BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1476—1480 (1969)

Nature of Acid Sites on the Surface of Silica-alumina. I. The Relation between the Acid Property of Sites and the Heat of Immersion

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(Received September 20, 1968)

The acidity and the acid strength of the sites of such solid catalysts as silica gel, alumina, and silica-alumina were determined by the *n*-butylamine titration method using the Hammett indicators. The distribution of the acid sites on the surfaces of these catalysts was found to vary with the outgassing temperature, and also with the alumina content in the case of silica-alumina. The heats of immersion of these catalysts in water and in an aqueous solution of *n*-butylamine were measured. The heat value corresponding to the difference between these two cases, as well as the number of acid sites, showed a maximum at contents of 10—20%. These phenomena are discussed with reference to the results of the diffuse reflection measurements.

Silica-alumina is widely used as a catalyst for such reactions as cracking, isomerization, and polymerization. Recently many studies of the nature of the catalytically-active sites[1-4] which are developed by the removal of chemisorbed water from the surface have been undertaken. The active sites thus generated possess acid properties; the Lewis-acid site can accept lone-pair electrons, and the Brönsted-acid site can donate a proton. It is thought that these acid sites play an important role in surface reactions. The distribution of these acid sites has been measured by various techniques, such as the indicator method[5,6] and the volumetric-base adsorption method.[7,8] However, no exact information on the nature of the surface of silica-alumina, has yet been obtained. In this work, the *n*-butylamine titration method using the Hammett indicators was employed to determine and characterize the acid properties of the surface of silica gel, alumina, and silica-alumina; the results will be discussed in relation to the heat of immersion caused by the interaction of water with acid sites. Furthermore, the spectra resulting from the diffuse reflection[9] of anthracene adsorbed on the samples from an *n*-hexane solution were measured in order to confirm the results obtained from the above experiments.

Experimental

Materials. The silica gel was prepared by the hydrolysis of ethyl ortho-silicate, which had been purified by distillation at 120—130°C. The product was washed with water by repeated decantation, kept standing overnight at 150°C, and then calcined at 600°C in air for 8 hr. Alumina was produced by hydrolyzing aluminum isopropoxide which had been previously purified by distillation under reduced pressure. The product was treated in the same way as in the case of silica gel. The silica-alumina was prepared by adding a suspension of aluminum isopropoxide in alcohol to the sol obtained by hydrolyzing ethyl ortho-silicate. The mixture was well

TABLE 1. SURFACE AREA OF SILICA-ALUMINAS WITH VARIOUS CONTENTS OF ALUMINA

Alumina content (wt%)	Surface area (m^2/g)
0	627
5	351
8	297
10	295
16	233
23	167
29	429
53	353
80	393
100	189

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1) M. W. Tamele, *Discussions Faraday Soc.*, **8**, 270 (1950).

2) O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955).

3) V. C. F. Holm, G. C. Bailey and A. Clark, *ibid.*, **63**, 129 (1959).

4) A. Clark, V. C. F. Holm and D. M. Blackburn, *J. Catalysis*, **1**, 244 (1962).

5) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

6) J. Kobayashi and I. Higuchi, *Shokubai (Catalysis)*, **4**, 49 (1962).

7) R. C. Richardson and S. W. Benson, *J. Phys. Chem.*, **61**, 405 (1957).

8) G. A. Mills, E. R. Boedecker and A. G. Oblad, *J. Am. Chem. Soc.*, **72**, 1554 (1950).

9) A. Terenin, V. Barachevsky, E. Kotov and V. Kolmogorov, *Spectrochimica Acta*, **19**, 1797 (1963).

stirred for 3hr at 120—130°C, and then treated as above. X-Ray analysis showed that the silica gel and silica-alumina were practically amorphous and that the alumina was of the γ-type. The specific surface areas of the samples evacuated at 300°C were determined by the B.E.T. method from the nitrogen adsorption. The results are listed in Table 1. The *n*-butylamine and benzene were purified by distillation, with several pieces of metallic sodium added to remove any moisture. The anthracene and the Hammett indicators were purified by recrystallizing them twice from a hot alcoholic solution.

Measurement of Acid Properties. The silica gel, alumina, and silica-alumina were dried at 100°C, 300°C, and 500°C for 3hr *in vacuo*. These samples were then dispersed into dry benzene, and the suspensions thus obtained were titrated with a 0.5 N benzene solution of *n*-butylamine using the Hammett indicators.[5] The treatment was made in a dry-box through which nitrogen gas flowed continuously. The amount of *n*-butylamine titrated corresponds to the number of acid sites.

Heat of Immersion. The heats of immersion of the samples were measured at 25°C in water and in an aqueous solution of *n*-butylamine by using a calorimeter equipped with a thermistor.[10]

Diffuse Reflection. An oxygen-free *n*-hexane solution of anthracene was added through a breakable joint to a sample dried at 300°C. After the adsorption equilibrium had been established, the *n*-hexane was sufficiently removed through a trap cooled with liquid nitrogen. The colored sample was then transferred into a cell used for the measurement of diffuse reflection, which was then cut off. The spectra were measured using a Hitachi-Perkin-Elemr 139 spectrophotometer, equipped with an attachment for the measurement of the diffuse reflection.

Results and Discussion

Acid Properties. The acid properties of the surfaces of silica gel, alumina, and silica-alumina show different characteristics as the evacuating temperature rises.

Figure 1 shows that silica-alumina has two acid-site groups; one group includes the strong acid sites in the range of $H_0 < -3.0$, and the other, the weak acid sites in the range of $6.8 > H_0 > 3.0$, where H_0 is the Hammett function. These are scarcely no intermediate sites between $H_0 = 3.0$ and $H_0 = -3.0$, as may be seen in the figure. The strong acid sites increase with a rise in the outgassing temperature. The acid property of alumina is quite different from that of silica-alumina, as is shown in Fig. 2. When alumina is heated at 100°C, weak acid sites alone develop. However, when the sample is treated at 300°C, strong acid sites also appear and the total number of acid sites increases. On the other hand, when heated at 500°C, all of the strong acid sites disappers. The total number of acid sites of silica gel is nearly

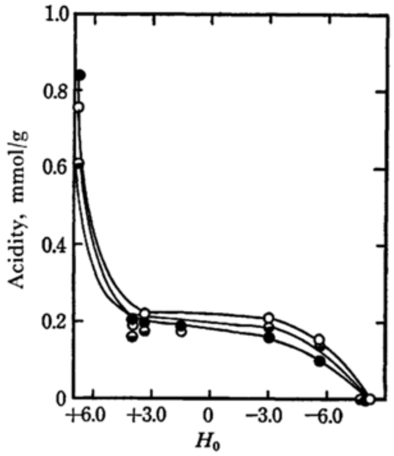

Fig. 1. Acidity *vs.* acid strength for 8.1% silica-alumina; degassing temperature: ● 100°C, ◒ 300°C, ○ 500°C.

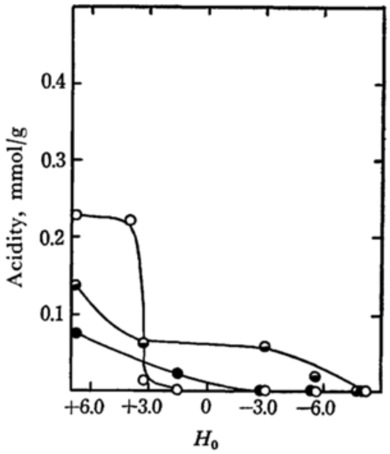

Fig. 2. Acidity *vs.* acid strength for alumina; degassing temperature: ● 100°C, ◒ 300°C, ○ 500°C.

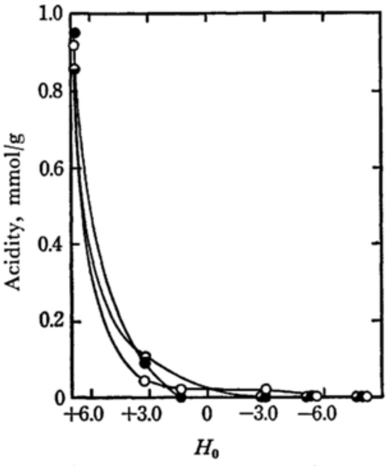

Fig. 3. Acidity *vs.* acid strength for silica gel; degassing temperature: ● 100°C, ◒ 300°C, ○ 500°C.

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[10] M. Miura, H. Naono, T. Iwaki, T. Kato and M. Hayashi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1623 (1966).

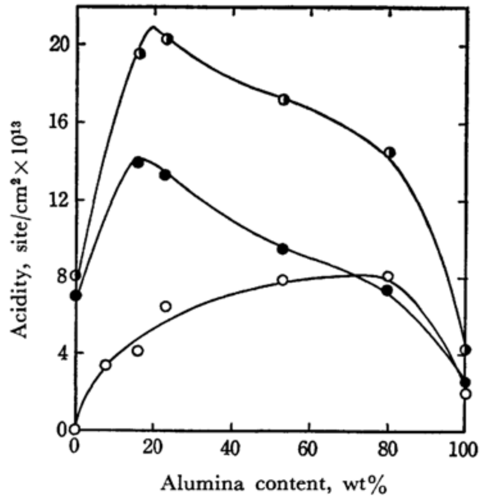

Fig. 4. Acidity of silica-alumina with various contents of alumina.

○: strong acid site, $H_0 < -3.0$

●: weak acid site, $+6.8 > H_0 > +3.0$

◑: total acid site, $H_0 < +6.8$

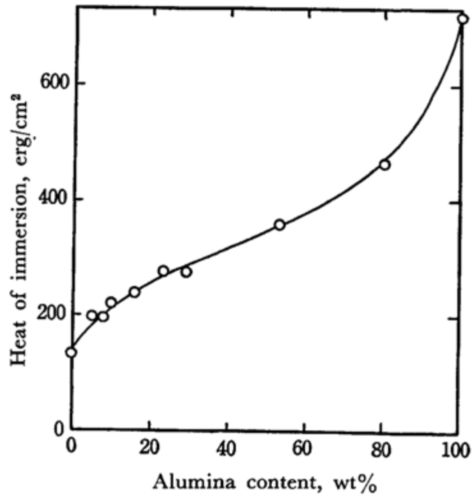

Fig. 5. Heat of immersion of silica-aluminas with various contents of alumina in water.

constant, regardless of the evacuating temperature, whereas more stronger acid sites appear with a rise in the temperature, as may be seen in Fig. 3.

The acid strength of silica-alumina also changes with the alumina content. Figure 4 shows the case of silica-aluminas evacuated at 300°C. The number of strong acid sites is almost zero for pure silica gel, but it increases with the alumina content until finally it again takes a low value for pure alumina. The maximum number of weak acid sites is at the content of 10—20%. Thus, the total number of sites is maximum at a content of about 20%. The aluminum atom originally hydrated in the surface layer of silica-alumina is dehydrated by evacuation at a high temperature. The naked aluminum atom thus produced may behave as a strong acid site, while the hydrated one may act as a weak acid site.[11] As the probability that the naked aluminum atoms will appear on the surface by evacuation increases with the alumina content, it may be generally predicted that the number of strong acid sites increases, and that of weak acid sites decreases, with an increase in the alumina content. The fact that the number of strong acid sites is less for alumina than for silica-alumina seems to be due to the difference in the mechanism of the generation of acid sites between these two materials.[12]

Heat of Immersion. The heats of immersion of silica-aluminas with various alumina contents in water are shown in Fig. 5. The heat evolved increases with the alumina content, as has been reported previously.[10] The factors responsible for the generation of the heat may be considered to be as follows: (1) the property of -OH groups on the surface, (2) the hydrogen bond between the -OH group and electronegative oxygen or the nitrogen atom in such molecules as water and *n*-butylamine, and (3) the distribution of acid sites on the surface. When the samples are immersed into water, the water molecule with nonbonding electrons generally makes a co-ordinate bond with the active acid site. The strong acid site is considered to contribute to heat generation more than the weak site does. The small amount of heat for silica gel may be due to the absence of a strong acid site on its surface and also to the weak dipole-dipole interaction of a water molecule having a large permanent dipole moment with the neutral -OH group. The gradual increase in the heat with the alumina content may be due to a slow increase in the number of strong acid sites on the surface. The large heat value for alumina may be caused mainly by the strong interaction of the negatively-charged -OH group[13] with the water molecule, since the alumina has a small number of strong acid sites.

When the samples are immersed into an aqueous solution of *n*-butylamine, more heat is generated than in the above case, as may be seen by comparing Figs. 5 and 6. The difference between the heat of immersion in water and that in the aqueous solution of *n*-butylamine is shown in Fig. 7. The amount of heat at a content of about 10% is characteristically large. The amount of *n*-butylamine adsorbed from the aqueous solution on the surface of silica-alumina is shown in Fig. 8, where the adsorbed amount was determined by means of

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[11] M. R. Basila, T. R. Kanter and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964).

[12] E. Echigoya, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **79**, 430 (1958).

[13] J. B. Peri, *J. Phys. Chem.*, **69**, 220 (1965).

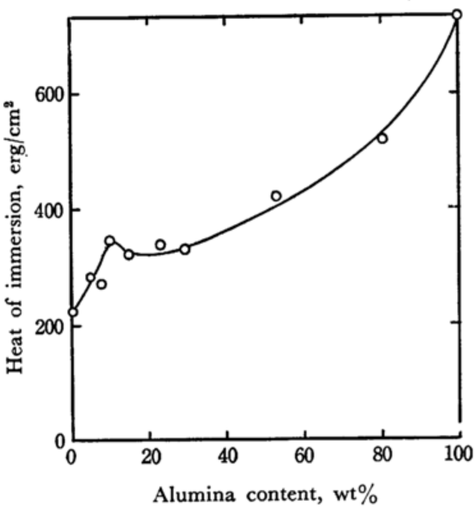

Fig. 6. Heat of immersion of silica-aluminas with various contents of alumina in the aqueous solution of n-butylamine.

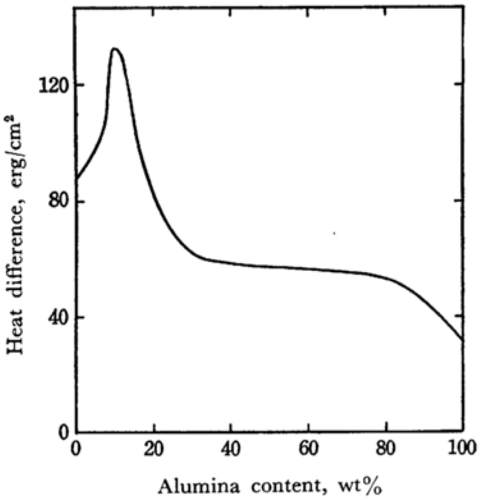

Fig. 7. Difference between the heats of immersion of silica-alumina with various contents of alumina in water and in the aqueous solution of n-butylamine.

an electrical conductivity method. The maximum amount of n-butylamine adsorbed is at a content of 10%, as may be seen in Fig. 8. Each of the curves in Figs. 7 and 8 bears a fairly good resemblance in shape to the curve of total acid sites shown in Fig. 4.

Diffuse Reflection. Anthracene was used as a molecular indicator because it is known that the spectra due to the interactions of anthracene with Lewis-acid site and with a Brönsted-acid site can be distinguished from each other.[14,15] A degassed n-hexane solution of anthracene was added to a sample evacuated at 300°C through a breakable joint, the whole was allowed to stand for 1 hr, and then the n-hexane was removed through the other breakable joint. Upon this treatment silica-alumina turned green and alumina, palegreen, but silica gel showed no change in color. According to the observation of the color change, only the strong interaction of anthracene with the acid sites can be observed. In the measurement of diffuse reflection, alumina shows a very weak absorption at 760 mμ; this is due to the carbonium cation radical arising from electron transfer from the anthracene molecule to the Lewis-acid site. This species was confirmed by ESR measurement. Silica-alumina with a content of 80% shows an absorption at 760 mμ, stronger than in the case of alumina; this was confirmed by a study of the ESR spectra.

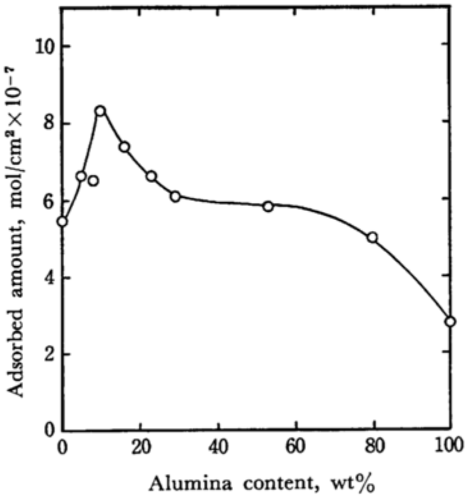

Fig. 8. Adsorbed amount of n-butylamine on the surface of silica-aluminas with various contents of alumina from the aqueous solution of n-butylamine.

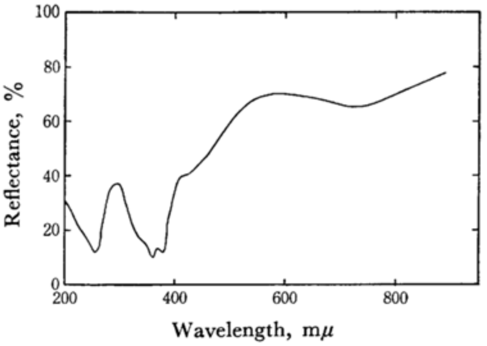

Fig. 9. Diffuse reflection spectrum of anthracene adsorbed on the surface of 10% silica-alumina.

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[14] W. I. Aalbergsberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049, 3055.

[15] A. I. Kitova and J. M. Varshavsky, *Dokl. Akad. Nauk SSSR*, **135**, 1395 (1960).

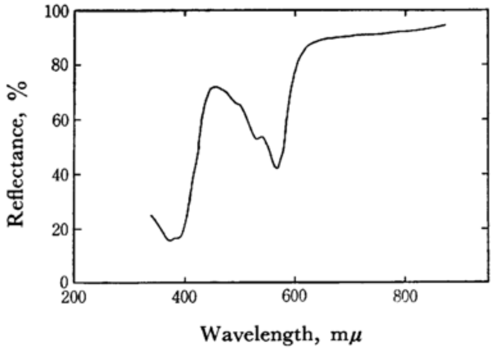

Fig. 10. Effect of water vapor on diffuse reflection spectrum of anthracene adsorbed on the surface of 10% silica-alumina.

On the other hand, silica-alumina with a content of 10% shows an absorption due to the interaction of anthracene with the Brönsted-acid site at 430 mμ in addition to that due to interaction with the Lewis-acid site at 760 mμ as Fig. 9 shows. Silica gel shows no absorption at either 760 mμ or 430 mμ.

When water molecules are adsorbed from the vapor phase through a third breakable joint, the color, the absorption bands at both 430 mμ and 760 mμ, and the ESR signal all disappear in the cases of alumina and silica-alumina, but new absorption bands at 530 mμ and 570 mμ appear in the case of silica-alumina with a content of 10%, as may be seen in Fig. 10. This new interaction is weak, since the color reverts to the original one when the system is evacuated. When anthracene is adsorbed and then water is adsorbed, it seems that water molecules squeeze themselves between the anthracene molecules and the sites on the surface. As a result, the absorption bands at 430 mμ and 760 mμ both disappear. This phenomenon suggests that the water molecule reacts with the acid sites more strongly than does anthracene, and also that the water molecule rather than *n*-butylamine is adsorbed preferentially on the sites from the aqueous solution of *n*-butylamine.

Conclusion. When silica-alumina is immersed into an aqueous solution of *n*-butylamine, the water molecule may preferentially interact with the strong acid sites and may weaken the site strength, as in the case described above. As a result, the strong acid sites may be transformed to weak ones, while the total number of the acid sites remains unchanged. If both the adsorbed amount and the heat value of *n*-butylamine depend principally on the total number of acid sites, the resemblance in shape among the curves of these three quantities (Figs. 4, 7, and 8) may be interpreted well.