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The Distribution of the Acid Strength on Zeolite Catalyst — Estimation from the Heats of Adsorption —

Yasuaki OKAMOTO, Toshinobu IMANAKA and Shiichiro TERANISHI

Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Machikaneyama, Toyonaka, Osaka

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The distribution of the acid strength on two zeolites, 13X and 10X, and on the copper form of X-type zeolite were estimated from the differential heats of *n*-butylamine adsorption in a benzene solution. The acid sites on these zeolites were revealed to have two kinds of acid strengths, that is, the cation-dependent one and the cation-independent one. The former corresponds to the stronger acid strength, and the latter, to the weaker. The IR spectra of the residual surface OH groups on these catalysts were also investigated. The strongest acid sites on each zeolite were considered to be those of the cation-dependent OH group which has the lowest frequency. The interaction between surface OH groups and immersed benzene was assumed to be a π-type hydrogen bond.

It is expected that the properties of catalytic reaction on an acidic catalyst can be explained in terms of the distribution of acid strength on it. The distribution of surface acid strength has usually been measured by means of the indicator method[1] and the volumetric-base adsorption method.[2,3] The former method, however, is incapable of measuring the acid strength of colored solids which include many cation-exchanged zeolites and other useful acidic catalysts. The number of useful indicators is limited, and their pKa values lie only between -8.2 and $+6.8$

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

[2] G. A. Mills, E. R. Boedecker and A. G. Oblad, *J. Amer. Chem. Soc.*, **72**, 1554 (1950).

[3] R. G. Richardson and S. W. Benson, *J. Phys. Chem.*, **61**, 405 (1957).

discontinuously. Therefore, this method has disadvantages for obtaining a continuous value and for providing both the stronger and weaker acid strengths. From the fraction of the base which desorbs slowly, the latter method allows some estimation of the number of effective acid sites and the average acid strength of the sites, as measured by the activation energies for desorption. As this method gives only the average acid strength, however, it is not effective in discussing the relation between the acid properties and the acid catalytic reactions. Consequently, the distribution of the differential adsorption heats of base must be measured in order to clarify the behavior of acidic catalysts of varying activities in terms of a site-energy distribution, that is, the number of acid sites and their individual strength.

Direct measurements of the adsorption heat of a base on acidic catalysts have been carried out by several workers. Richardson and Benson[3] measured the heat of adsorption of trimethylamine on Davison DA-1 cracking catalysts at 300°C with a crude adiabatic calorimeter, but gave only average values. Chessick and Zettlemoyer[4,5] determined quantitatively the site-energy distributions on attapulgite, silica-aluminas, and kaoline cracking catalysts on the basis of immersional heats in butylamine.

In this paper, the differential heats of the adsorption of *n*-butylamine in benzene are used for the elucidation of the acid-strength distributions on zeolites. Moreover, the relation between the acid strength and the frequencies of the IR adsorption bands of the residual surface OH group is discussed.

Experimental

Materials. The molecular Sieves, 13X and 10X, were supplied by the Union Carbide Company. In order to prepare copper-form X-type zeolite (CuX), sodium ions in 13X zeolite were 48.1% exchanged in a conventional method for Cu(II) with a copper sulfate solution. The *n*-butylamine was of a commercial grade and was used in adsorption experiments as a benzene solution. The benzene was purified by dehydration with sodium metal and subsequent distillation. The concentration of *n*-butylamine in benzene was determined in the following manner. *n*-Butylamine in benzene was extracted from the benzene phase to the water phase by pouring water into it, and then it was neutralized with a dilute aqueous HCl solution in the water phase, using phenolphthalein as an indicator. The normality of the amine solution was in the range of 0.165—0.0025 N.

Procedure. After zeolite had been treated in a glass ampoul at 400°C for several hours under a vacuum, it was used in the adsorption experiments. The over-all heat, which evolved when the treated zeolite was immersed in a benzene solution of *n*-butylamine at 25°C, was measured with a micro calorimeter manufactured by the Applied Electric Lab., Ltd. The amount of amine adsorbed on zeolite was elucidated by washing the immersed zeolite with benzene several times and then by using the neutralization method described in the previous section in connection with a material balance.

The amounts of *n*-butylamine adsorbed on zeolite from the gas phase were determined with a thermanobalance at different temperatures. Zeolite was dehydrated to a constant weight in a flowing stream of nitrogen at 400°C and then cooled to an adsorption temperature in it. *n*-Butylamine was introduced on the dehydrated, constant-weight zeolite at that temperature by the passage of nitrogen gas through a saturator containing *n*-butylamine. The increase in weight in comparison with that of the dehydrated zeolite is due to the physically- and chemically-adsorbed *n*-butylamine. In order to determine the amount of *n*-butylamine chemisorbed, the zeolite saturated with *n*-butylamine was flushed with nitrogen gas in order to remove the physically-adsorbed *n*-butylamine. After this treatment, the increase in weight was considered to reflect the amount of *n*-butylamine chemisorbed at that temperature.

The behavior of the residual OH groups on these zeolites was observed by means of studying the infrared spectra with a Hitachi IR spectrometer. The disks of zeolites were heated at 200—300°C in an IR cell under a vacuum. The disks were prepared by pressing zeolites between two polished stainless steel plates to a pressure of about 5 ton/cm^2.

The H-D exchange reaction of OH groups on the zeolites used was carried out with D_2O (supplied by the Merck Co.) in an IR cell at 400—500°C.

Results and Discussion

The surface properties of zeolite are assumed to be dependent on the amount of water on the surface. Figure 1 shows that the heats of immersion for 13X and 10X zeolites in benzene vary with the preheating temperature. The value for 13X

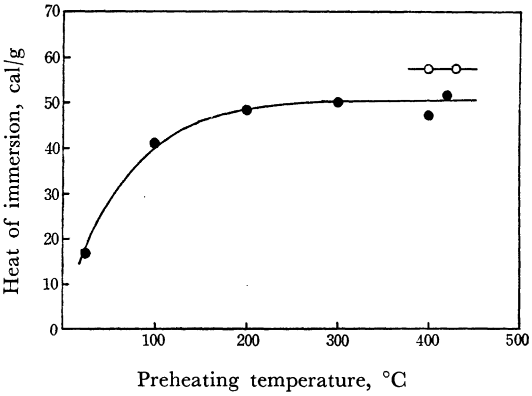

Fig. 1. Dependency of immersion in benzene on preheating temperature.
● 13X, ○ 10X

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4) J. J. Chessick and A. C. Zettlemoyer, *J. Phys. Chim.*, **62**, 1217 (1958).

5) A. C. Zettlemoyer and J. J. Chessick, *ibid.*, **64**, 1131 (1960).

gradually increases up to about 300°C and then becomes constant at about 400°C. The heats of immersion contain the surface energy of the solid and liquid and the energy of interaction between the surfaces of the solid and molecules in a liquid. Thus, it may be supposed, from the constancy of the heats of immersion, that the interaction between them is not dependent upon the preheating temperature beyond about 300°C. When these catalysts are dehydrated in a flowing stream of nitrogen gas at an incremental temperature, the change in their weights becomes constant beyond about 300°C. It is revealed by the IR spectra that the change in their weights is due to the adsorbed water. The amount of water adsorbed depends on the treating temperature as does the heat of immersion. The results suggest that the properties of the surfaces of the 13X and 10X zeolites are dependent mainly on the amount of adsorbed water and that they remain almost constant beyond 300°C.

The distribution of the acid strength on an acidic catalyst is expressed as that of the differential heats of adsorption of a base on its acid site. In our experiments, the acid-strength distribution of zeolites is determined from both the differential heats of the adsorption of *n*-butylamine in benzene and the amount of *n*-butylamine chemisorbed from the benzene phase.

The total heat which evolved in the system when zeolite was immersed in a benzene solution of *n*-butylamine includes the heat of the immersion of zeolite in benzene and the adsorption heats of *n*-butylamine on the acidic sites. When the sum of the coverage of the immersed benzene and that of the adsorbed base is assumed to be unity, the following equations can be derived;

$$\theta_A + \theta_B = 1 \tag{1}$$

$$Q_T(\theta_A, \theta_B) = Q_A(\theta_A, \theta_B) + Q_B(\theta_A, \theta_B) \tag{2}$$

where θ_A and θ_B are the coverages of the adsorbed *n*-butylamine and the immersed benzene respectively; Q_T, the total heat evolved in the system (cal/g); Q_A, the evolved heat due to adsorbed *n*-butylamine, that is, the integral heats of adsorption (cal/g), and Q_B, the evolved heat due to immersed benzene (cal/g). If the interactions between adsorbed *n*-butylamine and immersed benzene are neglected, $Q_B(\theta_A, \theta_B)$ is $Q_B^\circ \times \theta_B$ and $Q_A(\theta_A, \theta_B)$ is $Q_A(\theta_A)$, where Q_B° is the heat of immersion in the absence of adsorbed *n*-butylamine. Therefore,

$$Q_T(m_A) = Q_A(m_A) + Q_B^\circ \times [1-(m_A/m_A^\circ)]$$
$$\theta_A = m_A/m_A^\circ \tag{3}$$

where m_A is the amount of *n*-butylamine adsorbed on acid sites on zeolite (mol/g) and m_A°, the saturated amount of it. Figure 2 shows the $Q_T(m_A)$ values of 13X, 10X, and CuX.

The m_A° value of each catalyst is deduced from the amount of *n*-butylamine adsorbed on zeolite from the gas phase, as determined with a thermanobalance at 25°C. The m_A° values are 2.7 mmol/g, 3.2 mmol/g, and 2.7 mmol/g for 13X, 10X, and CuX respectively. Figure 3 shows clearly that $Q_A(m_A)$ consists of two straight lines. The differential heat of the adsorption of *n*-butylamine is obtained from Eq. (3):

$$dQ_A(m_A)/dm_A = dQ_T(m_A)/dm_A + Q_B^\circ/m_A^\circ \tag{4}$$

On the basis of the value of $dQ_A(m_A)/dm_A$ calculated from Eq. (4), Figure 4 shows the acid-strength distribution on these zeolites in terms of the differential heats of adsorption; that is, the acid strength and the ordinate show the acidity corresponding to each acid strength. It is interestingly found that acid sites of each zeolite have a distinct distribution of differential heats of adsorption with two peaks, indicating two kinds of acid strengths. The stronger acid site varies with the

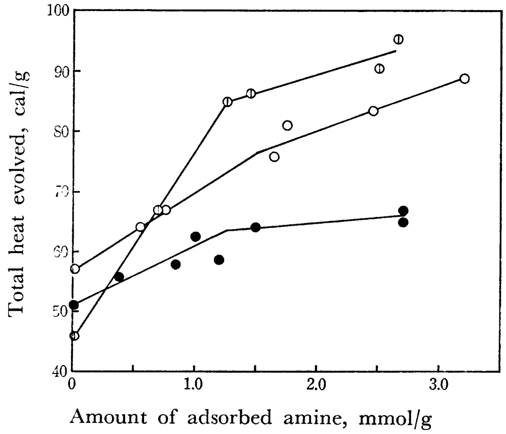

Fig. 2. Total heat evolved in system *vs.* amount of adsorbed *n*-butylamine.

● 13X, ○ 10X, ⦶ CuX

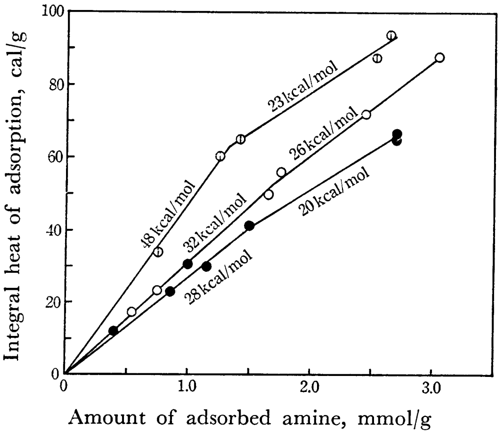

Fig. 3. Integral heat of adsorption of *n*-butylamine *vs.* amount of adsorbed amine. Numerical values are differential heats of adsorption calculated from Eq. (4).

● 13X, ○ 10X, ⊖ CuX

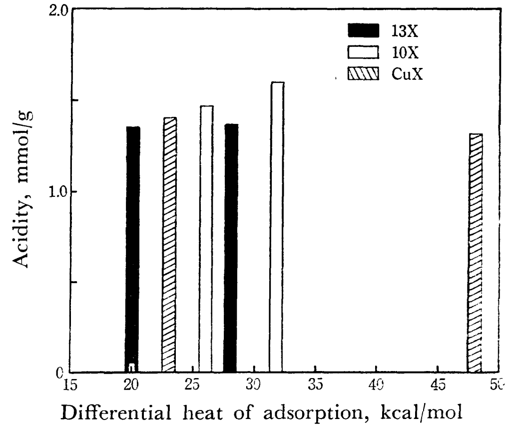

Fig. 4. Distributions of acid strength.

three zeolites used, but the weaker one is about constant. Therefore, the stronger acid site is cation-dependent, and the weaker one is cation-independent. It is considered that the reaction activities of these catalysts are dependent on the stronger one rather than on the weaker one. Thus, it is well and quantitatively shown that the activity of a reaction on cation-exchanged zeolite changes with the kind of the cation on zeolite.

The distribution of acid strength is estimated from the amount of *n*-butylamine adsorbed from the gas phase at an incremental temperature. Figure 5 shows the amounts of *n*-butylamine chemisorbed at various desorption temperatures. The curves are divided into two parts; one is in the region of desorption temperatures lower than about 150°C, while the other is in a higher temperature region than this. This behavior of the adsorbed amine also suggests that the acid sites on the zeolites have two kinds of acid strengths. This result is in agreement with that from the calorimetric method.

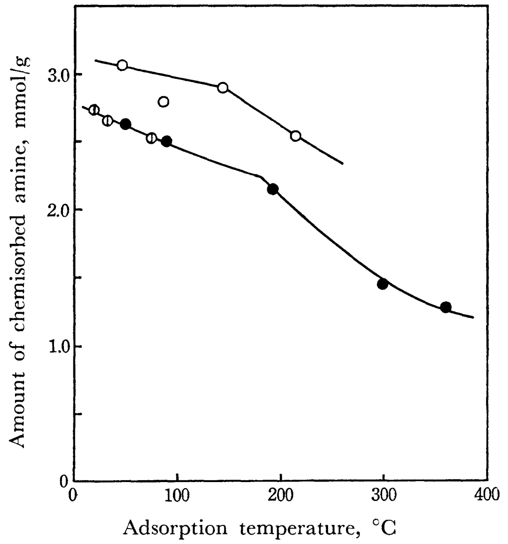

Fig. 5. Temperature dependency of chemisorbed amount of *n*-butylamine.

● 13X, ○ 10X, ⦶ CuX

It has been reported[6] that the acid sites of zeolite which is pretreated under a vacuum at 400°C consist almost entirely of Brönsted acid, that is, of residual surface OH groups. Therefore, the distribution of acid strength which is estimated here from the calorimetric method corresponds to that of the acid strength of the Brönsted acid sites. The acid strength of the Brönsted sites is deduced to be depend on the frequency of the residual OH group. It has previously been shown [7-9] that each zeolite has a few kinds of residual surface OH groups. It is interesting, therefore, to clear up the relation between the distribution of acid strength and that of the frequencies of the surface residual OH groups on zeolites. In this paper, the IR spectra of zeolites were investigated. The stretching vibrations of surface OH groups appear in the region of 3750 cm^{-1}—3600 cm^{-1}, but in this region

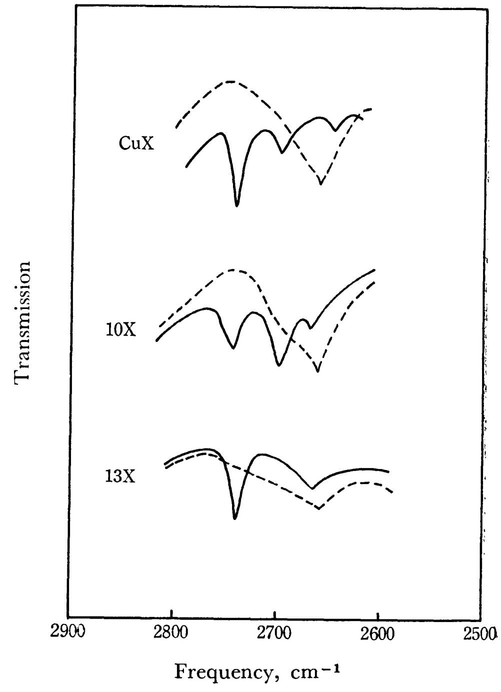

Fig. 6. Effect of adsorbed benzene on zeolite, solid line; IR spectra of residual surface OD groups on zeolite, dotted line; after introduction of benzene.

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[6] J. W. Ward, *J. Cat.*, **11**, 251 (1968).

[7] L. Bertsh and H. W. Habgood, *J. Phys. Chem.*, **67**, 1621 (1963).

[8] J. L. Carter, P. J. Lucchesi and J. C. Yates, *ibid.*, **68**, 1385 (1964).

[9] C. L. Angell and P. C. Schaffer, *ibid.*, **69**, 3463 (1965).

of the spectrum, the stretching vibrations of OH groups of water adsorbed on KBr windows appear also and the transmission of infrared rays is small because of their large divergence. Thus, the surface residual OH groups were turned into OD groups with D_2O. The solid lines in Fig. 6 show the IR spectra of the OD groups on the zeolites used. 10X and CuX have three species of residual OD groups, while 13X has only two. These OD groups are classified into two groups according to the dependency on the cation of the zeolite; that is, group (I) contains OD groups which are independent of the kind of the cation, while in group (II) they are dependent on it. Group (I) contains the 2733-cm^{-1} band on 13X, 10X, and CuX, and the 2699-cm^{-1} band on 10X and CuX, while group (II) includes the 2645-cm^{-1}, 2665-cm^{-1}, and 2668-cm^{-1} bands on CuX, 10X, and 13X respectively. It is shown above that the acid sites of zeolites have two kinds of acid strengths, namely, the cation-independent and cation-dependent acid strengths. The relation between the distribution of the acid strength and the behavior of residual surface OD groups can be obtained on the basis of these observations. Figure 7 shows that the differential heat of the adsorption of *n*-butylamine on the stronger acid sites depend linearly upon the frequency of the OD group which is lowest one on each zeolite. Therefore, it may be concluded that the stronger acid sites, which are cation-dependent, correspond to the cation-dependent OH group which has the lowest frequency. It may also be deduced that the reaction activity on zeolite generally depends on the lowest frequency of the residual OH group.

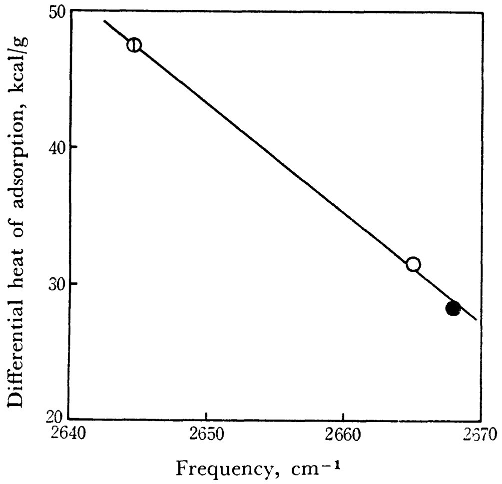

Fig. 7. Relation between differential heats of adsorption on *n*-butylamine and frequencies of residual surface OD groups.
● X, ○ 10X, ◐ CuX

As the heats of the adsorption of *n*-butylamine were measured in benzene, the surface OH groups were affected by the immersed benzene. The influence of the immersed benzene can be estimated from the change in the IR spectra of the OH group due to adsorbed benzene. The dotted lines in Fig. 6 show that the spectra of surface OH groups are broadened and that these groups are shifted to lower frequencies. The behavior of these group is the reverse of the adsorption and desorption of benzene molecules. When the surface OH group is hydrogen-bonded, the spectrum shows a similar behavior. On the basis of this fact and the properties of benzene, it may be concluded that the changes in the spectrum are due to the interaction between the π-electron system of the benzene molecule and the surface OH groups, that is, the π-type hydrogen bond.[10]

Conclusions

The acid-strength distribution of zeolite was estimated from the differential heats of *n*-butylamine adsorption in benzene. The acid strengths of the zeolites used were of two kinds, cation-dependent and cation-independent. The residual surface OH groups are classified into two groups, the cation-dependent group, which has the lowest frequency, and the cation-independent one. The stronger acid site, whose strength is dependent on the cation corresponds to the cation-dependent OH groups on zeolites which have the lowest frequencies. The π-electron system of the benzene molecule adsorbed on zeolite interacts with residual surface OH groups; this interaction are estimated to consist of a π-type hydrogen bond.

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[10] G. A. Galkin, A. V. Kiselev and V. I. Lygin, *Trans. Faraday Soc.*, **60**, 431 (1964).