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Abstract

Full Text

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G. M. PANCHENKOV, Z. V. GRYAZNOVA, and I. M. KUVSHINNIKOV

ION EXCHANGE ON ALUMINOSILICATE CATALYSTS IN AN ALKALI FLOW AT SHORT CONTACT TIMES

(Presented by Academician A. V. Topchiev, January 19, 1957)

Aluminosilicate catalysts, which are of great industrial importance, have been the subject of a number of studies ([1–9]). Many works have been devoted to elucidating the nature of the acidity and exchange capacity of aluminosilicates ([2–7]). However, complete clarity has not yet been achieved. The present work is devoted to further study of the mechanism of ion exchange in aluminosilicate catalysts. For this purpose, the kinetics of ion exchange under dynamic conditions in alkaline and neutral media was studied.

In the work, an industrial catalyst of composition 14% Al_2O_3, 86% SiO_2, and a catalyst of composition 37% Al_2O_3, 63% SiO_2, prepared by mixing the corresponding hydrogels followed by drying to a temperature of 100°, were used. Some portions of the catalyst were calcined at temperatures of 500, 750, 1100, and 1300° C. The catalyst had the form of cylinders 4 mm high and 3 mm in diameter. A crushed catalyst, sieved through screens from 200 to 350 mesh, was also used. The experiments were carried out under dynamic conditions with various flow rates of NaOH, LiOH, and KOH solutions. To conduct experiments under dynamic conditions, a catalyst layer one tablet thick was placed in a crucible with a No. 1 glass filter. The alkali solution flowed through the crucible at a constant rate. The solution that had passed through the catalyst layer was collected in flasks, which were changed at definite time intervals. The alkali concentration in the sample was determined by titration with phenolphthalein. The results of the ion-exchange experiments in an alkaline medium are presented in Figs. 1 and 2. In these figures the ordinate gives the value a—the number of milligram-equivalents of H^+ exchanged in 100 g of catalyst by a given volume of solution; the abscissa gives the volume of solution passed through the catalyst layer at a definite rate.

Table 1

Dependence of the ion-exchange rate (referred to concentration) on the heat treatment of a catalyst of composition 14% Al_2O_3, 86% SiO_2

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No.	Calcination temperature, °C	Calcination time, h	V/C
1	100	10	45
2	500	8	40
3	500	16	30
4	750	16	30
5	1100	4	24
6	1300	2	4

As can be seen from Fig. 1, for ion exchange under dynamic conditions the usual saturation curve is obtained. The initial section of this curve (Fig. 2) is well approximated by two straight lines. The tangents of the angles of inclination of the rectilinear segments characterize the rates of ion exchange. The value of the tangent of the angle of inclination of the second segment (V) depends on the flow rate and is proportional to the concentration of the solution. The rate of ion exchange also depends on the degree of preliminary heat treatment of the catalyst.

Calcination was carried out in a stream of dry air. Since the rate of the process V is proportional to the concentration of the solution, Table 1 used the function V/C, which does not depend on concentration.

On the basis of our experiments on the kinetics of hydrocarbon conversion on aluminosilicate catalysts and the data of Table 2, it may be concluded that, in order to obtain a catalyst with constant activity, it is necessary to subject it to heat treatment for no less than 16 hours at a temperature of 500–700°C.

The kinetic curves of ion exchange of aluminosilicate catalysts deactivated by calcination at 1100 and 1300° have linear initial portions of the curve without a break. When the catalyst is calcined to 1100°, a decrease in its volume (shrinkage) by 10% is observed, but the catalyst still retains considerable

Fig. 1. Kinetics of ion exchange under dynamic conditions on an uncalcined industrial catalyst. $C_{\mathrm{NaOH}} = 0.007\,N$, $v_n = 0.2$ ml/min

Fig. 2. Ion exchange under dynamic conditions: I –uncalcined industrial catalyst; $C_{\mathrm{KOH}} = 0.010\,N$, $v_n = 2.8$ ml/min; II –uncalcined catalyst of composition 37% Al_2O_3, 63% SiO_2; $C_{\mathrm{NaOH}} = 0.055\,N$, $v_n^* = 13.6$ ml/min; III –industrial catalyst calcined at 500° for 16 h; $C_{\mathrm{NaOH}} = 0.010\,N$, $v_n = 3.5;\ 3.1;\ 2.9$ ml/min; IV –powdered industrial catalyst calcined at 500° for 16 h; $C_{\mathrm{NaOH}} = 0.010\,N$, $v_n = 2.96$ ml/min

acidity. When calcined to 1300°, the shrinkage reaches 60%, and the acidity falls almost to zero.

For an uncalcined catalyst the kinetic curves sometimes do not start from zero. As additional studies have shown, this is due to the presence of ammonia adsorbed by the catalyst. This same factor, as well as different moisture contents,

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also explains certain differences in the rate of ion exchange under identical conditions. If the catalysts had been preliminarily calcined, good reproducibility of the results was invariably observed. In Fig. 2, curve III describes the results of three experiments carried out under identical conditions with a catalyst calcined at 500° for 16 hours. As can be seen from the graph, all

points of the three experiments lie well on one curve. Experiments with the powdered catalyst are described by a continuous curve without a break in the initial section, and the rate of exchange increases 20-fold (Fig. 2, IV).

Table 2

Values of the quantities a_0 and a_0'. A bed one pellet thick. Catalyst of composition 14% Al_2O_3, 86% SiO_2

Normality of the starting alkali C_{init}	Flow rate, v_n, ml/min	a_0, meq H^+/100 g	a_0', meq H^+/100 g
Uncalcined catalyst	**Uncalcined catalyst**	**Uncalcined catalyst**	**Uncalcined catalyst**
0.006	2.4	7.0	2.0
0.006	4.0	6.8	4.0
0.010	2.5 (LiOH)	8.7	3.3
0.010	2.8 (KOH)	8.0	3.1
0.010	2.5	8.5	3.3
0.010	2.7	4.8	1.3
0.010	3.0	8.0	3.0
0.015	2.5 (LiOH)	5.5	2.3
Avg.		7.2	
0.055	3.1	30	6.5
0.055	4.8	20	6.5
0.055	3.6*	17.6*	12.0*
Bed 4 cm thick	**Bed 4 cm thick**	**Bed 4 cm thick**	**Bed 4 cm thick**
0.007	3.5	8.5	2.0
0.011	0.5	8.0	2.8
Avg.		8.2	
0.098	1.8	46	20
Bed one pellet thick. Catalyst calcined at 550-750°	**Bed one pellet thick. Catalyst calcined at 550-750°**	**Bed one pellet thick. Catalyst calcined at 550-750°**	**Bed one pellet thick. Catalyst calcined at 550-750°**
0.010	2.9	3.2	1.3
0.010	3.1	3.2	1.0
0.010	3.5	3.0	1.0
0.010	3.8	3.1	1.6
Avg.		3.1	

* The experiment was carried out with a catalyst of composition 37% Al_2O_3, 63% SiO_2.

The most probable cause of the break in the kinetic curves is the difference in accessibility of the surface and internal (located inside the pores and between the pellets) exchange-capable centers of the catalyst. In this case, the break is explained by completion of the neutralization of the surface centers. Their amount can be determined graphically. If the surface and internal processes of ion exchange proceed successively, one after the other, then the amount of surface acid centers is determined by the ordinate of the break a_0; if, however, the processes proceed in parallel, then this quantity is determined by the point of intersection of the extension of the second segment of the kinetic straight line with the ordinate axis a'. The values of the ordinates a_0 and a' are given in Table 2. The study was carried out with NaOH solution and only in individual cases, indicated in Table 2, with LiOH and KOH solutions.

At sufficiently low alkali concentrations (up to $0.015\,N$), it is almost entirely neutralized by surface hydrogen ions. In this case, a successive process of neutralization of surface and internal hydrogen ions is observed and, consequently, the value a_0 determines the number of surface hydrogen ions. With an increase in alkali concentration, there is enough of it to carry out the neutralization of surface and internal ions simultaneously. In this case, the number of surface ions is determined by the value a_0'. It is seen from Table 2 that, for the uncalcined industrial catalyst, the amount of surface hydrogen ions of the catalyst is approximately equal to 7 meq per 100 g of catalyst, and for calcined catalysts, 3 meq per 100 g of catalyst. For the uncalcined catalyst of composition 37% Al_2O_3, 63% SiO_2, $a_0' = 12$, which is natural, since it is known that a catalyst of composition 30% Al_2O_3, 70% SiO_2 possesses maximum acidity. It has the largest number of exchange centers in general, and of surface centers in particular.

For an alkali concentration of about $0.1\,N$, a visible increase in the quantities a_0 and a_0' is observed. This can be explained by the fact that, at such concentrations, part of the alkali is consumed in dissolving the catalyst [10].

Studies with solutions of LiOH, NaOH, and KOH showed that the nature of the alkali ion does not affect the value of a_0'.

On the basis of the data obtained, it is evident that the slowest stage of the entire process is diffusion into the depth of the pores. At the break point, after completion of the process of surface neutralization, the rate of exchange is determined only by diffusion into the depth of the pores. Thus, the reason why smooth curves were not obtained, but rather curves with a break, is the abrupt change in the rate of the process. This view of the cause of the break is confirmed by data on ion exchange of an aluminosilicate catalyst under dynamic conditions in a solution of neutral salts. In this case there is no break in the kinetic curve, because the ion-exchange process proceeds approximately 10^3 times more slowly than in an alkali solution. The absence of a break in the

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kinetic curve for ion exchange of an aluminosilicate catalyst calcined to 1100° and to 1300° can be explained in the same way. At a temperature of 900–1000°, aluminosilicate decomposes into γ–Al_2O_3 and mullite ([11]), which are weaker acidic agents than alumosilicic acids. In this case the rate of the neutralization process is sufficiently low, and no break is observed. Another confirmation of the ion-exchange mechanism considered above is the absence of a break point on the kinetic curves during neutralization of a ground catalyst with an alkali solution (Fig. 2, *IV*). The latter does not permit the break in the kinetic curves to be explained by the assumption of the presence of acids differing in strength.

Danforth' s studies ([12]) show that the dependence of catalytic activity on the degree of poisoning of catalysts by alkali solutions is described by a broken line with two breaks. The author calls attention only to the second break. Meanwhile, in all cases another break is observed on the curve at the point where the catalyst has absorbed 2 meq per 100 g of catalyst. This is in good agreement with our results for catalysts that had undergone heat treatment.

Thus, one may arrive at the following conclusion: by neutralizing an aluminosilicate catalyst with an alkali solution, it is possible easily and rapidly to determine the concentration of external active centers on it. It should be noted that this method cannot be general for all acid and oxide catalysts, but is suitable only in cases where the rates of ion exchange on the surface and in the depth of the pores differ greatly.

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