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APPLICABILITY OF DSC-TG METHOD TO THE STUDY OF ADSORPTION PHENOMENA

— WATER VAPOR ADSORPTION ON TiO_2 —

By

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Differential scanning calorimetry (DSC) and thermal gravimetry (TG) have been widely used for the studies on the thermal properties of materials. The purpose of the present work is to examine the applicability of these methods to the study of surface phenomena by using the water vapor adsorption on TiO_2 as an example.

The instrument is specially designed (Rigaku Denki Co. Japan) for allowing to treat sample under vacuum (10^{-6} mmHg) and to measure simultaneously the heat and weight changes caused by adsorption or desorption of gases under a controlled temperature. The sample of TiO_2 was prepared from $TiCl_4$ by hydrolysis with NH_4OH in solution of $(NH_4)_2SO_4$ and calcination of the precipitate at 500°C for 3 hr in air. The sample had a structure of anatase with a surface area of ca. 70 m^2/g. Helium used as a carrier gas was purified by passing through a liquid N_2 trap containing molecular sieve (13 X). Flow rate was ca. 80 ml/min. The reference material was α-Al_2O_3 which has a small surface area. It was preliminarily confirmed that the adsorption of water vapor on α-Al_2O_3 is negligible compared to that on the sample. Calibration of the heat evolved was carried out by the heat of fusion of Ga (spectrographically standardized, Johnson-Matthey Co., melting point, 29.75°C).

Measurements were carried out by the following procedure.

(A) **Temperature scanning measurements:** The sample was evacuated at 450°C for 2 hr, cooled down under vacuum to a room temperature, and then subjected to the water vapor adsorption overnight. After the complete attainment of the adsorption equilibrium, the sample was evacuated at room temperature for 2 hr and then the temperature scanning was initiated in the dry He flow with a

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heating rate of 20°C/min. After the measurements, the same temperature scanning was repeated to examine the shift of base lines. A typical result for TG is shown in Fig. 1. Desorption takes place over a temperature range from ca. 100 to 300°C. The total weight decrease was about a hundredth of the sample weight and reproducible within 10%. The total weight decrease gives the adsorption of 4–5 water molecules/100 Å^2, in good agreement with the literature value[1] obtained by a successive ignition-loss method. The DSC curve simultaneously obtained shows a corresponding heat absorption with two broad peaks at 120°C and 190°C, indicating the presence of two types of the adsorbed water on the catalyst. These peak temperatures satisfactorily reproduce the literature values of 125° and 215°C observed on anatase by a TPD method[2]. Though the peak temperatures are reproducible, the amount of the heat absorbed varies largely from run to run. Therefore, further quantitative analysis was not made.

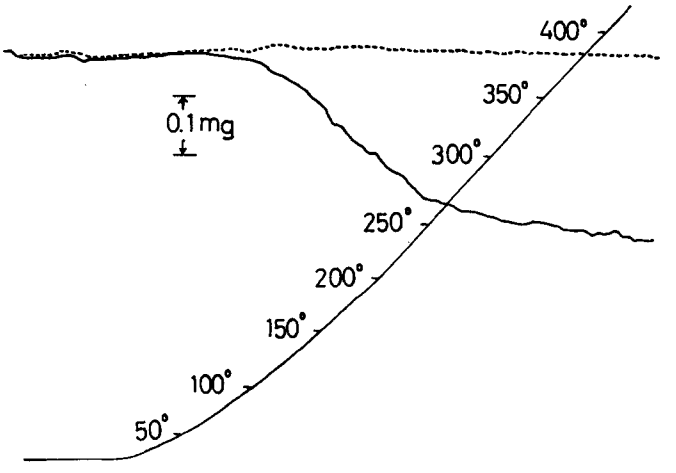

Fig. 1. Weight change during the desorption of water from TiO_2 surface (29.2 mg) by the temperature scanning (20°C/min) under the dry He flow.

(B) **Constant temperature measurements:** The sample was first pretreated at 500°C for 2 hr under the dry He flow and then cooled down to 32°C. Adsorption and desorption of water vapor were observed by switching the flowing gas to H_2O-saturated He and then to the dry He at 32°C. Results are shown in Fig. 2. A sharp heat evolution peak (curve 1) appears upon the introduction of the water vapor. The heat evolution completes within a few minutes. Another peak for the heat absorption caused by the desorption is much smaller than that of the adsorption, indicating the presence of irreversibly adsorbed water. The weight

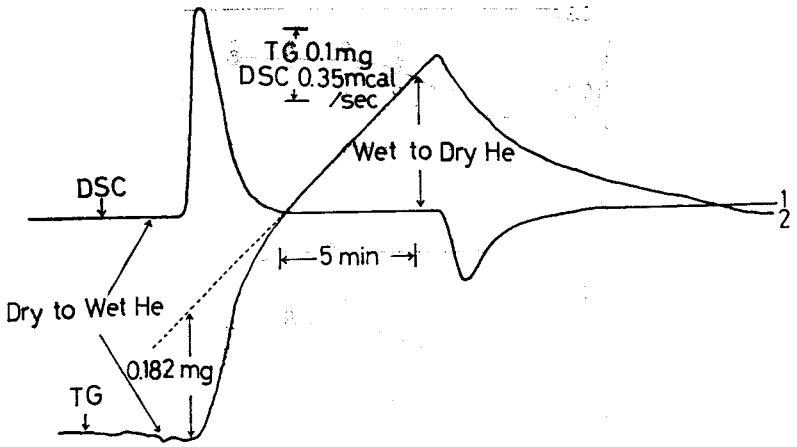

Fig. 2. Heat (curve 1) and weight (curve 2) changes simultaneously observed during the adsorption and desorption of water at a constant temperature of 32°C, sample weight; 6.3 mg.

change (curve 2 in Fig. 2) shows a steep increase during the first few minutes and then a slow one which continues in a linear manner even after completion of the heat evolution and extends for more than 10 minutes. The latter slow increase is independent of the quantity of the sample as well as the flow rate, and is observed even in the blank test without the sample and the reference material. Therefore, this gradual increase is due to other origins such as the water adsorption on the sample holder of the balance. The amount of adsorption was estimated by extrapolating the linear part of the slow increase to time zero as shown by the dotted line in Fig. 2. The amount of the adsorption thus estimated was confirmed to be proportional to the weight of the sample. Another measurement was conducted on the same sample in order to estimate the amount of the water reversibly adsorbed: namely, after the baseline of curve 2 became constant under the dry He flow at 32°C, the water vapor was again introduced and the weight and heat changes were followed. From these successive measurements, the amount of the irreversible adsorption on the sample preheated at 500°C is obtained as ca. 4 water molecules/100 Å^2. This is in good agreement with that obtained by the temperature scanning method. The amount of the reversible adsorption is estimated as ca. 10 water molecules/100 Å^2. The heats of the irreversible and reversible adsorptions are 17 and 8 kcal/mol, respectively. The reversible adsorption is taken as the physisorption, although its heat of adsorption is slightly smaller than the value calculated from the literature value of the heat of immersion[3] as well as the heat of condensation of water, 10.5 kcal/mol.

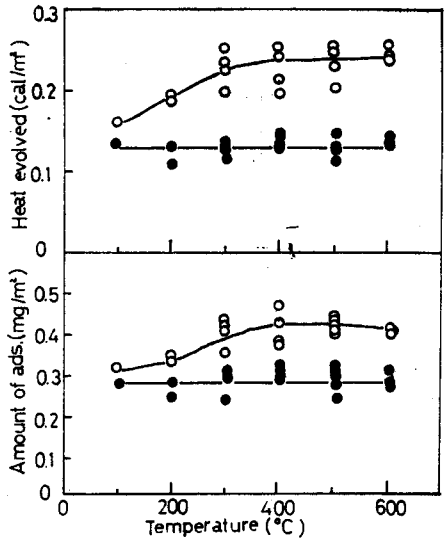

Fig. 3. Plots of the amount of heat evolved by water adsorption and the amount of adsorption for the unit area of 1 m^2 against the pretreatment temperature of TiO_2.
○: total change, ●: reversible part.

The data obtained by the constant temperature measurements are summarized in Fig. 3 for the sample preheated at various temperature after the attainment of the equilibrium of the water vapor adsorption at room temperature. The data scatter to a considerable extent, but the total amount of adsorption and the total heat evolved (○) have a tendency to increase with the pretreatment temperature, whereas their reversible parts (●) are almost independent of the pretreatment temperature. It is also to be noted that the complete removal of the adsorbed water is attained at the pretreatment temperatures higher than 300°C.

The following two conclusions are drawn from the present study: (I) The present instrument can follow the heat and weight changes down to 0.1 mcal/sec and 0.1 mg, respectively, sufficient to follow the changes caused by adsorption which takes place on the total surface area of the order of 1 m^2. (2) Measurements at a constant temperature produce much more precise data than those of the temperature scanning data. The heat change obtained by the temperature scanning method gives only a qualitative information on the adsorption.

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