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Abstract

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KINETICS OF THE CATALYTIC DEHYDROGENATION OF ISOPROPYL ALCOHOL IN THE PRESENCE OF TRANSITION METALS OF THE FOURTH PERIOD

The kinetics of the dehydrogenation of alcohols over catalysts—iron, cobalt, and nickel—has been little studied. There are only a few works with a nickel catalyst deposited on a support, in a flow system ([1,2]), and without a support—in a static system ([3]). Meanwhile, this reaction can serve as a model in the study of the above-mentioned catalysts, which are extremely widespread in practice.

In the present work we investigated the kinetics of the dehydrogenation of isopropyl alcohol over metallic iron, cobalt, and nickel obtained by precipitation. The iron catalyst was obtained by precipitating iron oxalate* with a 50% solution of oxalic acid from a 50% solution of ferrous sulfate. The precipitate was washed with distilled water until the wash waters gave a negative reaction for the sulfate ion and was decomposed in a stream of electrolytic hydrogen at 400° for 6 hours. The cobalt and nickel catalysts were prepared by precipitating the corresponding hydroxides with ammonia from a 20% solution of the corresponding nitrate salt. The precipitate was washed with distilled water until the wash waters gave a negative reaction for NO_3. The cobalt and nickel hydroxides were decomposed in a stream of air at 400°, and the oxides obtained were reduced with electrolytic hydrogen at 200, 250, 300, and 350° for 3 hours at each temperature. Between experiments the catalyst was regenerated with hydrogen for 45–60 min. The isopropyl alcohol and acetone used in the investigation had physical constants coinciding with literature data. The experiments were carried out in an ordinary flow apparatus ([4]). It was established that the catalysts studied, in the temperature interval examined (for iron and cobalt up to 250°, for nickel up to 215°), carry out exclusively the dehydrogenation of isopropyl alcohol to acetone. The gas formed was pure hydrogen, as shown by gas analysis. The catalyzate contained only acetone and unreacted alcohol, which was established by its distillation.

As was shown earlier ([2,5]), the dehydrogenation of alcohols obeys the general kinetic equation for monomolecular catalytic reactions in a flow, derived by one of the authors ([6]). In the case of the dehydrogenation of alcohols without impurities, this equation has the form:

$$\frac{dm}{dl} = k\frac{(A_1 - m)}{A_1 + (z_2 + z_3 - 1)m}, \tag{1}$$

where k is the reaction rate constant, A_1 is the feed rate of the starting substance, z_2 and z_3 are the relative adsorption coefficients of ketone and hydrogen, m is the amount of hydrogen evolved per minute, and l is the length of the catalyst layer.

After integration of equation (1), we obtain:

$$k = (z_2 + z_3)A_1 \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1)m. \tag{2}$$

The relative adsorption coefficients entering into equation (2) were determined by a reaction-kinetic method based on the decrease in the reaction rate when a known amount of the reaction product is added to the initial substance. The magnitude of the reaction rate during passage of the mixture and its comparison with the reaction rate during passage of the pure substance show to what extent the added substance is adsorbed on the active sites of the catalyst. The magnitude of the adsorption coefficients was calculated by the formula*:

$$z = \frac{B_1(2H - Y) - HY}{(1 - B_1)Y}, \tag{3}$$

where $B_1 = A_1/\Sigma A_r$; $Y = m/\Sigma A_r$; $H = Y_0/(2 - Y_0)$. Here Y is the degree of conversion in experiments with mixtures, and Y_1 is that with the pure substance.

Table 1

Relative adsorption coefficients z_2

Catalyst	Temperature, °C	$z_2 = a\ /a$
Iron	210	0.66 ± 0.02
Iron	230	0.70 ± 0.07
Iron	240	0.71 ± 0.06
Cobalt	206	0.45 ± 0.03
Cobalt	221	0.48 ± 0.03
Cobalt	238	0.45 ± 0.03
Nickel	166	1.51 ± 0.03
Nickel	182	1.35 ± 0.06
Nickel	198	1.16 ± 0.10

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* But not by reduction of oxides with hydrogen, which is completed only at the temperature of appreciable sintering.

Catalyst	Temperature, °C	$z_2 = a\ /a$
Nickel	209	1.00 ± 0.02

Table 2

Relative adsorption coefficients z_3

Catalyst	Temperature, °C	$z_3 = a_{H_2}/a$
Iron	200	0.20 ± 0.02
Iron	220	0.05 ± 0.02
Iron	235	0.06 ± 0.02
Iron	247	0.10 ± 0.02
Cobalt	204	1.03 ± 0.03
Cobalt	223	1.02 ± 0.08
Cobalt	238	1.04 ± 0.01
Nickel	172	0.39 ± 0.01
Nickel	184	0.25 ± 0.02
Nickel	197	0.16 ± 0.01
Nickel	206	0.11 ± 0.01

The relative adsorption coefficients were determined from the rate of dehydrogenation of binary mixtures of the reaction products with the initial alcohol. In this case the volumetric rate of the alcohol in the experiment with the pure substance was equal to the total volumetric rate of the alcohol and the reaction product in the experiments with mixtures. To check the constancy of the catalyst activity, experiments with mixtures were alternated with experiments with the pure substance. Tables 1 and 2 give the results of determining the adsorption coefficients. The adsorption-displacement curves, constructed from five points at each temperature, had the general form observed in (5,8).

As is seen from Tables 1 and 2, the relative adsorption coefficients of acetone and hydrogen on iron and cobalt catalysts do not depend on temperature. A dependence of the adsorption coefficients on temperature is observed only in the case of nickel, on which the relative adsorption coefficients of both products decrease with increasing temperature. The dependence of these adsorption coefficients on temperature is logarithmic, as is evident from Fig. 1, where the dependence of $\lg z$ on $1/T$ is plotted. A logarithmic dependence of the relative adsorption coefficients on temperature was also observed in other works (2,8) and is consistent with the view that treats adsorption coefficients as equilibrium constants of the adsorption process. From

* Calculation of the relative adsorption coefficients by the exact method (7) shows that, in the cases studied by us, the approximate formula (3) makes it possible to calculate these quantities with satisfactory accuracy.

Fig. 1. Dependence of the logarithm of the relative adsorption coefficients of acetone and hydrogen on reciprocal temperature on a Ni catalyst

Figure 1: Fig. 1. Dependence of the logarithm of the relative adsorption coefficients of acetone and hydrogen on reciprocal temperature on a Ni catalyst

the data obtained, the differences between the heats of adsorption of hydrogen, acetone, and isopropyl alcohol were calculated from the formula:

$$\lambda_{\text{prod}} - \lambda_{\text{sp}} = -\frac{4.57\,(\lg z''/z')}{1/T_1 - 1/T_2}. \tag{4}$$

The values obtained were: $\lambda_{\text{ac}} - \lambda_{\text{sp}} = 3.7$ kcal/mole and $\lambda_{\text{H}_2} - \lambda_{\text{sp}} = 14.5$ kcal/mole. In the case of iron and cobalt, the heats of adsorption of the alcohol and the reaction products are equal or close to one another, as follows from the independence of the adsorption coefficients from temperature ([9,10]).

Fig. 1. Dependence of the logarithm of the relative adsorption coefficients of acetone and hydrogen on reciprocal temperature on a Ni catalyst

The adsorption coefficients were then used to calculate the reaction-rate constants at different temperatures. In order to determine the true activation energy of dehydrogenation, a series of experiments was carried out with each catalyst at different temperatures and constant space velocity. To calculate the rate constants, the values A_1, m, and $z_2 + z_3$ were substituted into formula (2). For the nickel catalyst

Table 3

Dehydrogenation of iso-C_3H_7OH on Fe; catalyst volume 5.6 ml; feed rate 0.15 ml/min; $A_1 = 45$ ml/min; $A_1' = 8.03$ ml/min per 1 ml catalyst; $z_2 + z_3 = 0.79$; $\varepsilon = 20\,000$ cal/mole; $k_0 = 7.08 \cdot 10^8$; $\varepsilon/\lg k_0 = 2.26 \cdot 10^3$

Experiment No.	Temp., °C	V_{H_2}, ml/min	m_{H_2}, ml/min per 1 ml catalyst	k	k_{calc}
3	200	2.28	0.407	0.409	0.403
7	200	2.24	0.400	0.406	0.403
5	210	3.31	0.592	0.606	0.630
2	220	5.32	0.950	1.004	0.966
1	227	6.66	1.19	1.27	1.26
4	232	7.64	1.36	1.47	1.55
6	235	9.03	1.61	1.76	1.78

Table 4

Dehydrogenation of iso-C_3H_7OH on Co; catalyst volume 7 ml; feed rate 0.15 ml/min; $A_1 = 45$ ml/min; $A_1' = 6.43$ ml/min per 1 ml catalyst; $z_2 + z_3 = 1.49$; $\varepsilon = 12\,400$ cal/mole; $k_0 = 8.03 \cdot 10^5$; $\varepsilon / \lg k_0 = 2.1 \cdot 10^3$

Experiment No.	Temp., °C	V_{H_2}, ml/min	m_{H_2}, ml/min per 1 ml catalyst	k	k_{calc}
5	183	5.80	0.828	0.943	0.890
7	189	6.25	0.894	1.00	1.05
8	194	7.33	1.05	1.20	1.21
6	198	8.67	1.24	1.44	1.38
2	199	8.90	1.27	1.49	1.42
3	210	11.20	1.60	1.96	1.88
1	211	10.96	1.57	1.92	1.95
4	218	13.20	1.89	2.33	2.42

the value $z_2 + z_3$ at the required temperature was found by interpolation of the straight lines of the logarithmic dependence (Fig. 1). The results obtained are given in Tables 3–5 and in Fig. 2. The linear dependence of $\lg k$ on $1/T$ is in agreement with the Arrhenius equation, which confirms the validity of equation (2). The true activation energy of alcohol dehydrogenation on Fe and Co was determined for the first time. In work (^{2}), for the dehydrogenation of butanol-2 over a nickel-on-quartz catalyst, $\varepsilon = 9.9$ kcal/mole was obtained, i.e., only slightly higher than here.

As the data show, the activation energy of dehydrogenation on the metals we studied decreases from iron to nickel. The activity of catalysts of transition metals of the fourth period increases with an increase in the atomic number of the metal and with a decrease in the interatomic distance.

Fig. 2. Dependence of the logarithm of the dehydrogenation rate constants on reciprocal temperature: *a*—on iron, *b*—on cobalt, *c*—on nickel

Table 5

Dehydrogenation of *iso*-C_3H_7OH on Ni; catalyst volume 0.5 ml; feed rate 0.15 ml/min; $A_1 = 45$ ml/min; $A_1' = 90$ ml/min per 1 ml catalyst; $\varepsilon = 8900$ cal/mol, $k_0 = 3.67 \cdot 10^5$; $\varepsilon / \lg k_0 = 1.6 \cdot 10^3$

Experiment no.	Temp., °C	V_{H_2}, ml/min	mH_2, ml/min per 1 ml catalyst	$z_k + z_s$	k	k_{calc}
1	185	8.8	17.6	1.54	20.54	20.65
2	196	12.0	24.0	1.32	29.20	26.10

Experiment no.	Temp., °C	V_{H_2}, ml/min	mH_2, ml/min per 1 ml catalyst	$z_k + z_s$	k	k_{calc}
3	175	7.0	14.0	1.78	16.33	16.60
4	186	9.0	18.0	1.46	21.13	21.13
5	211	14.6	29.2	1.09	35.67	34.70
6	168	6.0	12.0	2.08	13.82	14.10
7	156	4.9	9.8	2.71	10.35	10.40
8	206	13.8	27.6	1.14	33.63	31.30

The new results obtained in the present work are important for elucidating the dependence of the catalytic activity of elements on their position in Mendeleev's periodic system.

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