produced on the surface. It may be seen from these discussions that the immersion phenomenon of alumina in water can be explained by the theory of rehydration, which is the second one of the two mentioned above. However, it is surprising that the immersion heats of the samples treated at 1100°C, on the surface of which the water contents are regarded as zero, are fairly large compared with those on silica samples.[1-4]

This fact seems to suggest that the wetting

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[8] W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **64**, 1196 (1960).

[9] R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Clornell University Press, Ithaca, N. Y. (1955).

[10] W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **63**, 1639 (1959).

of the surface of aluminoxane should be considered significant. In order to solve the problem of the wetting degree of the aluminoxane surface or, in other words, the problem whether or not the rehydration of the aluminoxane surface is significant in the sample treated at 1100°C, the kinetic study of the hydration is needed for alumina samples. The heats of immersion of α-alumina are considerably greater than those of γ-alumina. Some authors have pointed out that the immersion heats of the amorphous silica in water are less than those of crystalline silica.[1,11] The reason for this phenomenon remains unclear. The strength of the bonding force of surface radicals with water molecules is, however, probably an important factor, in addition to the concentration of the surface radicals.

Summary

1) The surface properties of two kinds of alumina have been studied by measuring the immersion heats and the water contents. The heat of immersion of alumina showed a maximum at about 600~650°C, which is considerably higher than the 200~300°C of silica, and the heat values were much greater than those of silica.

2) It has been concluded that the rehydration process of dehydrated sites plays an important role in the case of the immersion of alumina in water. The heats of hydration calculated from the immersion heats of α- and γ-alumina were 15.8 and 9.60 kcal./mol. water respectively.

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[11] W. H. Wade, R. L. Every and N. Hackerman, ibid., **64**, 355 (1960).