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Heats of Immersion of Silica-alumina in Nonaqueous Solvents

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The heats of immersion of silica gel, alumina, and silica-aluminas in benzene, cyclohexane, and a solution of *n*-butylamine in benzene have been studied in connection with the acid properties of the surfaces. It was found that *n*-butylamine interacts more strongly with the surfaces of silica-aluminas than is the case in an aqueous system, which was previously investigated. Further, the interactions of benzene with the surfaces of silica-aluminas were discussed on the basis of the results of the adsorption isotherms of benzene on the surfaces.

Silica-alumina is one of the most important catalysts for various acid-catalyzed reactions.[1] These catalytic actions are considered to be connected with the acid sites on the surface of silica-alumina. In our previous study,[2] the surface properties of silica-aluminas with different contents of alumina were investigated by examining the relation between the property of the acid site and the heats of immersion in water and an aqueous solution of *n*-butylamine; it has been found that the molecule interacts preferentially with the strong acid sites and weakens the site strength. Therefore, it may be of interest to investigate the heats of immersion of silica-alumina in nonaqueous solvents. In this work, the heats of immersion of silica gel, alumina, and silica aluminas were measured in benzene, cyclohexane, and a solution of *n*-butylamine in benzene. Further, the interaction of benzene with the surfaces of the samples was discussed by examining the adsorption isotherms of benzene on the surfaces.

Experimental

Materials. Silica gel, alumina, and silica-aluminas with a content of 10% alumina, 10% SA, and that of 50% alumina, 50% SA, were prepared by the hydrolysis of ethyl ortho-silicate and/or aluminum isopropoxide by a procedure similar to that described in a previous paper.[2] The specific surface areas of the samples evacuated at 300°C for 3 hr were determined from the nitrogen adsorption by the BET

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[1] K. Tanabe and T. Takeshita, "Acid-Base Catalysis," Sangyo Tosho Pub. Co. Ltd., Tokyo (1965), p. 179.

[2] M. Miura, Y. Kubota, T. Iwaki, K. Takimoto, and Y. Muraoka, This Bulletin, **42**, 1476 (1969).

method. The results are given in Table 1. The surface area of silica-alumina exhibits a low value at a content of 10% alumina; this is analogous to the previous finding.[2]

Benzene and cyclohexane were purified by distillation, with several pieces of metallic sodium added to remove any moisture.

Heat-of-immersion Measurement. Prior to the measurements, the samples were evacuated at 300°C for 3 hr in a vacuum of 10^{-5} mmHg. The heats of immersion of these samples in benzene, cyclohexane, and a solution of *n*-butylamine in benzene were measured at 25°C by using a calorimeter[3] which was improved so as to be able to hold four ampoules at a time. Since trace quantities of water dissolved in these liquids have a significant effect on the heat value, the water was removed by an activated molecular sieve in the following way. After each of these liquids had been placed in the calorimeter, a large quantity of the molecular sieve was added to the liquids. Next, after a thermal equilibrium in the system had been established, an ampoule containing the molecular sieve was broken in order to dehydrate the liquid completely just before another ampoule containing a sample was broken for the measurement of the immersional heat.

Adsorption Measurement. The adsorption isotherms of benzene on the samples were volumetrically determined at 25°C by using an adsorption apparatus equipped with greaseless Teflon cocks. The equilibrium pressure of benzene vapor was measured by means of a mercury manometer.

Results

The heats of immersion of the samples in benzene and cyclohexane are shown in Fig. 1 as a function of the alumina content. The heat value in benzene ranged from 82 to 110 erg/cm², and that in cyclohexane, from 48 to 77 erg/cm². The heat values of silica gel in benzene and cyclohexane were similar to those reported by Whalen.[4] In Fig. 2, the heats of immersion of these four samples in a 1 M solution of *n*-butylamine in benzene are shown as a function of the alumina content. In the figure, the heats of immersion in water and the aqueous solution of *n*-butylamine are also presented for comparison.[2] The adsorption isotherms of benzene on the surfaces of silica,

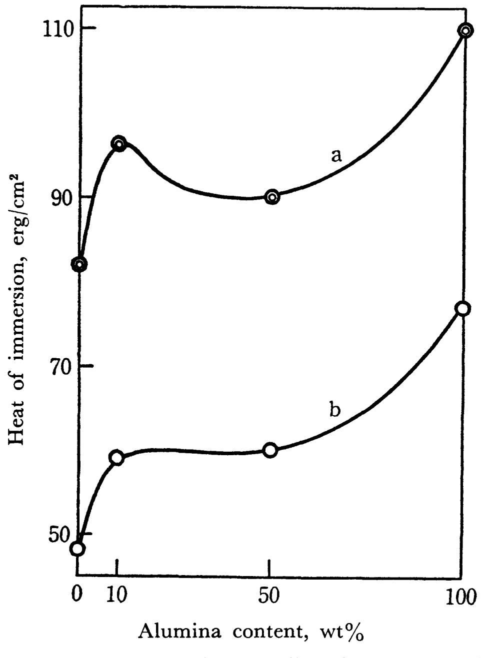

Fig. 1. Heats of immersion of silica-aluminas as a function of alumina content; (a) in benzene and (b) in cyclohexane.

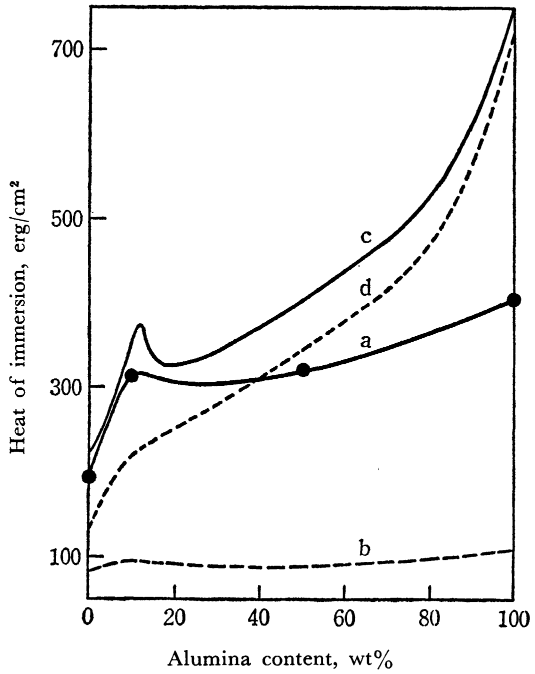

Fig. 2. Heats of immersion of silica-aluminas as a function of alumina content; (a) in the solution of *n*-butylamine in benzene, (b) in benzene, (c) in the aqueous solution of *n*-butylamine, and (d) in water.

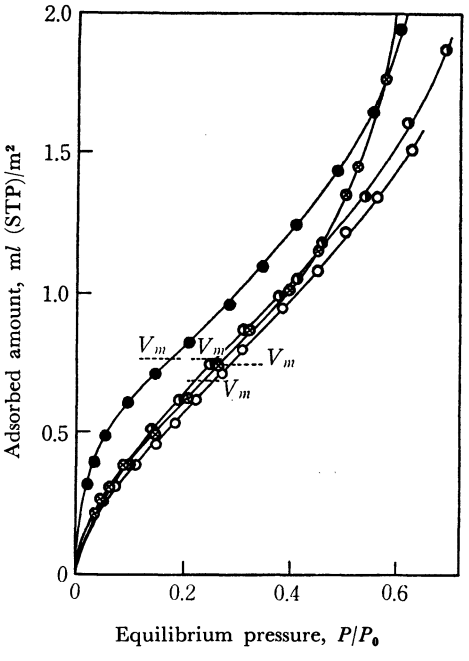

Fig. 3. Adsorption isotherms of benzene on the surfaces of the samples;
○: silica gel, ◑: 10% SA, ⊗: 50% SA, ●: alumina.

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[3] M. Miura, H. Naono, T. Iwaki, T. Kato, and M. Hayashi, *Kogyo Kagaku Zasshi*, **69**, 1623 (1966).

[4] J. W. Whalen, *J. Phys. Chem.*, **66**, 511 (1962).

silica-aluminas, and alumina are shown in Fig. 3. The dotted line in the figure shows a monolayer volume, V_m, estimated from the BET plots.

Discussion

When the silica-alumina is evacuated at a high temperature, such as 300°C, some hydroxyl groups bound with the aluminum atoms of the surface of silica-alumina are removed, resulting in the formation of strong acid sites which consist of Brönsted- and Lewis-acid sites,[5] whereas the remaining aluminol groups may act as weak acid sites. As for the silica, there is no strong acid site in spite of the presence of silanol groups on the surface. The alumina surface has aluminol groups and Lewis-acid sites. In our previous study,[2] the acidity of silica-alumina was obtained as a function of the alumina content, and it was found that the number of acid sites was at a maximum at an alumina content of 10—20%.

As can be seen in Figs. 1 and 2, the immersional-heat values of silica-alumina in benzene and cyclohexane did not vary much with the alumina content; this is unlike the case in water, where the heat value increased appreciably with the alumina content. The factors responsible for the generation of the heat in water have been considered to be the property of the surface hydroxyl groups as well as the number and strength of the acid sites.[2] The heat values of 10% SA in benzene and cyclohexane were larger than, respectively, the values estimated from the sum of the contributions of silica and alumina. This phenomenon may be interpreted on the basis of the contribution of the large number of acids sites on 10% SA to the generation of the heat in a nonpolar solvent.

The difference between the heat values in benzene and the solution of *n*-butylamine in benzene is remarkably larger than that between those in water and an aqueous solution of *n*-butylamine, as may be seen in Fig. 2. In the absence of water, as expected, *n*-butylamine interacts strongly with these samples; it seems probable that the remarkably large heat arises from the strong interaction of *n*-butylamine with the strong acid site, especially with the Lewis-acid site on the surface of alumina.

On the basis of the adsorption isotherms of benzene on the samples in Fig. 3, let us examine the interaction of benzene with the surface. The monolayer volumes, V_m, resemble one another though the adsorption isotherm on alumina is located higher than the others. The monolayer volume was converted to the benzene surface area, S_B, by assuming the cross-sectional area of benzene molecule to be 40.3 Å^2.[6] The ratio of the benzene area to the nitrogen area, S_B/S_{N_2}, for each sample is listed in Table 1. The benzene molecules adsorbed do not cover all the nitrogen area, suggesting that particular sites for benzene molecules are present on the surface. The number of sites where the benzene molecule can be adsorbed is about 2 per 100 Å^2. This number of sites does not correspond to the number of acid sites. Benzene molecules may be adsorbed not only on the acid sites, but also on other sites, such as those of silanol groups.

The interaction of the benzene molecule with the polar surface of a solid is considered to originate from: (a) the van der Waals interaction, (b) the Coulomb interaction between the surface and π-electrons of benzene, and (c) the dipole-induced dipole interaction. The last interaction (c) may be negligibly small compared with the other interactions.[7] On the other hand, the interaction of the cyclohexane molecule with the surface may arise from only the van der Waals interaction.

The immersional-heat values of the samples in benzene in Fig. 1 are larger by 30—37 erg/cm^2 than those in cyclohexane. The difference between the heat values in benzene and cyclohexane, ΔH, is given in Table 1. If the difference between the surface enthalpy of benzene, 67.6 erg/cm^2, and that of cyclohexane, 57 erg/cm^2, is disregarded, and if the cyclohexane surface area is equal to the S_B, the ΔH value may be the contribution of the interaction of π-electrons of benzene with the surface, as a rough estimate. The interaction energy, q, which is obtained by dividing the ΔH value by the monolayer volume, V_m, is presented in the last column of Table 1. As for silica, this value is in good agreement with that given by Kiselev and Poshkus.[8] They obtained, from the heat of adsorption, a value of 2—3 kcal/mol for the energy of interaction between the π-electron of benzene and hydroxyl groups on the surface of silica. Since the π-electron acts as an electron donor in this interaction, the relatively large energy for 10% SA may be ascribed to the contribution of the large number of acid sites.

Table 1. Surface area, number of site for benzene, and difference between heat of immersion in benzene and that in cyclohexane

Material	S_{N_2}(m^2/g)	S_B/S_{N_2}	Site/100Å^2	ΔH(erg/cm^2)	q(kcal/mol)
SiO_2	352	0.81	2.0	34	2.4
10% SA	215	0.84	2.1	37	2.6
50% SA	362	0.75	1.9	30	2.3
Al_2O_3	179	0.84	2.1	33	2.3

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[5] M. R. Basila, T. R. Kanter, and K. H. Rhee, *ibid.*, **68**, 3197 (1964).

[6] S. J. Gregg and K. S. W. Sing, "Adsorption, Surface Area and Porosity," Academic Press, London and New York (1967), p. 80.

[7] N. Okuda, *Nippon Kagaku Zasshi*, **82**, 1118 (1961).

[8] A. V. Kiselev and D. P. Poshkus, *Dokl. Akad. Nauk SSSR*, **120**, 834 (1958).