An Approach to Test the Bonding Force of Chemisorbed Water on Metal Oxides

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On the surface of metal oxides exposed to the atmosphere there exist usually water molecules adsorbed both physically and chemically. The bonding force or the easiness of removal of these water molecules, especially of chemisorbed water, on the surface of metal oxides must vary with the nature of the solids.

Several methods have been developed to study the removal of water molecules adsorbed on the surface of metal oxides: the semiquantitative detection by infrared spectroscopy,[1] the estimation of the whole surface water by water content measurements,[2] and the chemical determination by using the characteristic reaction of surface hydroxyl groups.[3] Fruitful results have been obtained by these methods on the removal behaviors of adsorbed water and on their effects on the surface properties of the solids, while the quantitative examinations on the removal of water molecules have not been reported. Kipling and Peakall[4] determined the rate of desorption by weighing the adsorbent in a vacuum after the saturation of the vapor, to distinguish the reversible adsorption from irreversible adsorption of the vapor.

This paper involves the quantitative approach to know the easiness of removal of water chemisorbed as hydroxyl groups on the surface of metal oxides. First, the sample is treated in the vacuum of 10^{-5} torr at a higher temperature (*e.g.* 600°C) to remove the whole physically adsorbed water and most chemisorbed water. Secondly, the adsorption experiment of water vapor is carried out volumetrically at 18°C to obtain the adsorption isotherm. In this process, both physical adsorption and chemisorption will occur. Next, this sample is evacuated at 30°C for 4 hr in the vacuum of 10^{-5} torr in order to desorb water molecules. In this operation only the removal of physically adsorbed water will occur. Again the adsorption isotherm of water is determined at 18°C as before. After the second adsorption measurement has finished, the sample is again evacuated at a higher pretreating temperature than 30°C. By repeating the adsorption measurement and the desorption treatment alternately, we can obtain a series of adsorption isotherms. The temperature of pretreatment is raised successively in each measurement. The isotherm obtained can be treated by the BET theory to calculate the amount of monomolecular adsorption (V_m).[5]

It is well known that the energy of chemisorption is definitely larger than that of physical adsorption. Therefore, we can expect that the temperature at which the desorption of chemisorbed water starts will be higher under a given pressure than that of physically adsorbed water. If there is a well-defined difference between the two temperatures, the sample pretreated in the higher temperature range will adsorb water vapor both physically and chemically on the surface. On the other hand, the sample pretreated in the lower temperature range will adsorb water vapor only physically. The value of V_m is considered to involve both the amount of physical monolayer coverage and that of underlying chemisorbed water. Thus it is plausible that the value of V_m increases sharply at the critical temperature characteristic to the nature of solid sample, when the V_m values are plotted against the temperature of pretreatment. This has been confirmed and interesting information obtained by the experiments performed on various metal oxides under these projections, and the results will soon be reported.

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