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Desorbability of Chemisorbed Water on Metal Oxide Surfaces. I. Desorption Temperature of Chemisorbed Water on Hematite, Rutile and Zinc Oxide

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The desorbability of water molecules chemisorbed on the surfaces of metal oxides has been investigated in the cases of α-Fe_2O_3, TiO_2 (rutile) and ZnO. Water vapor adsorption isotherms were determined on the samples treated at various temperatures in a vacuum of 10^{-5} Torr. The BET V_m-values of water adsorption were plotted against the temperature of the pretreatment. The curves obtained show a sharp increase at a moderate temperature which is varied by the nature of solid substance. This fact makes us conclude that, at this temperature, the chemisorbed water on oxide surfaces starts to be removed. The variation in the desorption temperature due to the nature of metal oxide is considered to come from the magnitudes of the bonding force of the surface hydroxyl groups to the surface metal atoms on each solid.

It has become clear that the surface of metal oxide is usually covered by hydroxyl groups in the atmosphere, which have serious effects on such surface properties as selective adsorbability, hydrophilicity, catalytic activity, and surface charge. Their existence and behavior have been investigated by various methods: specific chemical reactions,[1] infrared absorption spectroscopy,[2-6] water-content measurements,[7,8] and nuclear magnetic resonance study.[9,10] However, we still have no exact knowledge of the temperature at which the desorption of chemisorbed water on oxide surfaces starts. The primary purpose of this investigation is to determine this temperature experimentally. Since the bonding force of surface hydroxyl groups to surface metal atoms should vary with the nature of the metal oxide,[11] the desorption temperature may be expected to be characteristic for each substance. The results of this study, therefore, can indicate the extent of the removal of hydroxyl groups on solid surfaces and, accordingly, give a criterion for powder conditioning.

Experimental

Materials. The samples used in this research were hematite (α-Fe_2O_3), rutile (TiO_2), and zinc oxide (ZnO). The hematite, presented by the Nippon Bengara Kogyo Co., had been produced by the calcination of ferrous sulfate. The rutile, presented by the Teikoku Kako Co., had been made by calcining titanium hydroxide formed by the hydrolysis of titanium sulfate. The zinc oxide, presented by the Sakai Chemical Co., had been produced by oxidizing zinc vapor in the atmosphere at a high temperature. The former two samples were repeatedly treated with 0.1 N nitric acid in order to remove basic impurities, carefully treated with 0.1 N ammonia water in order to remove acidic impurities, thoroughly washed with distilled water, and dried at 110°C in the atmosphere.

Measurement of Surface Area. The surface areas of the samples were determined by the BET method using nitrogen, assuming the area of a nitrogen molecule to be 16.2 Å^2. The specific surface areas obtained for α-Fe_2O_3, TiO_2, and ZnO were found to be 13.8, 9.43, and 4.31 m^2/g respectively.

Measurement of Water Vapor Adsorption. The principle of the present investigation was to repeat the measurement of the water vapor adsorption on the same sample, while varying the conditions of the pretreatment. The volumetric method was used to determine the adsorption isotherms of water vapor, and an oil manometer was used to read the equilibrium pressure of the vapor. A sample of about 10 m^2 in total area was taken for every adsorption measurement. Prior to the first measurement of water vapor adsorption, the sample was treated at a high temperature (600°C for α-Fe_2O_3 and TiO_2, 450°C for ZnO) in a vacuum of 10^{-5} Torr in order to remove all the physically-adsorbed water and most of the chemisorbed

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water. Then the adsorption experiment of water vapor was carried out at a room temperature (10°C for α-Fe_2O_3, 18°C for TiO_2 and ZnO). Thus, we obtained the first adsorption isotherm. Subsequently, this sample was degassed at 30°C for 4 hr in a vacuum of 10^{-5} Torr in order to desorb water molecules. The preliminary tests showed that the desorption equilibrium can be attained within 4 hr in this process. Again the adsorption isotherm of water vapor was determined at the same temperature as before. After the completion of the second adsorption measurement, the same sample was again evacuated at a higher temperature (*e. g.,* 50°C) than 30°C. In the successive experiments the temperature of the pretreatment was raised step by step. By repeating the adsorption measurements and the desorption treatments alternately, we obtained a series of adsorption isotherms of water vapor.

Measurement of Water Content. The water content of the samples was determined volumetrically by using the same equipment as was used to measure the water-vapor adsorption. The same initial pretreatment as was given to the sample for the adsorption measurement was given to the original sample (600°C for α-Fe_2O_3 and TiO_2, 450°C for ZnO), and then the sample was exposed to saturated water vapor. This sample was degassed at 30°C for 4 hr in a vacuum of 10^{-5} Torr. By keeping the vacuum system closed, the water molecules adsorbed were evaporated at a given higher temperature (*e. g.,* 50°C) for 4 hr and trapped in a vessel kept at the temperature of liquid nitrogen. The amount of the condensed water was determined volumetrically at room temperature after reevaporation. This procedure was repeated on the same sample at various evaporation temperatures up to 1000°C. Since the number of water molecules remaining on the surface at 1000°C was found to be negligibly small, we calculated the water contents at various temperatures by assuming the water content at 1000°C to be zero.

Infrared Absorption Spectrum. The technique of absorption spectroscopy[2)] was applied to the surface species of the samples described above. The infrared spectra were measured with an apparatus of the Japan Spectroscopic Co. (IR-G). A small disk of the sample was prepared for infrared spectroscopic measurement at every step of the treatment.

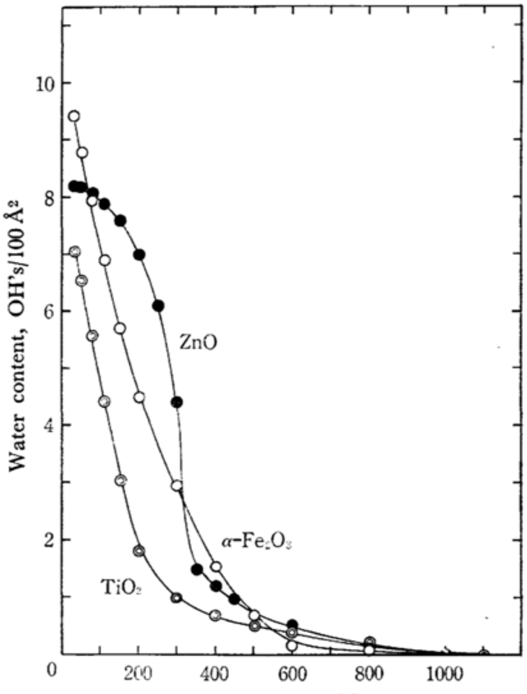

Fig. 1. Water content of α-Fe_2O_3, TiO_2, and ZnO at various temperatures.

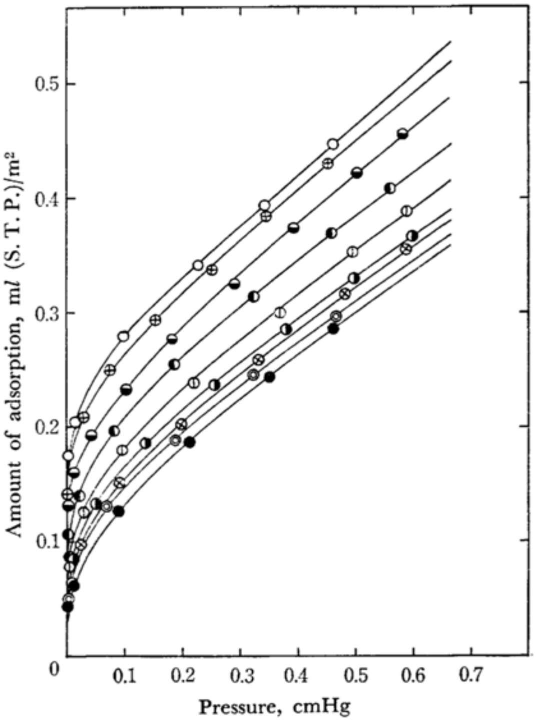

Fig. 2. Adsorption isotherms of water vapor on α-Fe_2O_3 pretreated at various temperatures; degassing temp. ○ 600, ● 30, ◎ 50, ⊗ 80, ◑ 110, ⦶ 150, ◐ 200, ◒ 300, ⊕ 400°C.

Results and Discussion

The water contents of α-Fe_2O_3, TiO_2 and ZnO are shown in Fig. 1 as a function of the pretreatment temperature. The numerical value of the amount is expressed by the number of surface hydroxyl groups on an area of 100 Å², assuming that the water molecules released have been chemisorbed as hydroxyl groups on the surface. It may be seen in Fig. 1 that all the samples lose adsorbed water greatly until 400°C, and then gradually until 800°C. At 1000°C almost all the water molecules have been removed from the surface. The water molecules released at higher temperatures are, of course, those chemisorbed on the surface, while those found at lower temperatures should have been adsorbed both physically and chemically. From the curves of the water content, however, the temperature at which the removal of chemisorbed water starts can not be recognized.

Figure 2 shows the adsorption isotherms of water on α-Fe_2O_3. The ordinate represents the amount of water adsorbed on the unit surface area of the sample in ml/m^2, which is then converted into the standard temperature and pressure. The first adsorption isotherm which was obtained after degassing at 600°C is much higher than the second one, which was obtained after degassing at 30°C. The amount adsorbed increases gradually with the rise in the pretreatment temperature and closely approaches the value of the original isotherm. All the isotherms are almost the same in shape, except that the amount adsorbed at zero pressure differs slightly from sample to sample.

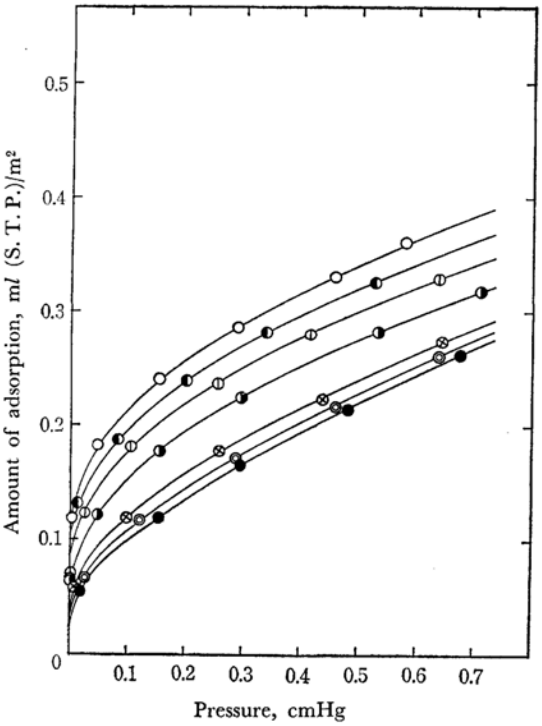

Fig. 3. Adsorption isotherms of water vapor on TiO_2 pretreated at various temperatures; degassing temp. ○ 600, ● 30, ◎ 50, ⊗ 80, ◑ 110, ⦶ 150, ◐ 200°C.

Figure 3 shows the adsorption isotherms of water on TiO_2. Although at first sight the characteristics seem to be the same as in the case of α-Fe_2O_3, the isotherms on TiO_2, after degassing at 30°C to 110°C, are close to each other and that of the 200°-degassed sample closely approaches the first adsorption isotherm.

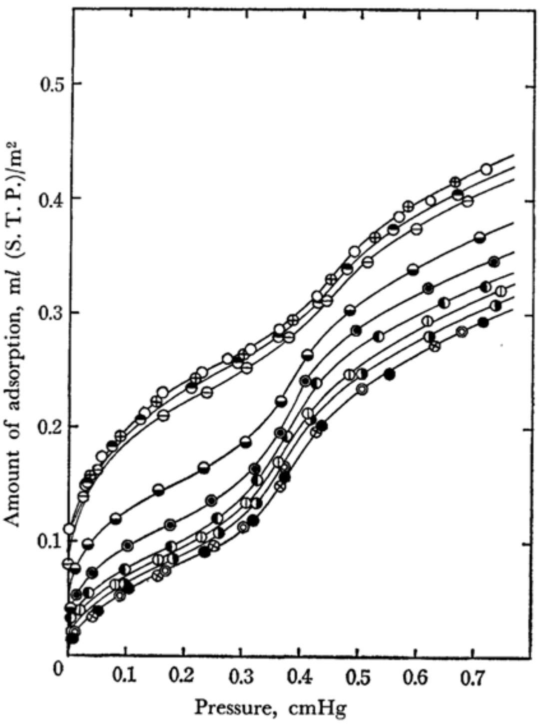

Fig. 4. Adsorption isotherms of water vapor on ZnO pretreated at various temperatures; degassing temp. ○ 450, ● 30, ◎ 50, ⊗ 80, ◑ 110, ⦶ 150, ◐ 200, ⊙ 250, ◒ 300, ⊖ 325, ◓ 350, ⊕ 400°C.

The adsorption isotherms of water on ZnO are given in Fig. 4. The shapes of these curves are quite different from those on TiO_2 and Fe_2O_3, representing a sharp increase in the amount adsorbed at a moderate pressure of the vapor. The appearance of such humps in the adsorption isotherm has been reported in other systems: carbon and adsorbates such as argon,[12] C_2H_5Cl, $CHCl_3$ and $CFCl_3$,[13] and cadmium bromide or sodium bromide and argon.[14] In the former systems, the surface of carbon was rather uniform and the hump appeared at the boundary between the first and second monolayers of an adsorbate. In the latter cases, the hump has been explained in terms of the interaction between adsorbate molecules and surface hydroxyl groups. In the case of metal oxide, we have no literature reporting the appearance of the hump on the adsorption isotherm. Detailed investigations of this phenomenon in the present system are now in progress. In any case, in the case of ZnO, the adsorption isotherms obtained on the sample treated above 300°C are extremely close to the first adsorption isotherm.

By applying the BET method[15] to the above data, the amount of the monolayer capacity of water on the unit surface, V_m, can be calculated.

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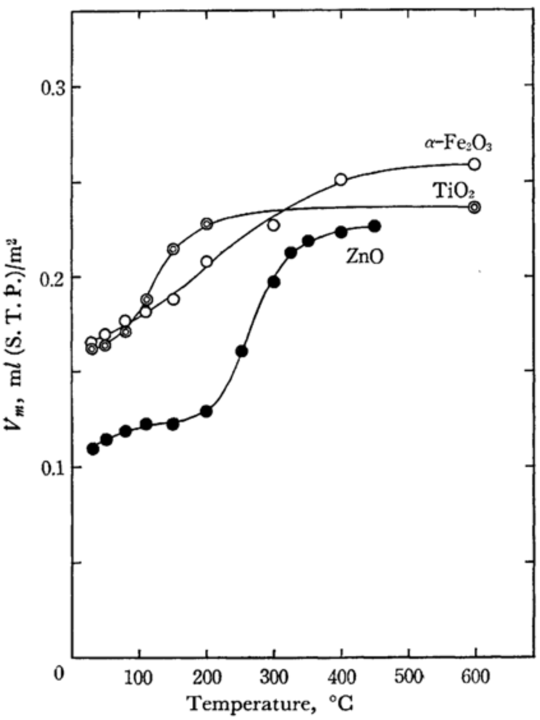

Fig. 5. Relation between V_m-value and pretreatment temperature.

BET plots were satisfactorily linear in the range of relative pressures from 0.05 to 0.35 in the cases of Fe_2O_3 and TiO_2, and from 0.05 to 0.20 in the case of ZnO. In Fig. 5 the V_m-values of the water adsorption are plotted against the temperature of the pretreatment. It may be seen from Fig. 5 that the V_m-values on TiO_2 and ZnO start to increase steeply at 110 and 200°C respectively, while in the case of Fe_2O_3 the value shows only a slow increase.

Even when a series of adsorption measurements were made in order from higher to lower pretreatment temperatures, the results obtained were quite reproducible. The reproducibility of the present experiments is satisfactory in this sense. This implies that the number of sites accepting water molecules is determined by the pretreatment conditions. The solid surface will be hydrated thoroughly after every adsorption measurement. Therefore, after treatments at moderate temperatures sites for both the physical and the chemical adsorption of water will be formed, the latter increasing in number with a rise in the pretreatment temperature.

It has been found that the rate of surface hydration on metal oxide is so fast that it seriously affects the value of immersional heat.[16] The V_m-value obtained, therefore, will contain both physical adsorption and chemisorption. Accordingly, the starting point of the sharp increase in V_m-values that is shown in Fig. 5 will correspond to the commencement of chemisorption in addition to the physical adsorption of water. Jurinak[17] assumed that only physical adsorption would occur on the samples of TiO_2 (anatase), α-Fe_2O_3, and α-FeOOH which were treated at 30°C in a vacuum of 10^{-6} Torr. Hollabaugh and Chessick[18] also considered that all the physically-adsorbed water might be removed near room temperature in a vacuum of 10^{-6} Torr. The present results substantiate the assumptions of these authors. From Fig. 5 we can find the temperature of pretreatment above which the reversible chemisorption sites for water abruptly increase. Moreover, this temperature is found to vary with the nature of the metal oxide, indicating that the surface hydroxyl groups bond to the surface metal atoms with a certain strength characteristic of each substance.

The desorption temperature of chemisorbed

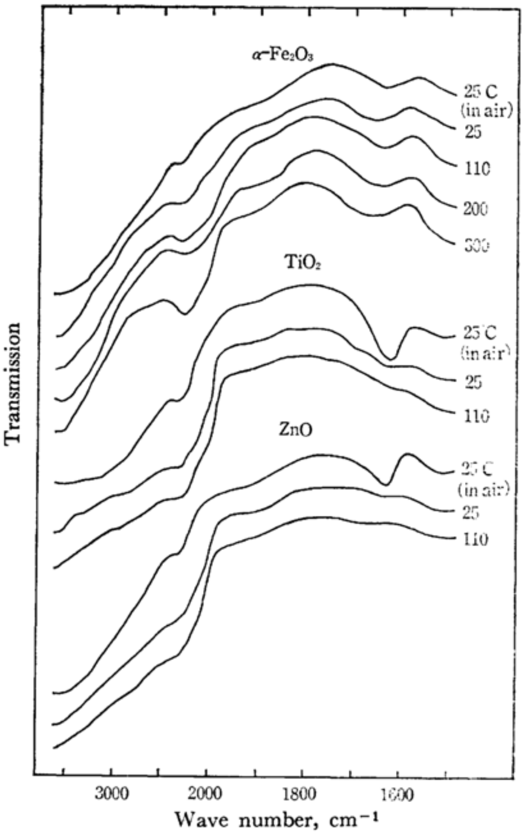

Fig. 6. Infrared absorption spectra of α-Fe_2O_3, TiO_2, and ZnO under various conditions of treatment.

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water is much higher in the case of ZnO than in the case of TiO_2. This means that the bonding force of hydroxyl groups to surface metal atoms on ZnO is much stronger than that on TiO_2. The reason for the difference between the two bonding forces may be explained by the structural or coordination factors of the solid substances concerned, but it is not clear at present. In the case of Fe_2O_3, there is no sharp increase in V_m-value. The desorption of chemisorbed water on Fe_2O_3 may start at such a low temperature that the removal of physically-adsorbed water can occur, and continue over a wide range of temperature. The heat of hydration, which was calculated by combining the data of immersional heat and of the water content of the powder, has been found to be 12.1 kcal/mol for Fe_2O_3,(19) and 23 kcal/mol for TiO_2 (rutile)(19) and ZnO.(16) These data have been interpreted in the following way: in the case of Fe_2O_3, the removal of chemisorbed water starts at a relatively low temperature, while on the other hand, the physically-adsorbed water remains until relatively high temperatures. This interpretation seems to be useful in the present case also.

Figure 6 shows the results of the infrared absorption spectroscopy of the three samples. The absorption band due to physically-adsorbed water appears near 1600 cm^{-1} on all the samples tested at room temperature in the atmosphere; it is extinguished by degassing in a vacuum of 10^{-5} Torr at room temperature in the cases of TiO_2 and ZnO, but it still remains in the case of Fe_2O_3 even after evacuating at higher temperatures. The difficulty of the desorption of chemisorbed water from Fe_2O_3 probably arises from the fact that water molecules have been adsorbed on the inner surface of Fe_2O_3. Healey *et al.*(20) suggested that the desorption of water vapor took place from the inner surface of ferric oxide powder. The X-ray data observed in connection with the present sample of Fe_2O_3 proved the crystallinity to be inferior to that of the other two samples. The behavior of adsorbed water on Fe_2O_3 suggests the existence of an inner surface on which nitrogen molecules can not be adsorbed at the temperature of liquid nitrogen.

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19) to be published.

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