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Difficulty of Establishing Adsorption Equilibrium in *n*-Butylamine Titration of Solid Acid Surfaces

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The Benesi or *n*-butylamine titration method[2] has widely been employed for determining the acid-strength distribution of solid acid surfaces. Applications[3,4] and variations[5] of the method have also been worked out. It was assumed so far that the adsorption equilibrium of both amine and indicator molecules with acid sites is attained on solid surfaces. However, no evidence has been given to show that the assumption is satisfied. Leftin and Hobson[6] showed that the intensity of a 550 mμ band due to benzeneazodiphenylamine (BADA) chemically adsorbed on silica-alumina became practically constant 30—40 hr after addition. Accomplishment of such a stationary state, however, does not necessarily indicate the validity of the assumption.

In the course of our studies we came across a remarkable phenomenon giving rise to a strong doubt about the validity of the assumption. The present paper deals with the findings.

A thin wafer (*ca.* 25 mg, 20×9 mm and about 0.1 mm thick) of a commercial silica-alumina catalyst (SA-1, Al_2O_3 13%)[3] was mounted on a holder, placed in a UV-cell,[7] and then activated by evacuation at 450 °C for 1 hr *in situ*. After transfer of highly dried and degassed decalin in a vacuum, followed by introduction of dried nitrogen gas, a decalin solution of *n*-butylamine was gently added through a pipette, without any agitation, into the cell in a dried nitrogen gas stream. The amount of addition was about 0.1 meq/g-catalyst, roughly corresponding to one-half of the acid content of SA-1 determined by *n*-butylamine titration with BADA as an indicator.[3] The cell was then allowed to stand at 50 °C without stirring. After 12 days, a solution of BADA in decalin (*ca.* 6×10^{-4} meq/g-catalyst) was admitted into the cell.

The resulting surface coloration and its change with time are shown schematically in Fig. 1. The indicator BADA is purple when adsorbed on acid sites, and yellow when adsorbed on poisoned acid sites or non-acidic sites.[3] Thus, in Fig. 1 yellow coloration indicates the poisoning of acid sites with the amine, the purple no poisoning with the amine, and no coloration the absence of BADA on the surface.

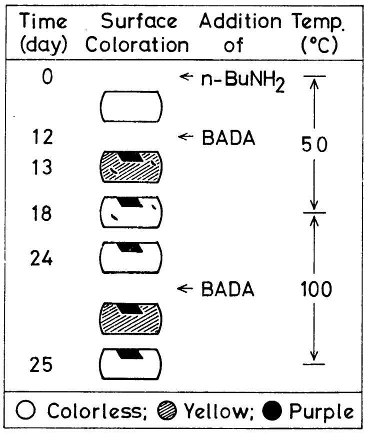

Fig. 1. Surface colorations of SA-1 wafer partially poisoned with *n*-butylamine.

In general, solid acid surfaces have been thought to have acid sites with different acid strengths. Acid sites of every acid strength should, on a macroscopic scale, be uniformly distributed over the surface of a wafer or of a catalyst particle. According to the prevailing theory of adsorption on such a heterogeneous surface,[8] at adsorption equilibrium basic molecules such as *n*-butylamine are distributed onto acid sites of every acid strength following the adsorption isotherm, a function of both the number and the strength of acid sites. Thus the adsorption of BADA onto the surface having reached adsorption equilibrium with *n*-butylamine will cause the surface to be uniformly colored at equilibrium. However, it should be noted that a macroscopically uniform distribution of basic molecules can be realized even though no adsorption equilibrium exists. The adsorption of basic molecules not followed with the desorption will yield an adsorption state far from equilibrium. Establishment of adsorption equilibrium thus needs desorption-readsorption cycles of basic molecules once adsorbed on the surface.

Macroscopic uniformity in the distribution of acid sites was proved by the fact that a uniform coloration occurred when BADA was added onto the wafer that had been immersed into a previously well-mixed decalin solution of *n*-butylamine (*ca.* 0.1 meq/g-catalyst) for 1—2 days at room temperature. The surface of a wafer partially poisoned with the amine would then have uniformly turned purple independently of the mode of poisoning, if there had existed adsorption equilibrium. However, this was not the case (Fig. 1). Essentially the same results were also obtained in separate experiments carried out in a similar way. No

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

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[8] For example, D. M. Young, and A. D. Crowell, "Physical Adsorption of Gases", Butterworths, London (1967), p. 247.

uniform coloration appeared during the course of standing for 25 days, indicating that the amine once adsorbed on acid sites was hardly desorbed or hardly migrated even at 100 °C, a temperature higher than the boiling point of the amine (77.8 °C). This was confirmed by the reappearance of the yellow upon the second adidtion of BADA (see Fig. 1). Such difficulty is also demonstrated by the fact that ethylamine is desorbed with an activation energy as high as about 20 kcal/mol from silica gel,[9] which is usually nonacidic or much less acidic than silica-alumina catalyst. All the facts are strongly negative against the establishment of adsorption equilibrium. Therefore, the local coloration in Fig. 1 is best explained as being due to the fact that the added amine molecules approach the surface, as a whole, irregularly or non-uniformly (as in the motion of a drop of ink allowed to fall into standing water), and then remain, without reaching adsorption equilibrium, on adsorption sites at which they first arrived. In both cases where the amine is added with stirring and where a previously well-mixed solution of the amine is used without stirring, the amine molecules should be allowed to approach uniformly the surface of catalyst, hence the subsequent addition of BADA probably yields a uniform surface coloration. However, it is highly unlikely that the desorption of the once adsorbed amine is accelerated and adsorption equilibrium thus reached.

The ordinary conditions for equilibration used in the *n*-butylamine titration method are much milder than those employed here; in the former, the temperature ranges from room temperature to 30 °C and the standing period from several hours to several days. Under such conditions, therefore, the adsorbed amine is probably far from equilibrium even if agitation is applied.

The yellow coloration of the wafer surface faded gradually with time, this being accompanied by the deepening of the purple (Fig. 1), indicating that the physically adsorbed BADA migrated onto acid sites not poisoned with the amine. The completion of this migration took at least 5 days at 50 °C. In fact, physically adsorbed BADA is desorbed with an activation energy as high as 16 kcal/mol from silica gel.[7] Thus it is concluded that even physically adsorbed BADA is desorbed or migrates with considerable difficulty.

It is very difficult for either *n*-butylamine or indicators, particularly the former, to reach adsorption equilibrium with acid sites under the usual conditions in the *n*-butylamine titration method. The difficulty is not effectively diminished for *n*-butylamine by raising the temperature to 50—100 °C. Such will also be the case with catalysts in the form of powder. Disregard of this difficulty might lead to an overestimation of the acid contents.

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