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The Surface Properties of the Silica-Titania System Prepared by the Hydrolysis of Metal Alkoxides

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The surface and bulk properties of silica-titania systems, prepared by the co-hydrolysis of silicon ethoxide and titanium tetrabutoxide, were investigated by measuring the heat of immersion, the adsorption of nitrogen, water, and ammonia, the X-ray diffraction, the DTA, and the TGA. It was found that the addition of silica to titania has a large suppressive effect on the crystal growth of anatase and on the transformation of anatase to rutile. The heat of immersion, the surface hydrophilicity (the surface area by water adsorption/the surface area by nitrogen adsorption) and the amount of ammonia adsorbed gave inverted sigmoid curves when the titania content was varied. Especially, the shape of the curve of the change in the heat of immersion coincides approximately with that of the surface hydrophilicity.

Recently, the methods of the preparation of metal oxides by the hydrolysis of metal alkoxides have often been reported. Such oxides synthesized by an ion-free process are suitable for the study of the surface properties of metal oxides. Meguro *et al.*[1,2] studied the surface properties of alumina-titania and silica-alumina systems prepared by the co-hydrolysis of metal alkoxides.

In this experiment, we have investigated the surface properties of the silica-titania system obtained by the co-hydrolysis of silicon ethoxide and titanium tetrabutoxide.

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[1] H. Murayama, K. Kobayashi, M. Koishi, and K. Meguro, *J. Colloid Interface Sci.*, **32**, 470 (1970).

[2] H. Murayama and K. Meguro, This Bulletin, **43**, 2386 (1970).

Experimental

Materials. Several samples of the silica-titania system were obtained by the co-hydrolysis of silicon ethoxide and titanium tetrabutoxide mixtures with different molar ratios. The purities of the alkoxides were checked by infrared analysis. The hydrolysis reaction was carried out by dropping a water-methanol mixture (water : methanol= 4:1 in weight) into a butanol solution of alkoxide (butanol : alkoxide= 1:1 in weight), keeping the total molar ratio of the water to alkoxide at 20:1. The water used was deionized and was then distilled. The alcohols used were of a reagent grade. After the liquid had been stirred for 10 hr at the boiling point, the precipitate was separated, washed with deionized water and then methanol, and dried at 100°C *in vacuo*. The dried samples were calcined for 2 hr in an electric furnace at temperatures from 500 to 1000°C. The samples calcined at 500°C were used for the study of the surface properties. The composition of the samples, as determined by X-ray fluorescence analysis were 21, 55, and 83 in the weight-percentage ratio: (titania)/(silica+titania); they will be designated as 4ST (silica : titania≒4:1 in weight), ST, and S4T respectively.

Apparatus and Procedure. The thermogravimetric and differential thermal analyses of the samples have been made by means of an automatic recording instrument of the Shimadzu Seisakusho Co.; the rate of heating was 10°C per minute. The X-ray diffraction patterns were recorded with a Geigerflex X-ray diffractometer of the Rigaku Denki Co., using Ni-filtered Cu radiation.

The heat of immersion was measured with a semimicro-calorimeter which had been devised in our laboratory.[3,4] A thermistor was used for measuring small temperature changes. A wide-mouthed, silvered Dewar flask with a 400 m*l* capacity served as the calorimeter vessel. It was attached to a Bakelite flange with stainless steel rings equipped with a Neoprene gasket. The calorimeter assembly included a small, 10 ohm heating manganin wire for calibration, a stirrer, a sample holder, and a thermistor. The whole assembly was immersed in a constant-temperature bath at 25°C. The heat evolved at immersion was calculated by means of galvanometer readings. The adsorption isotherms of nitrogen at −195°C, of water at 25°C, and of ammonia at 260°C were determined by means of a conventional, volumetric, gas-adsorption apparatus. For the water adsorption, the apparatus was maintained at 25°±0.5°C in an air thermostat. Each sample for water adsorption was outgassed at 100°C for 1 hr at 10^{-5} Torr and then cooled to 25°C prior to the adsorption studies. The nitrogen and water-surface areas of the samples were calculated by the BET formula, using 16.2 and 10.8 Å^2 for the cross-sectional areas of the nitrogen and water molecules respectively.

The compositions of all the samples were measured with a Rigaku Denki X-ray vacuum spectrograph by means of X-ray fluorometry.[5] The analyser crystal was ethylenediamine ditartrate. The chromium target was adjusted at 45KV, 12 mA (for Si) and 30KV, 6mA (for Ti). The X-radiation was detected by a proportional counter (90% Ar+10% CH_4) and discriminated as follows: for Si: base line, 70/1000, and channel width, 100/100, and for Ti: base line, 80/1000, and channel width, 100/100.

Results and Discussion

(*i*) *Differential Thermal Analysis, Thermogravimetric Analysis, and X-Ray Investigation.* Typical results of the differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) are shown in Fig. 1. The DTA of the samples are given in Fig. 1; they are characterized with an endothermic peak at 150°C and a small broad exothermic peak at 250—400°C. The endothermic peak is supposed to be due to the loss of adsorbed water, while the exothermic peak is supposed to be caused by the oxidation of a chemically-adsorbed solvent, which seems to be identified by the weight loss shown in the TGA curves at the same temperature. Therefore, in order to avoid the effect of the adsorbed solvent on the surface property, the chosen temperature of calcination was 500°C.

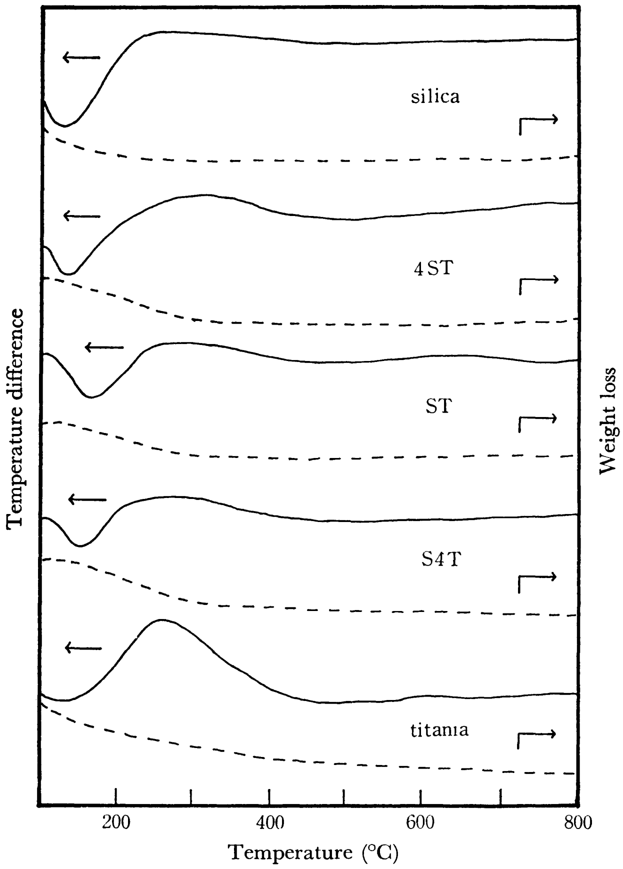

Fig. 1. DTA (solid lines) and TGA (dotted lines) curves of the silica-titania systems.

Typical X-ray diffraction patterns of the samples are shown in Fig. 2. The patterns of the silica calcined at 100—1000°C showed an almost amorphous structure. Broad lines characteristic of anatase are seen in the patterns of the titania heated at 100°C. These broad lines became sharper with a rise in the temperature of calcination. Moreover, the lines of rutile begin to appear in the patterns of the product calcined at 600—700°C. The silica-titania systems have different X-ray patterns from the parent oxides, but they show no lines which are not found in the patterns of the parent oxides. The X-ray-diffraction study showed that the addition of silica to titania has a large suppressive effect on the

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[3] K. Meguro, M. Koishi, and N. Okabe, *Kogyo Kagaku Zasshi*, **68**, 2055 (1965).

[4] K. Meguro, M. Koishi, M. Aizawa, N. Uchino, K. Matsumoto, H. Kimoto, Y. Kumaki, and H. Sawai, *Kogyo Kagaku Zasshi*, **69**, 1724 (1966).

[5] A. Leonard, S. Suzuki, J. Fripiat, and C. De Kimpe, *J. Phys. Chem.*, **68**, 2608 (1964).

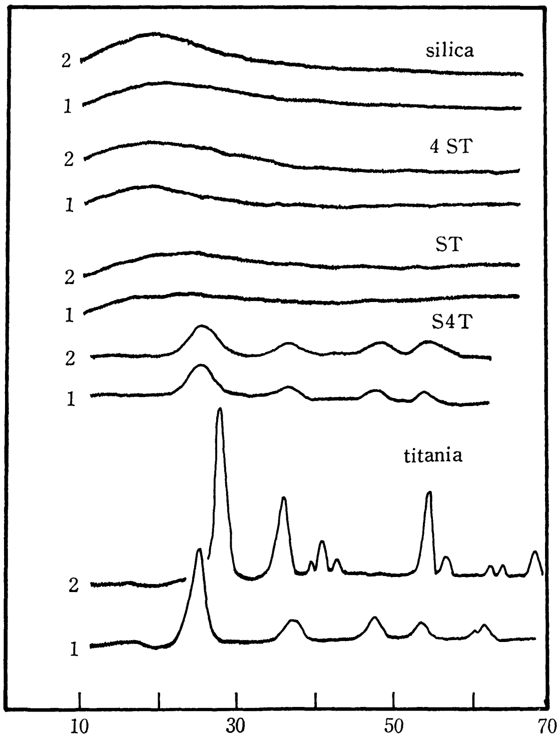

Fig. 2. X-Ray diffraction patterns at different temperatures (1:500°C 2:800°C) of the silica-titania systems.

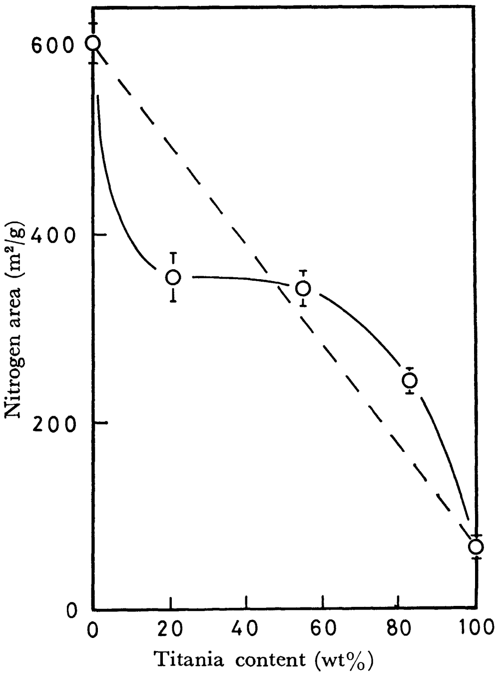

Fig. 3. The change of the nitrogen surface area of the silica-titania systems calcined at 500°C with composition. Dotted line, the dry-mixed oxides.

crystal growth of anatase and on the transformation of anatase to rutile. This effect was evidenced by the fact that the samples of 4ST and ST remained amorphous even when the calcining temperature was raised to 800°C. In the case of S4T, which has a higher titania content, only broad lines of anatase was observed in the calcination at 500°C; this anatase pattern remained the same up to 800°C. This suppressive effect increases as the silica content increases. Typical patterns are shown in Fig. 2. It is well known that the rate of the anatase-rutile transformation is affected by the presence of foreign ions, entering either substitutionally or interstitially.⁶⁾ From the suppressive effects on the crystal growth and the transformation, it may be supposed that the silica-titania systems prepared by the co-hydrolysis are different in structure from simple mechanical mixtures of dry silica and titania.

(*ii*) *Specific Surface Area.* The specific surface areas of the samples obtained by nitrogen adsorption change with the titania content, giving a sigmoid curve, as is shown in Fig. 3, in which the surface area is plotted as a function of the weight percentage of titania. This is compared with the straight dotted line in Fig. 3, which shows the theoretical surface area as calculated as the mechanical mixtures. In practice, however, the specific surface areas of the samples do not change proportionally with the composition, but give a sigmoid curve. The surface area decreases steeply between silica (600m²/g) and S4T (348m²/g), gradually decreases between 4ST and S4T (239m²/g), and then decreases steeply again between S4T and titania (63.9m²/g).

(*iii*) *Water Adsorption and Heat of Immersion.* Figure 4 represents the specific surface area derived from the water adsorption versus the composition of the silica–titania systems. The curve of the surface area versus the composition in Fig. 4 is not a straight line, as might be expected in the case of a simple mixture of dry silica and titania.

Healey and his co-workers⁷⁾ have shown that the ratio of the apparent surface area, as determined by the water adsorption, to the total area, as determined by the nitrogen adsorption, is a direct measure of the fraction of the hydrophilic surface present in a finely-

TABLE 1. SURFACE PROPERTIES OF THE SILICA-TITANIA SYSTEM CALCINED AT 500°C FOR2 hr

Sample composition wt % (TiO_2/SiO_2+TiO_2)	X-Ray diffraction	S_{N_2} (m^2/g)	S_{H_2O} (m^2/g)	S_{H_2O}/S_{N_2} × 100	H_i (erg/cm^2)	Amounts of NH_3 adsorbed (ml/m^2)
0	amorphous	600	81.3	14	119	0.001
21	amorphous	348	155	44	303	0.0124
55	amorphous	343	203	59	346	0.0166
83	weak anatase lines	239	142	60	332	0.0380
100	weak anatase lines	63.9	55	86	506	0.105

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6) R. D. Shannon, and J. A. Pask, *J. Amer. Ceram. Soc.*, **48**, 391 (1965).

7) F. H. Healey, Y. F. Yu, and J. J. Chessick, *J. Phys. Chem.*, **59**, 399 (1955).

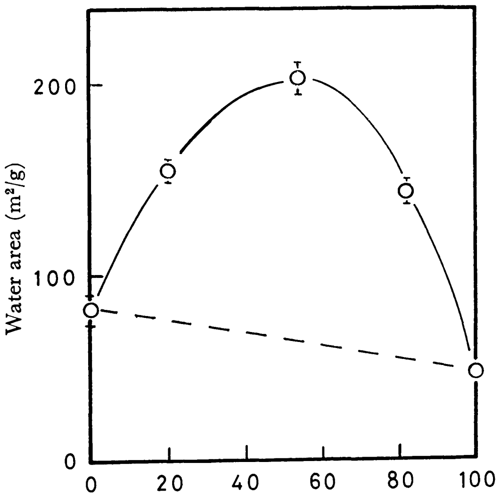

Fig. 4. The change of the water surface area of the silica-titania systems with composition. Dotted line, the dry-mixed oxides.

divided solid. The ratio may also be considered to be a measure of the hydrophobicity; the smaller the ratio the more hydrophobic the surface. Therefore, the surface hydrophilicity in percentage may be expressed as: (the surface area by water adsorption/the surface area by nitrogen adsorption) × 100. The change in the surface hydrophilicity of the samples is illustrated in Fig. 5 as a function of the titania content. The straight dotted line in Fig. 5 shows the theoretical surface hydrophilicity calculated as were the mechanical mixtures. It is noticeable that the experimental hydrophilicity deviates from the straight line. The hydrophilicity of the samples rises steeply between silica (14%) and 4ST (44%), rises gradually between 4ST (60%), and then again rises steeply beween S4T and titania (86%).

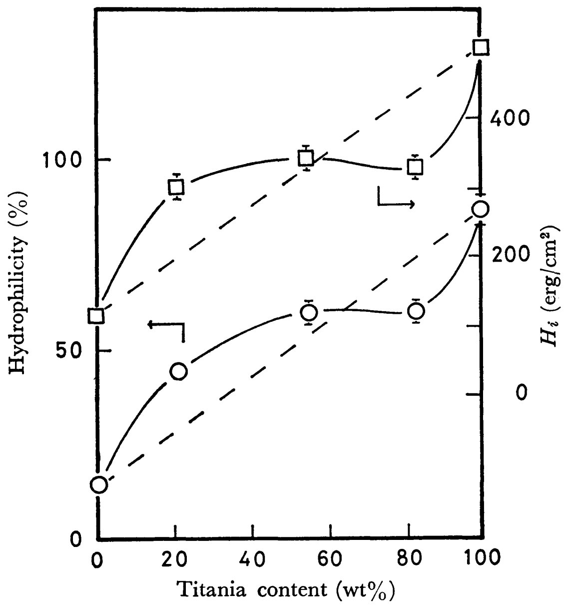

Fig. 5. The change of the heat of immersion and the surface hydrophilicity of the silica-titania systems with composition. □-Heat of immersion. ○-Surface hydrophilicity. Dotted lines, the dry-mixed oxides.

The change in the heat of immersion with the composition of the samples is represented in Fig. 5, in which the heat of immersion is plotted as a function of the titania content. The straight dotted line in Fig. 5 shows the theoretical heat of immersion calculated as were the mechanical mixtures. The heat of immersion increases steeply between silica (119erg/cm^2) and 4ST (303erg/cm^2), changes gradually between 4ST and S4T (332erg/cm^2), and then increases greatly between S4T and titania (506erg/cm^2). The crystal structures of silica, 4ST, and ST are almost amorphous, while those of S4T and titania are anatase. From these results, it may be concluded that the heat of immersion of the samples is not affected by the change in the crystal structure. The change in the surface hydrophilicity with the composition approximately coincides with that of the heat of immersion, as is shown in Fig. 5. The same results have been reported on alumina-titania[1] and silica-alumina[2] systems. The coincidence of the changes in the surface hydrophilicity of these samples with the composition and those of the heat of immersion of these samples with the composition can be explained as resulting from the fact that alumina, silica and titania surfaces are usually covered with hydroxyl groups, which act as primary adsorption sites for polar molecules. Since the surface hydrophilicity has an intimate relation with surface hydroxyl groups, the coincidence of this curve with that of the heat of immersion is reasonable.

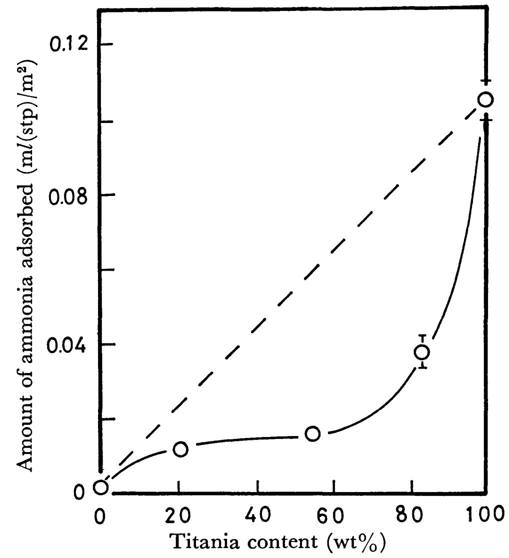

Fig. 6. The change of the amount of ammonia adsorbed on the silica-titania systems with composititon. Dotted line, the dry-mixed oxides.

(*iv*) *Surface Acidity.* Another important character of the surface of the silica-titania system is the surface acidity. The ammonia adsorption isotherm at 260°C, where the highest equilibrium pressure was about 10Torr, was determined.[8,9] The surface acidity of the samples was determined by the adsorption of ammonia at 260°C. The shape of the adsorption

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[8] T. Shiba and E. Echigoya, *Nippon Kagaku Zasshi*, **76**, 1046 (1955).

[9] J. J. Fripiat, A. Leonard, and J. B. Uytterhoeven, *J. Phys. Chem.*, **69**, 3274 (1965).

isotherms of the samples is that of the Langmuir type. The saturated amount of the adsorption of ammonia can be calculated from the Langmuir equation; the calculated values of the saturated adsorption are listed in Table 1. Figure 6 shows the relation between the amount of ammonia and the titania content in the silica-titania system. In this case, the amount of ammonia adsorbed on the samples does not change proportionally with the titania content. The straight dotted line in Fig. 6 shows the theoretical value of ammonia adsorption, calculated as were the mechanical mixtures. The change in the surface acidity with the titania content shows an inverted sigmoid curve like those of the heat of immersion and of the hydrophilicity. This suggests that there is a relationship between the sites responsible for the ammonia adsorption and the surface hydroxyl groups. This suggestion agrees with the results of Stöber.(10)

It should be noted that the observed values of the silica-titania system, such as those of the nitrogen area, the water area, the surface hydrophilicty, the heat of immersion, and the surface acidity, are very different from those obtained on the assumption that this system is composed of a simple mechanical mixture of the two components. These deviations may originate in the method of the preparation of the systems; they suggest that the surface structures of the systems prepared by the co-hydrolysis of these metal alkoxides are different from those of simple mechanical mixture of dry silica and titania.

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10) W. Stöber, *Kolloid-Z.Z.Polym.*, **145**, 17 (1956).