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MICRO-CALORIMETRIC DETERMINATION OF THE DISTRIBUTION OF ACID STRENGTH ON SILICA-ALUMINA CATALYST

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The distribution of the acid strength on silica-alumina catalyst was expressed quantitatively on a scale of the differential heat of adsorption of n-butylamine which was determined by calorimetric method. The method will be expected as the fundamental method for determining the distribution of acid strength on solid acid catalyst.

Solid acid catalysts play important roles in basic reactions of hydrocarbons, such as polimërization, isomerization, alkylation and decomposition. Many studies have been done on the determination of acidity and the distribution of acid strength on the catalyst surface.[1) - 6)] Recently, Zettlemoyer and Chessick reported that the energy distribution of acid sites on attapulgite could be developed from heat of immersion measurements.[7)]

In this study, the method using micro-calorimeter is presented to determine the distribution of acid strength on solid surface.

It may be supposed that adsorbed basic molecules occupy acid sites successively from strong to weak sites. Therefore, on the asumption mentioned above, the differential heat of adsorption decreases with increase of coverage on surface, if the distribution of acid strength exists on solid surface. If the differential heat of adsorption can be obtained at each surface coverage, these differential heat curve as a function of surface coverage may reflect the spectrum of acid sites on catalyst surface. In the present study, the coverage on solid surface was increased continuously and the heat of adsorption was measured at each coverage.

A micro-calorimeter was used for measuring the heat of adsorption of n-butylamine on silica-alumina in benzene solution. The micro-calorimeter equipped two symmetric cells was

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consisted of an aluminum block having large heat capacity. A known amount of n-butylamine - benzene solution could be admitted into both cells by operation of servo-motor of auto-titration system which was connected by tubing to the micro-calorimeter.

F.C.C silica-alumina catalyst was supplied by The Catalyst and Chemicals Industries Company (12.5 wt % Al_2O_3, B.E.T surface area 610 m^2/g, 100~150 mesh).

n-Butylamine was of a G.R. grade and used as a solution of benzene (0.1 mol/l) .

Silica-alumina catalyst was calcined for 3 hours at 550 °C. 30 ml benzene and 1.5 g silica-alumina were introduced into the sample cell and 30 ml benzene into the reference cell and then calorimeter was kept under constant temperature at 25 °C for overnight to attain temperature equilibrium. Then, a known amount of 0.1 mol/l n-butylamine - benzene solution was added into both cells. The catalyst slowly lost the heat evolved to its surrounding and gradually re-established the thermal equilibrium again. In the case of porous solid, silica-alumina catalyst, about 12 hours was needed for losing the heat evolved in the system because the diffusion rate of n-butylamine molecules and the rate of heat transfer in pores of silica-alumina were significantly low. The heat evolved was determined by comparing the area under the time-temperature curve (plot of thermocuple e.m.f. vs time) which was recorded on recorder with that of the calibration curve. The calibration curve, heating-cooling curve on recorder, was made by sending known amount of electrical joule energy through the heater in the calorimeter. Thus, this titration and calibration process was repeated till no heat evolved at about 0.05 coverage intervals.

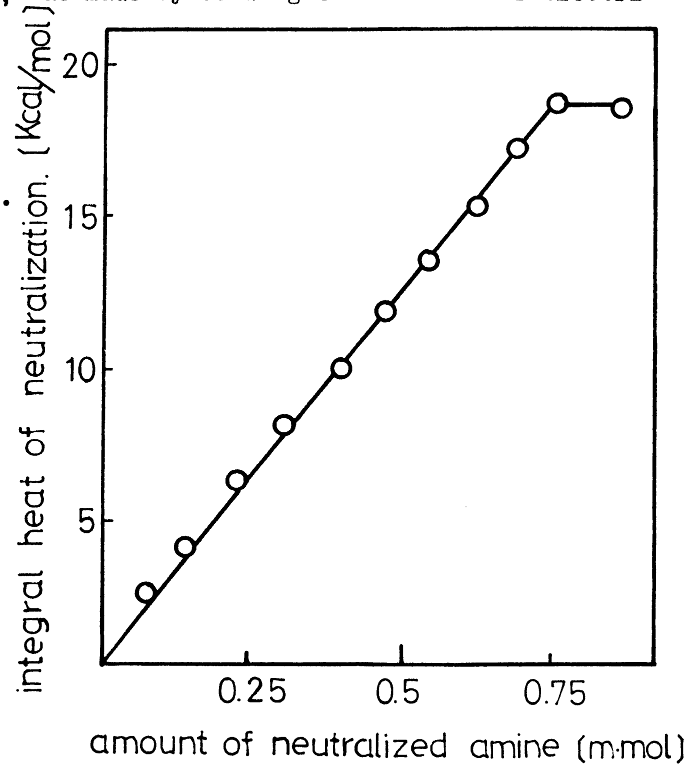

Fig.1 Integral heat of neutralization vs amount of added amine.

Prior to the experiments, measurements of the heat of neutralization the following homogeneous acidic solution were performed. That is, the acidic solution (H_2SO_4- benzene 0.1 mol/l solution) was titrated with n-butylamine - benzene solution and the the correlation between the heat of neutralization and the amount of added amine was examined. Because H_2SO_4 - benzene solution had no distribution of acid strength, the heat of neutralization was in proportion with the amount of added amine. The differential heat of neutralization was constant in this acid-base system, approximately 16.1 Kcal/mol (Fig.1).

In the case of silica-alumina catalyst, it is interesting to note that the integral heats of adsorption were divided in three straight lines against the amount of adsorbed amine, indicating the existence of three kinds of acid sites (Fig.2).

The differential heats of adsorption which were obtained from the slopes of the integral curve (Fig.2) were plotted against surface coverage (Fig.3). Fig.3 shows that the differential heat of adsorption determined experimentally decreased with increase of surface coverage and agreeded well with the asumption mentioned previously.

The strongest acid sites corresponded to the differential heat of adsorption of n-butylamine at approximately 11.2 Kcal/mol, moderately strong sites at 7.2 Kcal/mol and weak sites at 3.7 Kcal/mol, and the amount of each site was 0.32, 0.33 and 0.23 m·mol/g-catalyst respectively.

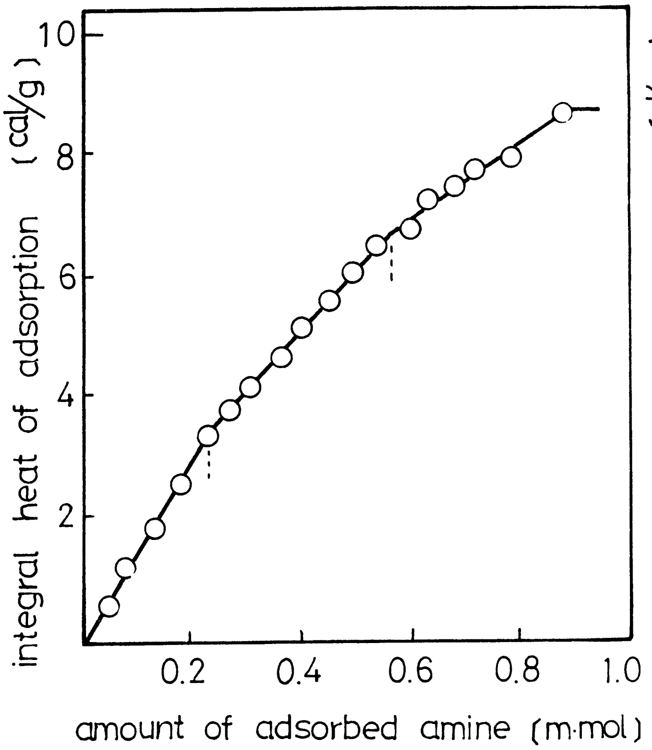

Fig.2 Integral heat of adsorption vs amount of adsorbed amine.

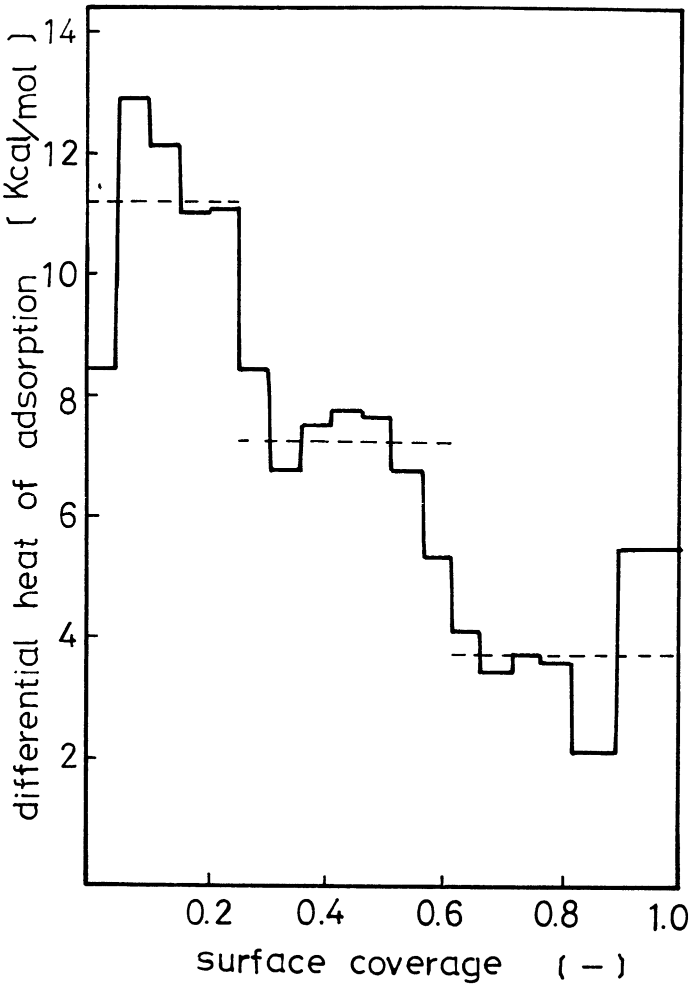

Fig.3 Differential heat of adsorption vs surface coverage.

Total acidity was obtained from amount of added amine, and was 0.88 m·mol/g-catalyst.

Considerable information on the distribution of acid strength on silica-alumina surface could be obtained by means of micro-calorimeter.

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