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Abstract

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KINETICS OF CUMENE CRACKING ON ZEOLITE 10X

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Studies of the catalytic properties of crystalline aluminosilicates—zeolites—have shown that highly efficient catalysts for a number of important processes can be obtained on their basis ([1–4]). The possibility of chemically modifying the surface of zeolites by ion exchange makes them very promising also for carrying out new catalytic reactions.

With respect to the cracking reaction, zeolites are, in their catalytic properties, quite close to amorphous synthetic aluminosilicates; however, owing to their molecular-sieve action, they possess greater selectivity. The insufficiency of the experimental data obtained to date on the catalytic properties of zeolites does not permit deeper comparisons of their properties with those of amorphous aluminosilicates. In this connection, it is of definite interest to carry out a systematic study of the catalytic properties of zeolites for those reactions that serve as model reactions in the study of amorphous aluminosilicate cracking catalysts.

In the present work, as one such reaction, the reaction of cumene cracking was studied; it is widely used in evaluating the activity of aluminosilicate catalysts. The investigation was carried out using two kinetic methods—the integral and the differential—whose application makes it possible to find all the principal quantitative characteristics of the process and to establish the boundaries of the regions in which the reaction proceeds.

As catalyst, a synthetic granular zeolite of type X in the calcium form (10X) from Linde (batch No. 106) was used. It was established that during prolonged operation (several tens of hours) as a catalyst for the cumene cracking reaction at 500°, the zeolite does not change its structure. This was shown by X-ray diffraction and adsorption studies of the original and used samples.

Table 1

Catalyst	Feed rate, mmol/2 · min	Degree of conversion, %
Zeolite	0.60	35.0
Houdry	0.66	60.6
Zeolite	0.79	27.0

Fig. 1

Figure 1: Fig. 1

Catalyst	Feed rate, mmol/2 · min	Degree of conversion, %
Houdry	0.86	55.7
Zeolite	1.18	16.0
Houdry	1.28	47.9

It was found that the zeolite has considerably lower activity in the cumene cracking reaction than a Houdry-type aluminosilicate catalyst (see Table 1). It was also found that at 450° the zeolite does not possess stable activity; at 475° and above, this catalyst operates with constant activity for three hours, which is reproduced after periodic regeneration of the sample. In all subsequent experiments a sample was used that had been brought to constant activity and regenerated.

The kinetics of cumene cracking by the integral method was studied at atmospheric pressure in the temperature range 475–550°. The dependence of the degree of conversion y on the reciprocal feed rate $1/v_0$ is given in Fig. 1. It is seen from the figure that, at all temperatures investigated, the initial portions of the curves up to values of $1/v_0 \sim 2$ are almost linear. It should be noted that on aluminosilicate catalysts this dependence, as a rule, is nonlinear. Treatment of the experimental data by means of

of the Frost kinetic equation[5] showed that, in contrast to aluminosilicate catalysts, the kinetics of cumene cracking on zeolite is not described by this equation.

To determine whether this is a consequence of the occurrence, in addition to the main cracking reaction, of any side processes, we carried out a complete analysis of the liquid and gaseous cracking products obtained at 550°. The analysis showed that the principal by-product is α-methylstyrene, i.e., the product of dehydrogenation of cumene. As was established earlier[6], the formation of α-methylstyrene is the result of thermal dehydrogenation of cumene. Our experiments on the thermal decomposition of cumene showed that, under the same conditions under which catalytic cracking was carried out, the thermal reaction begins only above 500°. At 550° and a feed rate of ~ 5 mmol/g · min, the gas yield is about 10%. By the same amount, in catalytic cracking, the degrees of conversion calculated from gas and from the benzene formed differ. On this basis we concluded that, in the temperature and feed-rate range studied, the zeolite brings about only the cracking of cumene with the formation of benzene and propylene. Thus, in this respect the zeolite and aluminosilicate catalysts possess identical properties.

Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2

Fig. 3

The kinetic study by the differential method was carried out on an apparatus with complete recirculation of the starting substance, described in work [7]. The design of the apparatus makes it possible to operate at low degrees of conversion, when the reaction rate can be measured directly

by the rate of formation of one of the reaction products—in our case propylene.

In Fig. 2, experimental data are presented, in the coordinates of the Arrhenius equation, on the dependence of the reaction rate w, referred to unit weight of catalyst, on temperature. It is seen from the figure that over the entire temperature interval the dependence of $\lg w$ on $1/T$ is linear. The observed activation energy, found from this dependence, is 35 ± 1 kcal/mole. Such a large value of the activation energy gives grounds for assuming that, despite the small pore size of the zeolite, cracking of cumene on it, at least up to 528°, proceeds in the kinetic region.

Fig. 4. Cracking of cumene with additions of benzene (δ). Dependence of $\lg w$ on $\frac{1}{T}$. 1—$\delta = 0$; 2—$\delta = 1$; 3—$\delta = 2$ and 4—$\delta = 3$

A linear dependence between $\lg w$ and $1/T$, from the standpoint of the Langmuir-Hinshelwood theory of heterogeneous kinetics, occurs if the reaction proceeds with zero or first order with respect to pressure. To establish which of these two cases is realized in the cracking of cumene on zeolite, we carried out experiments at different pressures: a—760, b—606, v—400, g—200 mm Hg (Fig. 3). It was found that the reaction rate is practically independent of pressure, and the experimental points corresponding to different pressures lie on one straight line (see Fig. 3). This quite unambiguously indicates that over the entire temperature interval the reaction proceeds according to zero order. Hence it follows that the observed activation energy coincides with the true one;

Fig. 4. Cracking of cumene with additions of benzene (δ). Dependence of $\lg w$ on $1/T$. 1—$\delta = 0$; 2—$\delta = 1$; 3—$\delta = 2$ and 4—$\delta = 3$

Figure 4: Fig. 4. Cracking of cumene with additions of benzene (δ). Dependence of $\lg w$ on $1/T$. 1—$\delta = 0$; 2—$\delta = 1$; 3—$\delta = 2$ and 4—$\delta = 3$

therefore the latter for the process of cracking cumene on zeolite is 35 kcal/mole. It should be noted that this value is quite close to the values of the activation energy on aluminosilicate catalysts. On the latter, however, zero order is observed, as we established, at substantially lower temperatures (up to 350—380°). Above 500° on aluminosilicate catalysts the reaction proceeds according to first order. This fact indicates that the adsorption coefficient of cumene on zeolite is much greater than on aluminosilicate catalysts; therefore zero order of the reaction is realized on zeolite at higher temperatures.

Thus it has been possible to show that on zeolite the kinetic mechanism differs substantially from the mechanism on aluminosilicate catalysts. This, in particular, may explain why on zeolite the kinetics of cumene cracking under integral-reactor conditions does not obey the Frost equation.

In order to determine the relative adsorption coefficient of benzene, we studied the effect of additions of it to cumene on the cracking kinetics. The results of the experiments are given in Fig. 4. With increasing concentration of benzene in the mixture, the character of the dependence of $\lg w$ on $1/T$ does not change; the observed activation energy also remains constant within the accuracy of the experiment. Hence it is not difficult to show that the heats of adsorption of cumene and benzene must be close to one another.

On the basis of the data obtained, with the aid of the equation

$$w = k\frac{1}{1 + z\delta},$$

in which δ is the ratio of the molar concentrations of benzene and cumene in the mixture, the values of the relative adsorption coefficient of benzene, $z_2 = b_2/b_1$, were found. It was established that in the interval 475–526° the value of z_2 is practically independent of temperature. The mean value of z_2 for this interval is 0.47, i.e., on the zeolite, cumene is adsorbed approximately twice as strongly as benzene. In this respect the zeolite also differs from aluminosilicate catalysts, on which, as we have established, the adsorption coefficients of cumene and benzene are close to one another.

Thus, the investigation carried out showed that on the crystalline aluminosilicate —zeolite 10X—the direction of the cumene cracking process is the same as on amorphous aluminosilicate cracking catalysts. The study of the reaction kinetics also made it possible to establish certain differences in the kinetic and adsorption mechanism of the process.

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Note: Figure translations are in progress. See original paper for figures.