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ON THE NATURE OF THE ACIDITY OF ALUMINOSILICATE CRACKING CATALYSTS

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The surface acidity of aluminosilicate catalysts has been studied in the works of many authors ([1]-[7]). However, the methods described in the literature make it possible either to estimate the acid strength only semi-quantitatively ([5], [6]), or to find the number of acid sites ([7]-[10]). A shortcoming of the methods used is the dependence of the results on the size of the molecule of the neutralizing base, inaccuracies in distinguishing chemical and physical adsorption, and diffusion complications ([11]). In addition, none of these methods, including the spectroscopic one ([12], [13]), can determine the nature of the acid being studied (protonic or aprotonic) and therefore does not make it possible to draw an unambiguous conclusion about the participation of any one type of acid in the cracking reaction. The difficulties in distinguishing the types of acid centers are connected with the absence of independent methods of determination and with their comparatively low surface concentration. Thus, the method of exchange adsorption allows preliminary hydration of aprotonic centers, while the other methods, based on the interaction of acid sites with amine molecules, allow the possibility of formation of a complex (catalyst · NR) both with protonic and with aprotonic centers.

As a possible way out of this difficulty, we chose the path of successive exclusion of one type of center and independent study of centers of the other type. In our earlier works ([4], [8]) it was shown that the method of exchange adsorption from salt solutions makes it possible selectively to remove the active centers of the aluminosilicate complex, practically without affecting the exchange centers of oxides, and, in combination with the kinetic method, to record accurately the catalytic activity of the samples as acid centers are removed.

In the present work it is shown that combining these two methods with the method of titrating aprotonic sites proves useful for the separate study of each type of acid and for elucidating their role in the cracking reaction.

Fig. 1

Figure 1: Fig. 1

For the study we took Al–Si* catalysts with increasing contents of Al_2O_3: 10/90, 30/70, 50/50, 80/20**, prepared by the method of joint mixing, as well as pure oxides of aluminum and silicon. Protonic acidity was determined by the exchange-adsorption reaction in solutions of the salts CH_3COOLi and CH_3COONa. Poisoning was carried out according to the procedure described by us earlier ([4], [8]). The activity of the initial and poisoned samples was determined by the cumene cracking reaction in a flow system at 475° ([4]). The experimental kinetic data were treated according to the equation of A. V. Frost for monomolecular heterogeneous reactions in flow ([14]).

As can be seen from Fig. 1, which presents the dependence of the rate constant on the amount of introduced Li and Na cations, for all the samples studied there is a linear decrease in activity with the introduction of additional amounts of cations, followed by a bend, after which the activity changes very little despite the introduction of considerable amounts of cations. In these experiments the limiting acidity, determined by extrapolating the first linear segment, was taken as the value of the proton acidity of cracking catalysts (Fig. 1). Such a definition is justified in view of the strict proportionality between the amount of introduced metal cations and the decrease in activity. On the flat segment this proportionality is violated: considerable exchange, as already mentioned above, changes the rate constant hardly at all. We are inclined to think that the bend in the straight line may be explained either by the continuation of exchange with OH groups of catalytically weakly active oxides Al_2O_3 and SiO_2, or by diffusion difficulties associated with an increase in the concentration of metal cations on the catalyst surface.

Fig. 1. Dependence of the rate constant α on the amount of introduced ions Li^+ (a) and Na^+ (b). 1 –30/70, 2 –50/50, 3–80/20

It follows from Fig. 1 that the maximum proton acidity and maximum activity were found for the sample of composition 30/70, somewhat lower for the 50/50 sample, and still lower for the 80/20 and 10/90 samples. The dependence of activity on the amount of adsorbed cations for the initial oxides is not shown in Fig. 1, since their rate constants are an order of magnitude smaller than for the Al–Si catalysts: 0.02 for SiO_2 and 0.01 for Al_2O_3. Ion exchange carried out with the initial oxides is also small (0.025 meq/g for Al_2O_3 and 0.070 meq/g for SiO_2) and lowers the rate constant of the cumene cracking reaction practically to zero. On this basis it may be said that the high exchange capacity and

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* In what follows, for brevity, aluminosilicate catalysts will be designated in abbreviated form as Al–Si.

** The numerator of the fraction corresponds to the weight percent content of Al_2O_3, and the denominator to SiO_2 in the catalyst.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

cracking activity are characteristic of the Al–Si complex, and not of the oxides entering into it.

It also follows from Fig. 1 that the slope of the rectilinear segments proved to be different for samples poisoned with Li and Na cations. This difference is apparently connected with the screening effect of the larger Na ions. To exclude the screening effect of the larger ion and to approach more closely the true value of the limiting acidity, in subsequent calculations the experimental data obtained in exchange with lithium cations were used. It is interesting to note that the exchange acidity determined from Fig. 1 by the extrapolation method coincides with the values of maximum exchange adsorption of these same samples calculated by us from the equation of the exchange-adsorption isotherm of E. N. Gapon (15). This agreement indicates the correctness of using the lithium cation to estimate the true number of exchange centers. An analogous conclusion—that the Li ion is capable of poisoning only one active center—was made by Danforth (19). The exchange-adsorption data made it possible to determine the fraction of active surface, which for the most active catalyst 30/70 proved to be equal to 2%. This value is in good agreement

in agreement with the calculation of the active surface from data on the restoration of the activity of calcined catalysts by introducing small amounts of water ([16]).

To determine the magnitude of the aprotonic acidity of the same samples and oxides, the thermometric method described by Trambouze ([2]) was used. The data presented in Fig. 2 are the averages of two repeated experiments. Fig. 2 presents the dependence of the rate constants of unpoisoned aluminosilicate catalysts and alumina on the magnitude of aprotonic acidity. This dependence is also rectilinear,

Fig. 2. Dependence of the rate constant α on the magnitude of aprotonic acidity for the initial (solid line) and poisoned samples of different composition (dashed line):
1–10/90, 2–30/70, 3–50/50, 4–80/20, 5–Al_2O_3

Fig. 3. Dependence of the rate constant α (I), protonic (II) and aprotonic (III) acidities on the catalyst composition

and the previous correspondence between activity and acidity is maintained. The greatest acidity corresponds to the sample of composition 30/70. The acidity of the initial samples decreases, as the activity decreases, to the value

Fig. 4. Dependence of the rate constant of the cumene cracking reaction on protonic acidity, determined by Li^+. 1 –30/70, 2 –50/50, 3 –80/20, 4 –SiO_2, 5 –Al_2O_3.

Figure 4: Fig. 4. Dependence of the rate constant of the cumene cracking reaction on protonic acidity, determined by Li^+. 1 –30/70, 2 –50/50, 3 –80/20, 4 –SiO_2, 5 –Al_2O_3.

of the aprotonic acidity of pure alumina, which shows a considerable value of Lewis acidity (0.43 meq/g), whereas silica shows a complete absence of this type of acidity. In the same figure the dashed line shows the change in the aprotonic acidity of the catalysts as they are poisoned by lithium cations. The slight decrease in aprotonic acidity upon poisoning (somewhat greater for the 80/20 sample) undoubtedly speaks in favor of the selectivity of this method with respect to aprotonic centers. It is necessary to note, however, that a certain decrease in the value of Lewis acidity upon poisoning is not the result of experimental error, but is connected with the lack of sharpness in distinguishing the nature of the acidic centers by this method, i.e., during titration with a Lewis base (in this case ethyl acetate), the protonic sites of the aluminosilicate structure are also partially titrated, which is especially noticeable for unpoisoned samples. If this were not so, the value of the Lewis acidity would not change upon poisoning, and the straight line of activity decrease would run parallel to the ordinate axis.

Our experiments on determining aprotonic acidity show its presence, and even in considerable amount, both in alumina and in Al–Si catalysts. Fig. 3 shows the dependence of the rate constant for cumene cracking over the initial catalyst samples, as well as of the protonic and aprotonic acidities, on their composition. The shape of the curves indicates that there is a definite dependence between activity and both types of acids. The parallelism of the acidity curves with one another indicates either the identity of the acidic centers, or that, in the formation of aluminosilicate catalysts, both forms of acidity arise. The first assumption is ruled out in connection with the fact that the initial

alumina and poisoned aluminosilicates have a high residual aprotonic acidity with practically complete loss of activity in the cracking reaction. Meanwhile, the slight decrease in Lewis acidity upon introduction of lithium cations and the disproportionately sharp decrease in the rate constant of the cracking reaction indicate that aprotonic acidity accompanies the appearance of protonic acidity when aluminum is introduced into the structure of silica, but by itself, without a proton (unhydrated), it does not participate in cracking. Thus, the second assumption, on the contrary, is confirmed by the presence of a large value of aprotonic acidity in alumina and poisoned samples with practically complete absence of cracking ability.

Fig. 4. Dependence of the rate constant of the cumene cracking reaction on protonic acidity, determined by Li^+. 1 –30/70, 2 –50/50, 3 –80/20, 4 –SiO_2,

5 $-Al_2O_3$.

The dependence of activity on protonic acidity, presented in Fig. 4, is rectilinear. The straight line passes through the origin, which indicates a direct and proportional relation between activity and protonic acidity.

These data undoubtedly show that the introduction of lithium cations into the catalyst lowers the cracking activity, and the number of introduced cations is strictly proportional to the number of active sites and is not connected with their adsorption on Lewis acid centers.

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REFERENCES CITED

1. T. H. Milliken, G. A. Mills, A. G. Oblad, Disc. Farad. Soc., **8**, 279 (1950).
2. V. Trambouze, J. Chim. Phys., **51**, 723 (1954).
3. K. G. Messerov, Usp. khim., **22**, 279 (1953).
4. K. V. Topchieva, Uch. zap. MGU, No. 174, 75 (1955).
5. Ch. Walling, J. Am. Chem. Soc., **72**, 1164 (1950).
6. H. A. Benesi, J. Am. Chem. Soc., **21**, 5490 (1956).
7. O. Johnson, J. Phys. Chem., **59**, No. 9, 827 (1955).
8. K. V. Topchieva, I. F. Moskovskaya, DAN, **101**, No. 3, 517 (1955).
9. J. D. Danforth, J. Phys. Chem., **58**, 1039 (1954).
10. G. A. Mills, E. R. Boedeker, A. G. Oblad, J. Am. Chem. Soc., **72**, 1554 (1950).
11. R. L. Richardson, S. W. Benson, J. Phys. Chem., **61**, No. 4, 405 (1957).
12. J. E. Mapes, R. P. Eischens, J. Phys. Chem., **58**, No. 12, 1059 (1954).
13. E. I. Kotov, Optika i spektroskopiya, **3**, issue 2, 115 (1957).
14. A. V. Frost, Vestn. MGU, No. 3-4, 11 (1946).

15. E. N. Gapon, ZhOKh, **3**, 144 (1933).

16. S. G. Hindin, A. G. Oblad, G. A. Mills, J. Am. Chem. Soc., **77**, 535 (1955).

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