BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2386—2389 (1970)

Surface Properties of the System SiO_2-Al_2O_3 prepared by the Hydrolysis of Metal Alkoxides

Hiroyoshi MURAYAMA and Kenjiro MEGURO

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

(Received February 16, 1970)

The mixtures of aluminum *s*-butoxide and silicon ethoxide in different molar ratio were hydrolyzed in aqueous alcohol. The precipitates were dried, and the growth and transformation of the crystals at calcination were estimated by X-ray diffractometry. The surface properties of the oxide powder were studied by means of the heats of immersion and the adsorption of nitrogen, water vapor and ammonia. The samples calcined at 500°C have surface areas 260—600 m^2/g. Heats of immersion and surface hydrophilicity with respect to the composition, from pure silica gel to pure alumina, have a fairly good resemblance to each other, but this is not found between the heats of immersion and surface acidity.

In the preceding paper,[1] we reported surface properties of the system Al_2O_3-TiO_2 prepared by the co-hydrolysis of metal alkoxides under ion-free conditions. The study of surface properties of silica-aluminas is extremely important and interesting from a catalytic point of view.[2–5] However, few investigations have been reported on the surface properties of amorphous silica-aluminas[6–8] obtained from metal alkoxides.

In the present paper, an investigation of the surface properties of silica-aluminas produced by hydrolysis of silicon ethoxide and aluminum *s*-butoxide under ion-free conditions is reported.

Experimental

Materials. The products of hydrolysis of metal alkoxides are usually free from ionic impurities.[9–12] It is therefore advantageous to use the co-hydrolysis of aluminium *s*-butoxide and silicon ethoxide, purified by distillation, to obtain ion-free silica-aluminas. Excess aqueous ethanol was poured, with vigorous stirring, into the various mixtures of these alkoxides in *n*-butanol. Stirring was continued for 15 hr at a temperature near boiling point. The precipitate was separated by centrifuging, thoroughly washed with alcohol (by decantation) to remove undecomposed alkoxides, finely ground, and then dried at 100°C until the residual pressure of gas was less than 10^{-5} Torr. Hydrolysis of these alkoxides was confirmed by infrared analysis. The dried products were calcined for 2 hr at temperatures 100—1000°C, and the resulting samples were kept in a desiccator. The compositions of the samples determined by means of X-ray fluorescence were 0, 35.0, 64.0, 80.5, 89.6, and 100 in weight percent ratio $Al_2O_3/(Al_2O_3+SiO_2)$, respectively.

Apparatus and Procedure. The compositions of all the samples were determined by means of X-ray fluorometry with a Rigaku Denki X-ray vacuum spectrograph.[6)] The analyser crystal was ethylenediamine ditartrate. The Cr-target was adjusted at 45 kV, 22 mA (for Al) and 45 kV, 12 mA (for Si). The X-ray radiation was detected by a proportional counter (90% Ar+10% CH_4) and discriminated as follows: for Al, base line 35/1000, channel width 100/100; for Si, base line 70/1000, channel width 100/100.

The differential thermal analysis curves were obtained with an automatically recording instrument, and the rate of heating was 10°C per minute. X-Ray diffraction patterns were obtained with a Geigerflex X-ray diffractometer of Rigaku Denki Co. The setting of the instrument was 35 kV, 15 mA for radiation on the target Cu*Kα*.

The calorimeter assembly for heats of immersion

---

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

[2] M. W. Tamele, *Discuss. Faraday Soc.*, **8**, 270 (1950).

[3] R. L. Richardson and S. W. Benson, *J. Phys. Chem.*, **61**, 405 (1957).

[4] J. N. Finch and A. Clark, *ibid.*, **73**, 2234 (1969).

[5] M. R. Basila, T. R. Kanter and K. H. Rhee, 145th ACS Meeting, New York, 1963, Abstr. Papers 26-I.

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

[7] J. J. Fripiat, A. Léonard and J. B. Uytterhoeven, *ibid.*, **69**, 3274 (1965).

[8] M. Sato, T. Kanbayashi, N. Kobayashi and Y. Shima, *J. Catal.*, **7**, 342 (1967).

[9] S. J. Gregg and K. H. Wheatley, *J. Chem. Soc.*, **1955**, 3804.

[10] J. F. Goodman and S. J. Gregg, *ibid.*, **1960**, 1162.

[11] M. R. Harris and G. Whitaker, *J. Appl. Chem.*, **12**, 490 (1962).

[12] G. C. Bye, J. G. Robinson and K. S. W. Sing, *ibid.*, **17**, 138 (1967).

[13] K. Meguro, M. Koishi, M. Aizawa, N. Uchino, K. Matsumoto, H. Kimoto, Y. Kumaki and H. Sawai, *Kogyo Kagaku Zasshi*, **69**, 1724 (1964).

measurement and the experimental techniques used were the same as previously described.[13] The calorimeter was the isoperibol type equipped with a thermistor temperature sensing element. All measurements were carried out at 25±0.1°C in water with samples evacuated at 100°C for 1 hr at 10^{-5} Torr before immersion.

Adsorption isotherms were determined at −195°C, 25°C and 260°C for nitrogen, water vapor, and ammonia, respectively, by using a conventional volumetric gas adsorption apparatus. For the water vapor adsorption the apparatus was maintained at 25±0.5°C in air thermostat. Each sample for water vapor adsorption was outgassed at 100°C for 1 hr at 10^{-5} Torr to remove physically adsorbed water and cooled to 25°C prior to the adsorption studies.

Results and Discussion

(i) Bulk Properties. The typical experimental results of X-ray analysis on the samples treated at different temperatures and the differential thermal analysis curve of the 0% ($Al_2O_3/Al_2O_3+SiO_2$) sample, that is pure silica gel, are illustrated in Fig. 1. The pure alumina, 100% ($Al_2O_3/Al_2O_3+SiO_2$) sample, is the same sample used in the previous study.[1] X-ray diffraction patterns of the 100% Al_2O_3 sample heated at 500°C for 2 hr possess only very few faint lines of γ-Al_2O_3. On the other hand, all other samples calcined for 2 hr at 500, 600, 700, and 800°C are amorphous to X-ray, as can be seen from the results given in Fig. 1.

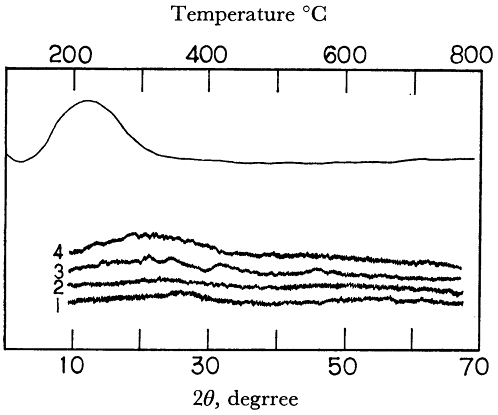

Fig. 1. X-Ray diffraction patterns at different temperatures (1: 100°C, 2: 500°C, 3: 800°C, 4: 1000°C) and differential thermal analysis curve of 0% ($Al_2O_3/Al_2O_3+SiO_2$) sample, that is pure silica gel.

Pure silica gel, 0% ($Al_2O_3/Al_2O_3+SiO_2$) sample, gives a differential thermal analysis curve which is characterized by the presence of a broad exothermic peak between 150—300°C, and a small endothermic peak at 120°C (Fig. 1). The first peak results from the loss of physically adsorbed water, and the last exothermic peak is attributed to the oxidation of chemically adsorbed butanol. The differential thermal analysis curves of other silica-alumina samples studied shows analogous features.

Changes of the surface properties of the system Al_2O_3-SiO_2 with composition were confirmed on these samples calcined at 500°C for 2 hr. Samples calcined below 500°C retain residues of butanol

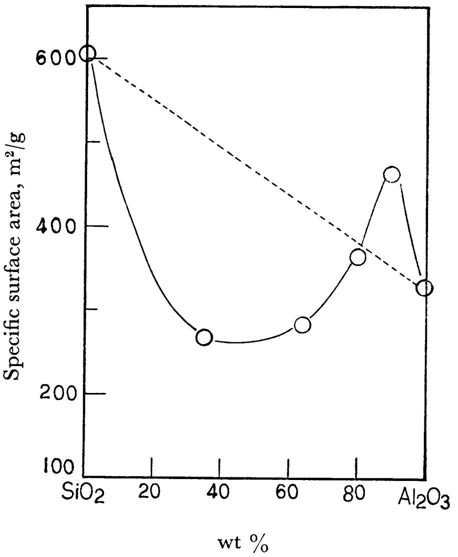

Fig. 2. Variation of specific surface areas of the system Al_2O_3-SiO_2 calcined at 500°C with composition. Dotted line is theoretical one under the assumption of additivity.

TABLE 1. SURFACE PROPERTIES OF THE SYSTEM Al_2O_3-SiO_2 PREPARED FROM ALKOXIDES FOLLOWED BY HEATING AT 500°C FOR 2 hr

Sample composition, % ($Al_2O_3/Al_2O_3+SiO_2$)	X-Ray analysis	S_{N_2} m²/g	S_{H_2O} m²/g	S_{H_2O}/S_{N_2} ×100	ΔH_i ergs/cm²	Amounts of NH_3 adsorbed cc/m²
100	broad γ·Al_2O_3	324	140	43	423	0.0185
89.6	amorphous	464	207	45	454	0.0259
80.5	amorphous	367	236	64	498	0.0327
64.0	amorphous	279	136	49	351	0.0348
35.0	amorphous	263	89.5	34	263	0.0424
0	amorphous	600	81.3	14	119	0.0009

---

14) F. H. Healey, J. J. Chessick and A. V. Fraioli, *J. Phys. Chem.*, **60**, 1001 (1956).

and water, and it is only above 500°C that the structures begin to show their crystalline nature.

(ii) Specific Surface Area. Specific surface areas have been determined by standard B.E.T. procedure, using 10.8 and 16.2 Å^2 for the molecular cross-sectional areas of water vapor and nitrogen, respectively.[14] Specific surface areas estimated from nitrogen and water vapor adsorption are given in Table 1. The variation of the specific surface area of the system Al_2O_3-SiO_2 with composition is represented in Fig. 2, in which the surface area is plotted as a function of Al_2O_3 contents (wt%) determined by X-ray fluorometry. The dotted line in Fig. 2 shows the theoretical specific surface areas of mixtures calculated under the assumption of additivity of surface area. The surface areas observed deviate from this theoretical line. The rise of Al_2O_3 contents decreases the specific surface area to a broad minimum of about 263 m^2/g obtained in the case of the 35.0% ($Al_2O_3/Al_2O_3+SiO_2$) sample, above which a slow increase in area occurs with further rise of Al_2O_3 content. The maximum in the specific surface area of silica-alumina is obtained in the case of 89.6% ($Al_2O_3/Al_2O_3+SiO_2$) sample.

Inspection of columns 3 and 4 of Table 1 reveals that the surface areas calculated from nitrogen adsorption are considerably higher than those calculated from the water vapor isotherms.

(iii) Surface Hydrophilicity and Heat of Immersion. Water vapor adsorption data were plotted as isotherms from which the monolayer capacity, V_m, was calculated by the B.E.T. method. The surface area, S_{H_2O} (m^2/g), was calculated from V_m, taking the molecular area of water vapor at 25°C as 10.8 Å^2. The results are given in column 4 of Table 1.

Healey *et al.*[15,16] have shown that surface hydrophilicity is represented as the ratio of total surface area to hydrophilic surface area. Thus it follows that

$$\text{Surface hydrophility}(\%) = S_{H_2O}/S_{N_2} \times 100,$$

where S_{H_2O} and S_{N_2} denote the specific surface areas as based on water vapor and nitrogen adsorption, respectively. The variation of the surface hydrophilicities of the system of Al_2O_3-SiO_2 with composition is listed in Table 1 and illustrated in Fig. 3, in which the hydrophilicities are plotted as a function of Al_2O_3 contents (wt%).

The data of heats of immersion of the system SiO_2-Al_2O_3 are shown in column 6 of Table 1. The variation in heats of immersion is represented in Fig. 3, in which the heats are plotted as a function of Al_2O_3 contents (wt%).

The dotted line in Fig. 3 shows the theoretical heats calculated under the assumption of additivity. The heats observed deviate from this theoretical line, and the rise of Al_2O_3 contents increase the heats to a maximum of about 500 erg/cm^2 obtained in the case of the 80.5% ($Al_2O_3/Al_2O_3+SiO_2$) sample.

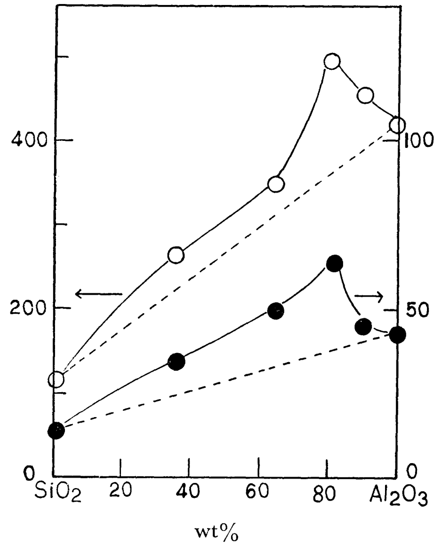

Fig. 3. Variation of surface hydrophilicities and heats of immersion of the system Al_2O_3-SiO_2 with composition.

● ----Surface hydrophilicity (S_{H_2O}/S_{N_2} X 100, percent).

○ ----Heat of immersion (erg per square centimeter).

Dotted lines are theoretical ones under the assumption of additivity.

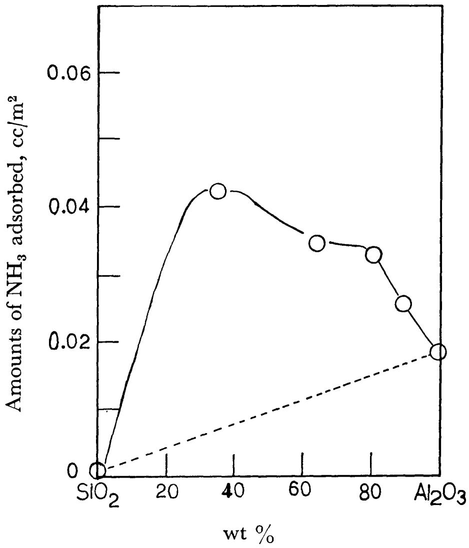

Fig. 4. Variation of amounts of ammonia adsorbed of the system Al_2O_3-SiO_2 calcined at 500°C with composition.

Dotted line is theoretical one under the assumption of additivity.

---

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

[16] A. C. Zettlemoyer, *Official Dig.*, **29**, 1238 (1957).

It is interesting to note that this tendency of the surface hydrophilicity coincides with that of heats of immersion. This strongly suggests a relationship between the magnitude of the heats of immersion and the concentration of hydroxyl sites on the surface, as pointed out by Young and Bursh,[17] and Zettlemoyer *et al.*[18]

(iv) Surface Acidity. The surface aciditiy of the system Al_2O_3-SiO_2 was determined by the chemisorption of basic gas (ammonia) at high temperature and low pressure. Ammonia adsorption isotherms at 260°C, where the highest equilibrium pressure was about 15 Torr, were determined[1] on all the samples studied after outgassing at 260°C for 1 hr at 10^{-5} Torr. The shape of the isotherms of all the samples studied is Langmuir's type. The amounts adsorbed at saturation per unit surface area calculated by the Langmuir equation are listed in Table 1 and illustrated in Fig. 4, in which the amounts of ammonia adsorbed are plotted as a function of Al_2O_3 contents. The rise of Al_2O_3 contents increases the amount of ammonia adsorbed to a maximum of about 0.04 cc/m^2 obtained in the case of the 35.0% ($Al_2O_3/Al_2O_3+SiO_2$) sample, above which a decrease in the amount of ammonia adsorbed occurs with further rise of Al_2O_3 contents.

From the fact[19] that silica gel does not behave as an acid-catalyst in the catalytic reaction such as propylene polymerization, it is reasonable to consider that its acidity is zero. The experiment on the ammonia adsorption at 260°C in the case of the 0% ($Al_2O_3/Al_2O_3+SiO_2$) sample gives near zero value (0.0009 cc, at S.T.P./m^2) for its acidity, as indicated in Table 1.

---

[17] G. J. Young and T. P. Bursh, *J. Colloid Sci.*, **15**, 361 (1960).

[18] A. C. Zettlemoyer, R. D. Iyengar and P. Scheidt, *J. Colloid Interfac. Sci.*, **22**, 172 (1966).

[19] S. E. Tung and E. Mcininch, *J. Catal.*, **3**, 229 (1964).