Surface Water Content of Metal Oxides. II. Measurement of Samples Containing Pores: Silica, Alumina and Silica-Alumina

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Two essentially different methods for determining surface water content, *i.e.*, a successive-ignition-loss method and chemical reaction of active hydrogen with methylmagnesium iodide, were applied to the measurement of samples containing pores: silica, alumina, and silica-alumina. It was found that the rate of reaction of methylmagnesium iodide with active hydrogen largely depends upon the pore size distribution. It took 20 min for completion of the reaction on the Aerosil sample having no pores, *ca.* 1 hr for alumina and silica-alumina which have peaks in the pore size distribution curve at radii 53 and 37 Å, respectively, and 17 hr for porous silica glass and silica gel which have peaks at radii 22 and 19 Å, respectively. The results obtained by the two methods were in good agreement with each other irrespective of the existence of pores in the transitional range. It was confirmed that the nature of the sample is decisive for the population of water content on metal oxides.

Surface hydroxyl groups on metal oxides have a significant effect on surface properties such as adsorbability,[1-4] catalytic behavior,[5,6] and electrification of the surfaces,[7,8] but a method for determining the surface hydroxyl groups has not been sufficiently established. Chemical reactions of surface hydroxyl groups with several reagents have been adopted by many authors to analyse the population of active hydrogen on solid surfaces.[9-13] We have applied the successive-ignition-loss method for the same purpose.[1,3,14,15] A comparison of these two methods was previously made[16] for the measurement of water content on a few metal oxides by use of methylmagnesium iodide. The results showed that methylmagnesium iodide reacts with hydrogens in surface hydroxyls of acidic or basic character, giving values of water content consistent with those obtained by the successive-ignition-loss method. It has become clear that simultaneous application of the two methods permits evaluation of the individual amounts of physisorbed and chemisorbed water.

We have examined the applicability of the two methods to the determination of surface water content on samples containing pores such as silica, alumina, and silica-alumina, and estimated the effect of the nature and origin of the oxide samples on the population of water content.

Experimental

Materials. Three kinds of silica were used, one being Aerosil-200 (Japan Aerosil Co.). The sample was washed with deionized water repeatedly to remove acidic impurities until the electrical conductivity of the suspension shows a minimum value, and then dried at 110 °C in air for 12 hr. The porous silica glass sample was prepared from sodium borosilicate glass (glass laboratory, Government Industrial Research Institute, Osaka). A sodium borosilicate glass rod was crushed and sieved to separate the fractions of 65—100 and 270<mesh. 100 g of glass powder was stirred in a 150 ml concentrated hydrochloric acid solution at 70—80 °C for 4 hr, and then washed with water. The acid- and water-washing procedure was repeated five times. Finally, the resulting porous silica glass was washed with deionized water until the electrical conductivity of the supernatant liquid settled down to an equilibrium value close to that of the deionized water, dried at 100 °C in air, and stored *in vacuo*. The porous silica glass sample was found to contain 4.0±0.1% B_2O_3 by the usual method of analysis using alkali fusion, separation from silica, and titration with sodium hydroxide.

The samples of silica gel, alumina, and silica-alumina were prepared by the same method as described previously.[15,17] Silica gel and alumina were produced by hydrolyzing ethyl orthosilicate and aluminum isopropoxide, respectively, and silica-alumina (SA-50) was prepared by mixing both component oxides of equal amount in weight in aqueous gel state. X-Ray analysis showed the three kinds of silica to be amorphous and alumina to be of η-type.

Determination of Water Content. The water content on a metal oxide was determined by two methods similar to those reported:[16] Zerewitinoff's method using methyl-

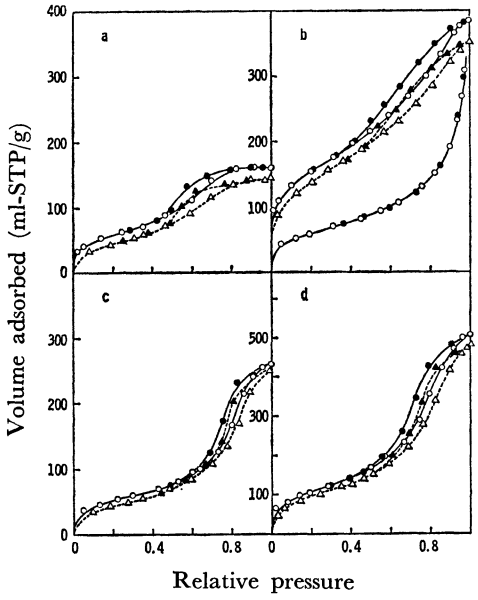

Fig. 1. Adsorption isotherms of nitrogen on porous silica glass (a), silica gel (b), Aerosil (b, the lowest curve), alumina (c), and silica-alumina (d). Open and shaded marks indicate adsorption and desorption respectively. Solid and broken lines indicate the isotherms on the sample treated at 100° and 800 °C respectively.

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TABLE 1. SPECIFIC SURFACE AREA AND PORE VOLUME OF METAL OXIDES

	Pretreatment temperature (°C)	Aerosil	Porous silica glass[a)]	Silica gel	Alumina	Silica-alumina
Surface area (m^2/g)	100	203	212	477	178	382
	300	205	204	536	185	386
	500	208	199	559	182	391
	800	197	177	509	166	349
	1000	175				
Pore volume (ml/g)	100		0.251	0.591	0.402	0.789
	800		0.224	0.543	0.387	0.747

a) 65—100 mesh

magnesium iodide and the successive-ignition-loss method. On analysing active hydrogen by means of Zerewitinoff's method, 0.2—0.5 g of a finely divided solid sample was evacuated in a small ampoule at elevated temperatures for 4 hr, sealed off *in vacuo*, and allowed to react with methylmagnesium iodide at 25 °C after breaking the ampoule in a *n*-butylether solution containing the Grignard reagent. The amount of methane gas evolved was measured by means of a gas burette. In the measurement of water content by means of the successive-ignition-loss method, the amount of water vapor expelled by heating at successively elevated temperatures was measured volumetrically; the water content in a sample treated at a certain temperature was obtained by summing up the amounts of water vapor expelled at temperatures higher than that indicated.

Measurement of Surface Area and Porosity. The adsorption-desorption isotherms of nitrogen were determined for each sample at the temperature of liquid nitrogen. The specific surface area was computed by applying the BET method to the nitrogen adsorption isotherm in the relative pressure range 0.05—0.30, in which the cross-sectional area of a nitrogen molecule was assumed to be 16.2 Å^2. The adsorption isotherms of nitrogen and the calculated specific surface area are shown in Fig. 1 and Table 1, respectively.

The porosity of the samples was calculated by applying the Kelvin equation to the desorption branch in the nitrogen isotherms,[18] where a correction for the thickness of the adsorbed layer on the walls was carried out by the method used by Clanston and Inkley.[19] The pore size distribution curves thus calculated for four samples except for Aerosil are illustrated in Fig. 2; the latter sample may be considered to have no pores in the sense of "transitional" range of Dubinin[18] because of the absence of hysteresis (Fig. 1). In Fig. 2 it can be seen that porous silica glass and silica gel have considerably small pores, both distribution curves exhibiting peaks at radii 22 and 19 Å, respectively; the latter has a broader distribution of pores than the former. The pores in alumina and silica-alumina are larger than those in the two kinds of silicas stated above, the distribution curves representing peaks at 53 and 37 Å, respectively. The pore volume can be calculated by assuming the saturated value in nitrogen adsorption isotherms of Type IV to correspond to the amount of nitrogen condensed in the pores (Table 1).

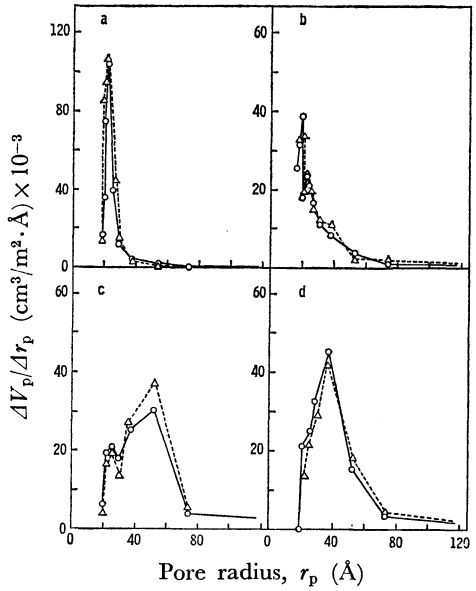

Fig. 2. Pore size distribution curve of porous silica glass (a), silica gel (b), alumina (c), and silica-alumina (d). Solid and broken lines indicate the values on the sample trated at 100° and 800 °C respectively.

Results and Discussion

Reaction Rate of Methylmagnesium Iodide. One molecule of methylmagnesium iodide reacts with one hydroxyl group or physisorbed water molecule to liberate one molecule of methane gas.[16] The amount of methane gas evolved from one gram of metal oxides is plotted against time (Fig. 3). We see that the evolution of methane gas is rapid in the case of Aerosil, and stops in *ca.* 20 min (Fig. 3a). The reaction is extremely slow on the surface of porous silica glass, being completed after 17 hr (Fig. 3b). The results for two kinds of porous silica glass samples having different particle sizes (65—100 and 270<mesh) are essentially the same. In the case of silica gel, the rate of reaction is as slow as that on porous silica glass (Fig. 3c). In alumina and silica-alumina (SA-50), the liberation of methane gas proceeds at a

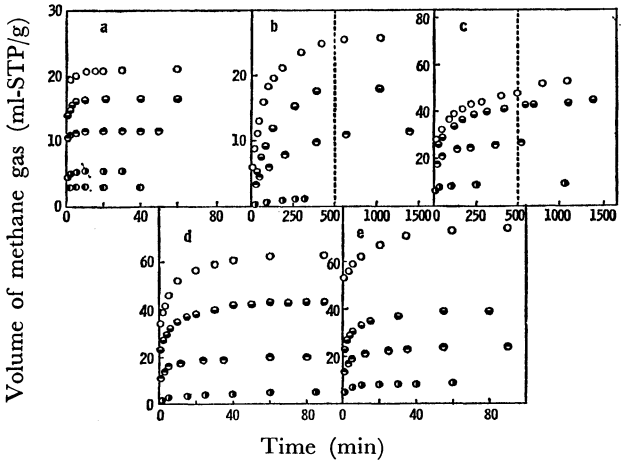

Fig. 3. Reaction of CH_3MgI with active hydrogen on Aerosil-200 (a), porous silica glass (65—100 mesh) (b), silica gel (c), alumina (d), silica-alumina (SA-50) (e); pretreatment temperature, ○: 100°, ◒: 300°, ◓: 500°, ◑: 800°, ◐: 1000 °C.

moderate rate, and ends in *ca.* 60 min (Figs. 3d and e).

A comparison of Figs. 1, 2 and 3 shows that the reaction rate of methylmagnesium iodide is closely related to the pore size distribution of metal oxides. In Aerosil samples, in which no hysteresis appears in the adsorption isotherm, the reaction is completed very rapidly (20 min), while in those having small pores the completion for the reaction requires a longer time. It takes about 60 min on alumina and silica-alumina having a peak at radii 53 and 37 Å, respectively, and about 1000 min on porous silica glass and silica gel having a peak at radii 22 and 19 Å, respectively. We can thus conclude that the rate of reaction of methylmagnesium iodide with active hydrogen on metal oxides is determined by the diffusion of the reagent into pores. The time required for the completion of the reaction gives a measure for the porosity of powders.

Dependence of Water Content upon the Nature and Origin of Samples. The water content obtained from the extreme value of methane gas evolved (Fig. 3) is plotted against pretreatment temperature (Figs. 4 and 5), along with those obtained from the successive-ignition-loss method. Figures 4 and 5 show that the values of water content measured by the two methods on each sample are in fairly good agreement with each other, as in other examples.[16] This indicates that the two methods tested here give mutually reliable data on surface water content in spite of their difference, even when the samples have pores of transitional sizes; a prolonged reaction time is required for the measurement by methylmagnesium iodide. It should be noted that the water contents in three kinds of silica are in fairly good agreement with each other, in spite of large differences in their origin and also in surface properties such as area and porosity. The

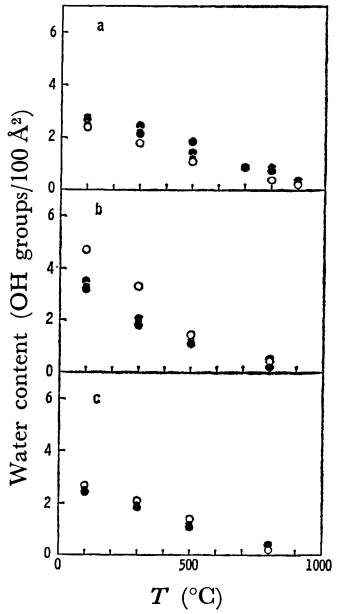

Fig. 4. Water content on Aerosil (a), porous silica glass (65–100 mesh) (b), silica gel (c), measured by the active hydrogen analysis (●) and the successive-ignition-loss method (○).

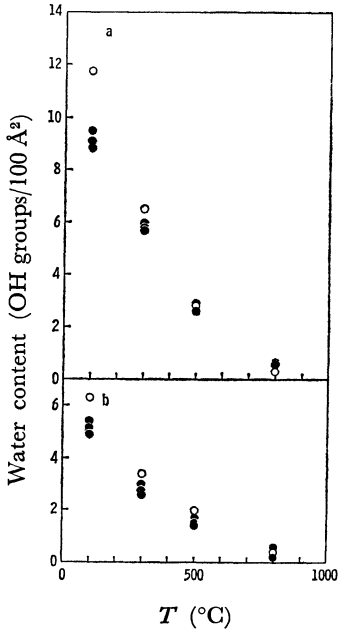

Fig. 5. Water content on alumina (a) and silica-alumina (SA-50) (b), measured by the active hydrogen analysis (●) and the successive-ignition-loss method (○).

water content in three kinds of 100 °-treated silica is *ca.* 3 OH/100 Å² (Fig. 4) which is much smaller than the values in the other oxides, but approximate to values estimated theoretically.[20]

A discrepancy between the two methods appears on porous silica glass treated at relatively lower temperatures: the successive-ignition-loss method gives a larger value. This might be due to the existence of extremely small pores which impede the diffusion of methylmagnesium iodide molecules, but permit the passage of condensed water molecules on outgassing. A similar discrepancy in the values of water content is observed on alumina and silica-alumina, when treated at lower temperatures (Figs. 5a and b). The same interpretation will also hold in these samples from the existence of pores of critical size. It can be expected that alumina and silica-alumina are easily hydrated to form aluminum atoms coordinated with water molecules or structural hydroxyl groups in the surface layer because of the well-known hydrophilic nature of aluminum ion. The latter situation will bring about a fairly large amount of observed water content on alumina as seen in Fig. 5a and also from previous results.[14,15]

It should be noted that the two methods give reliable values of water content in the process of heating the samples, especially in a range of smaller value of water content such as <2 OH/100 Å². From the fact that water evolution from the metal oxide surface at higher temperatures arises from the condensation dehydration of surface hydroxyls, it can be inferred that isolated surface hydroxyl groups which might remain on metal oxides at elevated temperatures can migrate to meet with each other on the surface, and that the migration occurs in the form of active hydrogens rather than hydroxyl groups themselves.

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