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CHEMISORPTION OF ISOPENTANE ON AN ALUMINA-CHROMIA-POTASSIUM CATALYST

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Many studies have been devoted to the problem of dehydrogenation of paraffin hydrocarbons in its various aspects; these were recently reviewed by Lyubarskii (^{1}). Among the catalysts used for this purpose, alumina-chromia catalysts occupy first place, especially those promoted with potassium (^{2}-^{4}). The results of studies of the phase composition, texture, and other physical properties of unpromoted alumina-chromia catalysts are described in works (^{5}-^{8}), and those of catalysts promoted with K_2O in article (^{9}). In studies of catalyst texture, not only N_2 but also other adsorbates were used—CH_3OH (^{10}), benzene (^{6}, ^{9}), and toluene (^{6}); however, chemisorption was neither observed nor studied in any of these works. In one of the early studies on adsorption (^{11}) on Cr_2O_3—MnO, chemisorption of CH_4, C_2H_6, and C_3H_8 above 300° was noted, but it was not studied in detail. This exhausts the data on the chemisorption of paraffins. The literature (^{12}, ^{13}) contains indications that high-temperature chemisorption of hydrocarbons on oxides should proceed reversibly by a dissociative mechanism and with a small activation energy. At the same time, it is believed (^{14}, ^{6}) that the slowest stage in catalytic transformations of hydrocarbons is their chemisorption. In light of the foregoing, it seemed important to try to detect and study in greater detail the chemisorption of paraffins and olefins at temperatures as close as possible to the temperature adopted for the dehydrogenation of paraffins. The present communication describes the results of a study of the adsorption of iso-C_5H_{12} on a standard catalyst for paraffin dehydrogenation, kindly provided to us by the authors of work (^{4}).

The texture of this catalyst, containing 84.6 wt. % Al_2O_3, 13% Cr_2O_3, and 2.4% K_2O, was determined by us (with the participation of A. L. Klyachko-Gurvich) from the adsorption of benzene vapor at 20° on an apparatus with quartz McBain balances: it has a specific surface area $S = 120$ m^2/g and an effective pore diameter of about 40 Å. Determination from argon vapor gave a value of $S = 135$ m^2/g, in good agreement with the determination from benzene vapor.

We studied the adsorption of isopentane by the capillary method described in work (^{15}). The amount of adsorbed isopentane (with correction for its content in the dead space of the apparatus) was measured with an accuracy up to 0.001 mmol. Isotherms measured at 20, 50, 100, and 150° (Fig. 1) and at 205, 241, 297, and 325° (Fig. 2) were well reproduced in repeated independent measurements. Before the start of each series of experiments, the catalyst was pumped out at 470–500° to a vacuum of the order of $1 \cdot 10^{-4}$. When the temperature is raised from 20 to 150°, the amount of iso-C_5H_{12} adsorbed at the same pressure decreases, and the form of the isotherms changes. The isotherm at 20° belongs to the type of polymolecular adsorption isotherms. Calculation by the BET equation from the data of this isotherm showed that 1 m^2 of surface is covered by 3.02 μmol of iso-C_5H_{12} at monolayer filling, and that the area occupied by 1 molecule of iso-C_5H_{12} on the catalyst surface is 56 $Å^2$. But already at

100–150° and pressures from 0 to 200 mm, the process proceeds in the region of small coverages (Henry region), in which adsorption depends linearly on pressure: $a = k \cdot p$, and the isotherm is a straight line passing through the origin. Such a course of the isotherm is one of the indicators of the homogeneity of the catalyst surface with respect to physical adsorption. Since another necessary indicator of such surface homogeneity is the independence of the heat of adsorption Q from the degree of coverage θ, this criterion also had to be checked. For this purpose, from the data of the isotherms at 20 and 50°, using the Clausius—Clapeyron equation

$$\frac{d \ln P}{dT} = \frac{Q}{RT^2},$$

we calculated the isosteric heats of adsorption of iso-C_5H_{12} on the catalyst studied (Table 1). As the coverage θ increases from 6 to 66% of a monolayer, the heat of adsorption Q changes little, which confirms the characterization of the surface as close to homogeneous. The very small decrease in Q may be connected with the interaction of iso-C_5H_{12} molecules with one another. At lower degrees of coverage θ, the heat of adsorption, determined from the isotherm data at 150, 205, and 241°, also remains constant, but it is smaller in magnitude than follows from the isotherms at 20 and 50° by extrapolation. Similar discrepancies have been described in the literature for other cases and were explained [16] primarily by the fact that, with increasing temperature, the distance between the adsorbed molecule and the catalyst surface increases somewhat.

Fig. 1. Adsorption isotherms of isopentane on an alumochromium-potassium catalyst for paraffin dehydrogenation. Black points—desorption

Table 1

a, μmol/m^2	2	1.5	1.0	0.5	0.2	0.075	0.050	0.025
θ, %	66	49	33	16	6			
Q, kcal/mol	9.6	9.9	10.4	10.5	10.7	7.5	7.2	7.5

Fig. 2. Adsorption isotherms of isopentane on an alumina-chromia-potassium catalyst at 150–325°

Figure 1: Fig. 2. Adsorption isotherms of isopentane on an alumina-chromia-potassium catalyst at 150–325°

Above 150°, in the initial part of the isotherms up to pressures of 10–15 mm, an increase in the amount of adsorbed substance is observed with increasing temperature. The isotherm changes from linear and reversible to convex and irreversible (205-325°, Fig. 2), of the Langmuir-isotherm type, reaching saturation. In this region adsorption proceeds very slowly. Our isotherms show that between 150 and 205° another type of interaction of iso-C_5H_{12} with the catalyst surface appears, ending at a pressure of 10–15 mm. Above these pressures the isotherms continue to remain linear and reversible, and equilibrium in these sections is established rapidly, while adsorption decreases with temperature. At temperatures up to 300°, decomposition of isopentane on the catalyst with desorption of the reaction products does not take place, as is evident, for example, from the 297° isotherm, whose desorption branch shows that a considerable amount of isopentane is chemisorbed. Although at 325° chemisorption also takes place and even to a greater extent than at 297°, its desorption branch could not be measured accurately because, during prolonged contact with the catalyst at these temperatures and pressures, iso-C_5H_{12} decomposed and reaction products desorbed from the catalyst. From the fact that at higher pressures the 325° isotherm retained a linear course, it follows that an insignificantly small amount of iso-C_5H_{12} underwent reaction at this temperature. At 350° it was not possible to measure the isotherm at all, since the reaction was already proceeding to a noticeable extent, as was evident from the increase in pressure in the system; in this experiment, products of the transformation of iso-C_5H_{12} on the catalyst were accumulated. Analysis of these products (carried out by Yu. A. Fedoninin, to whom we ex-

our sincere gratitude) on an MI-1035 mass spectrometer showed that they contained (vol. %): C_3H_8 28; CH_4 25.6; C_2H_6 16.7; C_2H_4 8; C_3H_6 6.2; C_2H_2 3.7; C_4H_{10} 2.8; C_5H_{10} 2.6; benzene 2.6; toluene 1.34. Thus, under stationary reaction conditions, as a result of very prolonged contact of isopentane with the catalyst at 350°, isopentane decomposes completely; moreover, not only cracking occurs, but also a series of consecutive reactions, including those leading to the formation of small amounts of aromatic hydrocarbons. Thus, under the conditions described above, the behavior of isopentane on the catalyst differed substantially from that observed in a flow system. As is known ($^{2-4}$), at short contact times in a flow system at 500-550°, dehydrogenation becomes the main process when paraffins are in contact with a catalyst of this type.

Fig. 2. Adsorption isotherms of isopentane on an alumina-chromia-potassium catalyst at 150–325° (the initial sections of the 297 and 241° isotherms are also shown on an enlarged scale).

Fig. 3. Dependence of the amount of isopentane chemisorbed on an alumina-chromia-potassium catalyst on temperature

Figure 2: Fig. 3. Dependence of the amount of isopentane chemisorbed on an alumina-chromia-potassium catalyst on temperature

a –150°, *b* –205°, *v* –241°, *g* –297°, *d* –325°, *e* –3 –repeated experiments. Black symbols –desorption.

The amount of chemisorbed isopentane changes exponentially with temperature (Fig. 3). It is, at 241°, 0.33%, at 297° 0.9, and at 325° 1.2% of the amount of isopentane adsorbed in a monolayer on the catalyst surface at 20°. The linear dependence of the logarithm of the amount of chemisorbed isopentane on the reciprocal temperature (Fig. 3) may be explained both by an increase in the number of chemisorption centers on the catalyst surface with increasing temperature and by an increase in the reactivity of the isopentane itself with temperature. Most likely, both of these factors act simultaneously.

In view of the fact that the experiments were carried out without circulation of isopentane vapors and in a closed system, different parts of which were at different temperatures (the ampoule with the catalyst being at a higher temperature than the rest of the apparatus), we did not obtain reliable data on the rates of chemisorption of *iso*-C_5H_{12}. Nevertheless, these rates could be estimated approximately by dividing the amount of chemisorbed isopentane by the time required to establish equilibrium. Thus, at 297° $a = 0.036$ mmol/g (for the entire catalyst charge) was reached in 96 h, and at 325° in 31 h. Since we had data for two temperatures at the same value of θ, we calculated (as follows from what was said above, again only approximately) the activation energy of chemisorption of isopentane on this catalyst. It proved to be equal to 15 kcal/mol.

Fig. 3. Dependence of the amount of isopentane chemisorbed on an alumina-chromia-potassium catalyst on temperature.

Thus, in the present study, for the first time the chemisorption of a paraffin hydrocarbon on a catalyst for paraffin dehydrogenation-dehydrocyclization and its variation with temperature and pressure has been measured,

and the activation energy of chemisorption was also approximately estimated. The data obtained indicate that the rate of chemisorption of isopentane increases rather rapidly with temperature and, consequently, at the temperature of dehydrogenation of paraffins (500° and higher) it should be fairly high. From the rapid increase in the number of chemisorption centers (estimated from the increase in the amount of chemisorbed isopentane) with temperature, it follows that at 500-550° a significant fraction of the catalyst surface must participate in chemisorption. Indeed, calculation from the graph in Fig. 3 extrapolated to 550° shows that at this temperature about 18.8% of the surface, calculated from the monolayer at 20°, should be capable of chemisorbing isopentane. Assuming that the reaction is undergone by activatedly adsorbed isopentane, it may be considered that about 0.2 of the entire catalyst surface participates at 550° in the dehydrogenation reaction. We are currently studying the chemisorption of isopentenes on this same catalyst.

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