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Water Content on Metal Oxides. I. Water Content on Silica Gel, Magnesium Oxide, Zinc Oxide, and Titanium Dioxide

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The surface water content has been determined on silica gel, magnesium oxide, zinc oxide, and titanium dioxide by means of active hydrogen analysis and by the successive-ignition-loss method. Except for magnesium oxide pretreated at 100 °C, it has been found that the water contents obtained from the two methods on every oxide tested are in good agreement with each other. The successive-ignition-loss method gives an extraordinarily high value of water content on magnesium oxide pretreated at 100 °C, probably because of the retention of inner hydroxyl groups. The present results indicate that the two methods are equally reliable for the quantitative determination of the water content on metal oxides. Moreover, the simultaneous application of both methods make it possible to estimate each amount of surface hydroxyl groups and physisorbed water molecules.

The surface hydroxyl groups on metal oxide play an important role in the adsorption of molecules. Several methods have thus far been examined in estimating the surface hydroxyl groups.[1-13] Morimoto *et al.* have studied the metal oxide surface by measuring the water content by means of the successive-ignition-loss method.[14-16] On the other hand, Fripiat *et al.* adopted Zerewitinoff's method to determine active

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hydrogen in the analysis of the water content on silica gel.[7)]

In order to obtain reliable data on the water content, it is desirable to compare the water content as determined by different methods and to investigate the characteristic features of each method. The water content on silica gel has been examined by various methods,[12)] but for the other metal oxides few works have been reported and different methods have not been compared. In connection with this problem, the active hydrogen analysis and the successive-ignition-loss method have been used for measuring the water content on several metal oxides pretreated at different temperatures. This paper will report the finding that both methods give, except in special cases, consistent data on the water content of silica gel, magnesium oxide, zinc oxide, and titanium dioxide.

Experimental

Materials. The metal oxides used in this work were silica gel, magnesium oxide, zinc oxide, and titanium dioxied. The silica gel was prepared by the hydrolysis of ethyl orthosilicate, which had been purified by redistillation.[17)] Zinc oxide furnished by the Sakai Chemical Co. was the sample which was prepared by burning zinc metal in air. Titanium dioxide furnished by the Teikoku Kako Co. was prepared by the hydrolysis of titanium sulfate; it was purified further by washing it with dilute ammonia water, nitric acid, and then thoroughly with distilled water. The magnesium oxide was synthesized *via* methylate. Twenty grams of magnesium metal (99.9% purity) were allowed to react with 300 g of purified methyl alcohol at 50—60 °C for 4 hr. The methyl alcohol solution of magnesium methylate thus obtained was kept at *ca.* 5 °C for one night. The crystals of magnesium methylate thus deposited were then further recrystallized from methyl alcohol. The magnesium hydroxide was made by hydrolyzing 30 g of magnesium methylate in 1000 g of distilled water at 60 °C for 7 hr. The excess water and methyl alcohol evolved by the hydrolysis were evaporated out. The magnesium oxide was obtained by calcining magnesium hydroxide at 800 °C for 3 hr in the atmosphere.

The methyl magnesium iodide used for active hydrogen analysis was synthesized by reacting 50 g of methyl iodide with 9 g of magnesium metal in 150 g of dried *n*-butyl ether at 60—70 °C for 4 hr. After the sedimentation of the excess magnesium metal, the supernatant solution was used for active hydrogen analysis.

Specific Surface Areas of the Oxides. The nitrogen adsorption isotherms were measured on the powdered samples at the temperature of liquid nitrogen. Assuming that the nitrogen molecular area was 16.2 Å^2, the surface areas of the powder were calculated by using the BET equation. The specific surface areas of silica gel, magnesium oxide, zinc oxide, and titanium dioxide pretreated *in vacuo* for 4 hr are given in Table 1.

TABLE 1. SPECIFIC SURFACE AREA OF METAL OXIDES

Pretreatment temperature (°C)	Metal oxides (m^2/g)			
	SiO_2	MgO	ZnO	TiO_2
100	423	67	6.4	9.7
200			5.5	
300	422	71	5.6	9.9
500	431	65	4.4	9.3
800	396	77		
1000	333			

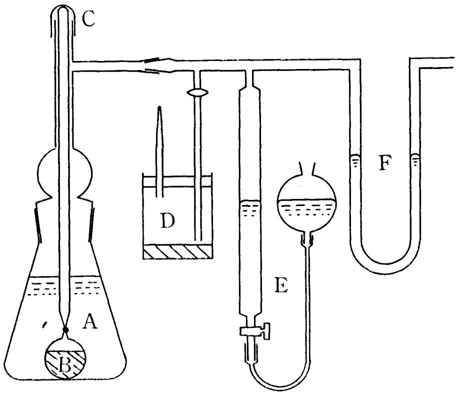

Fig. 1. Apparatus for active hydrogen on metal oxide.
A, methyl magnesium iodide solution; B, oxide powder; C, rubber cup; D, dry box (P_2O_5); E, gas burette; F, balance manometer.

Water-content Measurement by Means of Active Hydrogen Analysis. The measuring apparatus for active hydrogen on metal oxide is shown in Fig. 1; it was constructed by modifying the apparatus used for the determination of the active hydrogen of organic compounds by Krynitsky *et al.*[18)] The oxide powder used at one time was 0.3—2.0 g; it was pretreated *in vacuo* for 4 hr in a thin-walled glass bulb. The degree of vacuum attained in the pretreatment was 10^{-5} Torr at 100, 200, and 300 °C, and 10^{-3} Torr at 500, 800, and 1000 °C. After the pretreatment had finished, the neck of the bulb was sealed off and connected to a glass rod by fusion. The bulb was then transferred into reaction vessel containing 80 ml of a methylmagnesium iodide solution, and then it was broken in the solution by pushing in a glass rod. Since the reaction between methylmagnesium iodide and active hydrogen on metal oxide generates methane gas, the gas volume was measured by means of a gas burette at appropriate intervals. Prior to the measurements, the apparatus was calibrated by using pure benzoic acid; the volume of methane evolved from the reaction of benzoic acid with methyl magnesium iodide was confirmed to coincide with the calculated value.

Water-content Measurement by Means of the Successive-Ignition-Loss Method. The water content in metal oxides was determined by a procedure described previously.[14)] By this method, water molecules can be removed from the surface through the condensation dehydration of surface hydroxyl groups; moreover, the physisorbed water, if present, can be desorbed.

Results and Discussion

Methane gas is evolved by the reaction of methylmagnesium iodide with the surface hydroxyl groups or with the physisorbed water molecules:[7)]

$$CH_3MgI + HO\text{-(oxide surface)} \longrightarrow CH_4 + MgIO\text{-(oxide surface)}$$

$$CH_3MgI + H_2O \longrightarrow CH_4 + MgI(OH)$$

[17)] T. Morimoto and H. Naono, This Bulletin., **45**, 700 (1972).

[18)] J. A. Krynitsky, J. E. Johnson, and H. W. Carhart, *J. Amer. Chem. Soc.*, **70**, 486 (1948).

The volume of methane gas, V(ml(STP)/g oxide), is given by this equation:

$$V = \left\{V_1 - \left(V_2 - \frac{W}{\rho}\right)\right\} \cdot \frac{1}{W} \cdot \frac{273}{273+t}$$

where V_1 is the volume as measured by means of a gas burette, V_2 is the volume of a glass bulb, W and ρ are the weight and density of the oxide powder, and t is the measuring temperature (23—27 °C). In Figs. 2 and 3, V is plotted against the reaction time at various pretreatment temperatures for silica gel, magnesium oxide, zinc oxide, and titanium dioxide. It can be seen from these figures that the evolution of methane gas ceases within 30—50 min.

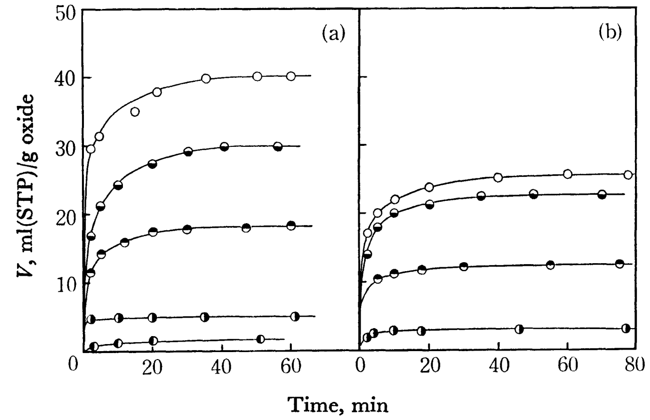

Fig. 2. Reaction of methylmagnesium iodide with active hydrogen on silica gel (a) and magnesium oxide (b). Pretreatment temperatures, ○: 100 °C, ◒: 300 °C, ◓: 500 °C, ◑: 800 °C, ◐: 1000 °C.

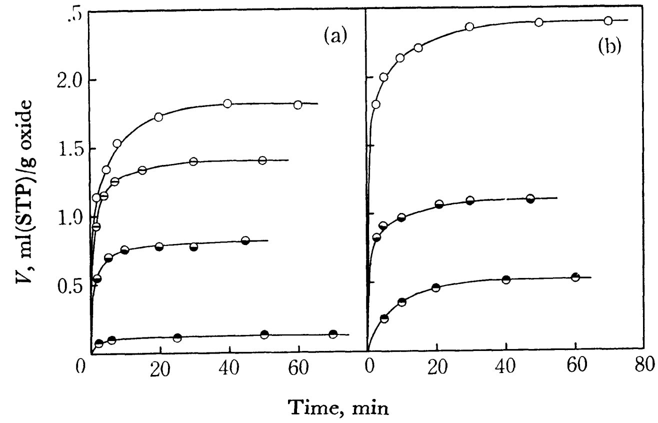

Fig. 3. Reaction of methylmagnesium iodide with active hydrogen on zinc oxide (a) and titanium dioxide (b). Pretreatment temperatures, ○: 100 °C, ⊖: 200 °C. ◒: 300 °C, ◓: 500 °C.

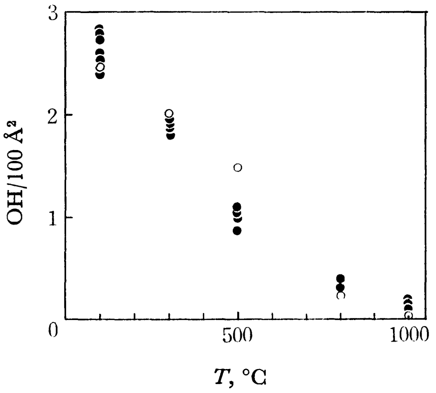

Fig. 4. Water content on silica gel measured by the active hydrogen analysis (●) and the successive-ignition-loss method (○).

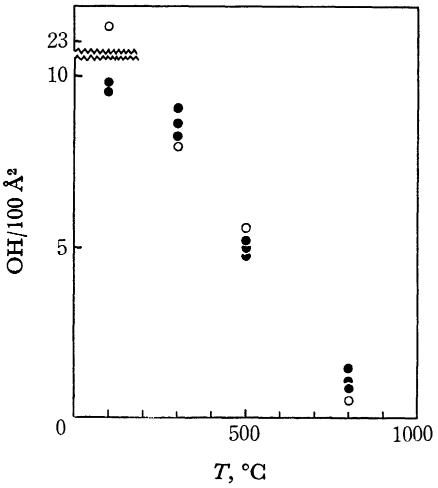

Fig. 5. Water content on magnesium oxide measured by the active hydrogen analysis (●) and the successive-ignition-loss method (○).

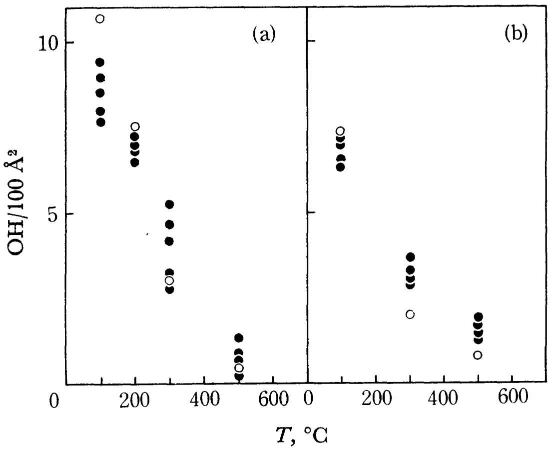

Fig. 6. Water content on zinc oxide (a) and titanium dioxide (b) measured by the active hydrogen analysis (●) and the successive-ignition-loss method (○).

In all the cases of oxides, the volume of the methane gas decreases with an increase in the pretreatment temperature; that is, the active hydrogen is removed from the oxide surface by pretreating oxides at elevated temperatures *in vacuo*. On the basis of the reaction of methylmagnesium iodide with the solid surface, we can calculate the water content on metal oxides from the amount of methane gas evolved. Taking into account the specific surface areas listed in Table 1, the water content can be expressed in the number of hydroxyl groups on an area of 100 Å², as is shown in Figs. 4—6. In these figures, the values of the water content, as determined by the active hydrogen analysis, are illustrated, together with those obtained by the successive-ignition-loss method.

Silica Gel. As can be seen from Figs. 2 and 3, the evolution of methane gas from silica gel occurs as rapidly as that from the other oxides, though the specific surface area of silica gel is much larger than those of the others. Furthermore, as may be seen from Fig. 4, the water contents on silica gel, as determined by the two methods, are in good agreement with each other. Therefore, it may be considered from these results that methylmagnesium iodide molecules react readily with all the active hydrogen atoms on silica gel.

Generally, on metal oxides pretreated at lower temperatures the surface may possibly retain physisorbed water molecules, together with chemisorbed water as surface hydroxyl groups, though only the latter exist on surfaces pretreated at higher temperatures. Here, it will be very interesting to analyze the water content into the surface hydroxyl groups and the physisorbed water. As has been stated above, one water molecule can be estimated to contain one hydroxyl group by the methylmagnesium iodide method, and two hydroxyl groups by the successive-ignition-loss method. Accordingly, when an appreciable amount of the physisorbed water exists on the metal surface, the water content obtained by the latter method should be larger than that obtained by the former one, as will be reported with regard to the water content on alumina pretreated at 100 °C *in vacuo*.[19] Since the water contents obtained on silica gel by the two methods accord well with each other, it may be concluded that only the surface hydroxyl groups exist on silica gel pretreated above 100 °C *in vacuo*.

Magnesium Oxide. Figure 5 shows that the water contents obtained on magnesium oxide by the active hydrogen analysis agrees fairly well those obtained by the successive-ignition-loss method, except for the sample pretreated at 100 °C. On 100 °C-treated sample, however, the two methods give very different values as to the water content; it is found to be 9.6 OH/100 Å^2 by the former, and 23.4 OH/100 Å^2 by the latter method. As has been described above, if physisorbed water exists on magnesium oxide, the latter method will give a larger value for the water content. Now, assuming that the difference between the values of the water content obtained by the two methods is due to the presence of the physisorbed water, we can calculate each of the surface hydroxyl groups and the physisorbed water. The calculation results in a negative value (-4.2 OH/100 Å^2) as the density of the surface hydroxyl groups. Thus, the large difference between the data obtained by the two methods cannot be explained only by the existence of physisorbed water.

With the successive-ignition-loss method it is possible to detect the hydroxyl groups in the inner layer of the solid besides those on the surface, because the oxide powder is ignited at elevated temperatures. On the contrary, in the active hydrogen analysis, only the surface hydroxyl groups can be determined, because methylmagnesium iodide molecules can react only the surface of the solid. The extraordinarily high value obtained by the successive-ignition-loss method stated above makes it possible to infer that the hydroxyl groups exist not only on the surface, but also in the inner layer of magnesium oxide crystals.

Assuming that a hydroxyl group is formed on a surface magnesium atom, the surface hydroxyl groups on the (100) face of magnesium oxide can be calculated crystallographically to be 11.3 OH/100 Å^2. The calculated water content approximates the value obtained by the active hydrogen analysis, being about twice as large as the value obtained by the successive-ignition-loss method. Thus, the water content obtained by the successive-ignition-loss method on the 100 °C-treated magnesium oxide corresponds to the two-layer coverage of hydroxyl groups. It is known that magnesium oxide is gradually changed into magnesium hydroxide by the reaction with water. Therefore, the value of 23.4 OH/100 Å^2 obtained on 100 °C-treated magnesium oxide may reasonably be said to originate from the chemisorption of water vapor from the atmosphere during preservation. On the samples treated above 300 °C, the two methods give similar results for the water content below the monolayer coverage, which shows that only the surface hydroxyl groups exist on magnesium oxide.

So far, methylmagnesium iodide has been mainly used for the determination of the hydroxyl groups on silica, which is known as a weakly acidic surface. On the contrary, magnesium oxide is well known as a basic solid; its basicity was intestigated by Tanabe and Yamaguchi by using bromo-thymol-blue as an indicator.[20] It is very interesting to note that the hydroxyl groups on such a basic solid as magnesium oxide react quantitatively with methylmagnesium iodide. In conclusion, all the hydroxyl groups on the acidic and basic surfaces can be measured quantitatively by means of the present active hydrogen analysis.

Zinc Oxide and Titanium Dioxide. The water content on zinc oxide and titanium dioxide is shown in Fig. 6 as a function of the pretreatment temperature. As can be seen from Fig. 6, the data obtained by different methods are, as a whole, in agreement with each other and the water content decreases remarkably with the increase in the pretreatment temperature. In these cases, an appreciable fluctuation of the data is observed in the active hydrogen analysis, probably because of the small quantities of methane gas evolved. A trend can be seen that the successive-ignition-loss method gives a slightly higher value in the water content on the 100 °C-treated zinc oxide than does the other method; this greater value may be attributed to the existence of the physisorbed water.

The above results lead to the conclusion that the surface hydroxyl groups can reasonably be measured quantitatively by both active hydrogen analysis and the successive-ignition-loss method. Furthermore, it is possible to estimate the values of both physisorbed water and surface hydroxyl groups by the simultaneous application of the two methods.

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