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Abstract

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ON THE DEPENDENCE OF THE ACTIVATION ENERGY ON THE RELATIVE ADSORPTION COEFFICIENT

We have investigated, over a wide temperature range, the activity of a series of nickel catalysts in the reaction of cyclohexane dehydrogenation,* in which nickel, in identical weight amounts, was deposited on various supports.

As follows from Table 1, the apparent activation energy of the cyclohexane dehydrogenation reaction Q, calculated by the Arrhenius equation, as well as the relative adsorption coefficient of benzene z_2, determined according to the formula given in work (3) and adsorption data (1), depend substantially on the nature of the support used. It was also shown that z_2 does not depend on temperature, while the relative adsorption coefficient of hydrogen z_3 is close to zero, i.e., hydrogen does not inhibit this reaction (4).

Table 1

No.	Catalyst	Q, kcal/mol	z_2	E, kcal/mol	No.	Catalyst	Q, kcal/mol	z_2	E, kcal/mol
1	Ni/Al_2O_3	9.8	4.0	12.8	4	Ni/kieselguhr	11.0	2.1	13.7
2	Ni/silica gel	4.8	7.3	14.0	5	Ni/Al_2O_3	10.8	2.05	13.0
3	Ni/Al_2O_3	10.0	2.1	13.0	6	Ni black	7.0	6.0	–

On comparing the data presented in Table 1, we established the following dependence between the apparent activation energy Q and the magnitude of the relative adsorption coefficient of benzene z_2:

$$Q = E - k \lg z_2, \tag{1}$$

where E and k are constants. This dependence is shown graphically in Fig. 1.

The general kinetic equation for monomolecular heterogeneous catalytic reactions in a flow, derived in (5), for our case, taking into account that the conversion percentage m was < 30 and that the reaction rate did not depend on

Fig. 1

Figure 1: Fig. 1

pressure, after a number of simplifications (^{6}) may be written in the following form:

$$m = \frac{KA_1}{\sum z_r A_r + K/2}, \quad (2)$$

where K is the rate constant, A_r is the number of moles of the r-th substance admitted into the reactor, and z_r is the relative adsorption coefficient of the corresponding substance.

* The catalysts were prepared by a method analogous to (^{1}). Nickel black—according to work (^{2}).

From the temperature dependence of the reaction rate constant, determined from equation (2), the true activation energy E was calculated; it is given in Table 1. The values of E for all the samples studied practically coincided. As follows from Fig. 1, the value of E corresponds to the initial ordinate of the straight line drawn. Thus, the constant E in equation (1) is the true activation energy.

For most of the catalysts we studied, the difference between E and Q is small and close to 3 kcal/mol; the exception is catalyst 2—nickel on silica gel—for which the apparent activation energy is three times smaller than the true one. It should be noted that for this catalyst sample the value of z_2 is maximal, and such a large discrepancy between E and Q follows from equation (1).

Fig. 1. Dependence of Q on $\lg z_2$ for nickel catalysts: *a*—from kinetics, *b*—from adsorption, *v*—for Ni black, *g*—according to the data of Balandin—Erbö (^{7,11})

Obviously, the apparent activation energy will be equal to the true one in the case where $z_2 = 1$, which was also found by one of the authors (^{7}) in studying the kinetics of dehydrogenation of cyclohexane and its homologues.

In addition, for catalyst 2 we also found a dependence of the value of z_2 on the amount of benzene in the initial mixture; moreover, as follows from Table 2, with increasing benzene content z_2 increases. The dependence of z_2 on the amount of benzene in the initial mixture is shown graphically in Fig. 2. In Table 1 for this catalyst we gave z_2 for mixtures containing a small amount of benzene.

Table 2

Dependence of z_2 on the composition of the C_6H_6—C_6H_{12} mixture for catalyst 2

C_6H_6, %	C_6H_{12}, %	z_2
10.1	89.9	6.0
17.4	82.6	7.5
34.5	65.5	8.0
56.9	43.1	20.0
70.2	29.8	$\gg 100$

The value of the relative adsorption coefficient characterizes the relative lifetime of the reaction-product molecules on the catalyst surface as compared with the molecules of the reacting substance (3). For catalyst 2, the benzene molecule remains on the catalyst surface 6-7 times longer than the C_6H_{12} molecule. In (8) it was indicated that sites with an intermediate adsorption strength should be catalytically active.

If it is assumed that the benzene formed as a result of the reaction is adsorbed primarily at the most active sites from the adsorption standpoint, then inhibition by benzene practically does not occur. Thus, from the temperature dependence of m we should obtain the true activation energies. However, as the percentage conversion m increases and the amount of benzene in the bulk and on the surface increases, the latter will accumulate more and more at sites with intermediate adsorption strength. Hence inhibition by benzene of the dehydrogenation reaction of C_6H_{12}, observed by a number of authors (4), will arise. This inhibition will lead, even under flow-system conditions, to the reaction being catalyzed not by the portion of the nickel surface that catalyzed the reaction at the beginning, but by a portion of the nickel surface partially covered to some extent with benzene. This effect, taking into account the ability of the π-electrons of benzene to interact with the d-electrons of nickel (9), should lead to a dependence

$$z_2 = f(m).$$

This dependence should appear more strongly for the catalyst that has larger values of z_2, since in this case benzene molecules will remain relatively longer on the catalyst surface. In this case, to determine the value of z_2 by the kinetic method, one should

take low-percentage mixtures, as we did for catalyst 2. The effect indicated above should lead to a distortion of the value of Q. In the literature there is indirect evidence for the phenomenon indicated above. One of us, together with Yur' ev,[10] studied Q as a function of the percentage of xylene in a xylene-dimethylcyclohexane mixture for the dehydrogenation reaction over Ni/Al_2O_3. It was shown that Q, up to a mixture containing 90% aromatics, does not depend on the composition of the mixture (in this case $z_2 = 1^7$). In addition, for the dehydrogenation of C_6H_{12} over a Ni-on-pumice catalyst we obtained $Q < 5$ kcal/mol (the catalyst is unstable) and $z_2 \sim 20$ even for mixtures containing 10% C_6H_6.

Fig. 2. Dependence of the relative adsorption coefficient of C6H6 on the composition of the C6H6—C6H12 mixture.

Figure 2: Fig. 2. Dependence of the relative adsorption coefficient of C6H6 on the composition of the C6H6—C6H12 mixture.

Fig. 2. Dependence of the relative adsorption coefficient of C_6H_6 on the composition of the C_6H_6—C_6H_{12} mixture.

Thus, the essence of the observed phenomenon reduces to the following: as long as the dehydrogenation reaction of C_6H_{12} over nickel catalysts proceeds on active sites with medium adsorption strength, which are not covered to a significant extent by C_6H_6 molecules, there is no inhibition and z_2 does not depend on m.

As soon as the coverage by benzene of sites with medium adsorption strength becomes appreciable, inhibition by benzene begins, leading to a dependence $z_2 = f(m)$, which is manifested especially readily in catalysts with large z_2. In order to determine the activation energy in this case, it is necessary to take this dependence into account. The value of E thus obtained for catalyst 2 agrees well with the value of E determined for the other catalysts (see Table 1). Another possible way of solving the problem is to use equation (1), from which E can be found graphically at $z_2 = 1$.

It is interesting to note that the data obtained by one of us for a series of dehydrogenation reactions of cyclohexane hydrocarbons over Ni/Al_2O_3[7] and Erbo' s data for Ni/BeO,[11] obtained using several other methods and equations, fit dependence (1) (Fig. 1). It is noteworthy that the value $E \simeq 14.0$ kcal/mol was obtained in our laboratory[12] for certain other supported nickel catalysts.

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