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A Direct Evidence for the Overestimation of Acidity Incidental to the Benesi Method

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Synopsis. Acid strength distributions of silica-alumina, silica-magnesia, and their mixtures were measured by the Benesi method. Overestimation of acidity has been demonstrated by the measurement that the acidity in the range $H_0 \leqq -3.0$ for the mixtures is larger than the value expected from additivity.

The amine titration method (the Johnson[1] and the Benesi[2] method), consisting essentially of titration of a solid acid by using butylamine and a series of Hammett indicators, has widely been employed[3] for determining the acid strength distribution of solid acids, which is in close connection with their catalytic activity.

The reliability of this method has not sufficiently been discussed. Matsuzaki *et al.*[4] initially pointed out that overestimation of acidity is to be involved in the Johnson method due to slow migration of the butylamine once adsorbed on weak acid sites to strong acid sites. Take *et al.*[5] experienced a difficulty in establishing adsorption equilibrium between butylamine and a thin wafer of silica-alumina even at 100 °C. From this phenomenon, they suggested the possibility that overestimation of acidity would be involved in the Benesi method for strong acid sites. The same suggestion was presented by Deeba and Hall[6] from their result obtained by column chromatography. However, such overestimation has not yet been given any experimental proof, especially for the Benesi method.

In this study, aiming at a direct demonstration of occurrence of the overestimation, mixtures of silica-alumina and silica-magnesia which possess strong and medium acid sites, respectively, were titrated by the Benesi method; the acidity for strong sites in the range $H_0 \leqq -3.0$ for the mixed samples has been found larger than that expected from additivity.

Experimental

Silica-alumina (Nikki Chem. Co., N631-L) was powdered to below 250 mesh and activated at 450 °C for 3 h in an electric furnace. Silica-magnesia was coprecipitated from an aqueous solution of sodium silicate and magnesium chloride by a similar way as reported by Ikebe;[7] the recipitate was dried at 105—110 °C and powdered to below 250 mesh, and the powder was calcined at 500 °C for 3 h befor use. Silica-alumina and silica-magnesia will be abbreviated as SA and SM, respectively. Mixtures of SA and SM were prepared simply by mixing the component powders. Benzene dried with silica gel was used as solvent. 4-Phenylazo-1-naphthylamine ($\mathrm{p}K_a = +4.0$), *p*-dimethylaminoazobenzene ($\mathrm{p}K_a = +3.3$), 4-(phenylazo)diphenylamine ($\mathrm{p}K_a = +1.5$), dicinnamylideneacetone ($\mathrm{p}K_a = -3.0$), benzylideneacetophenone ($\mathrm{p}K_a = -5.6$), and anthraquinone ($\mathrm{p}K_a = -8.2$) were used as indicators in the form of 4×10^{-3} mol dm^{-3} benzene solution. Butylamine solution in benzene of 0.1 mol dm^{-3} was used as titrant.

SA, SM, and their mixtures (1:1 and 1:2 in weight) were titrated by the Benesi method in the following procedure: A mixture of 0.4 g powder and 5 ml solvent was taken in each of several 50 ml Erlenmeyer's flasks and known amounts of amine were added to each flask. In this way, a series of samples was prepared in which each sample had a different amount of base added. The samples were tightly stoppered and shaken at 30 °C for 1—2 d, and then a portion of each slurry (*ca.* 1 ml) was transferred into each of several test tubes. A small amount of indicator (20—50 µl) was added to each sample and the color was observed. The acid strength distribution was determined from the amount of amine required to discolor the acid color of each indicator substantially. The transfer of slurry and addition of indicators were repeated after 1 d shaking to confirm the duplication of the preceding measurement. All the above procedure was performed in dry air to avoid moisture contamination.

Results and Discussion

The acid strength distributions obtained for SA and SM are shown in Fig. 1. SA has a 0.2 mmol g^{-1} acidity in the range $H_0 \leqq -3.0$ for strong acid sites and a 0.075 mmol g^{-1} acidity in $-3.0 < H_0 \leqq +4.0$ for medium ones. SM has a 0.35 mmol g^{-1} acidity in $-3.0 < H_0 \leqq +4.0$ but none in $H_0 \leqq -3.0$. These results are in qualitative agreement with the results obtained by Benesi.[1]

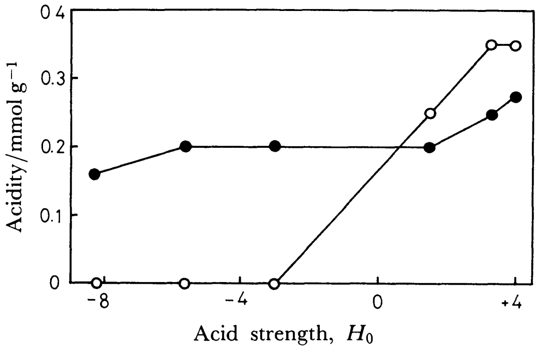

Fig. 1. Acid strength distributions of silica-alumina and silica-magnesia.
●: silica-alumina, ○: silica-magnesia.

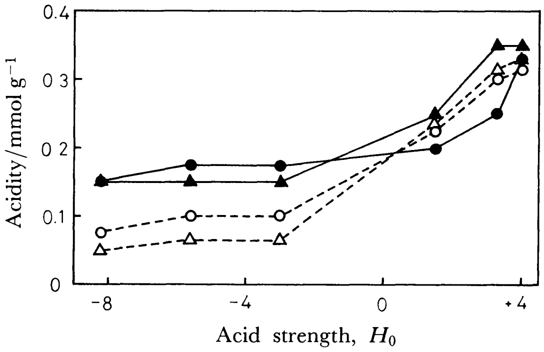

Fig. 2. Acid strength distribution of the mixtures.
● and ▲: Experimentally obtained, ○ and △: calculated from distribution of each solid for SA: SM=1:1 and 1:2, respectively.

Figure 2 shows the acid strength distributions for the mixtures of SA and SM (solid lines) in weight ratios 1:1 and 1:2. The distributions expected on the basis of additivity from the distributions of each solid are also shown in Fig. 2 (broken lines). If there is no overestimation in operation, the solid and the broken line should coincide with each other and the acidities in $H_0 \leqq -3.0$ for the 1:1 and 1:2 mixtures should be 1/2 and 1/3, respectively, of the acidity for SA given in Fig. 1. The observed acidity in $H_0 \leqq -3.0$ is, however, about two or three times larger than that expected from the distributions of each solid on the basis of the mixing ratios. Thus, these results have demonstrated the occurrence of overestimation. The degree of overestimation corresponds to 86% of the medium acid sites in SM for both the cases. Matsuzaki *et al.*,4) Take *et al.*,5) and Deeba and Hall6) pointed out that butylamine adsorbs on acid sites substantially irreversibly. With the irreversibility taken into account, the observed overestimation is attributable to the irreversible adsorption of amine not only on strong sites but also on relatively weak sites. Thus, when the acid color of dicinnamylideneacetone has disappeared, the whole acid sites in $H_0 \leqq -3.0$ and the greater part of the acid sites in $-3.0 < H_0 \leqq +4.0$ will be taking part in the adsorption of amine.

For the range $-3.0 < H_0 \leqq +4.0$, the acidities of the mixtures are in agreement with those expected from the acidities of each solid within experimental errors. However, this agreement does not necessarily conclude the absence of overestimation in the medium and weak ranges $-3.0 < H_0$ since if overestimation should be operative in these ranges, weak acid sites in $+4.0 < H_0$ would be included in the estimate for the range $-3.0 < H_0 \leqq +4.0$ and since the present study made no measurement on the presence of any acid sites in the range $+4.0 < H_0$; thus, it is left to future experimental check whether or not these medium and weak ranges are free from overestimation.

Recently, it has been observed that some portions of butylamine or Hammett indicators adsorbed on strong acid sites of silica–alumina can migrate,8) and that no overestimation occurs when a mixture of silica–alumina and nickel sulfate containing medium acid sites ($-3.0 < H_0 \leqq +1.5$) is subjected to a measurement by the Benesi method.9) These results are different from the present findings. The difference cannot be explained reasonably at this stage for lack of detailed knowledge about the behavior of amine and indicators adsorbed on the surface of solid acid.

References

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

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

3) T. Yashima and N. Takahashi, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 501 (1978).

4) I. Matsuzaki, Y. Fukuda, T. Kobayashi, K. Kubo, and K. Tanabe, *Shokubai*, **11**, 210 (1969).

5) J. Take, Y. Nomizo, and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, **46**, 3568 (1973).

6) M. Deeba and W. K. Hall, *J. Catal.*, **60**, 417 (1979).

7) K. Ikebe, *Kogyo Kagaku Zasshi*, **61**, 437 (1958).

8) I. Matsuzaki and S. Mishima, *Shokubai*, **21**, 211 (1979).

9) I. Matsuzaki and S. Mishima, *Shokubai*, **22**, 238 (1980).