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Academician A. A. BALANDIN and P. TETENI

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Abstract

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KINETICS OF THE DEHYDROGENATION OF ALCOHOLS OVER A PRECIPITATED COPPER CATALYST

The kinetics of the dehydrogenation of alcohols of various structures over copper was studied in the authors' works ($^{1-7}$). In these works it was shown that the rate and activation energy of alcohol dehydrogenation do not depend (^{1,2}), or depend only slightly (^{4,5}), on their structure. It was also established (^{7}) that the adsorption coefficients of ethyl, *n*-propyl, and isopropyl alcohols on a copper catalyst are identical.

In the present work, the kinetics of the dehydrogenation of alcohols differing considerably in structure was investigated: ethyl alcohol, isopropyl alcohol, benzyl alcohol, and cyclohexanol. In addition to determining the activation energy of these alcohols, such work is also of interest from the standpoint of studying the adsorption of different alcohols on this catalyst.

In contrast to earlier works, in the present work a copper catalyst was used that was prepared by precipitating copper hydroxide with ammonia from a 20% solution of copper nitrate. The copper hydroxide was decomposed in a stream of air at 400°, and the copper oxide obtained was reduced with electrolytic hydrogen at 150, 200, 250, and 300°, for 6 hours at each temperature. After each experiment the catalyst was regenerated with hydrogen. The substances used had physical constants coinciding with the data in the literature. The hydrogen required for preparing the mixtures used in determining adsorption coefficients was obtained by electrolysis of a 20% KOH solution, purified from traces of oxygen by passing over copper at 380–400°, and dried over $CaCl_2$. The experiments were carried out in the usual flow apparatus used in the laboratory of organic catalysis of Moscow State University. The feed of the initial substances was effected automatically from a syringe with an electric motor (feed accuracy ±0.005 ml/min). Collection and measurement of the volume of gas evolved as a result of the reaction were carried out with an automatic gas meter of the Patrikeev system. It was established that, in the temperature range studied (180–280°), for all four alcohols mentioned the catalyst investigated effected exclusively dehydrogenation. The gas formed was pure hydrogen (the purity of the gas was checked by gas analysis). The catalyzate contained unreacted alcohol and the corresponding aldehyde or ketone, as shown by distillation of the catalyzate. Experiments with catalyst grains of different sizes show that the investigations were carried out in the kinetic region.

As was proved in (^{8,9}), the dehydrogenation of alcohols obeys the general kinetic equation for monomolecular catalytic reactions in a flow system, derived by one of the authors (^{10}). In the case of 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 rate of feed of alcohol; m is the rate of hydrogen evolution; for the remaining notation see (^{8}).

Hence, after integration 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 definite amount of the reaction product or of a foreign substance was added to the initial substance. The magnitude of the decrease in the reaction rate indicates to what extent the added substance is adsorbed on the active sites of the catalyst.

The value of the adsorption coefficient z was calculated from the formula [11]

$$z = [B_1(2H - Y) - YH]/[(1 - B_1)Y], \tag{3}$$

where

$$B_1 = A_1/\Sigma A_r; \qquad Y = m/\Sigma A_r; \qquad H = Y/2 - Y^*.$$

We note that the values of the adsorption coefficients calculated from (3) do not differ greatly from the values obtained by applying the simpler formula [12], derived for lower degrees of conversion:

$$z = \left(\frac{m_0}{m} - 1\right) \Big/ \left(\frac{100}{p} - 1\right), \tag{4}$$

where p is the percent of alcohol in the mixture; m_0 is the value of m for pure alcohol.

The relative adsorption coefficients were determined from the rate of dehydrogenation of binary mixtures of reaction products with the initial alcohol. In this case the volumetric rate of alcohol in the experiment with the pure substance was equal to the total volumetric rate of alcohol and 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. The independence of the relative adsorption coefficients from the volumetric feed rate was verified. Tables 1 and 2 give the results of the determination of the adsorption coefficients. The adsorption-displacement curves had a form analogous to those observed earlier for other substances [12].

Table 1

Relative adsorption coefficients z_2 (ratio of the adsorption coefficients of aldehydes and ketones to the adsorption coefficients of the corresponding alcohols).
Precipitated copper catalyst

Substance	Temp., °C	z_2
CH_3CHO/C_2H_5OH	250	0.68 ± 0.03
CH_3CHO/C_2H_5OH	275	0.67 ± 0.005
$(CH_3)_2CO/i\text{-}C_3H_7OH$	189	0.64 ± 0.01
$(CH_3)_2CO/i\text{-}C_3H_7OH$	212	0.57 ± 0.01
$(CH_3)_2CO/i\text{-}C_3H_7OH$	230	0.64 ± 0.03
$C_6H_5CHO/C_6H_5CH_2OH$	244	1.33 ± 0.07
$C_6H_5CHO/C_6H_5CH_2OH$	269	1.34 ± 0.06
$C_6H_{10}O/C_6H_{11}OH$	212	1.23 ± 0.07
$C_6H_{10}O/C_6H_{11}OH$	238	1.24 ± 0.02
$C_6H_{10}O/C_6H_{11}OH$	244	1.16 ± 0.08
$C_6H_{10}O/C_6H_{11}OH$	250	1.16 ± 0.02

Table 2

Relative adsorption coefficients z_3 (ratio of the adsorption coefficient to the adsorption coefficients of various alcohols).
Precipitated copper catalyst

Alcohol	Temp., °C	$z_3 = \alpha_{H2}/\alpha_{sp}$
C_2H_5OH	223	0.55 ± 0.04
C_2H_5OH	239	0.50 ± 0.03
C_2H_5OH	266	0.56 ± 0.05
$i\text{-}C_3H_7OH$	189	0.30 ± 0.01
$i\text{-}C_3H_7OH$	212	0.30 ± 0.02
$i\text{-}C_3H_7OH$	216	0.38 ± 0.04
$i\text{-}C_3H_7OH$	230	0.37 ± 0.02
$C_6H_5CH_2OH$	235	0.52 ± 0.03
$C_6H_5CH_2OH$	265	0.54 ± 0.02

Alcohol	Temp., °C	$z_3 = \alpha_{H2}/\alpha_{sp}$
$C_6H_{11}OH$	212	0.52 ± 0.03
$C_6H_{11}OH$	238	0.48 ± 0.03

The obtained values of the relative adsorption coefficients of acetaldehyde and hydrogen differ from the values obtained in earlier works [3,6] and close, respectively, to unity and zero. However, the catalyst used in the cited works was obtained by calcina-

* Y in the expression for H denotes the depth of conversion in the experiment with the pure substance.

by the treatment of copper nitrate and reduction of the resulting copper oxide with hydrogen. On the other hand, the independence of the relative adsorption coefficients from temperature established in previous work (in the case of

Fig. 1. Dependence of the logarithm of the reaction-rate constant on reciprocal temperature in the dehydrogenation of alcohols:
a—ethyl alcohol, *b*—isopropyl alcohol, *v*—benzyl alcohol, *g*—cyclohexanol

a copper catalyst) is confirmed by our experiments. The relative adsorption coefficients of acetone were found to be close to the values calculated by us from the data of work ([2]) and equal to 0.77 ± 0.02. The remaining adsorption coefficients on copper were not determined in other works.

Table 3

Dehydrogenation of C_2H_5OH on Cu. Catalyst volume 4 ml; feed rate 0.126 ml/min; $A_1 = 11.25$ ml/min · ml catalyst; $z_2 + z_3 = 1.21$; $\varepsilon = 12800$ cal/mol; $k_0 = 6.65 \cdot 10^5$; $\varepsilon / \lg k_0 = 2.2 \cdot 10^3$

Experiment No.	Temp., °C	V_{H_2}, ml/min	m_{H_2}, ml/min · ml cat.	k	$k_{\text{calc. at } \varepsilon=12800 \text{ cal/mol}}$
6	217	4.40	1.10	1.18	1.22
7	222	5.23	1.31	1.44	1.50
2	231	6.36	1.59	1.79	1.77
3	240	7.87	1.97	1.23	1.97
1	247	9.37	2.34	2.67	2.67
5	247	9.14	2.28	2.58	2.67
4	256	11.00	2.75	3.23	3.28

Table 4

Dehydrogenation of isopropyl alcohol on Cu. Catalyst volume 4 ml; feed rate 0.164 ml/min;

$A_1 = 12.07$ ml/min · ml cat.; $z_2 + z_3 = 0.96$; $\varepsilon = 10700$ cal/mol; $k_0 = 1.89 \cdot 10^5$, $\varepsilon/\lg k_0 = 2.03 \cdot 10^3$

Experiment No.	Temp., °C	V_{H_2}, ml/min	V_{H_2}, ml/min · ml cat.	k	$k_{\text{calc. at } \varepsilon=10700 \text{ cal/mol}}$
6	191	6.20	1.55	1.66	1.55
3	200	7.93	1.98	2.17	1.99
1	210	9.48	2.37	2.64	1.61
5	215	10.73	2.68	3.07	2.91
2	223	11.67	2.92	3.34	3.34
4	232	14.77	3.69	3.97	4.16
7	242	17.17	4.29	5.28	5.22

As is evident from Table 2, the relative adsorption coefficients of hydrogen do not depend on temperature. It follows from this ([13], [14]) that the heats of adsorption of the corresponding alcohols are equal to the heat of adsorption of hydrogen and, consequently, are equal to one another. As is known from the literature ([15], [16]), the heats of condensation of the alcohols studied by us differ rather substantially, within the range from 9.3 kcal/mol for ethyl alcohol to 12.06 kcal/mol for benzyl alcohol. The heats of physical adsorption of the alcohols studied by us, in the case of their physical adsorption on the catalyst, should have differed, since the heats of physical ad-

sorption are usually close to the heats of condensation. The equality of the heats of adsorption of these alcohols on the catalytically active surface indicates the participation of chemical forces in the process of adsorption of the alcohols during catalysis.

Determination of the relative adsorption coefficients of the dehydrogenation products made it possible to determine the true activation energies of dehydrogenation of the alcohols studied by us. To determine the rate constants, the corresponding adsorption coefficients from Tables 1 and 2, as well as the values of m (determined at various temperatures) and A_1, were substituted into equation (2). The results obtained are given in Tables 3, 4, 5, and 6 and in Fig. 1. The true activation energies of dehydrogenation

Table 5

Dehydrogenation of benzyl alcohol on Cu. Catalyst volume 4 ml; feed rate 0.21 ml/min; $A_1 = 11.37$ ml/min · ml cat.; $z_2 + z_3 = 1.87$; $\varepsilon = 12300$ cal/mol; $k_0 = 2.92 \cdot 10^5$; $\varepsilon/\lg k_0 = 2.25 \cdot 10^3$

No. of experiment	Temp., °C	V_{H2} ml/min	m_{H2} ml/min · ml cat.	k	k calculated at $\varepsilon = 12300$ cal/mol
6	229	4.60	1.15	1.27	1.27
1	230	4.43	1.11	1.24	1.33
3	242	6.30	1.58	1.79	1.73
4	252	7.36	1.84	2.17	2.17
5	262	9.24	2.32	2.83	2.70
4	274	10.90	2.73	3.43	3.42

Table 6

Dehydrogenation of cyclohexanol on Cu. Catalyst volume 4 ml; feed rate 0.21 ml/min; $A_1 = 11.12$ ml/min · ml cat.; $z_2 + z_3 = 1.70$; $\varepsilon = 11100$ cal/mol; $k_0 = 3.34 \cdot 10^5$; $\varepsilon / \lg k_0 = 2.01 \cdot 10^3$

No. of experiment	Temp., °C	V_{H2} ml/min	m_{H2} ml/min · ml cat.	k	k calculated at $\varepsilon = 11100$ cal/mol
4	196	7.66	1.92	2.25	2.24
7	198	7.44	1.86	2.19	2.26
3	209	10.17	2.55	3.03	3.03
5	214	10.87	2.72	3.40	3.39
1	224	13.23	3.31	4.32	4.19
6	231	14.03	3.51	4.72	5.00
2	236	16.10	4.02	5.72	5.58

of alcohols on this catalyst have been determined for the first time. In the earlier work (4), on a copper catalyst prepared by another method, the true activation energy of dehydrogenation of ethyl alcohol was determined, coinciding with the value found by us (12.8 kcal/mol).

The data obtained show that the structure of the hydrocarbon radical of the alcohol has little effect on the magnitude of the activation energy of dehydrogenation on this metallic copper catalyst. Even such radicals, different in their character, as phenyl and methyl in ethyl and benzyl alcohol, do not exert a significant influence. The insignificant influence of the hydrocarbon radical on the activation energy confirms the multiplet theory and is explained by the fact that the influence of the framework substituent is manifested almost equally (17) both on the magnitude of the bond between atoms within the molecule that is broken during the reaction and on the bonds of the atoms of the reacting molecule with the atoms of the catalyst.

Moscow State University
named after M. V. Lomonosov

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