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Abstract

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ON THE INFLUENCE OF THE NATURE OF METALS ON THEIR CATALYTIC ACTIVITY

According to A. A. Balandin' s multiplet theory (^{1}), a necessary condition for catalysis is a structural and energetic correspondence between the reacting chemical bonds in the substrate and the catalyst. From structural correspondence follows (^{2}) the principle of conservation of the valence angle, about which many authors have written (see, for example, (^{3})). This principle requires the existence of a regular relationship between catalytic activity, and consequently the activation energy, and interatomic distances in the case of catalysts constructed in the same way. The existence of such a relationship has been confirmed in a number of cases (Eckell (^{4}), Rubinstein (^{5}), Beeck (^{6})). On the other hand, electronic theories of catalysis (which in the USSR are being developed chiefly by S. Z. Roginskii (^{7}) and F. F. Vol' kenshtein (^{8})) require the existence of a relationship between catalytic activity and the electronic properties of a solid catalyst. Therefore some investigators compare the catalytic activity of a metal with the work function (^{9}), with the incompleteness of the *d*-shell (^{10,11}), with the *d*-character of the metallic bond (^{12,13}), and also with magnetic properties (^{14}).

Table 1

Comparison of the values of the activation energy of dehydrogenation of isopropyl alcohol with the physical properties of the metallic catalysts studied

	Fe	Co	Ni	Cu	Pd	Ag	Pt
Atomic number	26	27	28	29	46	47	78
ε, kcal/mol	20.0	12.4	8.9	10.7	18.0	19.5	17.2
Crystal structure	A2	A3	A1	A1	A1	A1	A1

	Fe	Co	Ni	Cu	Pd	Ag	Pt
Interatomic distance (17), Å	2.48	2.51	2.49	2.56	2.75	2.89	2.77
Work function (18), V	4.36	4.18	4.86	4.47	4.82	4.28	5.29
Content of electron *d*-vacancies	2.2	1.7	0.6	0.0	0.60	0.0	0.55
d-Character of the metallic bond, %	39.7	39.5	40.0	36.0		36.0	44.0
Heat of atomization, kcal/mol	99	102	101	81	110	65	122

The authors of the present work have studied in detail the kinetics of the dehydrogenation of alcohols over various metallic catalysts (15,16). For the theory of catalysis it is of interest to compare the activation energies obtained with quantities characterizing various properties of the metals used as catalysts. Such a comparison is made in Table 1 for the dehydrogenation of isopropyl alcohol. As was shown by a special investigation in the case of a copper catalyst (15), the kinetic constants characterizing the dehydrogenation of various alcohols depend little on the structure of the alcohol. This is an obvious consequence of the identical orientation of the alcohols. Consequently, the results of investigations of the kinetics of dehydrogenation of isopropyl alcohol may, with a high degree of probability, be extended also to other alcohols, so that the results of Table 1 have a sufficiently general character.

Consideration of Table 1 shows that, for metals having a crystal lattice with close

Fig. 1. Dependence of the activation energy of dehydrogenation of isopropyl alcohol on the smallest interatomic distance in the crystal lattice of the metal (A1 and A3 lattices)

Figure 1: Fig. 1. Dependence of the activation energy of dehydrogenation of isopropyl alcohol on the smallest interatomic distance in the crystal lattice of the metal (A1 and A3 lattices)

packing (face-centered A1 or hexagonal A3), a parallelism is observed between the activation energies and the interatomic distances. In the range investigated, as is seen from Fig. 1, with increasing distance between metal atoms d, the activation energy of alcohol dehydrogenation ε increases. This increase is linear, in contrast to the dependence of the activity (a, not ε) on d in works ($^{4-6}$), where a maximum is observed. The existence of a regular dependence between the activation energy and the interatomic distance is in agreement with the multiplet theory. Conversely, upon examination of Table 1 it turns out that separately taken electronic properties (including the work function and the percentage of d-character), as well as the heat of atomization, cannot explain the course of change in the value of the activation energy. In this case no direct parallelism is observed between individual electronic properties and the activation energy. However, this does not contradict the essence of the electronic theory of catalysis. It is clear that the structural and energetic factors are also based on the structure of matter from electrons and nuclei. However, to explain catalysis there is apparently required a rather complex combination of electronic properties, whereas in structural (and energetic) factors this combination often already exists in ready-made form.

Fig. 1. Dependence of the activation energy of dehydrogenation of isopropyl alcohol on the smallest interatomic distance in the crystal lattice of the metal (A1 and A3 lattices)

In the present work the kinetics of dehydrogenation of isopropyl alcohol on metallic silver, platinum, and palladium was studied experimentally. Platinum and palladium were obtained by reduction from chloroplatinic and chloropalladic acids with formalin according to N. D. Zelinskii. The silver catalyst was prepared by reduction with hydrogen of silver oxide obtained by precipitation from an aqueous solution of

Table 2

Relative adsorption coefficients of acetone (z_2)

Catalyst	T-ature, °C	$z_2 = a \ /a$
Ag	250	1.00 ± 0.03
Ag	267	0.98 ± 0.05
Ag	289	0.96 ± 0.05
Pt	235	0.30 ± 0.03

Fig. 2. Dependence of $\log m$ on $1/T$ for the dehydrogenation of isopropyl alcohol: a—on Ag, —on Pt, —on Pd

Figure 2: Fig. 2. Dependence of $\log m$ on $1/T$ for the dehydrogenation of isopropyl alcohol: a—on Ag, —on Pt, —on Pd

Catalyst	T-ature, °C	$z_2 = a\ /a$
Pt	248	0.32 ± 0.03
Pt	268	0.30 ± 0.06

Table 3

Relative adsorption coefficients of hydrogen (z_3)

Catalyst	T-ature, °C	$z_3 = a_{H2}/a$
Ag	257	0.47 ± 0.09
Ag	272	0.44 ± 0.05
Ag	287	0.47 ± 0.04
Pt	226	0.32 ± 0.04
Pt	244	0.42 ± 0.04
Pt	256	0.45 ± 0.05
Pt	272	0.54 ± 0.08
Pt	282	0.60 ± 0.01

$AgNO_3$. The procedure for carrying out the kinetic measurements was described earlier ([10,11]). The calculation of the reaction rate constants k was carried out by the formula

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

obtained from the general kinetic equation derived by one of the authors ([19]) (here A_1 is the volumetric rate of passage of alcohol, m is the volume of hydrogen evolved in 1 min, in ml at N.T.P., z_2 and z_3 are relative

adsorption coefficients of acetone and hydrogen). To calculate the rate constants of the reaction, it was necessary to determine z_2 and z_3 for the reaction products, as is evident from formula (1). These quantities were determined by the reaction-kinetic method [20]. The determination procedure and calculation method are described in [15,16]. The data obtained are given in Tables 2 and 3.

Fig. 2. Dependence of $\log m$ on $1/T$ for the dehydrogenation of isopropyl alcohol: a—on Ag, —on Pt, —on Pd

In order to determine the activation energy of the dehydrogenation of isopropyl alcohol, separate series of experiments were carried out at various temperatures and at a constant volumetric flow rate. To calculate the values of k in formula (1), the values A_1, m, and $(z_2 + z_3)$ were substituted. For the platinum catalyst, z_3 increases with increasing temperature (see Table 3); therefore, the

Table 4

Dehydrogenation of iso-C_3H_7OH on Ag
(catalyst volume 10 ml; flow rate 0.16 ml/min; $A_1 = 47.4$ ml/min; $A_1' = 4.74$ ml/min per 1 ml catalyst; $z_2 + z_3 = 1.44$; $\varepsilon = 19500$ cal/mol; $k_0 = 2.31 \cdot 10^8$; $\varepsilon/\lg k_0 = 2.27 \cdot 10^3$)

Experiment No.	Temp., °C	H_2, ml/min	m_{H_2}, ml/min per 1 ml catalyst	k	k_{calc}
1	228	1.14	0.114	0.123	0.119
7	232	1.22	0.122	0.125	0.140
3	236	1.85	0.185	0.190	0.164
6	244	2.08	0.208	0.223	0.226
2	254	3.30	0.330	0.341	0.327
4	270	4.93	0.493	0.536	0.555
5	287	8.80	0.880	1.010	0.920

Table 5

Dehydrogenation of iso-C_3H_7OH on Pt
(catalyst volume 1 ml; flow rate 0.16 ml/min; $A_1 = 47.4$ ml/min, $A_1' = 47.4$ ml/min per 1 ml catalyst; $\varepsilon = 17200$ cal/mol; $k_0 = 7.36 \cdot 10^7$; $\varepsilon/\lg k_0 = 2.12 \cdot 10^3$)

Experiment No.	Temp., °C	m_{H_2}, ml/min per 1 ml catalyst	$z_2 + z_3$	k	k_{calc}
1	206	1.62	0.56	1.63	1.75
6	210	2.12	0.58	2.16	2.08
7	219	2.76	0.61	2.88	2.86
5	225	3.20	0.64	3.26	3.52
4	230	3.90	0.66	4.07	4.24
3	231	4.23	0.66	4.39	4.24
2	245	6.92	0.72	7.28	6.56
8	245	5.85	0.72	6.12	6.56

value of z_3 for the required temperature was found by interpolation from the plot of $\lg z_3$ versus $1/T$. The true activation energy of the re-

Table 6

Dehydrogenation of iso-C_3H_7OH on Pd (catalyst volume 1 ml, flow rate 0.15 ml/min; $A_1 = 45.0$ ml/min; $A'_1 = 45.0$ ml/min per 1 ml catalyst;
$\varepsilon = 18000$ cal/mol)

Experiment No.	Temp., °C	m_{H_2}, ml/min per 1 ml catalyst	Experiment No.	Temp., °C	m_{H_2}, ml/min per 1 ml catalyst
7	249	1.77	8	268	3.33
1	250	1.82	3	280	4.71
2	257	2.53	4	288	6.56
6	268	4.20	5	296	7.70

the reaction was determined for the dehydrogenation of isopropyl alcohol on silver and platinum, since for these catalysts the relative adsorption coefficients of the reaction products had been determined. For palladium, an approximate activation energy was determined, calculated from the tangent of the angle of inclination of the straight-line dependence of $\lg m$ on $1/T$. The values obtained are given in Tables 4-6 and Fig. 2. As is seen from Fig. 2, the points lie, with satisfactory accuracy, on Arrhenius straight lines. The activation energies found are placed in Table 1, as are the activation energies from works (15, 16).

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