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Next 3 Page(s) In Document Denied

MECHANISM OF OXIDATION OF METHYL ALCOHOL TO FORMALDEHYDE ON OXIDE CATALYSTS

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Abstract: In this paper a mechanism is proposed for the oxidation of methyl alcohol to formaldehyde on a Fe_2O_3-MoO_3 catalyst. The oxidation process can be described by an oxidation-reduction mechanism. The rate of the oxidation of methyl alcohol at a temperature of 270°C is given by the expression:

$$r = \frac{k_1\, p_{Me}}{1 + 0.5(k_1/k_2)(p_{Me}/p_{O_2})}.$$

The ideas on the oxidation-reduction mechanism are confirmed in a later part of this paper by results of the investigations: a) by the rate of interaction between methyl alcohol and catalyst without participation of oxygen in the gaseous phase, b) by the rate of interaction between oxygen and partially reduced catalyst without participation of methyl alcohol in the gaseous phase. The discussion presents a more detailed analysis of the ideas on the course of partial processes in catalytic oxidation of methyl alcohol with the participation of lattice oxygen of the catalyst. A comparison of the experimentally determined rate constants for the partial processes and for the oxidation shows that the suggested mechanism is of physical significance.

1. INTRODUCTION

The mechanism of oxidation of methyl alcohol to formaldehyde on oxide catalysts has so far not been dealt with in the literature [1,2]. There are neither experimental data nor theories as regards to the course of partial processes involved in this industrially important catalytic reaction. The experimental work of Peterson and Adkins [1] is only concerned with the study of a suitable composition of oxide catalysts on the basis of Fe_2O_3 and MoO_3 and with the verification of their catalytic activity in the oxidation of methyl alcohol. The authors arrived at the conclusion that the most suitable catalyst is a mixture containing both oxides in equimolecular amounts. The results of this work served as the basis for a number of patents [2] relating to the preparation of these catalysts. A property common to all Fe_2O_3-MoO_3 catalysts is their high activity at relatively low reaction temperatures of 200 - 330°C and their selectivity in the oxidation of methyl alcohol to formaldehyde.

The opinions of various authors [3,4] about the mechanism of catalytic oxidation differ. Some workers [5-8] prove on the basis of their experiments that the lattice oxygen of oxide catalysts participates in the catalytic process, while others [9-13] refute this idea.

Mars and Krevelen[14,15] have recently published interesting results of a study on the mechanism of oxidation of various organic compounds (benzene, naphthalene, anthracene) on vanadium pentoxide. They have proposed a kinetic equation for a two-stage oxidation-reduction mechanism on the basis of an analysis of data on the over-all oxidation rate, but without presenting any further proof to support this mechanism.

In view of the existence of such divergent opinions as regards the mechanism of catalytic oxidation processes it was interesting to study in detail the mechanism of another oxidation reaction, namely the oxidation of methyl alcohol to formaldehyde on a mixed MoO_3-Fe_2O_3 catalyst, in order to obtain some experimental proofs and ideas concerning the mechanism of oxidation-reduction processes involved in the oxidation of methyl alcohol.

2. EXPERIMENTAL

2.1. *Starting materials*

For all our measurements we employed a catalyst containing 17.5% by weight of Fe_2O_3 and 82.5% by weight of MoO_3. The grain size of the catalyst was in the range from 0.3 to 0.6 mm. The bulk weight of the catalyst amounted to 1.02 g/ml. The surface area of the catalyst, as determined by the BET method from the adsorption of krypton at 76°K, for the surface of the krypton molecule of 21 $Å^2$, was 6.9 m^2/g. The mean radius of the pores of the catalyst, determined by means of a high-pressure mercuryporometer, was 950 Å. The pore volume in the range of radii of 100 - 3.5 $\times 10^6$ Å amounted to 0.39 ml/g.

The methyl alcohol was of p.a. purity, refractive index $n_D^{20°}$ = 1.3295, vapour tension at 20°C 98.0 mm Hg. Its water content was 2.5 $\times 10^{-3}$ % by weight.

2.2. *Measurement of oxidation rate*

The rate of catalytic oxidation of methyl alcohol to formaldehyde was measured in a throughflow integral reactor at atmospheric pressure. The accuracy of dosing the individual substances (CH_3OH, N_2, O_2), expressed by the standard deviation, was 3% of the respective value.

By preliminary experiments and calculations we found that the rate of oxidation of methyl alcohol on the catalyst is neither influenced by internal nor by external diffusion. The temperature gradient between the main gas stream and the surface of the catalyst was likewise negligible. The formaldehyde content in the reaction products after absorption in water was determined titrimetrically by means of sodium bisulphite. The content of by-products (CO, CO_2, CH_4) was estimated chromatographically [16]. Under experimental conditions of kinetic measurements, no oxidation by-products of the reaction were found.

2.3. *Measurement of the rate of oxidation-reduction processes*

The rate of interaction of methyl alcohol and catalyst without participation of oxygen in the gaseous phase and the interaction of oxygen and partially
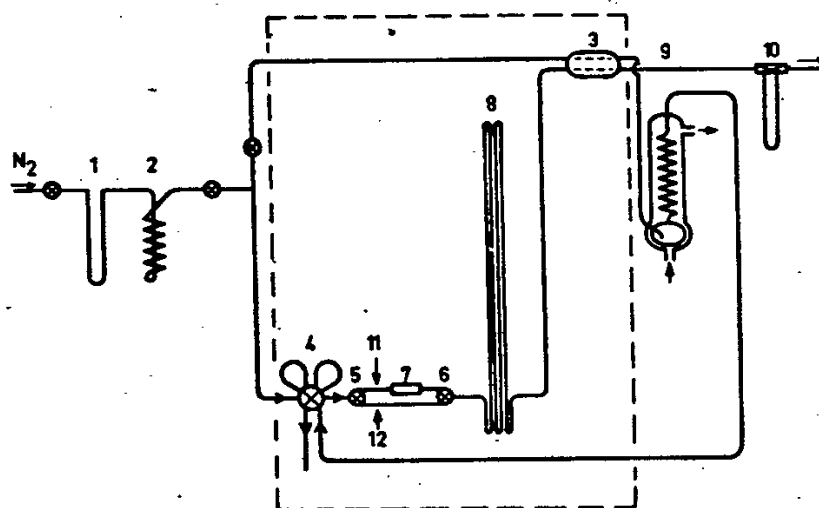
Fig. 1. Microcatalytic chromatographic pulse apparatus.

1. Copper wire heated to 300°C.
2. Freezing trap (-76°C).
3. Heat conductivity cells.
4. Dosing cock with free volumes of 5.2 and 8.4 ml.
5,6. Two-way cocks.
7. Microcatalytic reactor.
8. Chromatographic column.
9. Temperature-controlled methyl alcohol saturator.
10. Flow meter.
11,12. Seals of silicone rubber for dosing with a syringe.

reduced catalyst without participation of methyl alcohol in the gaseous phase were investigated by means of a microcatalytic chromatographic pulse method [17], adjusted to our experiments. The diagram of the apparatus is presented in fig. 1. The carrier gas, nitrogen, was freed from traces of oxygen on copper wire at 300°C in the reactor 1 (O_2 content < 0.01% by weight) and from traces of water by freezing trap 2, cooled to -76°C. An appropriate volume of methyl alcohol vapour in nitrogen, prepared in saturator 9 at a controlled temperature, was introduced into the carrier gas by means of eight-way dosing cock 4, equipped with two constant volumes of 5.2 and 8.4 ml respectively. The volume of the mixture was displaced from the dosing cock into reactor 7 at the velocity of the carrier gas.

The time for the passage of each dose of reactants through the catalyst bed was determined by the total volume of the dosed gas mixture, the free volume of the catalyst bed and the velocity of the carrier gas. The time for the passage of one dose DF volume 5.2 ml of the dosing cock was always 5.43×10^{-3} hours and for volume of 8.4 ml was 8.83×10^{-3} hours. In this arrangement and with successive dosing it was possible to ascertain the composition of the product as a function of the over-all time of the passage (i.e. time of passage of one dose multiplied by the total number of doses) of the reactants (CH_3OH or O_2) of constant composition through the catalyst bed. The over-all time of the passage could be set according to the number of individual doses. In each experiment methyl alcohol was introduced first and then oxygen in the way described.

The scattering of chromatographic analysis was in the range of ± 10% of the measured concentration.

2.4. *Sorption measurement*

The interaction between methyl alcohol or oxygen and catalyst was also investigated in a static sorption apparatus with a McLeod manometer in the usual arrangement. The accuracy of measurement of volume variations was in the range of $\pm 4\%$ of the mean value of the volume measured. A sorption vessel of quartz with a sample of the catalyst was fitted with two gold electrodes for measuring the changes of electrical conductivity at an alternating voltage of a frequency of 1 mc/sec.

The content of H_2O, CO and CO_2 in the mixture of reaction products after complete oxidation of methyl alcohol was determined from the pressure change in the apparatus brought about by freezing-out of the products into traps successively cooled by solid CO_2 and liquid N_2. The experimental arrangement did not permit us to ascertain changes in the concentrations of the individual components of the mixture with time.

3. RESULTS

The experimentally determined relationship between the conversion x and the value W/F in the integral reactor for an oxidation temperature of $270^{\circ}C$, range of methyl alcohol concentration in the feed of 1.5 - 7.5% by volume and oxygen concentration of 5 - 40% by volume is presented in figs. 2 and 3.
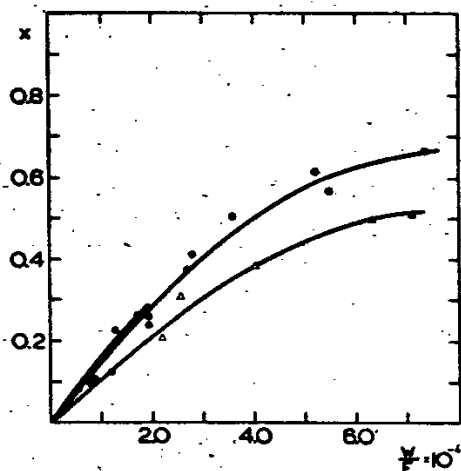

Fig. 2. Plot of conversion of methyl alcohol to formaldehyde versus time factor W/F at $270^{\circ}C$ for partial pressures of methyl alcohol and oxygen in the feed.

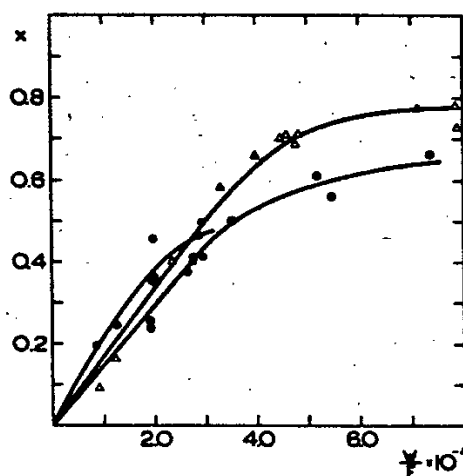|	$o^p Me$	$o^p O_2$
Δ	11.4	38.0
◐	34.2	38.0
●	57.0	38.0

Fig. 3. Plot of conversion of methyl alcohol to formaldehyde versus time factor W/F at $270^{\circ}C$ for partial pressures of methyl alcohol and oxygen in the feed.

	$o^p Me$	$o^p O_2$
◐	34.2	38.0
Δ	34.2	152.0
●	34.2	304.0

Table 1
Interaction of methanol or oxygen with 1 g of catalyst at 270°C.

Dose number	Dose of CH_3OH (μmol)	CH_2 formed (μmol)	Dose of O_2 (μmol)	O_2 consumed in regeneration (μmol)
1	620	200	-	-
2	-	-	224	82
3	620	210	-	-
4	-	-	224	75
5	620	210	-	-
6	-	-	224	92
7	620	215	-	-
8	620	38	-	-
9	620	36	-	-

The results of the investigations of the interaction between methyl alcohol and catalyst or between oxygen and partially reduced catalyst are given in table 1. The first part of this table (doses 1 - 7) shows the results of analyses of the products after alternating repetition of the oxidation cycle (odd dose numbers) and the regeneration cycle (even dose numbers). The second part presents the results obtained in successive dosing of methyl alcohol without re-oxidation of the catalyst (doses 7 - 9). Under the experimental conditions described, only very small amounts of oxidation by-products were formed: 5 - 10 μmols of CO + CO mixture and 3 - 5 μmols of methylal. In regeneration of the catalyst by oxygen, neither carbon-containing oxidation products nor water vapour were found in the carrier gas.

Fig. 4 presents the results of another series of experiments carried out in the microcatalytic reactor at a temperature of 270°C. These results are plotted in a coordinate system permitting determination of the rate constants of partial processes and of the amount of available lattice oxygen in the cat-
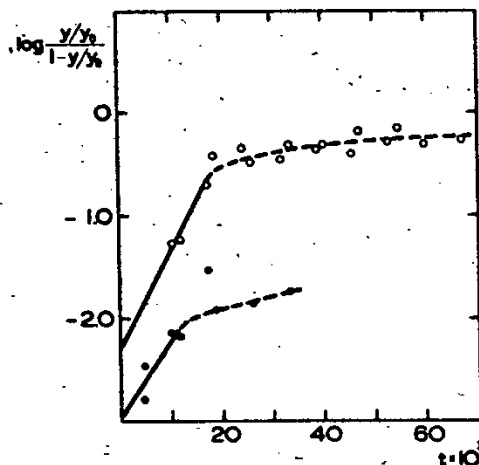

Fig. 4. Plot of $\log \dfrac{y/y_0}{1 - y/y_0}$ versus mean time of passage of methyl alcohol or oxygen through catalyst bed at 270°C.
$P = 1.222$ atm, $z = 0.9$ cm, $G = 3.84 \times 10^4$ μmol h^{-1}cm^{-2}.
● methyl alcohol, $y_0 = 0.666$.
○ oxygen, $y_0 = 0.209$.

alyst. On the y-axis is plotted a function containing the ratio of the mol fractions of methyl alcohol or oxygen in the reaction products and in the feed (y/y_0). On the x-axis is plotted the total mean time of the passage of methyl alcohol or oxygen through the catalyst bed.

Table 2
Results of measurement of the degree of reduction and re-oxidation of the catalyst in the static apparatus (weight 1.0 g of catalyst).

Dose of CH_3OH (μmol)	μmols formed			μmols bound
	$CH_3OH + H_2O$	CO_2	CO	O_2
88	120	50	21	68

Table 2 shows the results of analyses of the products after complete oxidation of a dose of 88.5 μmols of methyl alcohol in the static apparatus. The last column of table 2 contains the numbers of μmols of oxygen consumed in re-oxidation of the partially reduced catalyst. In the experiment, the initial value of the resistance of the sample, prior to its impregnation with methyl alcohol, changed from 0.90 MΩ to 0.50 MΩ after complete oxidation of the methyl alcohol. After re-oxidation of the catalyst by oxygen, the electric resistance of the catalyst sample rose again up to 1.1 MΩ

4. DISCUSSION

4.1. *Interpretation of kinetic data*

Both constituents of the mixed Fe_2O_3-MoO_3 catalyst may exist in a state of lower valency, as it is also the case e. g. with V_2O_5. During the catalytic oxidation of methyl alcohol we observed that the catalyst changes its initial yellowish-green colour into greyish blue. Both these circumstances induced us to interpret the results of kinetic measurements (figs. 2 and 3) for the time being only formally (as was also done by Mars and Krevelen [14, 15]) for the oxidation of other organic compounds on V_2O_5) on the basis of our postulate regarding the two-stage oxidation-reduction mechanism:

$$CH_3OH(g) + K_{ox} \xrightarrow{k_1} CH_2O(g) + H_2O(g) + K_{red} \qquad (1)$$

$$O_2(g) + K_{red} \xrightarrow{k_2} K_{ox} \qquad (2)$$
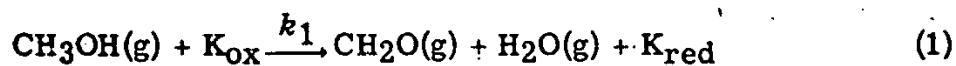
The equilibrium is in both stages shifted to the right sides of eq. (1) and (2), and it is possible, therefore, to consider in the kinetic equations only the reaction rates from left to right. The rate of the process (1) is given by the equation:

$$r_1 = k_1 p_{Me}^m \theta^p \qquad (3)$$

where

$$\theta = \frac{X}{X_0} .$$

The rate of the process (2) is defined by the equation:

$$r_2 = k_2 p_{O_2}^{n} (1 - \theta)^{q} . \tag{4}$$

On assumption that $p = q = 1$ and for steady state, when the rates of the both processes (1) and (2) are equal, it is possible to derive an expression for the oxidation of methyl alcohol:

$$r = \frac{k_1 p_{Me}^{m}}{1 + (\alpha k_1 p_{Me}^{m}/k_2 p_{O_2}^{n})} , \tag{5}$$

and an expression for the degree of reduction of the catalyst:

$$\theta = \frac{1}{1 + (\alpha k_1 p_{Me}^{m}/k_2 p_{O_2}^{n})} . \tag{6}$$

Eq. (5) can be integrated for the throughflow integral reactor. The last column of table 3 presents the kinetic equations in integral form for the exponents m and n. Treatment of the experimental data (figs. 2 - 4) by the method of least squares with the use of an automatic computer led to the most probable values of the rate constants of both partial processes (1) and (2); these values are given in table 3 for all combinations of reaction orders taken into consideration. Moreover, we calculated the standard deviation with which both constants k_1 and k_2 satisfy the given integrated kinetic integration. The standard deviation thus represents a certain criterion of the suitability of interpretation of experimental data. The least value of the standard deviation was found in the case of the rate constants for combinations of the order $m = 1$ and $n = 1$, or 0.5. In our further considerations we shall discuss, therefore, the simplest kinetic equation (5) and (6), which is of first order for both methyl alcohol and oxygen. The relatively good agreement between experimental data and the proposed kinetic equation ($s_1 = 9\%$, $s_2 = 12\%$) indicates that our assumption regarding the values of exponents p and q in eq. (3) and (4) is acceptable and that the rate of oxidation of methyl alcohol on the MoO_3-Fe_2O_3 catalyst can be described by means of the two-stage oxidation-reduction mechanism according to eq. (5).

The value of the constant k_2 is approximately half that of the constant k_1. This indicates that, as also in the oxidation of other organic compounds on V_2O_5 [14,15] a greater effect upon the rate of oxidation of methyl alcohol must be ascribed to the second partial step - regeneration (re-oxidations) of the catalyst.
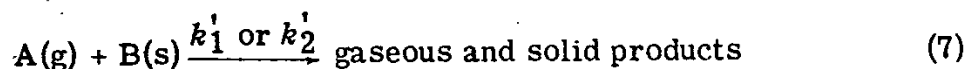
4.2. *Rates of partial processes in the oxidation of methyl alcohol and their physical significance*

The interpretation of the results obtained in the measurement of the over-all rate of oxidation of methyl alcohol to formaldehyde induced us to study in greater detail the rates of both partial processes (1) and (2). Either of them represents in principle, a reaction of similar type proceeding between the gaseous and the solid phase:

8

Table 3
Rate constants for catalytic oxidation of methanol on Fe_2O_3-MoO_3 catalyst at 270°C.

Reaction order m CH_3OH	n O_2	k_1	s_1 (%)	k_2	s_2 (%)	Integrated velocity equation
1	0.5	7.9×10^{-7} mol g^{-1} mm Hg^{-1} sec^{-1}	9	9.4×10^{-5} mol g^{-1} mm Hg$^{\frac{1}{2}}$ sec^{-1}	13	$\dfrac{W}{F}\dfrac{o^p \text{Me}}{\ln(1-x)} = -\dfrac{1}{k_1} + \dfrac{4\alpha}{k_2}\dfrac{o^p\text{Me}\,[o^pO_2 - (o^p\overset{\frac{1}{2}}{O}_2 - \frac{1}{2}o^p\text{Me}\,x)^{\frac{1}{2}}]}{\ln(1-x)}$
1	0	2.8×10^{-5} mol g^{-1} mm Hg^{-1} sec^{-1}	52	6.9×10^{-6} mol g^{-1} sec^{-1}	6	$\dfrac{W}{F}\dfrac{1}{x} = -\dfrac{1}{k_1}\dfrac{\ln(1-x)}{o^p\text{Me}\,x} + \dfrac{\alpha}{k_2}$
0.5	0	4.9×10^{-6} mol g^{-1} mm Hg$^{-\frac{1}{2}}$ sec^{-1}	38	1.4×10^{-5} mol g^{-1} sec^{-1}	48	$\dfrac{W}{F}\dfrac{1}{x} = \dfrac{2}{k_1}\dfrac{[1 - (1-x)^{\frac{1}{2}}]}{o^p\overset{\frac{1}{2}}{\text{Me}}\,x} + \dfrac{\alpha}{k_2}$
1	1	8.3×10^{-7} mol g^{-1} mm Hg^{-1} sec^{-1}	9	3.1×10^{-7} mol g^{-1} mm Hg^{-1} sec^{-1}	12	$\dfrac{W}{F}\dfrac{o^p\text{Me}}{\ln(1-x)} = -\dfrac{1}{k_1} + \dfrac{2\alpha}{k_2}\dfrac{\ln[o^pO_2/(o^pO_2 - \frac{1}{2}o^p\text{Me}\,x)]}{\ln(1-x)}$
0.5	0.5	4.4×10^{-6} mol g^{-1} mm Hg$^{-\frac{1}{2}}$ sec^{-1}	12	1.9×10^{-6} mol g^{-1} mm Hg$^{-\frac{1}{2}}$ sec^{-1}	16	$\dfrac{W}{F}\dfrac{o^p\overset{\frac{1}{2}}{\text{Me}}}{[1-(1-x)^{\frac{1}{2}}]} = \dfrac{2}{k_1} + \dfrac{4\alpha}{k_2}\dfrac{o^p\overset{\frac{1}{2}}{O}_2 - (o^pO_2 - \frac{1}{2}p\text{Me}\,x)^{\frac{1}{2}}}{o^p\overset{\frac{1}{2}}{\text{Me}}[1-(1-x)^{\frac{1}{2}}]}$

I. 2

$$A(g) + B(s) \xrightarrow{k_1' \text{ or } k_2'} \text{gaseous and solid products} \tag{7}$$

where $A(g)$ is either methyl alcohol or oxygen and $B(s)$ is the catalyst in oxidized or partially reduced form. The rate of the reaction (7) can be described by a kinetic equation similar to eq. (3) or (4):

$$r_i' = k_i' p_A X \quad \text{or} \quad r_i' = k_1' P_{y_A} X, \quad i = 1, 2 . \tag{8}$$

For the same reasons as in the preceding chapter, the rate of the reverse reaction has been neglected in eq. (8). From a comparison of eq. (8) and (3) or (4) follows that

$$\frac{k_1}{X_0} = k_1' \quad \text{or} \quad \frac{k_2}{X_0} = k_2' , \tag{9}$$

where X_0 represents the concentration of available lattice oxygen atoms or vacant places of the catalyst for the reaction (7). In formulating the velocity equation (8), we assumed that the available oxygen (i. e. a small fraction of the total amount of oxygen in the catalyst) or the vacant places are uniformly distributed in the surface layers of the catalyst and therefore equivalent in the reaction with a molecule from the gas phase.

The velocity equation (8) cannot be integrated in a simple way for each partial process, because not only the composition of the gas phase but also that of the solid phase changes during the reaction. It is not possible to attain for either of the partial processes (1) and (2) a steady state as in the case of the over-all catalytic rate of oxidation of methyl alcohol in the presence of gaseous oxygen molecules. For the integral reactor, where the gas molecules A continually pass through the bed of the solid B and react, it is possible to set up the material balance in an elementary volume of the bed for the substance A and thus formulate and solve the respective partial differential equations [18]. The solution of the differential equations leads to the determination of the relationship between the composition of the gas phase after its passage through the bed of the solid and time in the form

$$\frac{y}{y_0} = \frac{\exp(-k_i' PX_0 z/G) \cdot \exp(k_i' P y_0 t)}{1 + \exp(-k_i' PX_0 z/G) \cdot [\exp(k_i' P y_0 t) - 1]} \tag{10}$$

For constant values P, z, G and y_0 it is possible, after substitution of the values C_1 and C_2 for both exponential expressions, to write eq. (10) in the linear form

$$\log \frac{y/y_0}{1 - y/y_0} = \log \frac{C_1}{1 - C_1} + t \log C_2 . \tag{11}$$

Plotting of the experimentally determined values $\log[(y/y_0)/(1-y/y_0)]$ against time, i. e. mean time of the passage of the substance A through the catalyst bed, leads to a linear relationship. From the slope and the section it is possible to calculate the values k_1' or k_2' and X_0.

In fig. 4, the experimentally ascertained relationships were plotted for the first stage (1) without participation of oxygen from the gas phase in the reactio, and for the second stage (2) without participation of methyl alcohol from the gas phase. From the first, linear part of the graph, which holds for the considered model of the reaction, we calculated the rate constants $k_1 = 1 \times 10^{-7}$ molg^{-1}mmHg^{-1}sec^{-1}, $k_2 = 0.6 \times 10^{-7}$ molg^{-1}mmHg^{-1}sec^{-1}, $(X_0)_1 = 1200$ μmol/ml or μmol/g, and $(X_0)_2 = 200$ μmol/ml or μmol/g.

The values of the partial rate constants and their ratio agree in order of magnitude with the values of the constants determined from the over-all rate of oxidation of methyl alcohol (table 3, for $m = n = 1$). With regard to the complexity and insufficient accuracy of the chromatographic experimental method, this results must be regarded as a good agreement and a proof that the suggested equation and mechanism are a formal description of the partial oxidation-reduction processes in the oxidation of methyl alcohol on the Fe_2O_3-MoO_3 catalyst.

The values of $(X_0)_1$ and $(X_0)_2$ indicate that the amount of lattice oxygen available for the reaction is lower than would correspond to 3420 μmol/g of O_2 for reducing MoO_3 to MoO_2 and Fe_2O_3 to FeO in 1 g of catalyst. It is interesting that the value $(X_0)_1 = 1200$ μmol/g approaches the value 1150 μmol/g, which represents the amount of oxygen in 1 g of catalyst that had to be taken to form the oxide Mo_4O_{11} in the catalyst. The crystallographic structure and the conditions of Mo_4O_{11} formation have recently been determined by Kihlborg [19]. For a more accurate estimation of the number of lattice oxygen layers participating in the reaction one would require to know the crystallographic structure of the mixed catalyst.

If we consider that the catalyst surface of 6.9 m^2/g could take up approximately 70 μmol of physically adsorbed oxygen in a monomolecular layer at 76°K, it is probable that the number of lattice oxygen atoms in the catalyst surface will actually be considerably lower. For this reason it is also probable that several surface layers of lattice oxygen of the catalyst or certain lattice oxygen atoms in some crystallographic positions participate in partial oxidation-reduction processes. The non-rectilinear part of the curves in fig. 5 indicates that within a certain time, when the lattice oxygen available for the reaction is exhausted, the rate of the diffusion of lattice atoms into positions where they can further react becomes effective. For this region the derived relations are no more valid.

Another interesting fact (table 1) is that both partial processes (1) and (2) can be arbitrarily repeated in succession indefinitely without lowering the activity of the catalyst. This also offers the possibility of utilizing the suggested mechanism in practical oxidation reactions conducted in two cycles.

The assumption that lattice oxygen atoms in the surface participate in the oxidation process is also supported by the results given in table 2 for the static apparatus. From the oxygen balance after complete oxidation of methyl alcohol on 1 g of catalyst, without oxygen in the gas phase, follows that the oxidation of methyl alcohol consumed 77 μmol of lattice oxygen of the catalyst. In its regeneration, the catalyst recombined with 68 μmol of

oxygen. The decreasing electrical resistance in the oxidation of methyl alcohol indicates essential changes in the physical properties of the catalyst. The vacant places formed by the consumption of lattice oxygen atoms are likely to participate together with the remaining free electrons in the conduction of the current (both constituents of the catalyst, MoO_3 and Fe_2O_3 are n-semiconductors). The increase of the electrical resistance of the catalyst, after re-oxidation, to a value nearer the initial one confirms the good regenerative property of the catalyst. Under conditions of re-oxidation, the catalyst is converted into its original state.

LIST OF SYMBOLS

C_1	Function of $\exp\left(\dfrac{-k_i' PX_0 z}{G}\right)$	
C_2	Function of $\exp\left(k_i' P_{y_0}\right)$	
F	Feed rate of methanol	$mol\ sec^{-1}$
G	Over-all gas flow rate	$mol\ cm^{-2}\ h^{-1}$
K_{ox}	Catalyst in oxidized form	
K_{red}	Catalyst in reduced form	
P	Total pressure	atm
W	Weight of catalyst	g
X	Amount of available oxygen or vacant places in catalyst at time t	$\mu mol g^{-1}$, $\mu mol\ ml^{-1}$
T	Temperature	
k_1	Rate constant of oxidation of methanol by oxygen from catalyst K_{ox}	$mol g^{-1} mmHg^{-1} sec^{-1}$
k_2	Rate constant of oxidation of catalyst K_{red} by oxygen	$mol g^{-1} mmHg^{-1} sec^{-1}$
m	Reaction order with respect to methanol	
n	Reaction order with respect to oxygen	
p	Reaction order with respect to	
q	Reaction order with respect to	
p_{Me}	Partial pressure of methanol at time t	mmHg
$_0p_{Me}$	Partial pressure of methanol at time t_0	mmHg
p_{O_2}	Partial pressure of oxygen at time t	mmHg
$_0p_{O_2}$	Partial pressure of oxygen at time t_0	mmHg
p_{H_2O}	Partial pressure of water at time t	mmHg
r	Rate of oxidation of methanol	$mol g^{-1} sec^{-1}$
r_1	Rate of oxidation of methanol by oxygen from catalyst K_{ox}	$mol g^{-1} sec^{-1}$

$\dot{r}_2$	Rate of oxidation of catalyst K_{red} by oxygen	$mol g^{-1} sec^{-1}$
t	Reaction time	h
s	Standard deviation	
x	Conversion of methanol to formaldehyde, $= \dfrac{p_{Fd}}{\alpha p_{Me}\,\beta}$	
y	Mol fraction of methanol or oxygen in the gas stream at time t	
y_0	Mol fraction of methanol or oxygen in the gas stream at time t_0	
z	Distance through bed, from inlet	cm
α	Number of oxygen molecules required for converting one methanol molecule to formaldehyde, $= 0.5$	
β	Correction factor for volume change during reaction, $= \dfrac{100}{100 + \frac{1}{2}\,x_0 p_{Me}}$	
θ	$= \dfrac{X}{X_0}$	

SUBSCRIPTS

o	Boundary values
s	Solid state
g	Gas state
1	First step of the oxidation-reduction mechanism
2	Second step of the oxidation-reduction mechanism

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INVESTIGATION OF CATALYST POISONING AND HYDROCARBONS CONVERSION MECHANISM IN REFORMING PROCESS

Kh. M. MINACHEV and G. V. ISAGULYANTS

Abstract: The poisoning of reforming catalyst with sulfureous compounds and the mechanism of cycloparaffins conversion in the reforming conditions were investigated with use of S^{35} and C^{14}.

The data obtained permit to drow conclusion of establishment of an equilibrium between the sulfureous compound in gas phase and that on the surface. The conversion of thiophan or other sulfureous compound to hydrogen sulfide does not affect apparently the establishment of this equilibrium.

It can be regarded as dealing with a chemisorption using electron pairs of sulfur.

As to hydrocarbon conversion process the data obtained do not evidence in favour of cyclohexene as intermediate product by benzene and methylcyclopentane formation from cyclohexane. That does not agree with the usual view of the conversion of hydrocarbons on bifunctional catalysts.

The large application of reforming process in petroleum industry using platinum-alumina, palladium-alumina, catalysts makes it urgent to investigate the stability of such catalysts against poisoning by sulfur compounds and the mechanism of hydrocarbons' conversion in this process.

We have investigated the influence of sulfur compounds on activity and stability of a series of reforming catalysts in the process of cyclohexane conversion, as an example, under conditions close to industrial ones. The poisoning by thiophene added to cyclohexane has been studied in the most detailed way.

The experiments have been carried out in a flow system at temperature of 450°C and pressure of 20 atm. The space velocity of hydrocarbon was equal to 2 hours^{-1} at hydrogen to hydrocarbon mole ratio of 5.

The catalysts have been prepared by impregnating support pellets (4 × 4 mm) with chloroplatinic acid [1,2]. The addition of thiophene to the feed mixture has been shown to lower the benzene content in catalysate. This decrease occur at the initial one or two hours of work, then the benzene content in catalysate is kept at a constant level for a long time and is independent of the total amount of thiophene having been passed through the catalyst [1]. This level is dependent upon the thiophene concentration in feed mixture and upon the metal content in the catalyst. It is found that if pure cyclohexane is passed over a catalyst after the passing of cyclohexanethiophene mixture, the benzene content in catalysate increases quickly
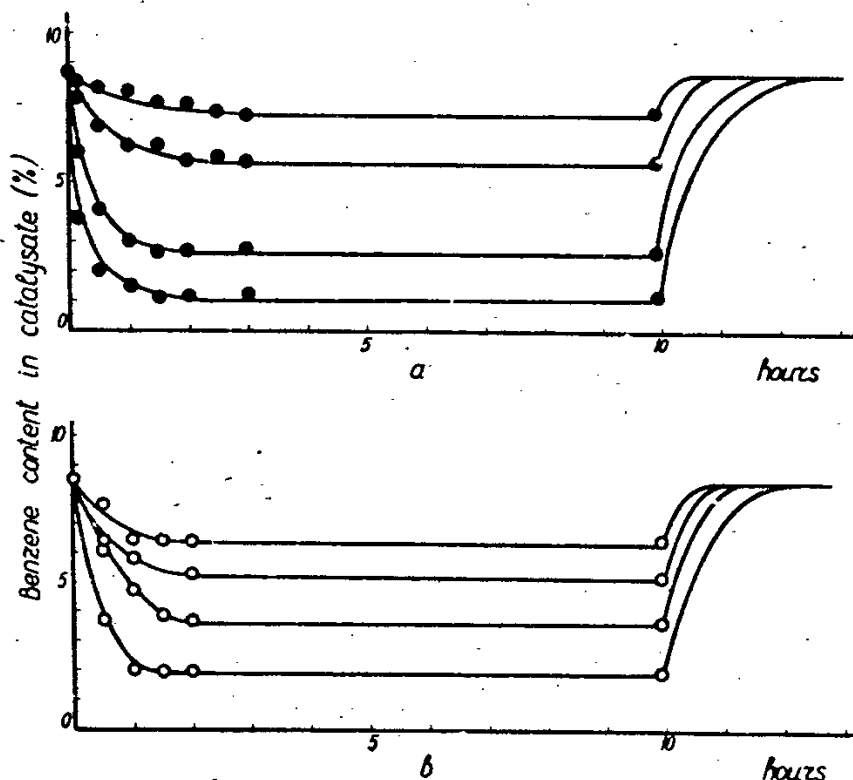
Fig. 1. Catalyst poisoning by thiophene during 10 hours and regeneration by pure cyclohexane.
  a) 5% Pt catalyst. 1 - 1% thiophene; 2 - 2% thiophene; 3 - 3% thiophene; 4 - 9% thiophene.
  b) 1% Pt catalyst. 1 - 0.3% thiophene: 2 - 0.79% thiophene; 3 - 2.1% thiophene; 4 - 6.24% thiophene; 5 - 9.33% thiophene.

(fig. 1) and reaches the value for a fresh, unpoisoned catalyst.

To investigate the cause of catalytic activity stabilisation the following should be determined: the sulfur amount deposited on the catalyst at different periods of poisoning, the dependence at this amount on the thiophene concentration in feed mixture etc. The runs using thiophene labeled with radioactive sulfur S^{35} were carried out [3,4] under above mentioned conditions. At predetermined time the samples of the catalyst were taken to determination of radiosulfur content. The regeneration of poisoned catalyst samples was carried out in a stream of pure cyclohexane. The radiosulfur content in the catalyst was determined also after the restoration of the initial activity.

Specimens for the measurement of radioactivity in the catalyst were prepared from a powder produced by thorough grinding a catalyst pellet in an agate mortar.

Radioactivity was measured by means of a thin mica endwindow counter with corrections made for self-absorption and S^{35} decay. The absolute sulfur content in the catalyst was found from comparison with the radioactivity of barium sulphate containing as it is well known 13.75% sulfur.

Catalysts samples containing 0.05-10% platinum were investigated using 98% cyclohexane - 2% thiophene mixture. The kinetics of sulfur deposition on 1% Pt catalyst is given in fig. 2, the sulfur amount in the catalyst after
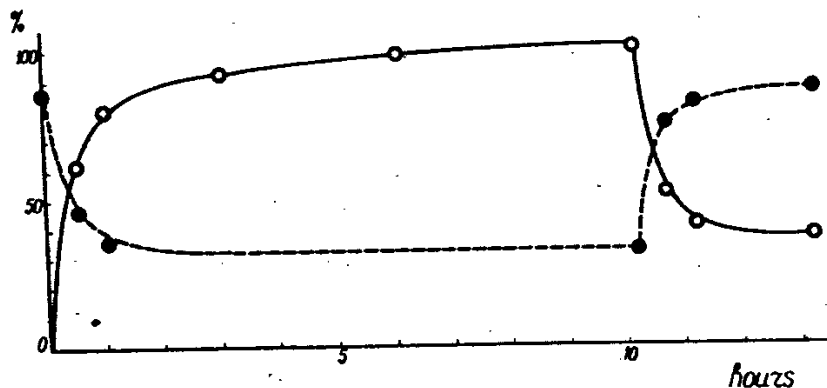
I. 10   3

Fig. 2. The ratio of sulfur amount deposited on 1% Pt catalyst to its
maximum value after 10 hours work, 1%; the removal of sul-
fur from catalyst when pure cyclohexane is passed. The ben-
zene content changes shown by dotted curve.

10 hours work (3.91 mg) being set equal to 100%. It is seen that 62.7, 80.6
and 92.3% sulfur deposit on the catalyst during 30 minutes, 1 hour, and
3 hours, respectively. The yield of benzene in products is shown by dotted
curve. It is interesting to be noted that the benzene yield falls with the in-
crease of the deposited sulfur amount.

Pure cyclohexane being passed through the catalyst, the fast process
of sulfur removal occurs, accompanied by restoration of dehydrogenation
activity. Nevertheless, the benzene yield attains the pre-poisoning value
after the removal of 70% sulfur. The further sulfur removal takes place
very slowly and is not accompanied by the activity change. The same re-
sult is obtained for 5% Pt catalyst. A penetration of sulfur into the catalyst's
bulk seems to occur in this case.

It is shown by special rund that sulfur is distributed through a catalyst
pellet with high extent of uniformity. The distribution of sulfur along the
catalyst's bed is also investigated. It is found that sulfur content decreases
in the direction from the front of the bed to its back. Sometimes this change
is about 25%.

The results obtained in investigation of the effect of platinum content in
the catalyst on the sulfur deposition are given in fig. 3. The runs were made
with cyclohexane containing 2% labeled thiophene. The sulfur amount in mg
is plotted versus the platinum content percentage. It is seen from these data
that as the platinum content changes from 0.05 to 10.0%, the amount of sul-
fur deposited on the catalyst increases continuously but not proportionally
to the metal content with a tendency to a limit value.

The dependence of catalyst's sulfur content on thiophene concentration
in cyclohexane was studied with 5% Pt catalyst. After the 10 hours work
catalysts were analysed for radiosulfur. The sulfur content in these cata-
lysts was 0.06-0.14 weight percent.

The plot of sulfur content versus the thiophene concentration in feed
mixture is given in fig. 4. The curve of fig. 4 is satisfactorily fitted by the
equation

$$A = \frac{\lambda P}{1 + \lambda P},$$ (1)
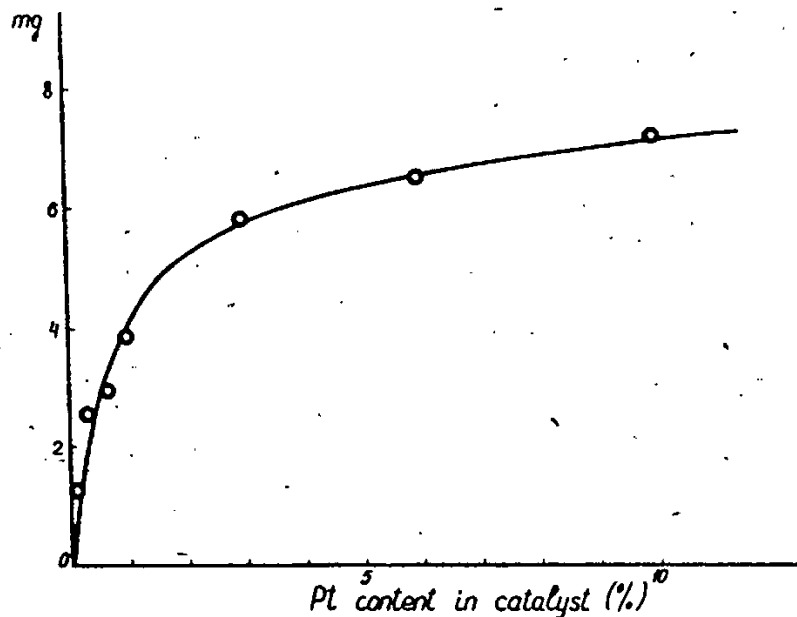
Fig. 3. Effect of metal content in catalyst on deposited sulfur
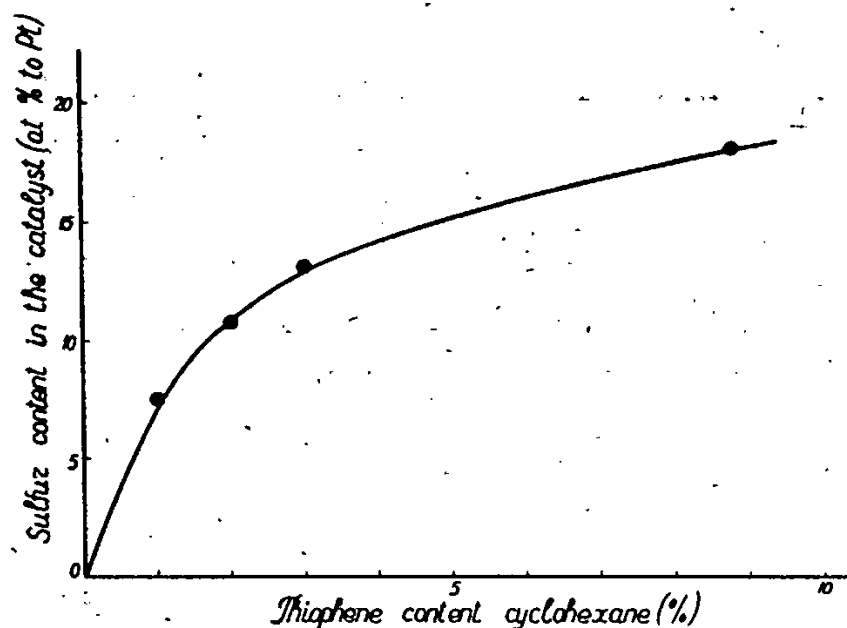amount (5) after 10 hours work with 2% thiophene.

Fig. 4. Effect of thiophene content in cyclohexane on sulfur
content in catalyst after 10 hours work.

where A is the sulphur amount, P is partial pressure of thiophene in cyclo-
hexane, λ is a constant. The Langmuir type dependence makes it possible
to state some suggestions regarding the poisoning mechanism which will be
dealt below.

It was found further that the benzene content in products varies linearly
with the sulfur amount in the catalyst (see fig. 5). Thus using eq. (1) the
benzene content may be determined.

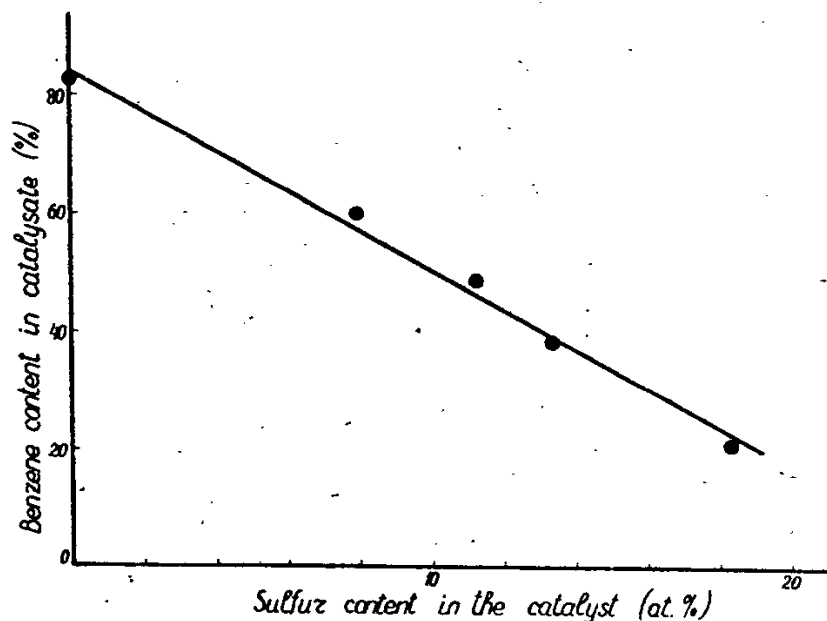When added to the feed mixture, thiophene and other sulfur compounds

Fig. 5. Benzene content in catalysate versus sulfur content in
the catalyst.

are known to convert readily into hydrogen sulfide, which contains the
main part of catalysate sulfur. It was found in our experiment that the sul-
fur compounds of different classes (thiophenol, diisoamylsulfide, thiophene,
ethylmercaptan, thiophane) produce almost the same poisoning action on the
catalyst. It suggests that the poisoning action is due to any product of sul-
fur compounds conversion which is common to various sulfur compounds.
This product may undergo hydrogenolysis resulting in removing sulfur from
the catalyst surface. The following facts oppose this standpoint.

   1. At small and middle thiophene contents in cyclohexane sulfur occurs
in products as hydrogen sulfide (less than 1% sulfur is detected as thiophene).
Thus only the front part of catalyst's bed is in contract with the feed sulfur
compound, that should result in much greater sulfur content in this part.
Nevertheless, as it was stated above, only a small decrease of sulfur con-
tent along the bed was observed, this being due probably to the decrease of
sulfur compound partial pressure as a result of dilution with hydrogen in
course of dehydrogenation. It can be readily illustrated by rough estimate.
The sulfur content in the seventh (last) layer of 6% Pt catalyst is equal to
76% as relative to the first layer at 2% thiophene in feed cyclohexane [4].
This content corresponds to the sulfur compound partial pressure of 0.066
atm. Under these conditions about 50% cyclohexane converts into benzene,
i.e., the hydrogen to hydrocarbon mole ratio becomes equal to 6.5. As a
consequence sulfur compound partial pressure falls to 0.05 atm. One can
find using the data of fig. 5 that as this partial pressure change takes place,
the sulphur content in catalyst falls to 81%.

   2. On the contrary, at high thiophene content in cyclohexane the cata-
lysates contain thiophene. It is not clear in this case why thiophene leaves
the catalyst's surface not being hydrogenolysed.

   These facts evidence in favour of establishment of an equilibrium be-

tween the sulfur compound in gas phase and that on the surface. The thiophene conversion with hydrogen sulfide as final product does not affect apparently the establishment of this equilibrium to any significant extent. This consideration is confirmed by the fact, that the sulfur content in catalyst is determined by the eq. (1). It may be regarded as dealing with a chemisorption using electron pairs of sulfur.

In this sense the constant λ should be considered as the adsorption coefficient. The observed fact of metal surface's uniformity with respect to sulfur appears to be interpreted as being due to high value of chemisorption heat. The developed consideration can be confirmed below as follows. As it was mentioned above, the benzene content in catalysates varies linearly with the sulfur content in the catalyst. If y denotes relative benzene content and x is sulfur content in the catalyst, then

$$y = ax + b .\tag{2}$$

It is evident that $b = 1$. If one expresses x as a fraction equal to the ratio of sulfur content to that leading to complete poisoning (when the whole of surface is blocked), one gets $a = -1$. Then from (1) and (2) the expression

$$y = \frac{1}{1 + \lambda P}\tag{3}$$

is obtained. It can be used for calculating benzene content in catalysates with various thiophene concentrations. For calculation we use the date obtained with 1 and 5% Pt catalysts.

Experimental [1,3] and calculated from eq. (3) values of y are given in table 1. The λ values are 21 and 11 atm^{-1} for the first and the second catalysts, respectively. The value is seen to vary as the platinum content changes. The calculations show that as the platinum percentage varies from 1 to 10 the λ value at first sharply falls then becoming constant. This course of λ appears to be an indirect result of surface heterogeneity.

Table 1

Benzene contents in catalysates (y) obtained experimentally and calculated in percent as relative to those with pure cyclohexane.

Catalyst	Thiophene content (%)								
	0.03	0.53	0.79	1.0	2.0	3	3.9	6.2	9
	y (%)								
1% Pt Obtained	98.9	76.1	66.2	55.4	31.4	–	28.6	19.7	–
Calculated	98	74	64	59	40.5	–	27	19	–
5% Pt Obtained	–	–	–	75.4	60	42.9	–	–	23.5
Calculated	–	–	–	76	59	48	–	–	24

Besides the dehydrogenation of hexamethyle rings, the mutual conversion processes of five- and six-membered rings are known to take place considerably under reforming conditions as a result of isomerisation. From

thermodynamical considerations the large yields of cyclohexane should not be expected in conditions used by us [5]. Benzene should be the main product, methylcyclopenthane yield must exceed that of cyclohexane considerably.

More detailed study of cyclohexane reforming was carried out [6] using 1% thiophene feed mixtures in presence of catalysts with various platinum content, catalysates being analysed by means of gas-liquid chromatographic column. The results are shown in table 2. It is seen from the table, that the benzene content in catalysates falls when thiophene is added, the methylcyclopentane content growing at the same time. The lower is the dehydrogenation activity of the catalyst, the greater is the methylcyclopentane content in catalysate. So addition of thiophene changes not only activity but also selectivity of the catalyst. It is interesting that with both pure cyclohexane and its thiophene mixtures a pressure increase from 20 to 60 atm results in a sharp growing of methylpentane content in catalysates, the benzene content being lowered at the same time.

The interesting data are obtained also with temperature variation. As thiophene content in feed cyclohexane increases from 1 to 3% at 450°C and 20 atm, methylpentane content in catalysates increases from 23.1 to 52.5% benzene content being lowered from 43 to 11.8%. The same antiparallel behaviour of methylcyclopentane and benzene is observed also at 500°C. The action of thiophene is similar when it is added to methylcyclopentane, as a result benzene content decreases but cyclohexane is not produced in large quantities in this case, a considerable yield being forbidden by thermodynamics. The mentioned data appear to be in bad accordance with the accepted mechanism of bifunctional catalyst's action based on dehydrogenation as a necessary stage of cyclane isomerisation [8-10]. It has been successfully shown recently by means of labeled atoms that the consecutive mechanism operates with cyclohexene as intermediate in the case of cyclohexane dehydrogenation into benzene on chromium oxide catalyst. The consecutive mechanism does not occur with renium catalyst. Since cyclohexane undergoes mainly dehydrogenation and isomerisation under the reforming condi-

Table 2
Effect of pressure on dehydrogenation and isomerisation of pure cyclohexane and its mixture with 6% thiophene at 500°C.
(Space velocity = 2 hr^{-1}; hydrogen:hydrocarbon = 5:1; Pt/Al$_2$O$_3$ catalyst used.)

Pressure (atm)	20		40		60	
Feed	Pure cyclohexane	Cyclohexane + 6% thiophene	Pure cyclohexane	Cyclohexane + 6% thiophene	Pure cyclohexane	Cyclohexane + 6% thiophene
Products:	Catalysate composition (%)					
Benzene	86.5	13.5	65.4	9.3	38.8	10.5
Methyl-cyclopentane	7.7	47.5	19.8	57.0	37.3	56.1
Cyclohexane	3.6	34.0	5.9	27.2	7.1	26.5
C$_5$-C$_6$ alcanes + gas	2.2	5.0	8.9	6.5	16.8	6.9

tions we made an attempt to detect cyclohexene as an intermediate product
in these two reactions using the above mentioned labeled atoms technique.
This work was carried out with two catalysts-rhenium and palladium on
alumina. Rhenium catalyst was chosen because it has been used in previous
investigation of benzene formation mechanism, as to palladium catalyst,
isomerisation of cyclohexane without thiophene took place on it to a greater
extent as compared to platinum. Alumina-palladium and alumina-rhenium
catalysts were prepared by impregnating alumina pellets with palladium
chloride and rhenium nitrate solutions (fluorated alumina was used in case
of palladium catalyst).

   Runs with pure cyclohexane and cyclohexene were carried out on alumi-
na-palladium catalyst preliminarily. Cyclohexane converted into benzene
and methylcyclopentane. Cyclohexene underwent dehydrogenation and iso-
merisation also but converted almost completely because of its greater re-
activity. Therefore we used in the runs with labelled atoms the mixture of
94.5 mole % cyclohexane and 5.5 mole % cyclohexane labeled with radio-
carbon. Liquid catalysates were analysed using gas-liquid chromatographic
column with a special device for radio-chemical analysis [12]. To obtain
more accurate data cyclohexene in some catalysates was converted into 1-
methoxycyclohexane-2-mercury chloride which was analysed for radioac-
tivity by means of thin mica end-window counter. The results of these runs
are shown in table 3.

   Activity of palladium catalyst with pure cyclohexane was stable. In case
of cyclohexane and its mixtures activity changed as it was expected, with
time and from run to run. The change of catalyst's selectivity was also ob-
served with respect to dehydrogenation and isomerisation activities. Cyclo-
hexene, pure or in mixture with cyclohexane, produced benzene and cyclo-
hexane in quantities which did not correspond to the stoicheometry of irre-
versible catalysis. It is seen from the data on products' radioactivity that
cyclohexene has practically no radioactivity but benzene and methylcyclo-
pentane are radioactive. It is clear from these results that cyclohexane
does not convert into cyclohexene under experimental conditions with cata-
lysts used, though it converts into benzene to a great extent (as high as 40%)
and with palladium catalyst into methylcyclopentane (as high as 8%). The
use of cyclohexane with high specific radioactivity and the very thorough
analysis for radioactivity in cyclohexene being taken into account, the data
obtained do not evidence in favour of cyclohexene as intermediate product
of dehydrogenation and isomerisation of cyclohexane. As to dehydrogenation
the data are in good accordance with those obtained previously for cyclo-
hexane dehydrogenation [11] and with the considerations of multiplet theory
of catalysis. As regards isomerisation the data obtained allow to conclude
that a mechanism of methylcyclopentane formation from cyclohexane is pos-
sible on bifunctional catalysts which does not involve as necessary stage
the cyclohexane formation or at least its desorption while transferring from
dehydrogenating sites to isomerisating ones on the active surface.

Table 3
Catalytic convertion of cyclic six-membered hydrocarbons under reforming conditions
(480°C; hydrogen pressure = 20 atm; hydrogen:hydrocarbon = 5:1).

Catalyst	Feed hydrocarbons	Space velocity, hr^{-1}	Catalyst's work time hours	Composition of liquid catalysates, mole %				Products' specific radioactivities in percent as relative to those of feed cyclohexane				Total radioactivity, %			
1% Pd-Al₂O₃	⬡	1.0	1.5	19.6	21.0	–	59.3								
			2.5	21.9	11.7	–	66.1								
			3.5	23.0	14.3	–	62.6								
1% Pd-Al₂O₃	⬡	2.0	1.5	7.1	19.5	3.1	70.3								
			2.5	6.2	27.5	3.6	62.7								
			3.5	7.5	26.4	4.6	61.5								
Without catalyst	94.5 mole% cyclohexene + 5.5 mole% cyclohexane	5 ml/hr	2.5	1.3	7.0	90.2	–								
1% Pd-Al₂O₃ *		2.5	2.0	31.9	36.7	11.9	19.5	0.5	14.2	0	1.9	3.0	90.5	0	6.5
			4.0	25.3	41.1	17.1	16.6	0.4	13.0	0	1.0	2.1	94.9	0	3.0
			5.0	31.6	40.7	12.6	14.7	14.0	12.7	0	0.9	2.8	94.8	0	2.4
			6.0	36.4	35.2	9.4	18.8	0.5	18.4	0	0.7	2.6	95.4	0	2.0
1% Pd-Al₂O₃		2.5	1.5	13.4	29.4	12.0	45.1	1.7	12.1	0.07**	1.9	4.9	76.5	0.2	18.4
			2.5	23.5	32.6	8.6	35.3	1.3	11.1	0.1***	1.9	6.6	78.6	0.2	14.5
			3.5	34.2	29.4	2.6	33.7	0.9	11.8	0	1.8	7.1	78.2	0	13.6
1% Pd-Al₂O₃		2.5	1.5	5.6	38.5	9.0	46.9	2.9	7.4	0	4.2	3.3	57.3	0	39.5
			2.5	12.1	30.3	5.5	51.5	1.8	7.6	0	2.2	5.5	62.7	0	31.8
			3.5	18.0	30.9	6.6	43.9	1.9	9.4	0	2.4	8.2	67.6	0	24.2
15% Re-Al₂O₃ ***		2.5	4.0	0.9	49.1	19.7	28.1***		7.3	0	3.6		78.1	0	21.9
			5.0	1.4	52.2	22.3	24.0		6.6	0	3.0		82.6	0	17.4
			6.0	1.1	63.6	13.9	17.7		7.1	0	4.5		84.5	0	14.8

* In run 5 space velocity was 0.6 hr^{-1}.
** Radioactivity of 1-methoxycyclohexane-2-mercury chloride as given for barium carbonate.
*** In run 8 hydrogen pressure was 5 atm radioactivity of methylcyclopentane was not estimated because of its exceedingly small amount in catalysates of this run.

10

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CHEMISORPTION AND INTERACTION OF HYDROGEN AND OXYGEN ON TRANSITION METALS

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Abstract: Chemisorption of hydrogen and oxygen as well as their interaction have been studied on evaporated films of molybdenum, nickel. palladium and rhodium at temperatures 78°K and 273°K. The results have shown that these metals differ in a characteristic way. The difference in behaviour of individual systems is probably connected with the strength of the chemisorption bonds.

1. INTRODUCTION

It was Faraday who first pointed out the connection between adsorption and heterogeneous catalysis and we know now that adsorption is a necessary prerequisite in heterogeneous catalysis. The relatively weak interactions of physical adsorption are probably not strong enough to activate the molecules of reactants and so these molecules must be activated by chemisorption.

The layer of chemisorbed molecules usually contains particles with different strengths of binding or even species of different chemical composition, especially when dissociation and probably also interaction of fragments (one with another or with gaseous molecules) takes place [1]. Two basic problems have to be tackled when studying heterogeneous activation: i) Is it sufficient that only some molecules are adsorbed whereas the others react directly from the gas phase, or is the adsorption of all molecules participating in reaction essential? ii) If the adsorbed layer consists of particles with different binding or of various kinds of particles, which of these are the most important in the catalytic reaction?

Attempts have been made to solve the first of these problems by analysis of kinetic data and examples can be found in the well-known papers of Rideal, Beeck and others [1]. Conclusions about the relative strength of bonds, drawn from the analysis of kinetics can be verified by direct measurements of corresponding values. Further, allowance can be made even for the variation in the strength of binding. Nevertheless, in no case do the kinetic analyses provide a direct proof of the mechanism of catalytic reactions.

A more fundamental contribution to this problem is the paper of Sachtler and Fahrenfort [2] in which it is shown that on gold the molecule HD can only be formed if both participants - hydrogen and deuterium - are adsorbed as atoms. The same holds for oxidation of hydrogen on gold. [3]. These conclusions are in agreement with the earlier experiments of Tamaru and his coworkers [4-6] with germanium, tin etc., upon which the so called Rideal

mechanism for H_2 - D_2 exchange did not operate. However, the experimental method used by these authors for obtaining their evidence is not applicable in the case of active transition metals. An attempt to solve this problem for palladium was made by Kazansky and Voevodsky [7] as early as 1957. These authors proved that during the reaction of a stoichiometric mixture of hydrogen and oxygen on the surface of a heated palladium tube the reaction preferentially consumed hydrogen diffusing through the tube. It is admissible to suppose that hydrogen atoms which had diffused reacted with oxygen before they recombined. So the results of Kazansky and Voevodsky provide evidence for the participation of adsorbed hydrogen atoms in the catalytic oxidation of hydrogen. In general, however, the question still remains open for solution.

In this paper we have tried to contribute to the solution of the problems mentioned above by a study of hydrogen - oxygen interaction on surfaces of metals. This system, which is attractive for the fundamental studies because of its relative simplicity, is also interesting from the point of view of the industrial purification of gases and of ultra-high vacuum technique [8].

2. EXPERIMENTAL PART

Adsorption and interaction of hydrogen and oxygen were studied on the evaporated films of molybdenum, nickel, palladium and rhodium. The experiments were performed in an all-glass apparatus equipped with mercury cut-offs and without any greased joints or stopcocks. Pressures in the range of 5 - 50 x 10^{-9} mm Hg were obtained after baking out the whole apparatus and outgassing the Bayard-Alpert gauge and the metal wire for four days. Films were condensed at 200°K and then sintered for 90 min at 330°K. Oxygen prepared by thermal decomposition of $KMnO_4$ was purified by freezing out condensable gases at 78°K. Hydrogen evolved by electrolysis was purified by diffusion through a palladium tube and by freezing out condensable gases at 78°K. When required, hydrogen was atomized by means of a hot tungsten wire. Analysis of hydrogen-oxygen mixture was performed by means of a calibrated Pirani gauge and a MacLeod gauge. The electrical resistance of the films was measured by a commercial Wheatstone bridge (Metra, Czechoslovakia) supplied with direct current. Required differential heats of adsorption were measured in a calorimeter of the Beeck type and with a Wheatstone bridge supplied with alternating current. Other details of the experimental technique as well as the method of evaluating the adsorption data corrected for thermal transpiration effect are given elsewhere [9, 10].

3. RESULTS

3.1. *Interaction of hydrogen with preadsorbed oxygen*
3.1.1. Molybdenum
The first series of experiments was performed at 273°K. The surface
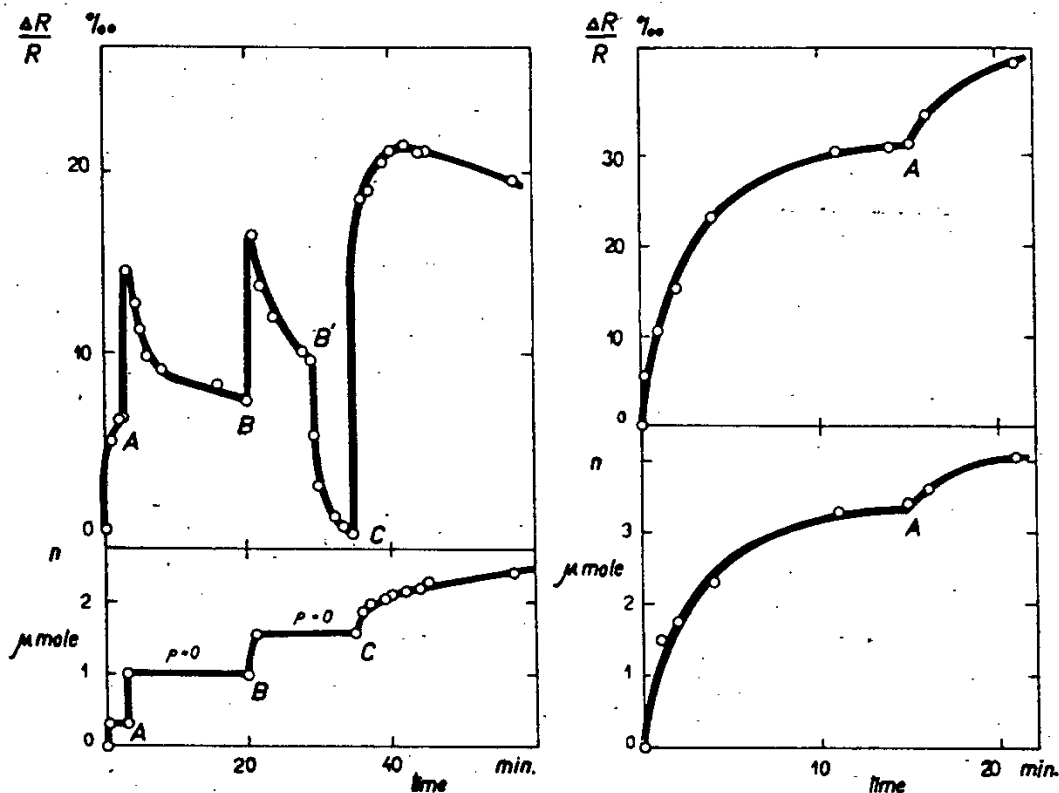
Fig. 1. Experiments with molybdenum. The relative change of the electrical resist-
ance of the molybdenum film during the sorption of atomized hydrogen at
273°K (a) and the time dependence of the sorption of atomized hydrogen in the
same experiment (b). The film was completely precovered by 3.8 μmoles of
oxygen. At O, A, B, C doses of hydrogen were admitted. B' - hot wire
switched off. (Another experiment with krypton showed that the sudden rise
at A, B, C was not caused by the heating of the film in the presence of gas.)
The relative change of the electrical resistance of the molybdenum film dur-
ing the sorption of atomized hydrogen at 78°K (c) and the time dependence of
the sorption of atomized hydrogen in the same experiment (d). The film was
completely precovered by 13.1 μmoles of oxygen. At O, A a dose of hydrogen
was admitted.

of molybdenum was covered to a known extent with oxygen and then the
adsorption of hydrogen was followed. This adsorption of hydrogen in-
creased the electrical resistance of such films just as the adsorption of
hydrogen on clean, uncovered films [11]. Furthermore, the extent of the
sorption of hydrogen did not indicate any interaction with preadsorbed oxy-
gen. A surface completely covered with preadsorbed oxygen did not sorb
any hydrogen at all. Even at 350°K * interaction of oxygen with hydrogen did
not take place. However, when hydrogen was atomized on a hot wire and then
admitted in the atomic form at 273°K to the surface completely covered with
oxygen, the curve of the time dependence of the film resistance revealed an
interaction between the adsorbed oxygen and admitted atomized hydrogen
(fig. 1a). As the decrease in the film resistance still continued when no
gaseous hydrogen was present (fig. 1b), it was the captured hydrogen which

* Note: The film was sintered at 360°K before this experiment.

evidently reacted. After switching off the atomization of hydrogen the sorp-
tion neither of molecular hydrogen nor of molecular oxygen continued. The
product of the interaction remained on the surface and blocked it.

It is interesting that the molybdenum surface covered by sorption of
molecular hydrogen at 78^OK adsorbed at this temperature (as compared
e.g. with nickel) only a relatively small amount of atomized hydrogen, but
the surface completely covered by oxygen captured the atomized hydrogen
nearly to the same extent as did the clean surface of the same area. In both
cases the atomized hydrogen increased the resistance of the film (fig. 1c,
1d).

3.1.2. Nickel

As reported at the Second Congress on Catalysis in 1960 [12], the extent
of hydrogen sorption on nickel decreased at 78^OK with the increasing extent
of oxygen preadsorption, which showed that hydrogen did not react with
oxygen at this temperature. This is also confirmed [13,14] by the fact, that
the electrical resistance of a film completely covered by preadsorbed
oxygen is increased by sorption of hydrogen at 78^OK as is the resistance of
the clean film.

However, the situation is quite different at 273^OK. At this temperature
hydrogen is trapped not only by the clean part of the nickel surface but also
by the preadsorbed oxygen. During this interaction the resistance of the film
decreased and the extent of hydrogen sorption was several times higher than
on the clean surfaces of the same area. However, such interaction between
molecular hydrogen and preadsorbed oxygen took place on nickel at 273^OK
only if at least a small part of the nickel surface had remained uncovered
by oxygen. This phenomenon can be most simply explained [14] by the as-
sumption that hydrogen can react only if adsorbed as atoms on the uncovered
part of the surface. In contrast, gaseous hydrogen atomized on the wire
could react at 273^OK without such restrictions on the extent of oxygen pread-
sorption.

Some features of this sorption of atomized hydrogen at 78^OK differ from
those on molybdenum. Nickel film covered by adsorption of molecular
hydrogen, adsorbed at 78^OK a further large amount of atomized hydrogen
and the electrical resistance of the film increased during this process [15].
The film completely covered by oxygen sorbed atomized hydrogen, too, but
the resistance of the film did not change (fig. 2a). The sorption of atomized
hydrogen at 78^OK on the surface completely covered by oxygen was of a
similar extent to the sorption of molecular hydrogen on the clean surface
of the same area (fig. 2b). The atomized hydrogen reacted at 273^OK with
preadsorbed oxygen and the resistance of the film decreased during this
reaction. However, with nickel there are no maxima (in contrast to molyb-
denum) on the curves of the time dependence of film resistance (fig. 2c, 2d).

In another experiment the surface of nickel was completely covered by
oxygen at 273^OK and then cooled to 78^OK. After it, the film was quickly
warmed to the temperature 273^OK and the change of the resistance, after
the temperature had been established, was followed. The same film was
cooled again to 78^OK and exposed to the atomized hydrogen. When the atom-
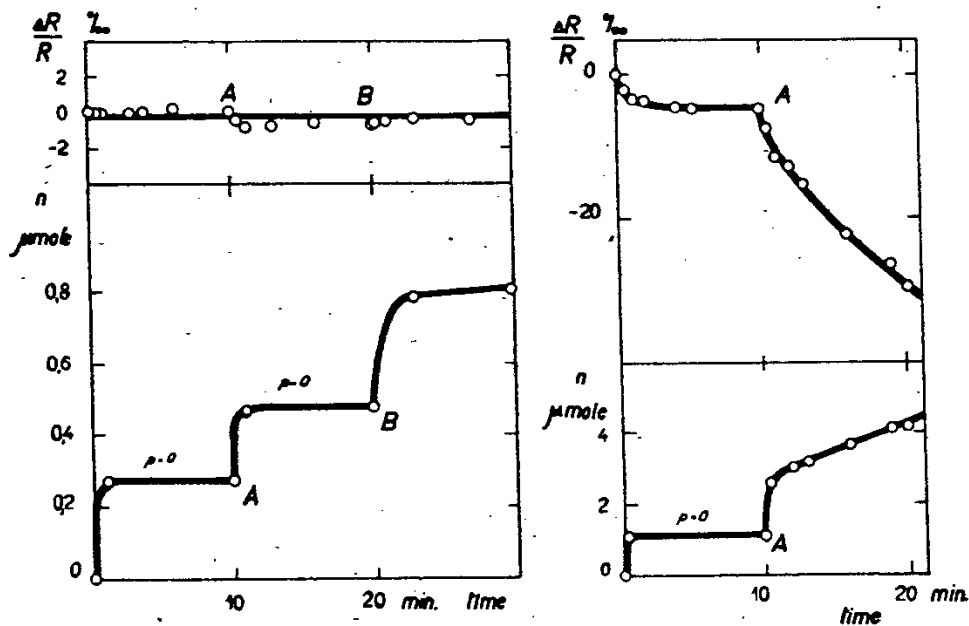
Fig. 2. Experiments with nickel. The relative change of the electrical resistance of the nickel film during the sorption of atomized hydrogen at 78°K (a) and the time dependence of this sorption in the same experiment (b). The surface was completely precovered by 1.95 μmoles of oxygen. At O, A, B, C a dose of hydrogen was admitted. The relative change of the electrical resistance of the nickel film during the sorption of atomized hydrogen at 273°K (c) and the time dependence of this sorption in the same experiment (d). The surface was completely precovered with 4.6 μmoles of oxygen. At O, A a dose of hydrogen was admitted.
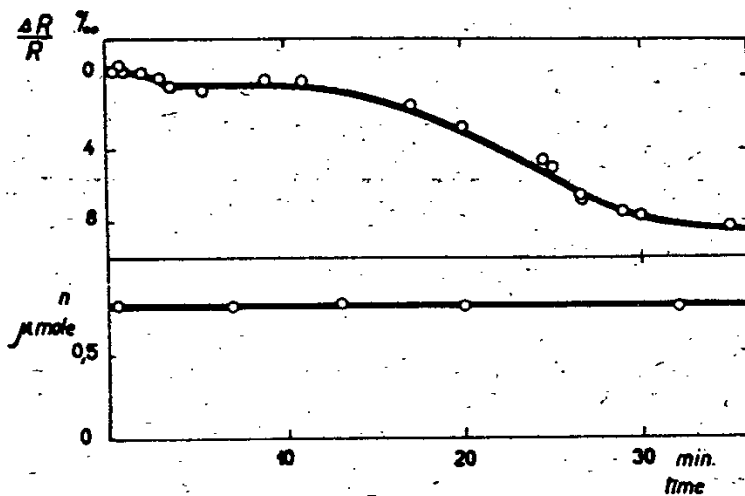
Fig. 3. The relative change of the electrical resistance of the nickel film at 273°K during the interaction of a complete oxygen layer with atomic hydrogen pre-sorbed at 78°K (a) and the time dependence of the amount of consumed hydrogen at 273°K in the same experiment (b). Atomization switched off, hydrogen pressure 1.5×10^{-2} mm Hg.

ization was switched off, the film was warmed quickly to 273°K and the resistance was followed. The shape of corresponding time dependence is shown in fig. 3a. No desorption occurred during warming the film as well
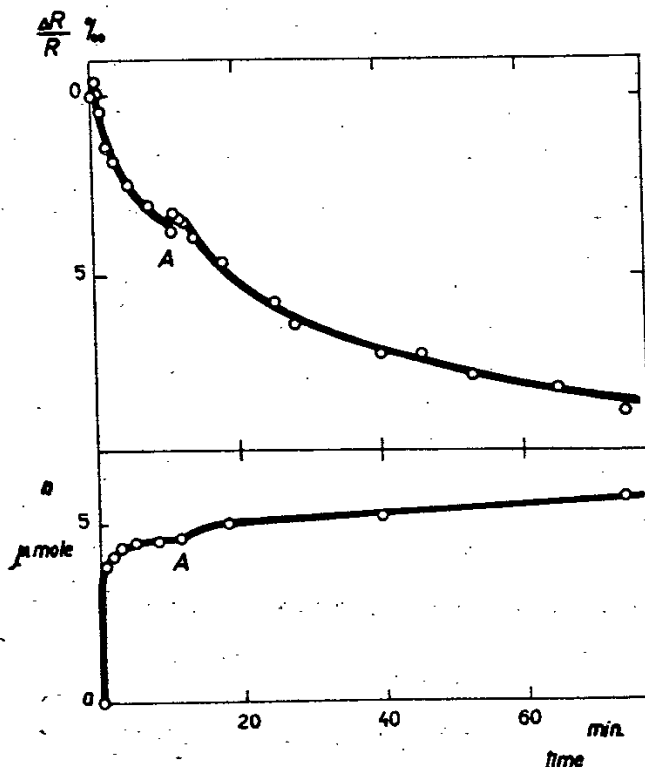
Fig. 4. Sorption of molecular hydrogen at 273°K on a composite film. The relative change of the electrical resistance with time (a) and the time dependence of the sorbed amount in the same experiment (b). At O, A a dose of hydrogen was admitted. Pressure during the slow process after A was in the order of 10^{-2} mm Hg.

as in the further course of interaction (fig. 3b). While the film covered by oxygen only maintained its resistance during this process at 273°K unchanged, the resistance of the film exposed to atomized hydrogen decreased slowly. Evidently, this decrease was caused by the interaction between hydrogen and oxygen.

A nickel film completely saturated by oxygen (such a film did not adsorb any molecular hydrogen) was covered after the oxygen preadsorption with a very thin layer of freshly evaporated nickel. According to a rough estimate based on the heating current and the time of evaporation, this layer was certainly thinner than 10% of the original nickel layer, and (according to the capacity of the original film for preadsorption of oxygen) had an area capable of adsorbing at most 0.15 μmole of hydrogen. Nevertheless, in a slow process the sorption of molecular hydrogen on this composite film reached a value of 0.6 μmole of hydrogen (fig. 4b) and after two hours the sorption was still continuing slowly. Both the extent of this sorption and the accompanying resistance decrease (fig. 4a) indicated that the interaction of hydrogen and oxygen was occurring. Hydrogen was probably adsorbed on the fresh nickel surface and diffused from it to sites in the oxygen layer. In none of these cases was the product of interaction desorbed from the surface of nickel.

3.1.3. Palladium, rhodium

Palladium films catalysed the reaction of hydrogen and oxygen at $273^{\circ}K$ very well. We found that the resistance alternately increased with oxygen chemisorption and then decreased again when molecular hydrogen was admitted and reacted with preadsorbed oxygen. Reproducible results were obtained when the sequence was repeated several times in the same experiment with the same film. The product of this interaction was most probably water. At $273^{\circ}K$ water evidently desorbs from the surface and does not inhibit further reaction.

Palladium absorbed hydrogen very strongly at $78^{\circ}K$. This process is exothermic and so the extent of absorption decreases with increasing temperature. The absorption of hydrogen in palladium at $78^{\circ}K$ [16] took place even when the surface was completely covered by oxygen, but with a slightly lower rate than the normal.

The adsorption of hydrogen on rhodium films [15] increased their electrical resistance both at $78^{\circ}K$ and $273^{\circ}K$. The change of the resistance was very small even for very thin films and the curve of resistance-coverage dependence did not have the same complicated character as in the case of e.g. nickel. The extent of hydrogen adsorption on rhodium at $273^{\circ}K$ was about one half that observed at $78^{\circ}K$. The form of the isobar suggests a comparatively low heat of adsorption of hydrogen. As far as the hydrogen-oxygen interaction is concerned, the behaviour of rhodium resembles that of palladium [16].

3.2. *Interaction of oxygen with preadsorbed hydrogen*

As already shown [15,16] oxygen reacted at $273^{\circ}K$ with preadsorbed hydrogen readily both on palladium and rhodium. At $78^{\circ}K$ oxygen sorption into the hydrogen layer was very fast on both these metals. On rhodium this fast sorption was accompanied by a rapid increase of the electrical resistance of the film to a value which remained constant a certain time. Rapid adsorption of oxygen also occurred at $78^{\circ}K$ on palladium irrespective of the extent of the hydrogen presorption. However, the size of the increase in the resistance associated with the oxygen adsorption depended on the amount of presorbed hydrogen and was negligible on films which had been saturated with hydrogen [16]. Oxygen was also sorbed very quickly at $78^{\circ}K$ by the layer of preadsorbed hydrogen on nickel. This sorption was accompanied by an instantaneous increase of the electrical resistance to a value which then remained constant. At $273^{\circ}K$ oxygen was again instantaneously sorbed but a very rapid increase of the resistance was followed by a slow decrease of the resistance. The greater part of this decrease took place without the presence of oxygen in the gas phase, indicating that the reaction was continuing in the adsorbed layer [14].

No desorption of hydrogen was apparent on the sorption of oxygen on palladium, rhodium and nickel at $78^{\circ}K$ and $273^{\circ}K$. However, on molybdenum about 35% of the adsorbed hydrogen was successively desorbed at $78^{\circ}K$ and $273^{\circ}K$ when small amounts of oxygen were admitted to the molybdenum film covered with hydrogen. The resistance of the film increased during this process to a value characteristic for the adsorption of oxygen on a clean molybdenum film [11].

No direct correlations of the catalytic activity of the four metals in the hydrogen-oxygen reaction can be found with the following quantities: the extent of sorption at $78^{O}K$, the shape of isobars, the change of the electrical resistance of the film during the sorption process, or the extent and the kinetic characteristics of the slow sorption process at $78^{O}K$. However, it seems that there exists a certain correlation with the energetics of adsorption. When the surface is covered to a high extent, the more endothermic of the heats q_1 and q_2 associated with the reactions [*]
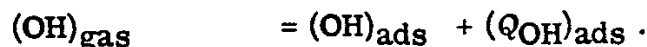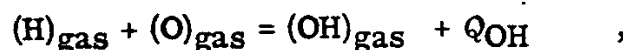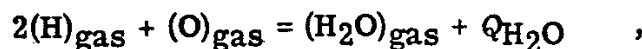
$$(O)_{ads} + 2(H)_{ads} = (H_2O)_{gas} , \qquad (1)$$

$$(O)_{ads} + (H)_{ads} = (OH)_{ads} , \qquad (2)$$

will represent the minimum possible value of the activation energy of the overall reaction. The value of q_1 and q_2 can be calculated from equations

$$q_1 = -2D(MeH) - D(MeO) + Q_{H_2O} ,$$

$$q_2 = -D(MeH) - D(MeO) + Q_{OH} + (Q_{OH})_{ads} ,$$

where D stands for the dissociation energy and the Q terms represent the heats of processes

$$2(H)_{gas} + (O)_{gas} = (H_2O)_{gas} + Q_{H_2O} ,$$

$$(H)_{gas} + (O)_{gas} = (OH)_{gas} + Q_{OH} ,$$

$$(OH)_{gas} = (OH)_{ads} + (Q_{OH})_{ads} .$$

With an assumption that the metal surface contains free valencies, the dissociation energies of the metal-adsorbate bonds can be easily calculated from the equation

$$Q_{H_2} = D(MeH) - D(HH) .$$

The heats Q_{H_2O} and Q_{OH} are given in the literature and the heat of adsorption of the OH group can be estimated according to Rüelchi and Delahay [21]. Calculations of the values of q_1 and q_2 were performed with the initial heats of adsorption and in some cases with the mean values of the heat [22-24] as well (table 1).

The highly endothermic values of q_1 and q_2 for molybdenum (and similarly for W, Cr, V, Ta, etc.) show that these metals will be inactive in the catalysis of the reaction between hydrogen and oxygen at low temperatures. The reaction (2) is not so highly endothermic on rhodium, palladium and platinum and reaction (1) is even exothermic. This might explain the easy formation of water on these metals even at low temperatures. According to the estimation of the endothermic effect nickel should favour reaction (1) in comparison with reaction (2) in contrast to what was found at $273^{O}K$. Thus reaction (1) is probably connected with a certain activation energy.

This simple calculation can be easily extended to the simultaneous reaction of several bonds in one molecule of oxide Me_mO_n, without change in the given conclusion.

[*] All equations are accompanied by an error of several RT.

10

Table 1
Heat effect of hydrogen – oxygen interaction on metals.

Metal	q_1 (kcal/mole)		q_2 (kcal/mole)	
Cr	-57 [1]			
Fe	-24 [1]	(-12) [23]	-21 [1]	(-40) [23]
Co	- 5 [1]			
Ni	-10 [1]	(0) [23]	-16 [1]	(-11) [23]
Mo	-51 [1]	(-31) [24]		
Rh	+11 [22]	(+18) [22]		
Pd	+15 [1]		- 4 [1]	
Ta	-75 [1]	(-58) [22]		
W	-69 [1]	(-56) [23]		
Pt	+15 [1]		- 4 [1]	

Figures in parentheses were calculated by means
of mean values of heat of hydrogen adsorption
(where experimental data were available).

The reaction of gaseous molecular hydrogen with preadsorbed oxygen
is less endothermic than the reactions (1) and (2). However, the latter re-
actions are probably accompanied by an activation energy mainly on account
of dissociation of hydrogen molecules. At least on nickel and molybdenum
this reaction does not take place at $273^\circ K$.

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THE ELECTRON SPIN RESONANCE STUDY OF FREE RADICALS ADSORBED ON CATALYSTS

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Abstract: The results obtained in ESR study of structure, nature of the bond with the surface and reactivity of free radicals adsorbed on various catalysts are reported. Adsorbed free radicals of two types were investigated: those bonded with the surface by a weak one-electron bond (for instance H atoms, CH_3, C_2H_5 radicals, etc.) and radicals formed as a result of charge transfer during adsorption of molecules possessing high electron affinity on the surface of n-semi-conductors (O_2^-, SO_2^-). The radicals of the first type can exist in high concentrations on the surface of insulators at low temperatures. They are very reactive, the strength of their bond with the surface is about 3-5 kcal/mole. Their recombination occurs at temperatures of about 130-150°K. The radicals of this kind can not be obtained on semi-conductors, as by trapping free electrons they are transformed to chemisorbed species.

Radical-ions of the second type were obtained by adsorption of O_2 and SO_2 molecules on reduced TiO_2. They are more stable and can be detected using the ESR method at room temperatures and somewhat higher temperatures. The role of adsorbed free radicals in heterogeneous catalysis is discussed on the basis of the results obtained.

1. INTRODUCTION

The investigation of active intermediate forms of chemical reactions by moern physical methods is one of the most important problems of chemical kinetics. This is so because the real mechanism of a chemical reaction can be determinated and its elementary processes investigated only after the identification of its intermediate products. Of particular interest is the investigation of active intermediates in heterogeneous catalysis, as they have hardly been investigated till now.

It is well known that the mechanism of a chemical reaction in homogeneous kinetics can be a molecular, an ionic or a radical one. But things are quite different for heterogeneous catalysts. In this case it is very difficult to draw a line of demarcation between these mechanisms. Moreover sometimes it is difficult to say what is meant by the terms "an adsorbed molecule, ion or radical" and to what extent do their properties differ from those of molecules, ions or radicals in the gas or liquid phase. The existing theories of heterogeneous catalysis admit the possibility of various mechanisms for elementary processes on catalytic surfaces. The multiplet theory developed by Balandin implies that the mechanism of heterogeneous catalysis is similar to that of molecular reactions. On the other hand, there

is much evidence that in reactions including electron transfer (for instance, oxydation-reduction reactions) the molecules of initial substances and the intermediates adsorbed on catalysts surface possess an electrical charge. The electron theory of catalysis proposed by Hauffe [1], Germain [2], Volkenstein [3] and Roginsky [4] is most suitable for interpreting the mechanism of these reactions.

The problem of the part played by free radicals in heterogeneous catalysis is of special interest. During the last thirty years, after the very important role played by free radicals in the mechanism of homogeneous reactions had been established, the radicals adsorbed on the catalyst surface were very often supposed to be active intermediate products in heterogeneous catalysis as well. This point of view was most clearly expressed both in the Volkenstein theory of heterogeneous catalysis and in the chain theory of catalysis worked out by Semenov and Voevodsky [4,5]. It must be stressed, however, that existence of adsorbed free radicals and their participation in heterogeneous catalysis has not yet been verified by using direct physical methods. At the same time modern physical methods and first of all the ESR method give great opportunities for investigating properties of free radicals not only in solids, liquids and gases, but also on the surface of catalysts. This report contains some results on the recent ESR investigation carried out in our laboratory on the properties of adsorbed free radicals.

Volkenstein's electron theory of catalysis postulated that there exist two kinds of surface-adsorbed free radicals: those yielded by dissociation of adsorbed molecules and those formed via electron transfer between adsorbed molecules and the catalyst. In the first case there seems to be equilibrium between the strong two-electron and the weak one-electron bond of the radical adsorbed, with the surface:

$$\ddot{R} \rightleftharpoons \dot{R} + e \,. \tag{1}$$
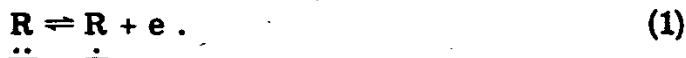
According to this theory the weak one-electron form of adsorption is highly reactive as in this case the adsorbed radicals have unpaired electrons and their properties must be close to those of free radicals. The radicals bonded with the surface by strong two-electron bonds are, however, not free as they have no unpaired electrons.

The free radicals of the other sort can appear by interaction of adsorbed molecules with free valences of the surface (electrons or holes). When the molecules possess high electron affinity, as in the case of oxygen, they can behave as acceptors trapping free electrons from the conductivity band:

$$\underline{O_2} \rightleftharpoons \underline{O_2^-} \,. \tag{2}$$

When the ionisation potential of the molecules is low, adsorption may occur on holes, and positively charged radical-ions may be formed. For instance:

$$\underset{++++}{O_2} \rightleftharpoons \underset{+\ \ ++}{O_2^-} \,. \tag{3}$$

We tried to investigate both forms of adsorbed free radicals. We did not try to detect them during the reaction, but we intentionally tried to obtain adsorbed free radicals in high concentrations by means of the adsorption of saturated molecules of a high electron affinity on the semi-conducting surface or by artificial dissociation of adsorbed molecules by photolysis or radiolysis. After we have studied properties of adsorbed radicals, we tried to make some conclusions as to the participation of these in heterogeneous catalysis.

2. THE PROPERTIES OF FREE RADICALS BONDED WITH THE SURFACE WITH A WEAK ONE-ELECTRON BOND

Ionizing radiation or the photolysis of frozen chemical compounds are the most widely used techniques for obtaining free radicals at low temperatures. The same techniques were applied to obtain adsorbed radicals bonded with the surface with a weak one-electron bond.

Catalysts with a known surface area were pretreated in a vacuum at 400-500°C. The compounds yielding radicals were adsorbed on the samples in such a way that surface coverage was essentially less than a monolayer. After the adsorption was completed, the samples were cooled to the liquid nitrogen temperature and irradiated with γ-rays from Co^{60} or with UV light of a PRK-7 mercury lamp. ESR spectra of irradiated samples were obtained on the ESR spectrometer EPR-2 ($\lambda = 3$ cm, the modulation frequency 1 Mc/s).

The low temperature of irradiation and recording of ESR spectra were chosen in order to minimize the recombination of adsorbed radicals and their reactions with the initial substances. In some experiments the catalysts with surface adsorbed radicals were warmed after irradiation in vacuum or in various gases up to room temperature in order to investigate the recombination of adsorbed radicals and their reactivity. Details of the experimental technique used are described in refs. 6-8.

Attempts were made to prepare adsorbed radicals on the following catalysts: SiO_2; Al_2O_3; $Al_2O_3.SiO_2$; MgO; ZrO_2; ZnO; NiO; activated charcoal.

The most interesting results were obtained for silica-gel. ESR spectra of the following radicals adsorbed on this substance were observed at 77°K: spectra of hydrogen and deuterium atoms (prepared by irradiation of SiO_2 preheated in a vacuum); methyl radicals (photolysis of CH_3I), ethyl radicals (radiolysis of adsorbed ethane), HO_2 radicals (photolysis of H_2O_2), C_6H_7 radicals (radiolysis of adsorbed benzene) [8-13].

Several of the spectra obtained are represented on the left side of fig. 1. Spectra of free radicals trapped at low temperatures in solid polycrystalline matrices are shown on the right side of this figure. Both side spectra are essentially similar although slightly different in some respects. Analysis of these differences can give some information on the structure of adsorbed radicals and the nature of their bonds with the surface.

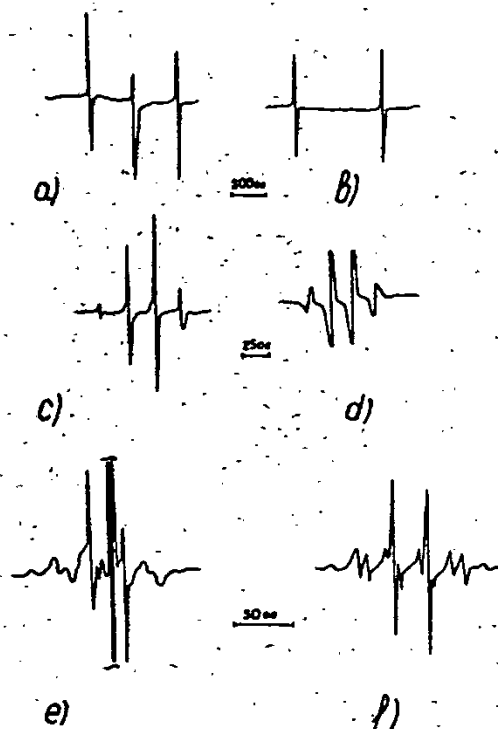Let us first consider the information which may be obtained from the

Fig. 1. Comparison of ESR spectra of free radicals adsorbed on the surface of
silica-gel with those of free radicals stabilized in solid polycrystalline
matrices at 77°K.
a) Spectrum of adsorbed H atoms (the signal in the central part of the
spectrum is due to radiation-induced defects).
b) Spectrum of free H atoms.
c) Spectrum of adsorbed methyl radicals.
d) Spectrum of methyl radicals in Xe-matrix at 77°K.
e) Spectrum of adsorbed ethyl radicals.
f) Spectrum of ethyl radicals in solid ethane at 77°K.

analysis of the hyperfine splitting in ESR spectra of adsorbed radicals. The
theory of ESR spectra shows that the hyperfine splitting, for instance, in
the H atom spectrum is proportional to the unpaired electron density on the
proton. When the adsorption of an H atom on the surface is accompanied by
the formation of one electron bond, the unpaired electron will be drawn
into the solid and its density on the proton must be reduced. Thus, the one-
electron bond of the adsorbed radical with the surface will be accompanied
with diminishing of the hyperfine splitting in the ESR spectrum.

Comparison of hyperfine splitting in the spectra of adsorbed radicals
with that for free radicals may, thus, give some information about the na-
ture of the bond of radicals with the surface. The corresponding data are
represented in table 1. The hf splitting in the ESR spectra of adsorbed radi-
cals may be seen to be only by a few percent less than that for free radi-
cals. The disturbing action of the surface on the unpaired electron cloud of
adsorbed radicals is thus very small.

Deformation of the electron cloud of adsorbed hydrogen atoms could be
estimated, besides, on the basis of an asymmetrical shape of the spectrum
components which is due to hyperfine anisotropy. The quantitative inter-

Table 1

Radical	The hf splitting in spectra of adsorbed radicals (Oe)	The hf splitting in spectra of free radicals (Oe)
H	506	510
CH$_3$	23.1	22-25
C$_2$H$_5$		
The hf splitting on α-protons	21.0	22.5
The hf splitting on β-protons	27.0	27.1

pretation of both effects mentioned was discussed in our paper [12] giving also rough estimation of the strength of a one-electron bond as being 3-5 kcal/mole.

Analysis of the amplitude ratios of components in ESR spectra of adsorbed alkyl radicals, as shown in fig. 1, made in the same paper, gives some information about the geometry of adsorption of these radicals and about their motion in the adsorbed state. Conclusion was drawn that there is a loss of two rotational degrees of freedom and there remains only one axis of rotation, that of the unpaired p-electron cloud when the methyl radicals are bonded to the surface by a one-electron bond due to the impelling of the unpaired electron cloud into the adsorbent (fig. 2). Interpretation of adsorbed ethyl radical spectrum shows that the radical "lies on the adsorbent surface on its side" (fig. 2b), and there is rotation (or oscillation) of its CH$_3$ and CH$_2$ groups relative to each other. Besides, there is one more kind of rotation of the whole radical as a result of which it, say, rolls along the surface (fig. 2b). The adsorbed alkyl polymer radical likewise "lies on its side".

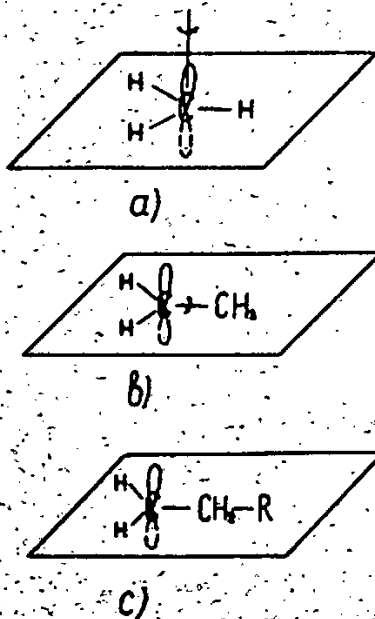The conclusion drawn from the analysis of ESR spectra that the strength

Fig. 2. Absorption scheme for alkyl radicals.

of the one-electron bond of adsorbed radicals with the surface is very small is in good agreement with the results obtained by studying recombination of adsorbed radicals at elevant temperatures. The ESR spectra of adsorbed radicals do not change at liquid nitrogen temperature during prolonged keeping of samples. As the temperature is raised to 130-150°K the signal intensity of adsorbed H atoms begins to decrease with time due to their recombination. The recombination of adsorbed alkyl radicals (ethyl and methyl) occurs at 200-250°K. In plotting the intensity of ESR spectra versus time at different temperatures we obtained kinetic curves of recombination of adsorbed atoms and radicals.

The recombination of adsorbed H atoms was found to follow the first order kinetic law with the velocity constant of recombination:

$$K = 10 \, e^{-2000/RT} \, \sec^{-1} \, . \tag{4}$$

The first order of this reaction seems to indicate that the rate-controlling step of the process is the surface migration of adsorbed atoms to the recombination centres. The energy of activation for this process must be close to the heat of adsorption of H atoms. Thus the value for $E = 2$ kcal/mole confirms our conclusion that the strength of one electron bond of adsorbed radicals with the surface is about a few kcal/mole.

Additional confirmation for the weakness of one-electron bond was obtained by investigation of the reactivity of adsorbed radicals. It was shown that at 140°K the adsorbed H atoms reacted with oxygen forming HO_2 radicals [9,10)

$$H_{ads} + O_2 \rightarrow HO_{2 \, ads} \, . \tag{5}$$

At 110-120°K H atoms react with ethylene [10). This process leads not to the formation of ethyl but of polymer radicals:

$$H_{ads} + n \, C_2H_4 \rightarrow CH_3\text{-}(CH_2)_{2n-2}CH_3 \, . \tag{6}$$
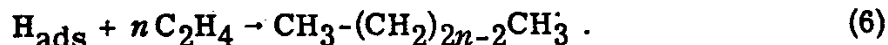
The adsorbed ethyl radicals and polymer radicals may react with oxygen to form peroxide radicals.

These results indicating very high reactivity of adsorbed free radicals give evidence for the low value of their heat of adsorption.

Besides radicals adsorbed on silica-gel, we tried obtaining them on the surface of other catalysts with various electronic properties. ESR spectra of hydrogen and deuterium atoms, ethyl radicals and C_6H_7, radicals adsorbed on the aluminium oxide, and also hydrogen atoms and C_6H_7 r radicals adsorbed on the surface of silica-alumina catalyst were obtained. At the same time ESR spectra of free radicals adsorbed on the surface of "good" semiconductors ZnO and NiO and "poor" semiconductors such as MgO and ZrO_2 could not be obtained using the technique described above. This appeared to be impossible even when semiconductors with molecules adsorbed on their surface in a monolayer were irradiated with fast 1.8 MeV electrons directly in the ESR cavity, at liquid nitrogen temperature. However, when surface coverage of the catalyst was greater than the monolayer, ESR spectra of radicals formed were observed.

These results may be interpreted in the following way. Free radicals

are known to possess considerable electron affinity, about 1 eV [14]. As a
result they can trap free electrons of the conductivity band of n-semicon-
ductors and be transformed to negatively charged particles, bonded with
the surface with strong two-electron bonds (see reaction (1)). The possi-
bility of such a process was proved experimentally by Myasnikov [15,16].
With p-semiconductors the transformation of a weak one-electron bond into
strong two-electron one can lead to the appearance of holes, for instance:

$$R + S \rightarrow R^- + S^+ . \tag{7}$$

The high rate of reactions (1) and (7) seems to account for our failure to ob-
tain free radicals adsorbed on semiconductors. In the case of insulators
these processes cannot take place due to absence of free electrons and holes.
As a result of it, high concentrations of adsorbed free radicals can be ob-
tained at low temperatures.
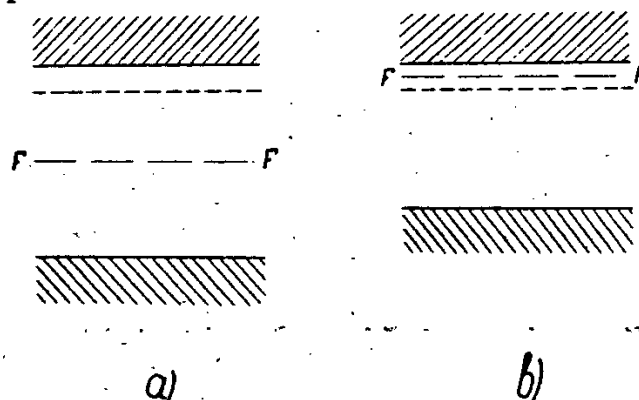
Fig. 3. Band model of adsorption of free radicals
on semi-conductors (b) and insulators (a).

The explanation proposed can be illustrated by the simple band mode
(fig. 3). The forbidden band width in insulators is known to be about 6-10
eV. In this case the Fermi level is in the middle of the forbidden band, in
other words about 3-5 eV lower than the bottom of the conductivity band.
When adsorbed free radicals trap free electrons, they may form ac-
ceptor levels located about 1 eV lower than the bottom of the conductivity
band in accordance with theoretical estimates [17,18] and experimental
data [16] (fig. 3a). As a result of it the acceptor levels are not populated and
the reaction (1) is shifted to the right. On the contrary the Fermi level in
n-semiconductors lies only some tenths of eV deeper than the bottom of the
conductivity band, i.e., higher than the acceptor levels (fig. 3b). Reaction
(1) is shifted to the left and all adsorbed free radicals are transformed to
strongly chemisorbed species.

3. RADICALS FORMED BY ADSORPTION OF MOLECILES POSSESSING HIGH ELECTRON AFFINITY ON REDUCED TiO$_2$

It was already pointed out that free radicals may be formed on semi-
conductors by adsorption of saturated molecules without dissociation in two

cases: when adsorption occurs on free electrons or holes. In the first case negatively charged radical-ions would appear, in the second the positively charged ones. There is much evidence to show that adsorption of various molecules on semi-conductors brings a change in their conductivity. These results show that adsorbed molecules trap free electrons from the conductivity band, but they cannot prove the formation of adsorbed free radicals.

Adsorbed radical-ions may be formed only if the free electrons are fully localized on the adsorbed molecules, or completely transferred to the solid. When electrons or holes are trapped only in part, the adsorbed free radicals will not be formed, but polarisation of adsorbed molecules will occur. Ionisation potentials of saturated molecules are known to be rather high (more than 10 eV [14]), whereas the work function of most solids is about 5-6 eV. On the basis of these facts complete transfer of electrons from adsorbed molecules to the adsorbent, accompanied by the formation of adsorbed positively charged radical-ions seems to be rather improbable. That is why we paid particular attention to the study of negatively charged ion-radicals.

The formation of negatively charged ion-radicals is evidently most likely to be expected when adsorption of molecules of high electron affinity occurs on semi-conductors, the Fermi level of which is most close to the bottom of the conductivity band. That is why we studied adsorption of oxygen and SO_2 on the surface of reduced TiO_2, possessing quasi-metallic conductivity.

A sample of anatase with a surface area of 56 m^2/g was reduced by heating in high vacuum at 500°C for 6-10 hours. Upon this treatment it did not exhibit an ESR spectrum and has a quasi-metallic conductivity. After the oxygen had been adsorbed at room temperature, the sample conductivity diminished and ESR signals could be observed. If adsorption took place at a low pressure of oxygen (about 1 mm Hg), two lines could be observed: a narrow one whose nature is not yet quite clear and a broad one with markedly expressed anisotropy of the g-factor ($g_{II} = 2.021$, $g_I = 2.011$) (fig. 4a). The second signal is due to adsorbed peroxide radicals formed by the adsorption of oxygen.

At high pressure of oxygen both the signals are broadened, when the pressure is higher than 10 mm Hg, they disappear. The effect is fully reversible: after oxygen was pumped off, the initial shape of signals reduced.
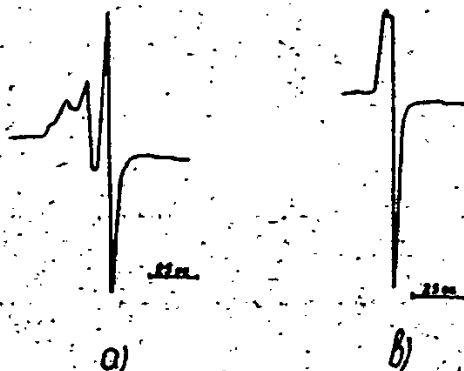

a)   b)

Fig. 4. ESR spectra of oxygen (a) and SO_2 (b) adsorbed on reduced anatase.

The broadening action of oxygen is more markedly expressed for the broad signal, than to the narrow one. This seems to indicate, the narrow signal to be due not to oxygen atoms or molecules adsorbed on the surface of TiO_2, but due to thd eefects in its volume on which free electrons are trapped.

The intensity of broad signal is close to the amount of oxygen molecules adsorbed (about 5×10^{18} spins/g). With samples kept for an hour at room temperature the broad signal intensity drops to a considerable extent, contrary to this in the presence of acetaldehyde it disappears in a few seconds. This result may point to a reaction of adsorbed peroxide radicals with acetaldehyde molecules.

The formation of adsorbed free radicals during adsorption of saturated molecules was also established for adsorption of SO_2 on reduced anatase. The ESR spectrum obtained is shown in fig. 4b.

4. ON THE PROBABLE ROLE OF ADSORBED FREE RADICALS IN HETEROGENEOUS CATALYSIS

The results reported indicate that the free radicals of two types can exist on the surface of the catalysts: those bonded with the surface with weak one-electron bond and formed as a result of charge transfer process by the adsorption of molecules possessing a high electron affinity. The structure and the nature of the bond with the surface of both types of adsorbed free radicals can be studied using the ESR method.

Let us try to discuss now the probably role of adsorbed free radicals in heterogeneous catalysis. Our results indicate that adsorbed free radicals bonded with the surface with weak one-electron bonds can exist in sufficient concentrations only on the surface of insulators or in the case when dissociative adsorption is not characteristic. Moreover the strength of their bonding with the surface is very small (only about few kcal/mole). This seems to exclude the participation of adsorbed free radicals of this kind in elementary acts at the surface of insulators, at least at high temperatures. Under these conditions adsorbed free radicals would readily desorb from the surface, initiating gas-phase chain reactions. At low temperatures they can also play the part of active intermediates in the inverse process, namely, recombination on the surface of free radicals from the gas phase.

On semiconductors, where dissociative adsorption is more probable, the participation of adsorbed free radicals bonded with the surface with weak one-electron bonds in heterogeneous catalysis is also questionable. First of all, at low temperatures their surface concentration will be very low. With rising temperature it might increase, but at the same time owing to the weakness of one-electron bonds the probability of their desorption from the surface will also rise to a very high degree.

It seems that free radicals of the second type, formed by charge transfer between adsorbed molecules and the adsorbent will play the part of active intermediates. The results reported show that they actually exist on the surface of semiconductors and seem to be highly reactive. It must be stressed, however, that we observed these radicals only in the most favour-

able case by adsorption of molecules of a high electron affinity on the sur-
face of a quasi-metallic semi-conductor. If the electron affinity of adsorbed
molecules or the Fermi level of the adsorbent were lower, adsorption
would lead rather to polarisation of adsorbed molecules and not to the for-
mation of adsorbed free radicals. An investigation of adsorbed species
formed in this case seems to be of great interest.

ACKNOWLEDGEMENTS

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STAT

CATALYTIC AND ACID PROPERTIES
OF BINARY OXIDE CATALYSTS BASED ON SILICA

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Abstract: The purpose of this work was to investigate the influence of chemical composition and heat treatment of silica-alumina, silica-zirconia and silica-magnesia catalysts on their physico-chemical and catalytic properties.

The properties of synthetic catalysts differ markedly from those of their components or mechanical mixtures because in the process of preparation a chemical interaction occurs between the substances entering into the composition of the catalyst.

The "strength" of acid centers on the surface of the catalysts studied is determined by their chemical nature and does not depend on the proportion of the components. With the increase of the contents of the metal oxide in the catalyst the concentration of acid centers on the surface passes through a flat maximum. The limit concentration of acid centers depends on the strength of the surface acid in the following way: the higher the acidity, the lower the limit concentration.

The catalytic activity of the contacts under investigation is caused by the presence of functional groups of acid nature on their surface. The catalytic activity of the catalysts with respect to dehydration of alcohols and cracking of cumene is directly proportional to the number of acid centers on their surface.

The rate constants of cumene cracking reactions, dehydration of isopropyl alcohol, dimerization of propylene and isobutylene referred to milliequivalent of acid centers change symbatically with the acidity of the catalyst.

1. INTRODUCTION

The characteristic feature of complex catalysts is nonadditivity of their physico-chemical and catalytic properties. In many cases the components are inactive while their mixtures have a high catalytic activity. Silica-alumina and silica-zirconia catalysts may be cited as an example of this phenomenon.

Fig. 1 shows the influence of the chemical composition of silica-alumina catalysts on their activity with respect to the decomposition of cumene. It is seen from the figure that the activity of binary mixtures is much higher than that of the mixture components.

The elucidation of the causes underlying catalytic properties of binary catalysts and the laws governing the formation of active substances is one of the most important problems of the science of catalysis.

In the present work the influence of the chemical composition and of heat treatment on the physico-chemical and catalytic properties of binary mixtures of aluminum, zirconium and magnesium oxides with silicic acid is investigated.

The catalysts were obtained by:
a) impregnation of silica gel with salt solutions;
b) hydrolysis of diluted alcohol solutions of ethyl ether of ortho-silicic acid
and of nitrate of the corresponding metal.

After washing and drying the samples were calcined for four hours at a
given temperature.

The surface area of the samples was determined by the B. E. T. method
[1] of nitrogen adsorption at -194°. The acidity was determined by the indi-
cator method and the number of acid centers by n-butylamine adsorption
[2,3,4].

2. INFLUENCE OF THE CHEMICAL COMPOSITION OF CATALYSTS ON THEIR ACTIVITY.

Earlier it was found that in the process of preparation there occurs an
interaction between zirconium hydroxide and silicic acid leading to the form-
ation of a chemical compound with a high catalytic activity [5]. In this work
this system was studied in greater detail. The investigation showed that all
silica-zirconia catalysts (even those containing only 0.1% ZrO_2) have a high
acidity: they are capable of ionizing the indicator with $pK = -8.2$.

High acidity of industrial silica-alumina catalysts was reported by a
number of investigators [3,6,7]. The silica-alumina catalysts investigated in
this work contained from 0.1 to 90% Al_2O_3. The samples containing less than
90% Al_2O_3 ionize anthraquinone ($pK = -8.2$); the samples with 90% Al_2O_3 and
10% ZrO_2 ionize the indicator with $pK = -3$.

Measuring the acidity of silica-magnesia catalysts showed that the compo-
nents as well as the mixtures containing less than 10% MgO practically pos-
sess no acidity. The samples containing 10% MgO (or more) are acids of mo-
derate strength. They are capable of ionizing the indicator with $pK = -3$.

The x-ray pictures of the samples containing from 10 to 30% MgO have
3 diffusive bands similar to those of talc. With the increase of the contents
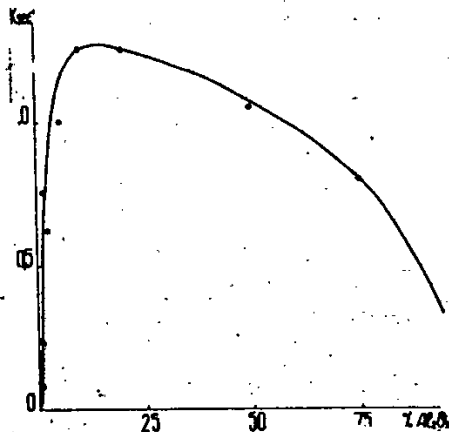of MgO there appear in addition the bands of MgO.

Fig. 1. The influence of Al_2O_3 content on the activity of silica-alumina
catalysts for cumene cracking reactions at 400°C.

The infra-red spectrum of a mechanical mixture of MgO and silica gel is additive: it shows the bands of MgO (1420 and 1450 cm^{-1}) and of silica (465, 800 and 1090 cm^{-1}). Spectra of the samples containing up to 30% MgO have the absorption band at 800 cm^{-1} characterizing free SiO_2. In the spectra of catalysts containing more than 30% MgO the absorption band of free MgO (1450 cm^{-1}) is present.

The most typical absorption bands in the spectra of the catalysts are the bands at 665 cm^{-1} and the band in the region of 1010 - 1090 cm^{-1}. The position of the band at 1090 cm^{-1} characterizing the vibration of the frame [SiO_4] depends on the chemical composition of the catalyst. With the increase of MgO contents the absorption maximum is displaced into the long wave region, which shows the decrease in the polymerization of tetrahedrons [SiO_4] owing to the intrusion of MgO ions into the frame.

Table 1

The influence of MgO contents in catalysts on the displacement of the absorption band at 1090 cm^{-1}.

% MgO	0	5	10	20	30	40	70
Displacement of the band at 1090 cm^{-1}	0	5	15	50	50	65	80

The intensity of the band at 665 cm^{-1} depends on the catalyst composition and the conditions of preparation of the catalysts. For the samples not subjected to aging the intensity of the band at 665 cm^{-1} is not great but when the period of aging is increased the intensity also increases. If the proportion between MgO and SiO_2 changes in the sample the intensity of the band at 665 cm^{-1} passes through a maximum in the range of 20 - 30 % MgO (fig. 2, curve 1).
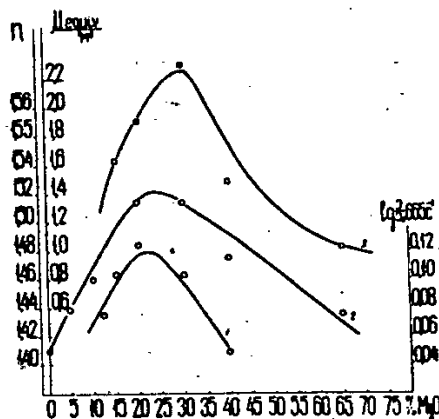
The Fig. 2. The influence of MgO content on catalyst properties:
1 – intensity change of the band at 665 cm^{-1};
2 – change of the refraction index;
3 – change of the concentration of acid centers on the surface.

The values of refraction indices (curve 2) and the concentration of acid centers (curve 3) change in the same way. These results show that silica-magnesia catalysts are not mechanical mixtures of MgO and SiO_2 but products of their interaction. The samples of the composition 30% MgO + 70% SiO_2 have the greatest quantity of interaction product. On the basis of similarity between the intensity curves of the band at 665 cm^{-1} and the concentration of acid centers on the surface we may suppose that acid properties of silica-magnesia catalysts are due to the formation of this substance.

The absorption band at 665 cm^{-1} is typical for absorption spectra of a number of magnesium silicates, such as talc and minerals containing magnesium in the fourfold configuration. But comparison shows that the catalyst properties are not identical with those of talc:1) talc crystallites are anisotropic, the refraction index is 1.53 - 1.58; the catalyst crystallites are isotropic, the refraction index depends on the composition, reaching for the sample containing 30% MgO the maximum value 1.51; 2) the thermograms of talc are characterized by endothermal effects at 120 and 870°. Exothermal effects within the range of 1000° are not observed. On the thermogram of the catalyst only the endothermal effect at 120° (removal of adsorbed water) is observed. At 855° there occurs an exothermal effect corresponding to the formation of clinoenstatite; 3) natural talc and synthetic talc do not have acid properties. The catalyst is an acid of mean strength.

The influence of the chemical composition of silica-magnesia catalysts on the position of the band at 1090 cm^{-1} and the value of the refraction index lead to the conclusion that the interaction products of MgO and SiO_2 are not compounds of constant composition. It is possible that MgO is bound with silica forming compounds of variable composition in which magnesium ions are in the fourfold configuration.

3. INFLUENCE OF THE CHEMICAL COMPOSITION ON THE NUMBER OF ACID CENTERS.

In fig. 3 a dependence of the number of acid centres on the surface of silica-zirconia catalysts on the contents of ZrO_2 is presented. It is seen from the figure that with the increase of the contents of ZrO_2 from 0.1 to 1% the number of acid sites increases in proportion to the concentration of zirconium dioxide. The increase of the contents of ZrO_2 in the samples from 1 to 10% causes a further increase in the number of acid centers, but the rate of the increase slows down. In the samples containing more than 10% ZrO_2 the number of acid centers remains practically unaltered.

If we assume that the molecule of zirconium dioxide reacts with silicic acid forming an acid center, then for the catalyst obtained by impregnation we can calculate the possible number of acid centers. The calculation has shown that in the case of the samples containing up to 1% ZrO_2 the number of acid centers is equal to the number of zirconium atoms on the surface. If the concentration of ZrO_2 is higher the number of the acid centers formed is less than the calculated one.

Fig. 4 gives the concentration change of acid centers on the surface of silica-alumina and silica-zirconia catalysts over a wide range of compositions. Curve 2 shows that with the change of the contents of zirconium dioxide from
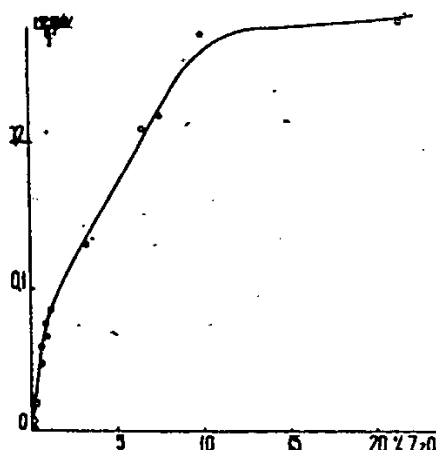
Fig. 3. Dependence of the number of acid centers
on the content of ZrO_2 in the catalyst.
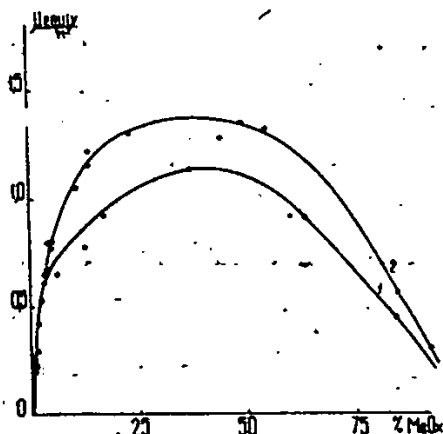
Fig. 4. Influence of the contents of Al_2O_3 and ZrO_2 in catalysts
on the concentration of acid centers on the surface.

15 to 57 mol.% the concentration of acid centers on the surface remains
approximately constant and is equal to about 1.3 microequivalent per m^2.

A similar dependence is observed for silica-alumina catalysts as well:
for low contents of Al_2O_3 in the catalyst the number of acid centers corre-
sponds to the calculated one. Over the range of 20-57 mol.% Al_2O_3 (which is
equivalent to the change of the ratio $SiO_2:Al_2O_3$ from 6.6 to 0.5) the con-
centration of the acid centers remains approximately constant and is equal
to about 1 microequivalent per m^2.

A slight change in the number of acid centers with the increase of the
contents of ZrO_2 or Al_2O_3 to more than 20 mol.% may be due to the following
reasons:

a) inaccuracy in the determination of the number of acid centers due to the
fact that there is a limit adsorption when their concentration on the surface
becomes high;

b) interaction between acid groups on the surface resulting in a decrease of
their effective concentration;

c) incomplete interaction between zirconium dioxide and silicic acid.

If the true concentration of acid centers on the surface of catalysts increased with the increase of the contents of metal oxide and the limit concentration found by us were due to the limit adsorption of n-butylamine molecules, then a considerable increase of the catalytic activity of the acid center equivalent would be expected. But as we shall prove below, this is not the case. Special experiments have shown that in the case of the samples obtained by coprecipitation, even with the equimolecular ratio of the components one fails to find free ZrO_2 and Al_2O_3. This shows that the assumption c) is baseless.

Presumably, the more probable is the second assumption according to which the effective limit concentration of acid centers on the surface is due to their interaction. In the case when hydroxyls are the acid centers they may interact, separating water and forming oxygen bridges. On the basis of the experimental data obtained in this work we can determine the apparent site area * of one acid group on the surface of silica-zirconia catalysts. One is led to think that in the region of low concentrations of zirconium dioxide (below 1%) when the number of acid groups is proportional to the contents of ZrO_2 and equal to the number calculated, the distance between the formed acid centers is great and a considerable interaction between them does not take place. The upper limit of this region is set by the concentration of acid groups equal to 0.25 microequivalents per m^2 (1% ZrO_2), whence the effective area of undisturbed acid centers is equal to 600 - 700 $Å^2$.

At maximum concentration of acid centers (1.3 micro-equivalents/m^2) the effective area of an acid center on the surface of a silica-zirconia catalyst is 130 $Å^2$.

For the silica-alumina catalysts the minimal effective area is larger, about 170 $Å^2$. These results show that the value of the effective area of a hydroxyl group on the surface of catalysts of high acidity is 10-20 times more than that of the effective area of a hydroxyl group on the surface of silica gel [8].

4. INVESTIGATION OF CATALYTIC ACTIVITY

Investigation of catalytic activity with respect to dehydration of isopropyl alcohol has shown that the catalytic activity of silica gel is close to zero.

The addition of only 0.1% zirconium dioxide to silica gel leads to the appearance of considerable acidity and catalytic activity. With the change of the contents of ZrO_2 in the catalyst, the specific activity and the concentration of acid centers change in a similar way.

With the change of the temperature of calcining from 425 to 850°C the catalytic activity becomes lower. As the surface area of the sample at these temperatures remains practically the same, the observed decrease of the activity may be caused both by a decrease of the number of active centers and the alteration of their nature.

Fig. 5 gives the dependence between the catalyst activity with respect

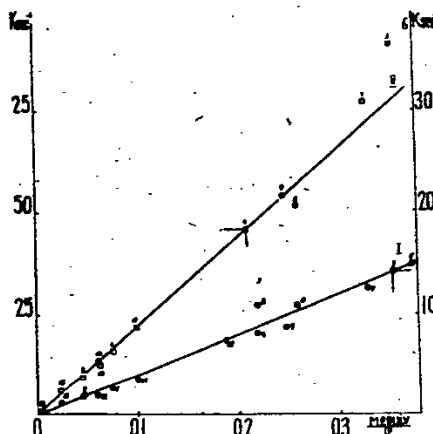* Further we shall call this value the effective area.

Fig. 5. Influence of the number of acid centers on the surface of
silica-zirconia catalysts on their catalytic activity.
1. Decomposition of ethyl alcohol.
2. Decomposition of isopropyl alcohol.
1 - 10% ZrO_2 - 500°; 2 - 10% ZrO_2 - 850°;
3 - 45% ZrO_2 - 500°; 4 - 45% ZrO_2 - 800°;
5 - 50% ZrO_2 - 500°; 6 - 50% ZrO_2 - 800°;
7 - 55% ZrO_2 - 800°; 8 - 55% ZrO_2 - 800°;
9 - 71% ZrO_2 - 500°; 10- 71% ZrO_2 - 750°;
11 - 85% ZrO_2 - 435°; 12- 85% ZrO_2 - 500°;
13 - 92.5% ZrO_2-425°; 14 - 92.5% ZrO_2 - 500°.

to the decomposition of ethyl and isopropyl alcohols and the number of acid
groups on the surface. As is seen from the figure, the activity of silica-zir-
conia catalysts is proportional to the number of acid centers on the surface:
within the limits of accuracy of determination the points for samples of dif-
ferent chemical composition calcinea at different temperatures lie on the
same direct line. This result shows that the decrease of the activity of silica-
zirconia catalysts after heat treatment is due to the decrease of the number
of acid centers and not to the change of their nature.

A linear dependence between the catalytic activity and the number of
acid centers on the surface is observed for the decomposition reactions of
cumene on the silica-alumina catalysts and for dehydration of isopropyl al-
cohol on silica-magnesia catalysts of various composition (fig. 6). The
same dependence was reported by several other authors between the number
of acid groups on the surface of catalysts and their activity with respect to
cracking reactions of cumene and polymerization of propylene on silica-
alumina catalysts [7,9,10].

The direct proportionality between the catalytic activity and the number
of active centers on the surface shows that the catalytic properties of the
substances studied are due to the presence of acid centers on their surface
and that the activity of any one acid center does not depend on the temperature
of calcining and the ratio of the components entering into the composition of
the catalyst.

The reaction rate constant referred to unity of acid centers is a charac-
teristic value for a catalytically active component and may serve as a ratio-
nal characteristic of substances possessing catalytic activity with respect
to the processes of acid nature.
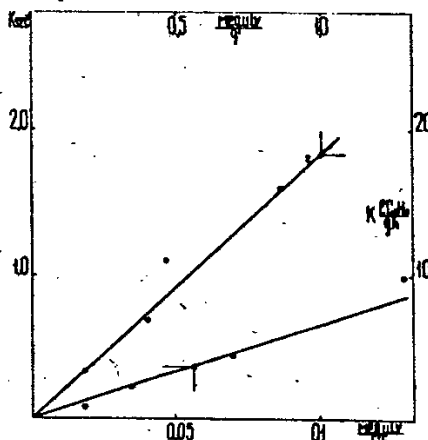
Fig. 6. Influence of the number of acid centers on the
surface of catalysts on their activity:
1) decomposition of cumene on silica-alumina
catalysts at 400°.
2) decomposition of isopropyl alcohol on silica-
magnesia catalysts at 325°.

For catalytic reactions occurring in the liquid phase in the presence of
proton acids a linear dependence between the function of acidity and the log-
arithm of reaction rate was found by a number of investigators [12,14]. It
was of interest to find out whether such regularities exist for solid oxides
possessing acid properties.

Table 2
The influence of the acidity of catalysts on their activity.

logarithm of reaction rate constants

Composition of catalysts	pK	dehydration of isopropyl alcohol (1/m.equiv.h)	dimerization of propylyne (1/equiv. hour)	dimerization of isobutylene (1/equiv.hour)
Al_2O_3-SiO_2	-8.2	3.75	4.1	-
ZrO_2-SiO_2	-8.2	2.25	2.75	4.0
phosphorous acid on silica gel	-5.6	1.47	1.6	3.6
MgO-SiO_2	-3.0	1.25	-	-
-metaphos-phorous acid on silica gel	-3	0.55	0.0	3.3

In table 2 data are given characterizing the influence of the acidity of
the catalysts studied by us on the activity of a unit of acid centers for dime-
rization processes of propylene, isobutylene and dehydration of isopropyl
alcohol.

As is seen from table 2 for all three reactions the reaction rates change symbatically with the strength of the acid groups of the catalyst. The discrepancy between the catalytic activity and the acidity of the silica-alumina catalyst is apparently due to inaccuracy in determining acidity because of the absence of a suitable indicator with pK less than -8.2. Probably the real acidity of this catalyst is much higher.

For various reactions the character of dependence of the reaction rate on the acidity of catalyst is different: the dependence of the dimerization rate of propylene on the acidity of catalysts is much more pronounced than it is for the dimerization rate of isobutylene. But for all reactions studied the dependence between the acidity and the catalytic activity is less pronounced than for homogeneous acid reactions. The coefficient α in the equation of Hammet is only 0.15 - 0.6 against 1 - 2 for homogeneous reactions.

The results obtained can be explained if we suppose that the greater part of the molecules of the reacting substances adsorbed on the surface of even a weakly acid catalyst is protonized, as a result of which the further increase of the acidity of catalysts can not change considerably the degree of ionization. Evidently the protonization of the molecules adsorbed on the solid surface proceeds easier than that of the dissolved ones.

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THE MECHANISM AND KINETICS OF ALDOLIC REACTIONS IN GASEOUS PHASE ON SOLID CATALYSTS WITH BASIC CHARACTER

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Abstract: The reactions between formaldehyde and nitromethane [1], formaldehyde and acetic-aldehyde [2], formaldehyde and acetone [3], formaldehyde and acetonitryle [4] were investigated in gaseous phase in the presence of silica gel catalyst containing various quantities of sodium (0.01, 0.03, 0.06, 0.08 moles Na/100 g gel).

The apparent reaction rate constants were determined for reactions (2), (3), (4) at $275^{\circ}C$.

In fig. 3 the dependence between apparent reaction rate constants and the sodium content in the catalyst, is platted. The rate constants show a linear dependence on the quantity of sodium in the gel. This fact confirms that the reaction rates are directly proportional to the basicity of the catalyst. On the other hand it was found the linear dependence between the acidities (pK) of the hydrogen donor molecules (CH_3CHO, CH_3COCH_3, CH_3CN) and the rate constants of the reactions with formaldehyde.

It confirms the previous established statement, that for this type of reactions (aldolic), the rate of reaction is directly proportional to the acidity of the hydrogen of donor molecules and the basicity of the solid catalyst.

1. INTRODUCTION

The reactions referred to as aldol reactions were described in several earlier papers. Aldol reaction is here considered to be one that occurs between a compound, (I), containing the carbonyl group and another, (II), containing a mobile hydrogen, namely:

$$A.B.C=O + H_2C.X.Y \rightarrow A.B.C=C.X.Y + H_2O ,$$

$$\text{(I)} \qquad \text{(II)} \qquad \text{(III)}$$
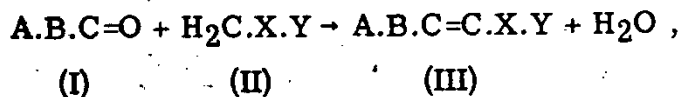
where B is a solid basic catalyst.

As compounds (I), aldehydes [1-10] and, as compounds (II), aldehydes [1-3], ketones [4], nitriles [5,6], nitroparaffins [8] and diketones [9] have been investigated.

Studies on the mechanism of the aldol reactions carried out over solid basic catalysts permitted the conclusion that it resembles that of the aldol condensation in the liquid phase [10]. In the first stage of reaction (1), the basic catalyst abstracts a proton from the carbonyl compound.

$$X.Y.CH_2 + B \rightarrow X.Y.CH^{(-)} + BH^{(+)} . \qquad (1)$$
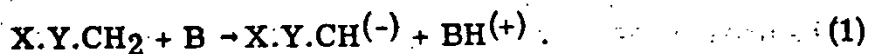
It is too early to answer the question whether the proton is completely transferred with formation of the conjugate acid $BH^{(+)}$, or the polarized complex $X.Y.CH...H...B$ is formed. This question will be studied further. The following stages of the aldol reaction, namely, reaction of anion (III) with carbonyl compound (I),

$$X.Y.CH^{(-)} + C=O \rightarrow X.Y.CH-C-O^{(-)} , \qquad (2)$$
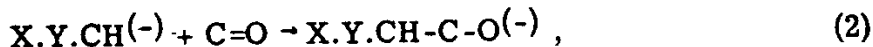
which constitutes the condensation proper and proceeds with formation of a new C-C bond, then regeneration of the catalyst,

$$X.Y.CH-C-O^{(-)} + BH^{(+)} \rightarrow X.Y.CH-C-OH , \qquad (3)$$

and abstraction of the water molecule from the resulting compound,

$$X.Y.CH-C-OH \rightarrow X.Y.C=C + H_2O , \qquad (4)$$

were found to proceed at a higher rate. The rate-determining stage should, therefore, be the reaction between the base and compound (II) containing the acidic hydrogen. If this is true, the over-all reaction rate, V, should be directly proportional to the acidity of compound (II) and basicity of catalyst B:

$$V = K_{(2)}K_B .$$

There were two methods to verify the above suggestion. By utilizing invariably the same standard reaction (2) ($K_{(2)}$ = constant), the apparent rate constant for that reaction carried out over silica catalysts containing varying amounts of sodium, was found to be directly proportional to the sodium content in the gel. The straight-line relationship holds true up to sodium contents of 0.081 g-atom Na/100 g silica gel. This fact together with consideration of the possible structure of active centres on the surface of the silica gels used, permitted the conclusion that the groups -SiONa constitute the active centres [8].
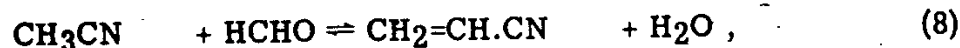
The first part of the present work deals with gas-phase aldol reactions of compounds (II) containing hydrogens of varying mobility ($K_{(2)}$ = variable) in the presence of the same catalyst (K_B = constant).

The following reactions were investigated:

$$CH_3NO_2 + HCHO \rightleftharpoons CH_2=CH.NO_2 + H_2O , \qquad (5)$$

$$CH_3CHO + HCHO \rightleftharpoons CH_2=CH.CHO + H_2O , \qquad (6)$$

$$CH_3COCH_3 + HCHO \rightleftharpoons CH_2=CH.COCH_3 + H_2O , \qquad (7)$$

$$CH_3CN + HCHO \rightleftharpoons CH_2=CH.CN + H_2O , \qquad (8)$$
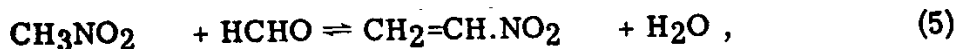
The carbonyl compound was always the same, namely, formaldehyde, and only the compound with mobile hydrogen was varied ($K_{(2)}$). The α-hydrogens are known to decrease in acidity in the order $CH_3NO_2 > CH_3CHO > CH_3COCH_3 > CH_3CN$; if the above-mentioned assumption concerning the mechanism of the aldol reaction is true, the V-values should yield a series that follows the type $V_5 > V_6 > V_7 > V_8$.

The kinetics and mechanism of reaction (6) were described earlier [9]. The present work makes use of a preliminary observation that reactions (7)

and (8) proceed in the gas phase according to the above scheme. In the presence of silica-sodium catalysts they are fairly efficient; their maximum yields are obtained at 300° and 450 - 500°C, respectively.

Reaction (5) failed to occur in the presence of those catalysts. At relatively low temperatures (150°C), the reaction mixture became oxidized with the nitro group. The products of the reaction were found to contain water, carbon dioxide and monoxide, amines and polymeryzates. Kinetic studies of reaction (5) were, therefore, a failure.

The second part of the present work is intended to determine the apparent rate constants of reactions (7) and (8) and to ascertain if in this case also exists, as does for reaction (5), a straight-line relationship between the apparent rate constant and catalyst sodium content.

The apparent rate constant was determined as the reciprocal of the contact time at 275°C within which the transformation took place in a definite degree. The temperature 275°C and the equimolar ratio of the reactants were chosen to make it possible to compare the resulting data with those obtained earlier for reaction (1).

2. EXPERIMENTAL

2.1. *Apparatus*

Experiments were carried out in a differential reactor described in an earlier paper [1].

2.2. *Catalyst*

Silica-sodium catalysts [9] were used. Pure-grade silica gel containing 0.003 g-atom Na+K/100 g and gels containing 0.010, 0.030, and 0.036 g-atom Na/100 g were examined.

2.3. *Reagents*

Commercial 30% formalin (with 5% methanol) was used as formaldehyde. Pure-grade acetone was purified by distillation and a fraction boiling at 55.5 - 56.0°C was used. Acetonitrile was distilled to collect a fraction boiling at 81 - 82°C.

The reaction mixture was made up of equimolar amounts of formalin, acetone and acetonitrile.

2.4. *Analysis*

Products of the reaction were analyzed chromatographically and chemically. Methyl vinyl ketone was determined bromometrically. Acrylonitrile in the presence of formaldehyde was determined by the method involving addition of n-dodecyl mercaptane to the double bond. (The method applies only for acrylonitrile-to-formaldehyde ratios greater than   ; when present in larger amounts, formaldehyde causes an error directly proportional to its content.)

3. METHOD

In each experiment, yields of reactions (7) and (8), based on acetone and acetonitrile, respectively, were evaluated from the products analysis data. The rate of dropwise addition of the reaction mixture, its composition and the catalyst volume were used to calculate the apparent contact time defined as the residence time of the gaseous products in the empty space equal to that occupied by the catalyst.

4. RESULTS

The yield versus contact time curves for reaction (7) carried out over different catalysts, and for reaction (8), are given in figs. 1 and 2, respectively. The curves show that for each catalyst the yield rises as the contact time is increased; for identical contact times, the yield is related to the content of sodium in the catalyst.
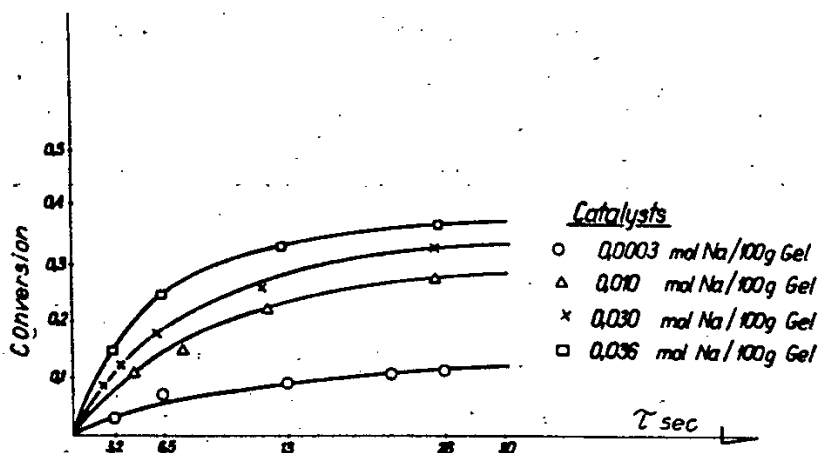
Fig. 1. Dependence of conversion upon τ.
Reaction: $CH_3COCH_3 + HCHO \rightarrow CH_2=CHCOCH_3 + H_2O$.
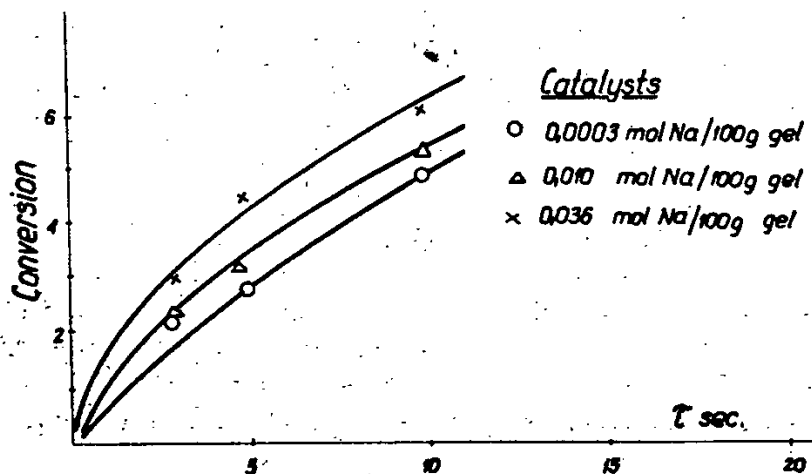
Fig. 2. Dependence of conversion upon τ.
Reaction: $CH_3CN + HCHO \rightarrow CH_2CHCN + H_2O$.
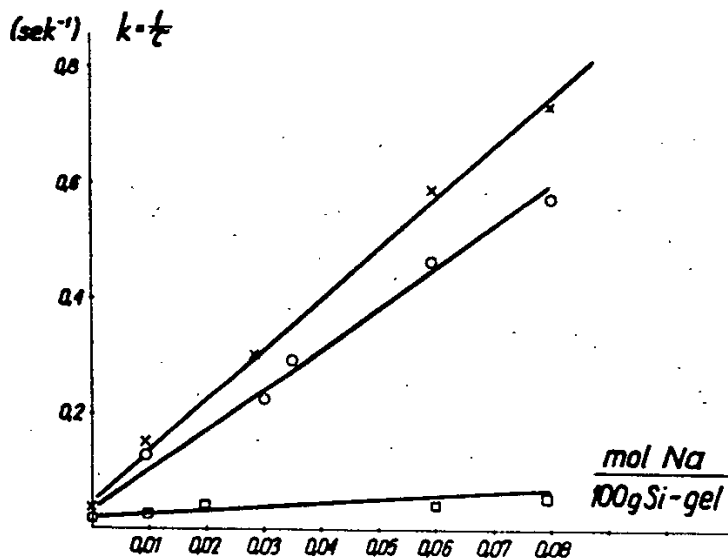
Fig. 3. Dependence between apparent reactor rate constant,
and sodium concentration in silica catalyst.
x CH_3CHO + HCHO $CH_2=CHCHO$ + H_2O.
o CH_3COCH_3 + HCHO $CH_2=CHCOCH_3$ + H_2O.
□ CH_3CN + HCHO $CH_2=CHCN$ + H_2O.
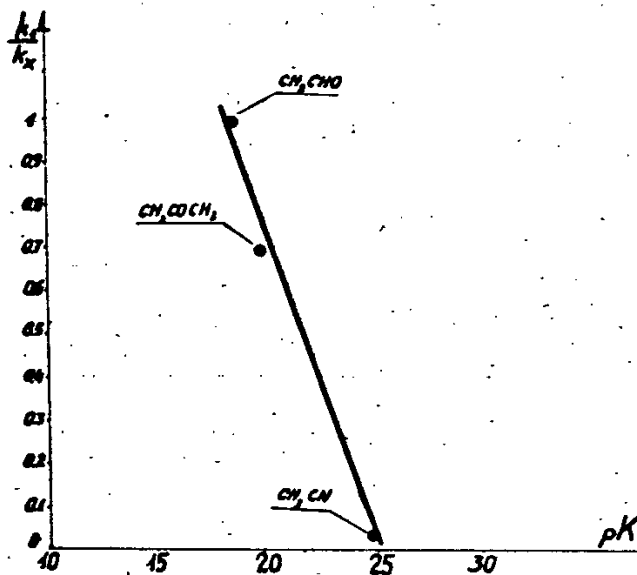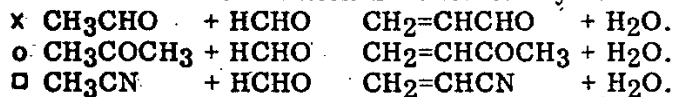
Fig. 4. Dependence between acidity of organic molecules
and reaction rate constants.

The data of Figs. 3 and 4 were used to calculate the apparent rate con-
stant, $k_{0.10}$, for reactions (3) and (4) over each catalyst as the reciprocal
of the contact time τ, for a yield of 0.10, namely,

$$k_{0.10} = 1/\tau .$$

The rate constant thus defined allowed to compare the present data
with those obtained for reaction (6) [9]. The 0.10 yield contact times for
reactions (7) and (8) with catalysts of reaction (2) were easy to read from
fig. 1, since for each catalyst the maximum yield was greater than 0.10.

On the other hand, maximum yield for reaction (3) was only 0.05; the contact time for the 0.10 yield was, therefore, assumed to be twice that for the 0.05 yield. This assumption burdened the data with an additional error but made possible their intercomparison.

The apparent rate constant versus catalyst sodium content curves for the two reactions are presented in fig. 3. For comparison, the data obtained for reaction (6) [9] are also plotted in fig. 3.

For catalysts containing less than 0.036 g-atom Na/100 g gel, the apparent rate constants of reactions (6), (7) and (8) are directly related to the sodium content.

The comparison of the three straight lines reveals their two characteristic features:

a. the lines do not pass through the origin of the reference frame and intersect the upper ordinate,

b. the lines have different slopes.

The first festure is applicable in terms of a primary activity of the silica gel containing no alkali metals. The slopes of the lines are related to apparent rate constants based on unit sodium content in the catalyst, i.e., $K_B = $ constant.

The relative apparent rate constants read from fig. 3 for the three reactions yield the following series:

$$K_{CH_3CHO} : K_{CH_3COCH_3} : K_{CH_3CN} = 1 : 0.07 : 0.04 .$$

On the other hand the acidities of hydrogenes of molecules which we apply are known.

If the assumption $v = K_2 K_B$ is right, there should be expected the lineal dependence between the acidities (pK) and the velocity constant of the reactions involved.

Table 1

	pK	k_{CH_3CHO}/k_x
CH_3CHO	19.7 [11]	1
CH_3COCH_3m	20.0 [11]	0.7
CH_3CN	25 [12]	0.04

Table 1 and fig. 4 show the dependence between pK and the apparent reaction velocity constants. In order to simplify this problem they are given as a ratio: k_{CH_3CH}/k_x.

As it is evident the points are ranged along the straight line. This diagram confirms our assumption concerning the mechanism of reactions of the aldolic type in the gaseous phase; on the other hand, it permits to foresee the velocity aldolic reaction in gaseous phase at this moment, when the acidity of the hydrogen donor molecules are known.

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STAT

STUDY ON CATALYTIC DEHYDROGENATION
OF C_6 - C_{10}-ALKANES

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1. INTRODUCTION

C_6 and above alkenes are valuable raw materials for manufacturing of a
number of important products, such as detergents, alcohols, carbonyl com-
pounds, etc. At present alkenes with double bonds on the end of the chain are
of the greatest interest. On polymerization of high-molecular unbranched
alkenes-1 lubricating oils are produced. The copolymerization of ethylene
with hexene-1, dodecene-1, hexadecene-1 has been carried out [1]. Isotactic
polymers with high melting points have been produced from branched alkenes-1
with tertiary and quaternary carbons [2]. Recently alkenes with double non-
end bonds are becoming to be used in synthesis processes. For instance, the
position of double bonds in alkenes is not important for oxosynthesis. Copo-
lymers have been produced from conjugated alkadienes (isoprene, butadiene)
and hexene-2 or heptene-2 [3].

The main methods to produce high-molecular alkenes are thermal crack-
ing of paraffins, synthesis from CO and H_2 on ferrous and cobalt catalysts and
polymerization of lower alkenes [3]. The first and the second methods (on fer-
rous catalysts) give mainly mixtures of normal alkenes-1 of various mole-
cular weights. The synthesis from CO and H_2 on cobalt catalysts produces
considerably less alkenes than that on ferrous catalysts; double bonds of these
alkenes are in different positions. The third method gives more or less
branched hydrocarbons with double bonds in the middle of molecules.

The development of new methods of the middle and higher alkenes pro-
duction are of high importance. The catalytic dehydrogenation of alkanes is
a rather tempting method. Our aim was to study C_6 - C_{10}-alkane dehydro-
genation, to find catalysts and conditions for a selective process to produce
corresponding alkanes, as well as to study possibilities of controlling the
reactions of dehydrogenation, dehydrocyclization and cracking. The given
material is the summation mainly of our studies on the problem.

C_6 and above alkanes might be divided conditionally into two groups:
1) isoalkanes, containing in their main chains less than 6 carbon atoms and
which therefore can not be aromatized directly without isomerization of
carbon skeleton;
2) n-alkanes and isoalkanes, containing in their chains 6 and more carbon
atoms which can be aromatized directly. Besides our studies, there are few de-

hydrocyclization of individual alkanes, as well as of their artificial and nat-
ural mixtures, and on dehydrogenation of C_4-C_5-alkanes, which had a close
bearing on the problem we were interested in.

2. STUDY ON DEHYDROGENATION OF ALKANES CONTAINING IN THEIR MAIN CHAINS LESS THAN 6 CARBON ATOMS

On the iso-hexane example we have shown that alkanes of this group can
relatively easily be dehydrogenated into iso-hexenes with rather high yields
close to equilibrium ones [14]. The chromia-alumina-potassium oxide-cata-
lyst which showed high activity in dehydrogenation of pentanes produced cata-
lysates of 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane with
86-89% yields, containing 32-40% alkenes, mainly corresponding to original
alkanes. The results are given in table 1.

Table 1
Composition of iso-hexanes catalysates (500°C, flow rate 0.5 hour^{-1},
30 cc of catalyst, 100 cc of hydrocarbon)

Hydrocarbon	Catalysate yield (wt.%)	Content in catalysate (wt.%)		
		Alkenes	Dienes	Aromatic hydro-carbons
2-methylpentane	86.0	32.0	2.3	2.2
3-methylpentane	88.3	38.9	0.7	1.8
2,3-dimethylbutane	89.2	40.1	4.5	1.5

Using this catalyst under somewhat different conditions 3,3-dimethyl-
butene-1 was produced from 2,2-dimethylbutane. The yield was 9%, also
rather close to an equilibrium one. When the reaction was carried out in
helium, as an inert diluent, the yield of 3,3-dimethylbutene-1 increased to
12%. Lorz et al. reached the same results when the reaction was carried
out in vacuum [15].

3. STUDY ON DEHYDROGENATION OF C_6-C_{10}-n-ALKANES

Fig. 1 shows the equilibrium alkene yields, obtained on C_2-C_6-n-alkenes
dehydrogenation, depending on temperature. The estimates were made ac-
cording to the data on the free energies of these hydrocarbon formation [16].
It is seen from the figure that the equilibrium yields of the corresponding
alkenes increase with increase of molecular weight of the original alkanes
and of reaction temperature. On dehydrogenation of higher alkanes the equi-
librium alkene yields are believed to be higher. However, the higher is the
molecular weight of the original alkane and the higher is the temperature,
the more possibilities there are for the side reactions to occur. Levitsky
indicates [17] that while estimating the equilibrium alkene concentrations the
side reaction stage, including the aromatization stage, should be taken into
account. Table 2 shows the equilibrium hexene yields estimated by Levitsky
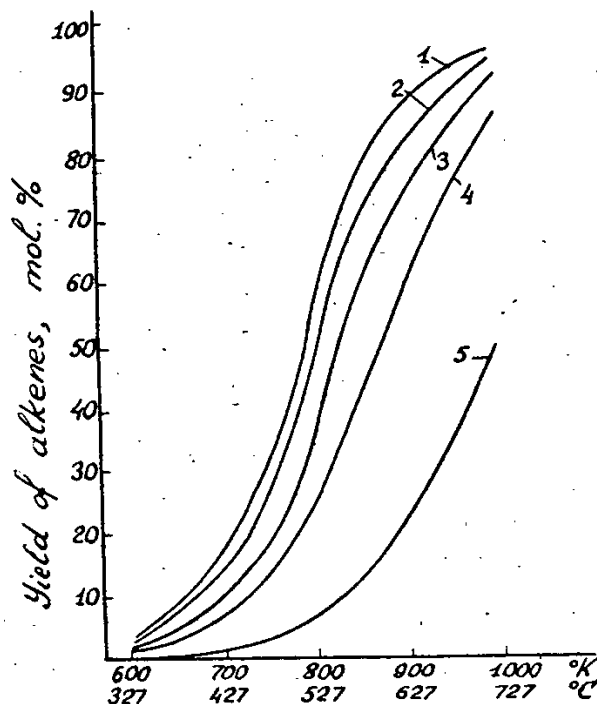
Fig. 1. Equilibrium yields of alkenes from $C_2 - C_6$-n-alkanes.
1 - n-hexane; 2 - n-pentane; 3 - n-butane; 4 - propane; 5 - ethane.

Table 2
The equilibrium hexene yields at different stages of n-hexane aromatization.

Benzene yield (mol.%)	Equilibrium hexene yield (mol.%)			Benzene yield (mol.%)	Equilibrium hexene yield (mol.%)		
	450°C	475°C	500°C		450°C	475°C	500°C
0	24.4	33.0	43.2	30	7.1	12.4	19.8
5	17.8	26.4	36.8	40	5.5	9.8	15.9
10	13.8	21.8	21.9	50	4.3	7.7	12.6
20	9.4	16.0	24.8	60	3.3	5.9	9.7

at different stages of n-hexane aromatization.

As it follows from the table, when benzene contents in the catalysates obtained at temperatures 450-500°C are 40-60% the equilibrium hexene yields are 3-16%. Alkene yields of the same order were obtained in the experiments on dehydrocyclization of n-alkanes. Levitsky compared the theoretical heptene yields with the experimental data by Grob [18], Obolentsev and Usov[19]. He assumed that the equilibrium constants of n-hexane and n-heptane dehydrogenation were equal. He came to the conclusion, that the stage of heptane dehydrogenation in these experiments was so high, that the heptene yields were determined not only by the rate of the forward reaction, but by the rate of the reverse reaction as well.

We have studied the behaviour of n-hexane on the conventional dehydrogenating chromia-alumina-potassium oxide-catalyst [20]. The thermodyna-

mic estimates have shown that under the experimental conditions the hexene equilibrium yields were 42-73%, in spite of the fact that the hexene contents in the catalysates varied only in the range of 9 - 12%, while the benzene content was up to 67%. The result obtained is of a principal interest, since in the previous studies on n-alkane dehydrocyclization it was considered that low yields of alkenes obtained from n-alkanes in the process of their aromatization provided evidence that only a negligible reverse reaction, the reaction of hydrogenation proceeded. On this basis the assumptions on the mechanism of alkane dehydrocyclization were made.

Thus in case the aromatic hydrocarbons are produced in the catalysis process at 450-500° the hexene yields will not exceed the corresponding values shown in table 2. However, provided one finds such dehydrogenating catalysts and such conditions under which the aromatization reaction does not take place at all or proceeds to a little extent, the alkene yields might be relatively high, as is seen from table 2.

It is known that aromatizing and dehydrogenating catalysts are of the same nature and the aromatization reaction thermodynamically is more advantageous. For instance, at 400°C and up n-hexanes are practically aromatized completely, while the equilibrium hexene yields at 400° are only ~ 12%.

Having examined the published data on n-alkane dehydrocyclization we found that the ratio of alkene and aromatic hydrocarbon yields depended both on the nature of catalysts and on the conditions under which the reaction proceeded. However, the alkene contents in the catalysate cannot be taken as a criterion of dehydrogenating capacity of a catalyst, for it is quite probable that a part of alkenes produced converted into aromatic hydrocarbons in the catalysis process.

In order to determine the stage of the proceeding of the aromatization and dehydrogenation reactions we carried out experiments both with n-hexane and isopentane (hydrocarbon from which aromatic hydrocarbons are practically not obtained under dehydrogenating conditions) under similar conditions. Studies were carried out on the effects of methods of chromia-alumina and chromia alumina-potassium oxide-catalyst preparation as well as of various alkaline additives on the ratio of dehydrogenation and aromatization reactions [21,22]. As a result of these studies a series of interesting regularities were found.

Our data confirmed that the nature of catalysts and methods of their preparation, in particular, the methods of introduction of alkaline additives (A) have considerable effects on the degree of the proceeding of the dehydrogenation and aromatization reactions. It is seen from table 3, where the selective data from the quoted works are shown.

It is seen from table 4 that catalysts with nearly the same dehydrogenating capacity (on isopentane) do not always give the same yields of aromatic hydrocarbons.

The dependence of isoamylene contents in the isopentane catalysate, of hexene and benzene contents in the n-hexane catalysate and of benzene content in the cyclohexane catalysate upon the duration of the experiments is shown in fig. 2. The dehydrogenation and aromatization reactions of these

Table 3

The effects of catalyst compositions and methods of their preparation
(500°C, flow rate 0.5 hour^{-1}, 30 cc of catalyst, 100 cc of hydrocarbon)

Catalyst	Yield on the hydrocarbon passed, wt.%		Ratio of yields		
	Alkenes		ben-zene	isoamylenes: benzene	hexenes: benzene
	from iso-pentane	from n-he-xane			
Catalyst composition					
Cr_2O_3	7.0	6.5	3.8	1.78	1.71
$Al_2O_3 + Cr_2O_3$	29.5	19.6	13.9	2.21	1.41
$Al_2O_3 + Cr_2O_3 + K_2O$	38.2	11.9	37.0	1.06	0.32
$Al_2O_3 + Cr_2O_3 + Na_2O$	36.8	12.0	22.5	1.67	0.53
$Al_2O_3 + Cr_2O_3 + PbO$	29.1	15.6	13.3	2.19	1.17
Method of preparation $Al_2O_3 + Cr_2O_3 + K_2O$ (90.7 : 5.6 : 3.7 mol.%)					
Impregnation of Al_2O_3 with $K_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$ solution	38.2	11.9	37.0	1.04	0.32
Impregnation of Al_2O_3 with KOH and $(NH_4)_2Cr_2O_7$ solution	37.9	11.9	28.3	1.34	0.48
Impregnation of Al_2O_3 with CrO_3 and K_2O_3 solution	39.3	13.3	22.0	1.80	0.60
Coprecipitated	29.2	5.0	24.0	1.22	0.21

hydrocarbons were studied with 17 different catalysts. Here are given only
selective data. As it is seen from the figure, the curves of dehydrogenation
(isopentane and cyclohexane) and of n-hexane aromatization are parallel
not in all cases. This statement does not correspond with Steiner's [23] main
assumption on which basis he came to the conclusion that the active centres
of oxide catalysts for the reactions of n-alkane dehydrogenation and dehydro-
cyclization were identical. Steiner states that the poisoning effect decreases
the dehydrogenation rate approximately to the same extent as the dehydro-
cyclization rate.

The observed regularities indicate that n-hexane dehydrocyclization re-
action apparently needs some additional changes of the catalyst nature which
are not necessary for dehydrogenation of isopentane or cyclohexane.

The direct proof of the existence of various active centres which are
responsible for proceeding of dehydrogenation and aromatization on the chromia-
alumina catalyst surface is our work on partial poisoning of the chromia-
alumina catalyst with cyclopentadiene or furfural [24]. In this work we showed
that the treatment of the chromia-alumina catalyst with cyclopentadiene or

Table 4

Isoamylene yields from isopentane, hexene and benzene yields from n-hexane
in terms of the hydrocarbon passed (the conditions are as in Table 3)
$Al_2O_3 + Cr_2O_3 + A$ (90.7 : 5.6 : 3.7 mol.%).

Catalyst		Isoamylenes	Hexenes	Benzene
A-K_2O	Impregnation of Al_2O_3 with $(NH_4)_2Cr_2O_7$ and $K_2Cr_2O_7$ solution	38.2	11.9	37.0
"	Impregnation of Al_2O_3 with $(NH_4)_2Cr_2O_7$ and KNO_3 solution	38.6	9.1	38.2
"	Impregnation of Al_2O_3 with $Cr(NO_3)_3$ and KNO_3 solution	40.8	11.9	28.1
"	Impregnation of Al_2O_3 with CrO_3 and K_2CO_3 solution	39.3	13.2	22.0
A-Na_2O	Impregnation of Al_2O_3 with $(NH_4)_2Cr_2O_7$ and $NaNo_3$ solution	36.8	12.0	22.5
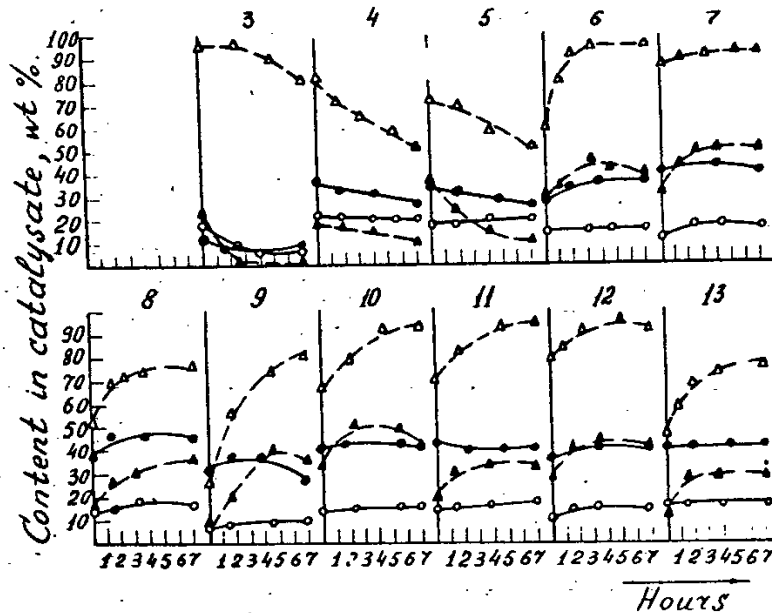
Fig. 2. Unsaturated (● - from isopentane, o - from n-hexane) and aromatic
(▲- from n-hexane, △ - from cyclohexane) hydrocarbon contents in
dependence upon the duration of catalyst work.
3 - Cr_2O_3;
4 - $Al_2O_3 + Cr_2O_3$ (precipitation);
5 - $Al_2O_3 + Cr_2O_3$ (impregnation);
6 - $Al_2O_3 + Cr_2O_3 + K_2O$ [$(NH_4)_2Cr_2O_7$ and $K_2Cr_2O_7$];
7 - same as above, KNO_3 instead of $K_2Cr_2O_7$;
8 - $Al_2O_3 + Cr_2O_3 + K_2O$ [$Cr(NO_3)_3$ and KNO_3];
9 - $Al_2O_3 + Cr_2O_3 + K_2O$ (precipitation);
10 - $Al_2O_3 + Cr_2O_3 + K_2O$ [$(NH_4)_2Cr_2O_7 + K_2CO_3$];
11 - $Al_2O_3 + Cr_2O_3 + K_2O$ [$(NH_4)_2Cr_2O_7 + KOH$];
12 - $Al_2O_3 + Cr_2O_3 + K_2O$ (grinding of wet salts);
13 - $Al_2O_3 + Cr_2O_3 + K_2O$ [$CrO_3 + K_2CO_3$].

furfural and its subsequent regeneration led to irreversible poisoning of its
dehydrocyclizating capacity without changing in its dehydrogenating activity.
This could be seen for example from table 5.

Table 5

Irreversible poisoning of chromia-alumina catalyst with cyclopentadiene
(500°, flow rate 2.1 hour^{-1}, 30 cc of catalyst, 100 cc of hydrocarbon).

Original hydrocarbon	Catalyst state	Average content in catalysate (wt.%)	
		Alkenes	Aromatic hydro-carbons
n-Hexane	Without poisoning	17.5	6
	After poisoning and regeneration	16.4	3
n-Nonane	Without poisoning	17.9	21
	After poisoning and regeneration	13.4	14
Isopentane	Without poisoning	26.1	–
	After poisoning and regeneration	26.1	–

The existence of dehydrogenating and dehydrocyclizating active centres
on the surface of chromia-alumina catalysts gave us hope to find conditions
for selective dehydrogenation of C_6 and above alkanes. Indeed, at 475^oC and
flow rate 2, 1 hour^{-1} in the presence of the chromia-alumina catalyst men-
tioned above we obtained a catalysate of n-hexane in 97% yield, containing
10% hexenes. The catalysate did not practically contain aromatic hydro-
carbons. Hexene yield on decomposed n-hexane was 74% [25]. At 427^oC and
flow rate 4.2 hour^{-1} the catalysate of n-nonane in 98.7% yield containing
8-9% nonenes was obtained. Aromatic hydrocarbons were also almost ab-
sent in it. The nonene yield on decomposed original hydrocarbon was 87% [26].

We also carried out (more or less selectively) the reaction of dehydro-
genation of C_6-C_{10}-alkanes with another oxide catalyst -K-5, technical
catalyst for n-butane dehydrogenation [27,28]. At 500^oC and flow rate 2.1
hour^{-1} aromatic hydrocarbons were produced on it only at an initial stage
of the experiment, then their formation practically terminated. The amount
of alkenes in the catalysate was maintained at 7-11% level. The number of
carbon atoms in molecules of the major portion of produced alkenes corres-
ponds to original alkanes. Isomerizing activity of both the chromia-alumina
catalyst and K-5 catalyst was extremely low under these conditions and
therefore the paraffin part of the catalysate consisted mainly of unchanged
original alkanes.

These first results of selective dehydrogenation of C_6-C_{10}-n-alkanes
undoubtedly are of theoretical interest. 10-12% yields of alkenes might be
of practical importance only if simple and accessible methods of their iso-

lation are developed. Our attempts to increase considerably alkene yields with other catalysts (metal, coal, chromic oxide on silica-alumina and others) failed. Alkene concentration and contact time of alkenes with the catalyst under conditions of selective dehydrogenation of n-alkanes (the process is carried out at comparatively high flow rates) are likely to be too negligible for aromatization to occur to a high extent. The increase of alkene concentration resulted from changes of reaction conditions leads to the beginning of the dehydrocyclization reaction. The higher is alkene concentration the higher is reaction rate. It seems that our large experimental material on n-alkane dehydrogenation and some published data permit to say that the formation of alkenes on oxide catalysts promotes to some extent the n-alkane dehydrocyclization process. We do not, however, eliminate the possibility of the formation of aromatic hydrocarbons directly from n-alkanes under some conditions.

In this connection our study on conversion of n-hexane on the chromia-alumina-potassium oxide-catalyst at low pressure is of some interest. Taking into account the fact that dehydrogenation of n-alkanes into corresponding alkenes is a reversible reaction proceeding with evolution of one mole of hydrogen per one mole of reacting n-alkane and the aromatization reaction is irreversible, we can assume that the reduction of partial pressure of mixture components will result in the increase of the alkene yield, hexenes in our case. We have studied this reaction at temperature 500^0 in vacuum and in helium atmosphere. All experiments were carried out at the same contact time. It is seen from fig. 3 that the reduction of partial pressure in the system results in the increase of benzene yield and in some reduction of hexene yield. We think that the fact can be explained only as follows: under the conditions of the reaction n-hexane dehydrocyclization occurs mainly through intermediate formation of hexenes.
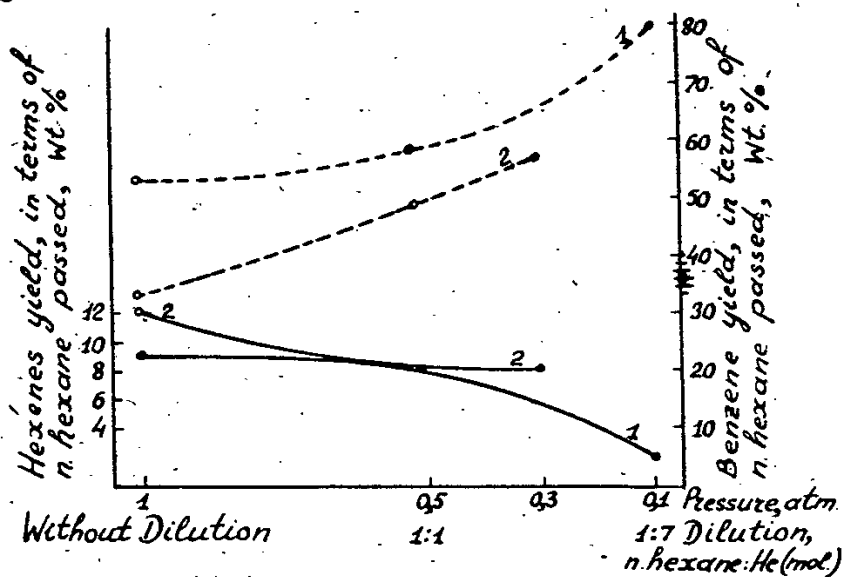

Fig. 3. Dependence of hexane (——) and benzene (----) yields upon the extent of dilution (1) and pressure (2).

We obtained important data at the unit with fluid bed oxide catalysts [29]. Using various chromia-alumina catalysts and changing process conditions

we could control the stage of side reactions (aromatization and formation of low-boiling alkenes) with reference to the main reaction of dehydrogenation. As it is seen from table 6 there are several ways to carry out n-alkane dehydrogenation reaction.

Table 6
Results of n-alkane dehydrogenation reaction on fluid bed oxide catalysts.

Hydro-carbon	Catalyst	Temper-ature ($^\circ$C)	Flow rate (hr^{-1})	Cataly-sate yield (wt.%)	Catalysate composition (wt.%)		
					C_6 or C_9-alkenes	Low boiling alkenes	Aromatic hydro-carbons
Selective dehydrogenation							
n-Hexane	Al_2O +Cr_2O_3	475	9.2	98	11	no	traces
n-Nonane	Al_2O_3+Cr_2O_3	500	9.2	95	8	no	2
Dehydrogenation with aromatization							
n-Hexane	Al_2O_3+Cr_2O_3+ +K_2O	575	5.0	76	20	no	25
n-Nonane	Al_2O_3+Cr_2O_3	600	9.2	77	19	6	15
Dehydrogenation with cracking							
n-Nonane	K-5	600	9.2	85	10	14	2
Dehydrogenation with cracking and aromatization							
n-Nonane	Al_2O_3+Cr_2O_3+ +K_2O	600	9.2	70	18	15	16

1. Selective dehydrogenation with the production of corresponding alkenes with yields of about 10%.

2. Dehydrogenation and aromatization; cracking to low-boiling liquid hydrocarbons does not occur at all or proceeds to a little extent. Such course of the reaction might have a practical importance for certain hydrocarbons, e. g. n-hexane. Hexenes as well as benzene produced from this hydrocarbon are valuable products.

3. Dehydrogenation and partial cracking to low-boiling liquid products; aromatic hydrocarbons are produced in very small amounts. It is of importance that cracking products in this case consist mainly of alkenes-1. This way may also be of great interest.

4. Dehydrogenation followed by cracking and aromatization.

In conclusion it should be noted that the main portion of alkenes produced by n-alkane dehydrogenation have a double bond nearer to the middle of the molecule. Regardless of the reaction conditions and catalysts, we always obtained hexene-2 and hexene-3 from n-hexane, heptene-2 and heptene-3 from n-heptane, octene-4 from n-octane, nonene-4 from n-nonane, decene-4 and decene-5 from n-decane. Only a larger part of cracking products, if they

were, consisted of alkenes-1. On the whole, this result corresponds with thermodynamic calculations.

4. CONCLUSIONS

1. The cases of 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane have shown that C_6-alkanes, the main chain of which contains less than 6 carbon atoms are comparatively easily dehydrogenated on the chromia-alumina-potassium oxide-catalysts producing corresponding alkenes with yields near to equilibrium ones.

2. The experiments have proved the existence of at least two kinds of active centres - dehydrogenating and dehydrocyclizating - on the surface of the chromia-alumina catalyst.

3. There have been found catalysts and conditions for practically selective dehydrogenation reaction of C_6-C_{10}-n-alkanes with production of $\sim 10\%$ of corresponding alkenes.

4. There has been shown the ability to control the stage of proceeding of dehydrogenation, dehydrocyclization and cracking reaction when the process occurs on fluid bed oxide catalysts.

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STAT

SELECTIVITY OF CATALYSIS AND BOND ENERGIES

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Abstract: In order to study the causes of the selectivity of catalysis the energies of the bonds of hydrogen, carbon and oxygen with the active centres of dehydrogenation and dehydration were determined for 25 oxides by the kinetic method.

For the rare earths a parallelism has been found between the bond energies and the magnetic moments of the metal ions.

It has been found that for the oxides of metals of the atomic number changing from 4 to 92 (with some data lacking) the energies of the bonds of the catalyst with oxygen, determined kinetically and thermochemically, vary almost in a parallel way.

A dependence between activation energies and ionic radii has been observed.
The results are discussed in terms of the multiplet theory.

1. According to the multiplet theory the selectivity of the catalytic action obeys the principles of the structural and energetical correspondence [1]. It follows from the latter that a doublet reaction, for instance AB + CD = AD + BC, the most active will be a catalyst, K, for which

$$Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK} = \tfrac{1}{2}(Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC}). \qquad (1)$$

Thus the selectivity depends upon bond energies.

Here the terms of the type Q_{AB} denote the bond energies of the reacting atoms in the molecule, and those of the type Q_{AK} are the energies of the bonds formed by these atoms with the catalyst surface. The average values for the bond energies Q_{AB} can be found in the tables. The knowledge of the bond energies Q_{AK} and their relation with the position of the elements in the Periodical System would be an important step forward in the solution of the problem of a cognizant choice of the catalysts [2].

With this aim in the N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR and in the Moscow State University the present authors and their younger colleagues started a systematic determination of the values of Q_{AK} using the kinetical method. The experiments have been described in papers recently published together with Dudzik, Ferapontov, Konenko, Matiushenko, Matiushenko, Naumov, Peng Be-sien, Revenko, Strszyżewski, Yui Tsi-tsyuang and others. The results obtained are generalized in this report.

The data for three standard reactions, i.e. the dehydrogenation of tetralin (I), the dehydrogenation of propanol-2 (II) and the dehydration of the

latter (III) are given below. According to the multiplet theory their index groups, i. e. the groups of atoms reacting in direct contact with the catalyst, are as follows:

$$
\begin{matrix}
\text{C - C} \\
| \quad | \quad \text{(I)} \\
\text{H \quad H}
\end{matrix}
\qquad
\begin{matrix}
\text{C - O} \\
| \quad | \quad \text{(II)} \\
\text{H \quad H}
\end{matrix}
\qquad
\begin{matrix}
\text{C - C} \\
| \quad | \quad \text{(III)} \\
\text{H \quad O}
\end{matrix}
\qquad (2)
$$
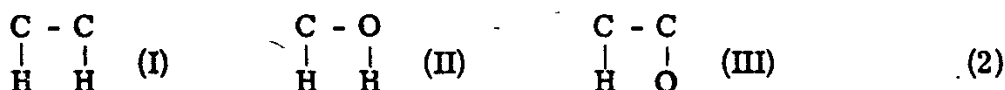
Metal oxides were used as catalysts; they were prepared by essentially one and the same method consisting in the precipitation by ammonia by aqueous solutions of nitrates.

The multiplet theory equations for reactions I, II and III in (2) are:

$$E_I = -2Q_{CH} + 2Q_{HK} + 2Q_{CK},$$

$$E_{II} = -Q_{CH} - Q_{OH} + 2Q_{HK} + Q_{CK} + Q_{OK}, \qquad (3)$$

$$E_{III} = -Q_{CH} - Q_{CO} + Q_{HK} + 2Q_{CK} + Q_{OK},$$

and

$$\epsilon_1 = -\tfrac{3}{4}E_I; \quad \epsilon_2 = -\tfrac{3}{4}E_{II}; \quad \epsilon_3 = -\tfrac{3}{4}E_{III}. \qquad (4)$$

Here E is the heat of formation of the corresponding intermediate multiplet complex, ϵ is the activation energy of the reaction. From the system of three equations (3) we find the three unknowns Q_{HK}, Q_{CK} and Q_{OK}, and by way of substituting ϵ for E and introducing the values $Q_{CH} = 98.7$; $Q_{OH} = 110.6$ and $Q_{CO} = 85.5$ cal (cf. ref. 3) instead of Q_{AB} we finally obtain for Q_{AK}:

$$Q_{HK} = \tfrac{1}{3}(-\epsilon_1 + 2\epsilon_2 + 2\epsilon_3) + 62.0,$$

$$Q_{CK} = \tfrac{1}{3}(-\epsilon_1 + 2\epsilon_2 - 2\epsilon_3) + 36.8, \qquad (5)$$

$$Q_{OK} = \tfrac{1}{3}(3\epsilon_1 - 2\epsilon_2 - 2\epsilon_3) + 48.6.$$

The results are summarized in table 1. For a lesser number of oxides a review has been given in ref. 4a).

For computation of Q_{AK}, in table 1 the values of ϵ_1, ϵ_2 and ϵ_3 given in this table have been used as a rule with the only exception of the items marked "m". This mark means that the mean values of ϵ_1, ϵ_2 and ϵ_3 were taken from different series of experiments and not solely from table 1. If for some reason ϵ_2 and ϵ_3 for the catalysis of propanol-2 could not be obtained, then for evaluating the values ϵ_2 and ϵ_3 for other substances including methanol, tert. butanol and formic acid were taken.

In the case of identical index groups in (2), but different extraindex substituents, the values ϵ for one and the same catalyst are found to be in close proximity to one another. Accordingly the same is true for the values Q_{AK}. Hence it follows that in the course of the reaction the index groups of the reacting molecules are actually oriented towards the catalyst in full agreement with the multiplet theory. In the next approximation the influence of the valency of the metal, and that of the nature, the number and the dis-

Table 1
Bond energies Q_{AK} (cal).

n	K	$r(Å)$	ϵ_1	ϵ_2	ϵ_3	Q_{HK}	Q_{CK}	Q_{OK}
4	BeO	0.32	–	16.4	20.1	49.8 *	19.6 *	66.5 *
12	MgO	0.74	–	24.9	26.3	–	–	–
13	Al_AO_3	0.57	–	–	13.0	–	–	–
21	Sr_2O_3	0.83	27.4	25.2	30.0	56.1	24.4	39.4
22	TiO_2	0.64	17.6 **	10.4	15.3 m	59.0	30.2	44.9
23	V_2O_3	0.67	23.8 **	20.6	20.9	56.5	26.5	43.6
24	Cr_2O_3	0.64	22.8 **	18.8	24.2 m	61.0	22.5	48.8
25	MnO	0.91	32.0 **	31.9	–	60.8 *	26.7 *	38.8 *
30	ZnO	0.78	–	14.9	–	48.6 *	23.1 *	61.7 *
31	Ga_2O_3	0.62	32.0	8.3	11.5	53.5	23.8	67.6
39	Y_2O_3	0.97	34.5	16.0	20.7	53.6	22.0	56.5
42	MoO_2	0.68	16.0	14.0	–	62.5 *	28.8 *	40.3 *
42	MoO_{3-x}	0.65	14.6	–	18.3 m	60.5 *	28.5 *	43.6 *
57	La_2O_3	1.04	51.0	24.3	28.0	47.5	17.2	64.9
58	CeO_2	0.92	32.0 **	21.1	27.8 m	56.2	21.2	49.0
59	Pr_2O_3	1.00	51.6	15.2	27.4	52.9	11.4	72.0
60	Nd_2O_3	0.99	44.8	17.4	26.0	52.8	16.0	64.7
62	Sm_2O_3	0.97	42.9	20.6	26.0	51.3	18.8	60.6
64	Gd_2O_3	0.94	43.3	14.7	25.6	54.8	15.0	65.2
66	Dy_2O_3	0.88	40.2	13.7	26.5	57.1	14.8	62.2
67	HO_2O_3	0.86	38.4	12.8	24.7	57.1	16.0	62.2
68	Er_2O_3	0.85	36.6	15.5	26.5	56.5	16.4	59.4
69	Tu_2O_3	0.85	38.8	18.3	17.0	54.9	18.0	57.4
70	Yb_2O_3	0.81	34.7	20.6	25.1	53.4	22.1	53.0
73	Ta_2O_5	0.66	–	–	23.8	–	–	–
74	WO_{3-x}	0.65	26.8	–	23.7	53.2 *	27.7 *	42.9 *
90	ThO_2	0.99	35.7	23.5	31.8	56.3	17.7	48.8
92	U_3O_8	0.93	36.3	20.0	18.5	48.9	25.6	40.3

* From other reactions.   **** For cyclohexane**

position of the atoms surrounding the active centre should also be taken into consideration. Thus, in the case of chromia Q_{OK} decreases markedly with the increasing valence of chromium [1]. The influence of the environs (particularly those dependent on method of preparation) is described [1] by the sublimation term λ. In a few cases the apparent ϵ were used instead of the true ones, but that was of no considerable effect [1] upon the values Q_{AK} found, because in these cases the extent of the reaction never exceeded 15-20%.

2. Let us begin the discussion of table 1 with the rare earths, for which most instructive results were obtained. As it is well known, the lanthanides comprise a series of 14 elements in which the 4f-shell is gradually filled up. The change of the atomic number n causes a consequent change of their various properties in two limiting types, i.e. the monotonous one (effected by the increasing nuclear charge) and the periodical one (due to particular stability of the configurations of 0; 7 and 14f-electrons).

Contrary to incomplete data of earlier authors, we found that catalytic properties of the rare earths differ considerably. Their values Q_{HK}, Q_{CK} and Q_{OK} differ too (cf. table 1):
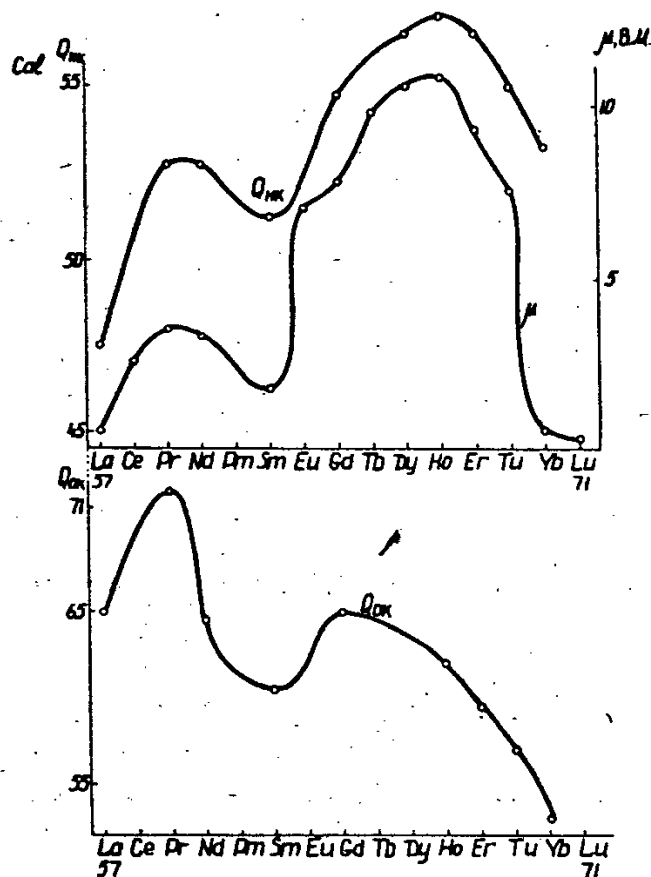
Fig. 1. Dependence of the bond energies Q_{HK} and Q_{OK}, in cal, and of the magnetic moment, μ, in Bohr's magnetons, on the atomic number n of the rare earth element.

The energies of the bonds with the catalysts proved to be a periodical function of n. The values Q_{HK} and Q_{OK} change [5] in a parallel way with the effective magnetic moment μ in which the periodical properties of the elements are expressed most evidently (fig. 1, μ in Bohr's magnetons). The lower exactitude of the relationship for Q_{OK} is probably caused by its known greater sensitiveness to foreign influence. The bond energy Q_{CK} varies inversely with μ (fig. 2).

The *activation energy* of the dehydrogenation of propanol-2, ϵ_2, also varies periodically and inversely with μ (fig. 2). In contrast with this fact the energy of activation of the dehydrogenation of tetralin, ϵ_1, varies in a different way, almost monotonously, in parallel with the ionic radii (fig. 3). At the same time the activation energy of dehydration of alcohol, ϵ_3, is practically constant; it decreases gradually from 28 (for La_2O_3) to 25.1 cal (for Yb_2O_3), with but few deviations (table 1).

The regularities found show that the bond energies (which depend upon the electronic structure) are more primary properties for catalysis than the activation energies. Indeed all the three values Q_{HK}, Q_{CK} and Q_{OK}
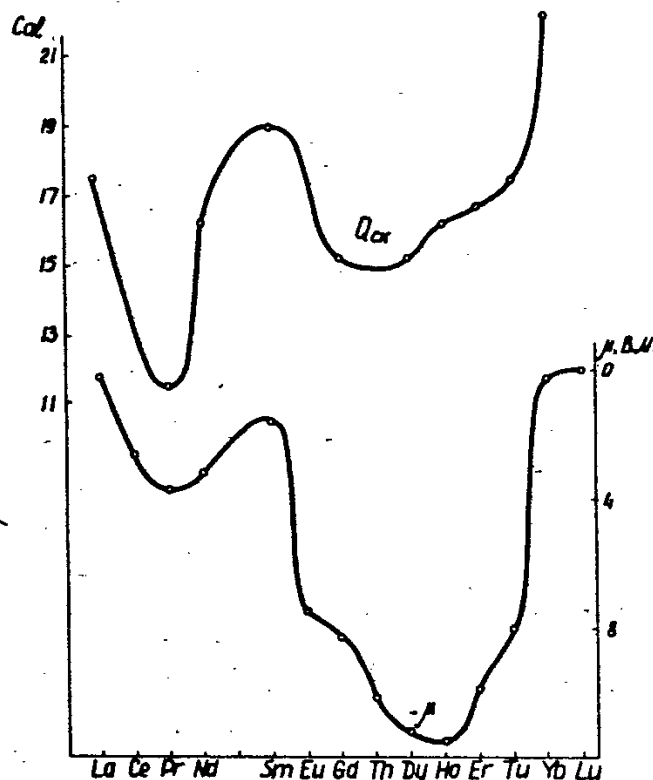
Fig. 2. Dependence of the bond energy Q_{CK}, in cal, and the activation energy of the dehydrogenation of propanol-2, ε_2, in cal/mole, and of the magnetic moment, μ, in Bohr's magnetons, on the atomic number n of the rare earth element.
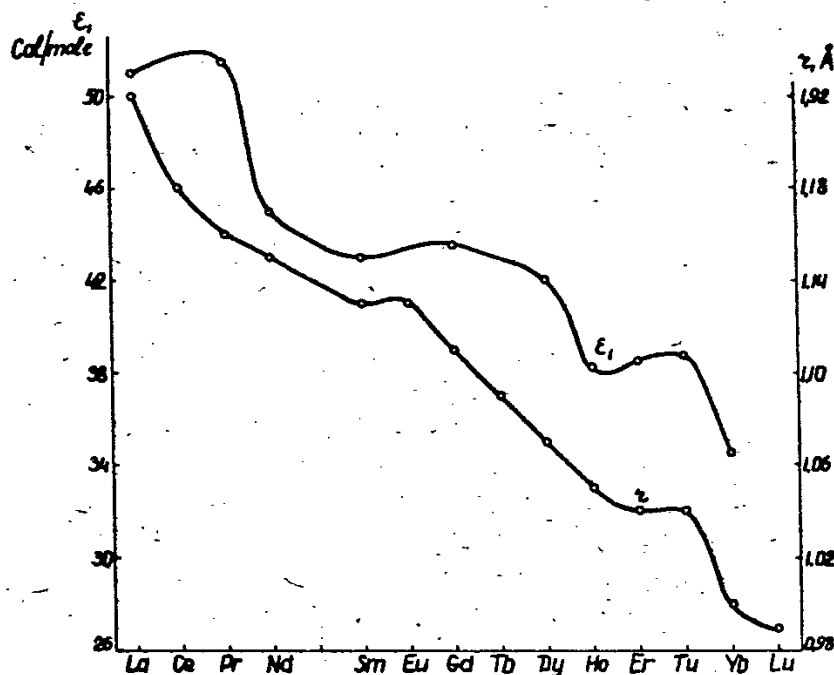

Fig. 3. Dependence of the activation energy of the dehydration of tetralin, ε_1, in cal/mole, and of the metal ion radius, r, in Å, on the atomic number, n.

vary periodically and are distinctly either parallel or inverse with one and the same value, μ, whereas ϵ_1 varies monotonously, ϵ_2 varies periodically and ϵ_3 is constant.

It is of interest to discuss the results from the structural standpoint too. An approximately linear relationship has been observed between ϵ_2 for the rare earths of the structure DS_3 and their lattice parameter a (fig. 4).
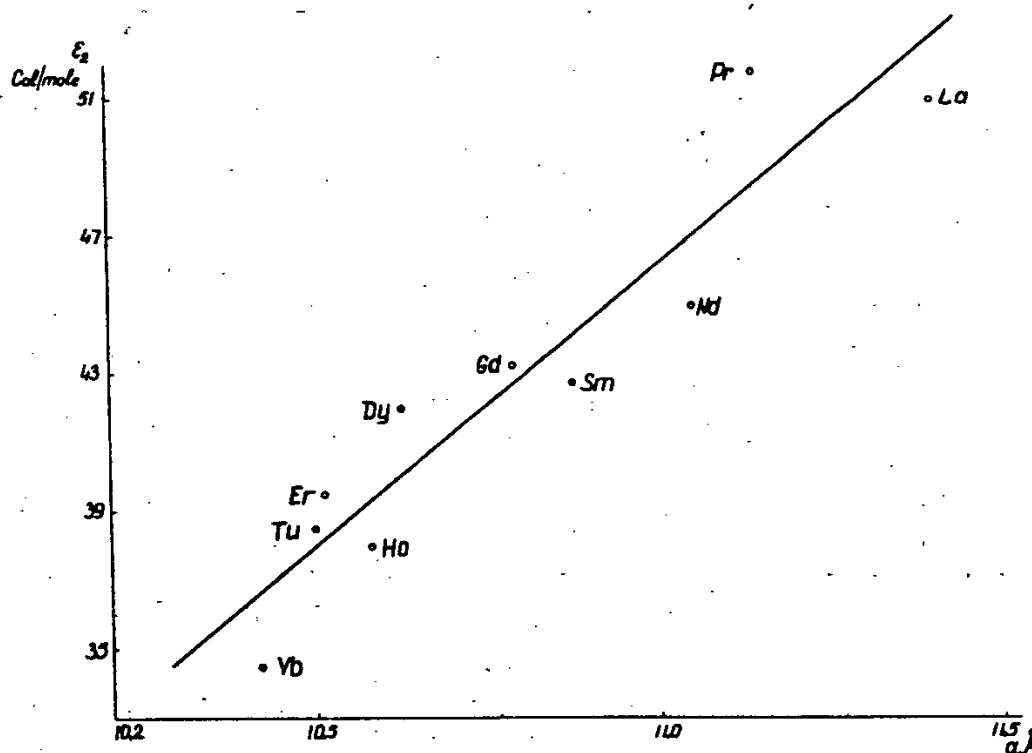

Fig. 4. Relationship between the activation energy of the dehydrogenation of tetralin, ϵ_1, cal/mole, and the constant of the crystal lattice of the rare earths, a, in Å.

The curve in fig. 4 is analogous to fig. 3 in [2] which is illustrated the linear relationship between ϵ_2 and the distance Me-Me on Co, Ni, Cu, Pd, Ag and Pt [2] (now amplified by the data for Re and Ru). Both cases, those of the rare earths and the transition metals, are explained by the principle of conservation of the valence angle.

The regularities found are important for the multiplet theory. They substantiate the energetical equations of the latter, since the parallelism of Q_{AK} with μ shows that Q_{AK} has a real physical meaning. On the other hand it confirms the principle of conservation of the valence angle based on this theory. The results are likewise of importance for the electronic theory of catalysis from the standpoint of which the role of the d-shells and the relationship between catalysis and the properties of transition metals were frequently discussed.

Thus the effect of the change in the electronic structure on catalysis discussed in the electronic theory is due to the resulting change in the energy of the bonds with the catalyst discussed by the multiplet theory.

By the way scandia has Q_{HK} and Q_{CK} values in proximity with those of yttria. Since yttria is usually discussed in common with the rare earths, the fact we found is in favour of the inclusion of scandia into the same group.

3. From the data obtained it follows that the catalytically active centres of the oxides consist mainly of metal atoms and not of oxygen ones. This is evidenced by the following facts:

(i) The Q_{AK} observed for metals and for oxides have the same order of magnitude; thus Q_{HK}, Q_{CK} and Q_{OK} for nickel [1] are equal to 55; 14* and 48.5, and for chromia 61.0; 22.5 and 48.8 cal.

(ii) In catalysis of alcohols it is unlikely that the oxygen atom is bound to the oxygen of the oxide because the formation of a peroxide is chemically impossible under the condition. The energy of the O-O bond is about 35 cal, whereas the observed Q_{OK} are higher, sometimes above 60 cal (table 1).

(iii) If the hydrogen or carbon atoms of the molecule were bound to oxygen atoms of the oxide, Q_{OK} should not change considerably when one oxide is substituted for another. However Q_{OK} varies within wide limits, i.e. from 72.0 for praseodymia to 29.8 cal for zirconia (cf. table 1).

(iv) If hydrogen and carbon were bound to the oxygen atoms of the oxide, a considerable variation in Q_{AK} might be expected if a sulfide instead of an oxide of the same metal should be used as a catalyst. However there is little difference between the actually observed values Q_{AK} for oxides and sulfides, e.g. for MoO_{3-x} and MoS_2 we have obtained: Q_{HK} 61.8 and 60.3; Q_{CK} 27.7 and 26.8; Q_{OK} 42.9 and 59.5 cal and similarly for WO_{3-x} and WS_2: Q_{HK} 57.0 and 58.0; Q_{CK} 29.6 and 26.8; Q_{OK} 61.3 and 54.2 cal respectively.

(v) For the rare earths the values Q_{HK} and Q_{OK} change parallely with μ of the metal ion and the values Q_{CK} inversely with μ (cf. above). Hence it follows that the nature of the metal plays a decisive role.

If the oxygen atoms are also a part of the complex active centre, then their influence can not be decisive, as it is seen from the facts mentioned above.

Further consequences follow from the conclusion that the reacting atoms are bound mainly with metal atoms of the oxide catalyst. From this one can expect that there exists a parallelism between the energies of the bonds of the oxygen of the reacting molecule with the oxide catalyst surface, $Q^K_{Me_nO_m}$, measured by the kinetic method (table 1), on the one hand, and the energies of the bonds of the metal with oxygen, found thermochemically, $Q^T_O\text{-Me}$, on the other. In part, $Q^K_{O\text{-}Me_nO_m}$ and $Q^T_{O\text{-}Me}$ are measures of one and the same property, namely the affinity of the metal to oxygen, but one value refers to the surface and the other one to the bulk on the oxide, and therefore they must differ only by the sublimation term λ.

In fig. 5 a plot of $Q^K_{O\text{-}Me_nO_m}$ and $Q^T_{O\text{-}Me}$ against n is given. The expected general parallelism between these curves is really observed [7].

* In this report the values Q_{CK} are always by 8.3 cal greater than in [1,2], because of a new value for the heat of atomization of carbon recently established [3]. This does not affect E in the eq. (1) and (3) because in their left and right hand parts the corrections are identical and cancel out.
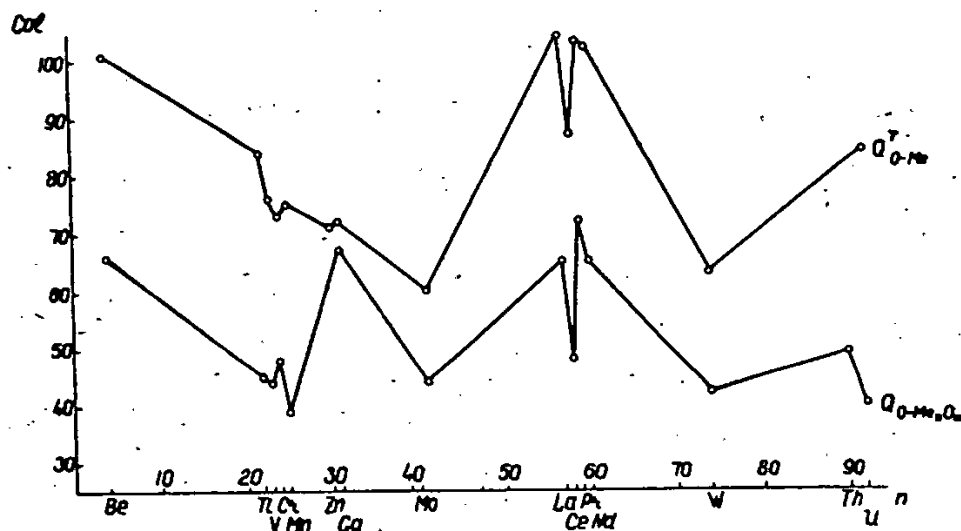
Fig. 5. Dependence of the bond energies $Q^K_{O-Me_nO_m}$ and Q^T_{O-Me} on the atomic number, n, of the metal in the oxide.

Such a parallelism primarily shows that in catalysis the atoms of the reacting species are adsorbed on the metal and not on the oxygen atoms. It shows secondly that $Q^K_{O-Me_nO_m}$ is a periodic function of the atomic number since, as it is known, Q^T_{O-Me} is a periodic function of n.

In fig. 5 the curve for Q^T_{O-Me} runs above that for $Q^K_{O-Me_nO_m}$ and there exist some deviations from the complete parallelism, outside the limits of experimental error. This is due to the influence of the correction sublimation term λ; one might not expect complete constancy of the latter for the different catalysts investigated in spite of the identical method of their preparation. Therefore the fact of such discrepancies is also in a qualitative accordance with the multiplet theory.
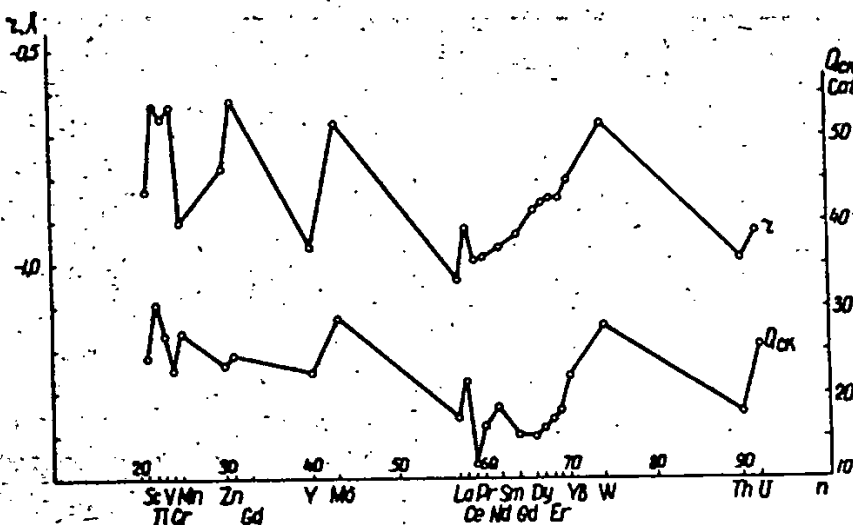
Fig. 6. Dependence of the bond energy Q_{CK}, cal, on the ionic radius of the metal, r, in Å.

4. It has been further found [4], that the values Q_{CK} for the oxide catalyst vary with n inversely to the ionic radius r of the metal of the oxide (fig. 6). For Q_{HK} and Q_{OK} there exists a similar dependence, but it is not so well expressed.

As regards ϵ_1 and ϵ_2 as a function of n, they change in the range from $n = 4$ to $n = 92$ (with some data lacking) almost in parallel [4] with the ionic radius, for the case of catalysts of an identical method of preparation. This can be seen for instance in fig. 7, where ϵ_1 is the activation energy of the dehydrogenation of cyclohexane (from our data and from paper [8]), and in fig. 8, where ϵ_3 is the activation energy of dehydration of propanol-2.

Fig. 7. Dependence of the activation energy of cyclohexane, ϵ_1, cal/mole, and of the ionic radius of the metal in the oxide, r, in Å, on the atomic number, n, of the metal in the oxide.
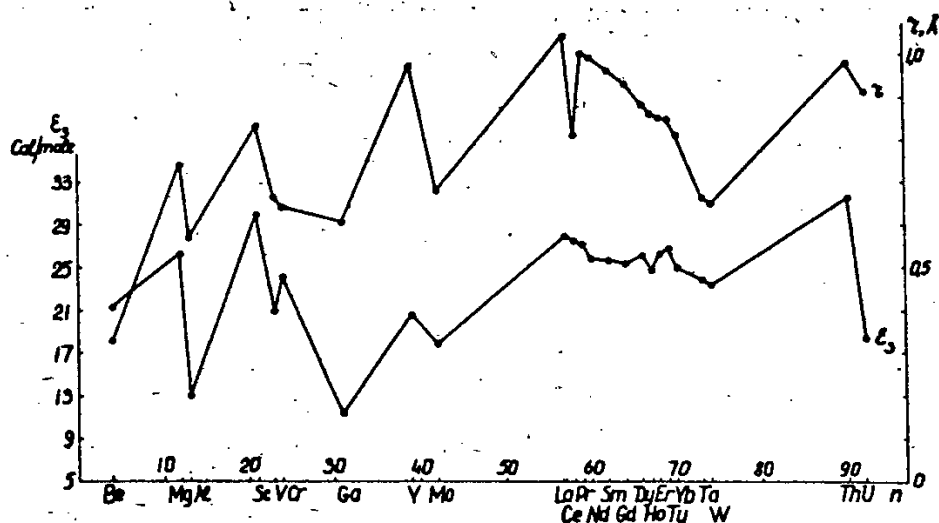
Fig. 8. Dependence of the activation energy of dehydration of propanol-2, ϵ_3, cal/mole, and of the ionic radius of the metal in the oxide, r, in Å, on the atomic number of the metal, n.

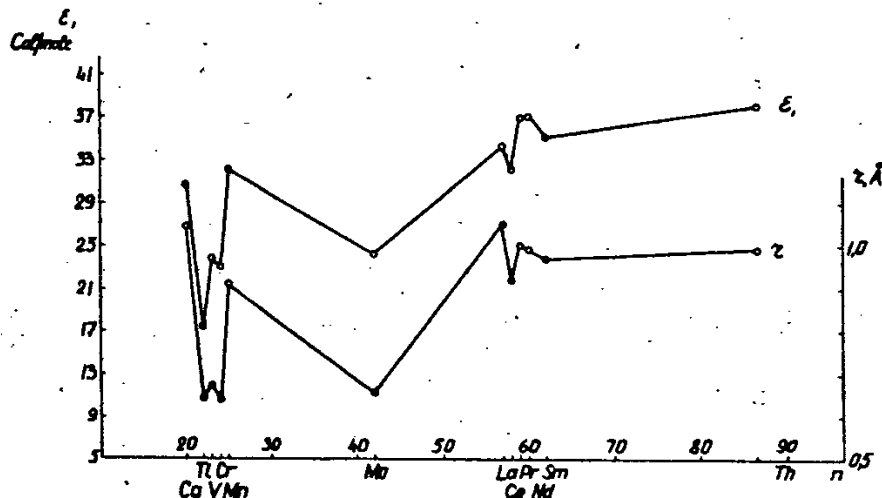The interesting relationships found evidence again that the energetical and structural factors in catalysis play an important role and that they are closely interconnected.

ACKNOWLEDGEMENT

Correlations shown in figs. 5-8 were established with the participation of V. A. Naumov.

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SOME DATA ON THE CORRELATION OF ADSORPTION PROPERTIES AND CATALYTIC ACTIVITY

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Abstract: The adsorption of hydrogen, cyclohexane, benzene, isopropanol and acetone was investigated by the kinetically on the catalytically active part of the nickel surface. It was stated, that the catalytically active part of the surface is characterized by mean adsorption of hydrogen, and weak adsorption of the other substrates. There were determined the energy of activation values of cyclohexane and isopropanol dehydrogenation and tert-butyl alcohol dehydration on six, differently prepared nickel catalysts. From the energy activation of values the bond strengths of H, C and O with the nickel surface were calculated. The obtained data supports the above mentioned conclusion on the character of adsorption as taking place on the catalytic surface. On the basis of the bond strength values a further suggestion can be made, that the catalytic reactions "select" the most appropriate part of the surface. This result was supported by the experiments on hydrogenation of ethylene in the presence of preadsorbed hydrogen.

1. INTRODUCTION

The correlation of adsorption and catalytic properties is one of the most important questions for the theory of catalysis. According to the first view the better the adsorption properties, the higher the activity of the catalysts. The great effect of the previous history of the catalyst on its catalytic activity is explained by the followers of the chemical theory of catalysis from this point of view [1]. This is true, however, only of the total activity depending on the surface area of the catalysts, but the relation between the adsorption capacity and the activation energy is more complicated. This is shown in the work by Beeck and his coworkers [2], who established, that the smaller the absolute value of the adsorption heat of hydrogen and ethylene, the higher the rate constant of hydrogenation of ethylene on several metal films. Balandin came to the conclusion, that both the too strong adsorption and the too weak one are disadvantageous with respect to catalytic activity, and that there is an optimum bond of adsorption for the catalytic reactions [3]. It is rather difficult to clear up this problem, because there are no data to state surely the character of adsorption taking place on the *catalytically* active part of the surface, considering that the adsorption taking place on the whole surface of the catalyst may not be identified with that taking place on the part of surface which is active in the catalytic reaction.

To study the problems mentioned above the adsorption of hydrogen as

well as the kinetics of dehydrogenation of cyclohexane and isopropanol, hy-
drogenation of ethylene and the dehydration of tert-butyl alcohol were in-
vestigated over Ni catalyst.

2. EXPERIMENTAL

The adsorption of hydrogen was measured in a BET volumetric appa-
ratus [4], the kinetics of dehydrogenation and dehydration were investi-
gated in a flow-system reactor [5], the hydrogenation of ethylene in a cir-
culating apparatus.

The measurements were carried out over metal nickel catalysts pre-
pared in several ways.

Catalyst no. 1. $Ni(OH)_2$ was precipitated from the solution of $Ni(NO_3)_2$
with NH_4OH and this was decomposed in air and H_2 stream
at 400°C.

Catalyst no. 2. $Ni(NO_3)$ was decomposed in argon stream and reduced in
H_2 stream at 400°C.

Catalyst no. 3. NiC_2O_4 was precipitated from solution of $NiSO_4$ with am-
monium oxalate and it was reduced in H_2 stream at 400°C.

Catalyst no. 4. Raney nickel.

Catalyst no. 5. Nickel formiate was decomposed at 400°C in H_2 stream.

Catalyst no. 6. Nickel carbonate was decomposed at 400°C in H_2 stream.

3. RESULTS AND DISCUSSION

3.1. Adsorption data obtained by the kinetic method

A new form of Balandin's kinetic method [6] for determining the ad-
sorption coefficients was developed, thereby rendering possible the deter-
mination of the absolute value of adsorption coefficients for the participants
of the catalytic processes. The data obtained by the kinetic method charac-
terize the adsorption of different substrates especially on the catalytically
active part of the surface.

The kinetics of dehydrogenation of cyclohexane, as it was previously
proved [7], in presence of additives, obeys the equation *

$$\frac{1}{w} = \frac{1}{k_1} + \frac{1}{k_2'} + \frac{1}{k_3'} + \frac{v_i}{v_1} \left(\frac{1 + b_i}{k_1}\right) \tag{1}$$

where w is the rate of reaction, k_1, k_2', k_3' are the rate constants of ad-
sorption of cyclohexane, of desorption of benzene and hydrogen respectively,
b_i is the adsorption coefficient of the additive; v_1 and v_i is the flow-rate of
cyclohexane and the additive, respectively.

Plotting $1/w$ against v_i/v_1 it can be shown that eq. (1) defines a straight
line with slope $(1 + b_1)/k_1$, in the case of mixture cyclohexane-argon: $1/k_1$
as than $b_i = 0$.

* To obtain this equation no supposition as regards which of the elementary reaction
steps is the rate-controlling one, was made.

Comparing the slope values obtained in two series of experiments the adsorption coefficient of additives can be calculated. In this way the adsorption coefficients of benzene and hydrogen were determined over the catalyst no. 1, the values of which are given in table 1 together with adsorption heat data calculated from these.

Table 1
Adsorption data relating to the adsorption of hydrogen and benzene on sample no. 1 (kinetic method)

Substrate	t (°C)	b (atm^{-1})	ΔH (kcal/mole)
H_2	278	0.87	
	293	0.57	24.1
	310	0.24	
	323	0.17	
C_6H_6	275	15.20	
	285	12.09	11.8
	304	8.59	
	314	7.50	

The kinetics of dehydrogenation of isopropanol in case of catalyst no. 1 was previously studied by one of the authors and Balandin [8]. It was established, that the reaction obeys the

$$k = \left(\frac{b_2}{b_1} + \frac{b_3}{b_1}\right)v_1 \ln \frac{v_1}{v_1-x} + \left(\frac{b_2}{b_1} + \frac{b_3}{b_1} - 1\right)x \qquad (2)$$

equation, where b_1, b_2, b_3 are the adsorption coefficients of isopropanol, acetone, hydrogen, respectively: k is the reaction rate constant; x is the quantity of isopropanol reacting during a time-unit.

The values of relative adsorption coefficients in equation (2) can be determined [9] by comparing the rate of the binary mixture with additives by the aid of the equation

$$\frac{b_i}{b_1} = \frac{(x_i/x_0) - 1}{(100/p) - 1}, \qquad (3)$$

where p is the concentration of alcohol in the mixture expressed in mol%.
Table 2 contains the relative adsorption coefficients of hydrogen, acetone, benzene, cyclohexane, isopropanol determined by the dehydrogenation rate of the different binary mixtures in the way mentioned above. Comparing the values of table 1 and 2 the data for the adsorption of isopropanol, acetone and cyclohexane can be calculated and are collected in table 3.

These data can be said to be quite reasonable when compared with those in the literature. The values of the heat of adsorption of hydrogen is of the same magnitude as that determined from the isosteric heat of adsorption over the same catalyst (table 4). The values of the heats of adsorption of isopropanol and acetone fall close to those determined by Gale et al. [10]

Table 2

Relative adsorption coefficients of hydrogen, acetone, benzene and cyclohexane to isopropanol. Sample no.1 (kinetic method) .

Substrate	t ($^{\circ}$C)	$\dfrac{b_i}{b_1}$	$\Delta H_i - \Delta H_1$ kcal/mole
index i: H_2 index 1: i-C_3H_7OH	172 184 197 206	0.39 0.25 0.16 0.11	-14.5
index i: C_3H_6O index 1: i-C_3H_7OH	166 182 198 209	1.51 1.35 1.16 1.00	- 3.7
index i: C_6H_6 index 1: i-C_3H_7OH	170 180 191 210	0.96 0.85 1.06 0.97	~ 0
index i: C_6H_{12} index 1: C_3H_7OH	161 170 178 188 207	0.18 0.24 0.26 0.32 0.43	- 7.8

Table 3

Data relating to the adsorption of the different substrates on sample no.1, $t = 250^{\circ}$C (kinetic method)

Substrate	b (atm^{-1})	$-\Delta H \left(\dfrac{kcal}{mole}\right)$	$\Delta G \left(\dfrac{cal}{mole}\right)$	ΔS (e.u.)
H_2	3.14	24.1	-1450	-43.3
C_6H_6	25.5	11.8	-2560	-17.8
C_6H_{12}	106.9	1.8	-4850	5.8
i-C_3H_7OH	124.7	9.6	-5000	- 8.8
C_3H_6O	89.8	13.3	-4680	-16.5

Table 4

The rate constants of ethylene hydrogenation (k') and the adsorption coefficient of hydrogen (b_{H_2}), at different quantities of preadsorbed hydrogen. Sample no.1, $t = 0^{\circ}$C.

V_{H_2} ml NTP.g^{-1}	k' min^{-1}	b_{H_2} 10^3 Torr^{-1}
0	2.714	100
0.45	2.140	32
0.54	1.800	19
0.60	0.451	13
0.67	0.162	11
0.80	0.115	7.8

in the case of NiO and that of benzene to that found by Rubinstein et al. [11] over alumina silicate catalyst. The value of the heat of adsorption for cyclo-hexane is lower than that determined by Rubinstein [12], moreover, it is lower than the heat of condensation of cyclohexane. Presumably this is in connection with the fact that, in case of Ni catalyst a dissociative, probably endothermic adsorption, takes place to some extent at lower temperatures, as has been confirmed by Galvey and Kemball [13], while Rubinstein observ-ed the change in character of the adsorption over alumina-silicate catalyst only at higher temperatures which seems to be quite reasonable.

By an investigation of the obtained absorption heat data it can be con-cluded that it is only in the case of hydrogen when "classical" chemisorp-tion on the catalytically active part of the surface is taking place. The isosteric heat values for hydrogen adsorption vary as a function of conver-age from 32.4 to 8.1 kcal/mole. Hence it can be seen, that the catalytically active part of the surface is not the most active one from the point of view of adsorption. This conclusion is especially supported by the data referring to the adsorption of benzene, isopropanol and acetone, from which it is clear that these substances are submitted to a physical adsorption and/or to a weak chemisorption as a result of which a mobile adsorption layer is form-ed as it is shown by the values of entropy of adsorption. Therefore, catalysis is not characterized by the strongest possible adsorption of the participants and, from the point of view of catalysis it is not the most active of the sur-faces which is the most favourable one.

This statement is also confirmed by the investigations on the hydrogen-ation of ethylene carried out over catalyst no. 1. Under the given circum-stances the rate of reaction proved to be of first order with respect to the pressure of hydrogen and independent of the pressure of ethylene, and so the measured rate constant represents the multiplication of the true rate constant and the adsorption coefficient of hydrogen

$$k' = kb_{H_2} \tag{4}$$

It was studied further to see how the rate-constant values of this reaction were influenced by the quantity of preadsorbed hydrogen. Table 4 sum-marizes the overall rate constant values, k', in the case of different quan-tities of preadsorbed hydrogen, as well as the values of b_{H_2} calculated by the Freundlich equation from the adsorption isotherm of hydrogen. The results are shown graphically in fig. 1.

It can be seen that the values of both the overall rate constants and the adsorption coefficients decrease with increasing quantity of preadsorb-ed hydrogen. The shape of the two curves, however, is not the same. The shape of the k' curve is not so steep as that for b_{H_2} and it has several sec-tions. Similar results were also obtained at two other temperatures.

The difference between the shape of the curves of k' and b_{H_2} can be explained supposing the preadsorbed hydrogen at lower coverage excludes the sites having lower activity from the point of view of catalysis. So it is clear and explainable only by the initial increasing of k values that the k' values representing the multiplication of k and b_{H_2} decrease in a smaller degree at the beginning than the b_{H_2} values. The break of the curve, and
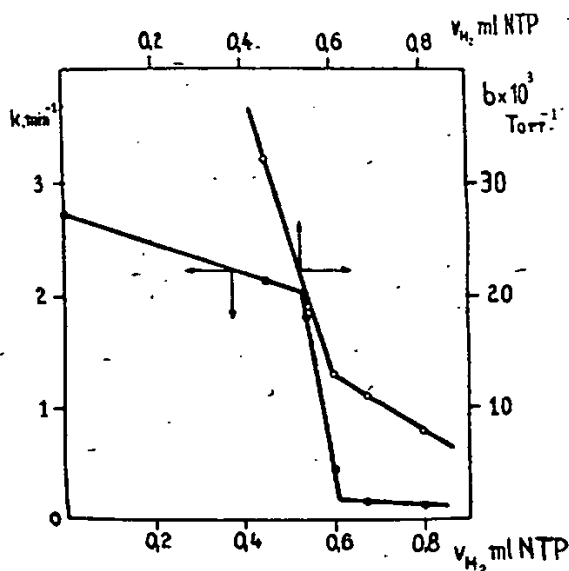
Fig. 1. Change of the overall rate constant,
k', (full ring) and of the adsorption
coefficient of hydrogen, b, (open ring)
as a function of the quantity of pread-
sorbed hydrogen on the surface of Ni
catalyst no. 1.

the steeper decreasing of the k' values after this break point is likely in
connection with the fact that the preadsorbed hydrogen increasingly ex-
cludes the parts of the surface having lower but optimum activity from the
point of view of catalysis and accordingly also the overall rate constant
and the b_{H_2} values decrease. The k' values at higher coverage are decreas-
ing to a smaller extent again and this fact is due likely to the phenomenon,
that the activity of sites changes only slightly with the coverage.

The statement that the catalytic reactions studied do not all take place
on the sites having optimum adsorption capacity, but rather on those having
smaller activity and that the centres for the optimum adsorption and for
optimum catalytic activity do not coincide, seems to be supported by the
experiments above.

3.2. *Influence of the method of preparation on the catalytic activity*

The statement, that it is not the most active part of the surface on
which the catalytic reactions take place raises a question, i. e., is it pos-
sible to obtain and in what degree differences between the activation energy
of reactions taking place on catalysts which have the same composition but
were prepared in different ways? It is reasonable to suppose that the sites
with optimum activity are "chosen" by the catalytic reaction and for the
same reaction the same activation energy is expected.

To study this problem the activity of six nickel catalysts prepared in
different ways were investigated. Three reactions were used to measure
the activity of catalysts: Dehydrogenation of cyclohexane and isopropanol
and dehydration of tert-butyl alcohol. The kinetics of the dehydrogenation

reactions were studied on the basis of eqs. (1) and (2), the applicabilities of which were verified by kinetic measurements of the catalysts prepared in different ways. The calculation of the rate constant of dehydration of tert-butyl alcohol was performed

$$k = v_1 \ln \frac{v_1}{v_1 - x} \qquad (5)$$

with the aid of equation (5).

The activation energy values are collected in table 5. Furthermore, in

Table 5

The activation energy values for dehydrogenation of cyclohexane and isopropanol and for dehydration of tert-butyl alcohol on the different nickel catalysts in kcal/mole unit.

Sample	C_6H_{12}	$i\text{-}C_3H_7OH$	$t\text{-}C_4H_9OH$
1	22.9	10.5	21.7
2	24.3	7.8	29.2
3	29.5	14.5	21.0
4	18.2	9.0	22.2
5	21.9	12.3	23.2
6	19.9	11.2	21.1

order to obtain data about the differences concerning the surface heterogeneity, the hydrogen adsorption on the different samples was studied by the volumetric method. These data are summarized in table 6.

Table 6

Hydrogen adsorption on different nickel catalysts investigated by the BET method.

Sample	Isotherm	v_{max} ml NTP/g	Converage $\sim = \frac{v}{v_{max}}$	$-\Delta H \frac{kcal}{mole}$
1	Freundlich	3.32	0.18 – 0.66	32.4 – 8.1
2	Freundlich	2.34	0.06 – 0.26	20.7 – 8.6
3	Langmuir $\sqrt{P}$	0.98	0.10 – 0.50	22.2 – 10.6
4	Freundlich	4.92	0.08 – 0.33	36.7 – 16.8
5	Langmuir $\sqrt{P}$	2.28	0.08 – 0.42	16.7 – 14.2
6	Langmuir $\sqrt{P}$	1.10	0.09 – 0.35	27.0

From the data of tables 5 and 6 it can be seen that there are considerable differences both in the adsorption of hydrogen and the activation energy values of the reaction taking place over different catalysts. As in the investigated reactions different combinations of the atoms C, H and O occur, it was reasonable to determine the interaction characterized by the bond energy between the individual atoms and catalytic surface according to Balandin's kinetic method [14] with regard to the bonds Ni-H, Ni-C and Ni-O (table 7). At the same time in this table the deviations between the values of bond energy mentioned above and the thermochemical ones are

Table 7
The strength of chemical bonds between the catalytic
surface and H, C, O atoms (in kcal units)

Sample	Q_{HNi}	λ_{HNi}	Q_{CNi}	λ_{CNi}	Q_{ONi}	λ_{ONi}	$\Sigma \lambda_{XNi}$
1	61.8	6.8	13.5	7.5	50.1	2.6	16.9
2	66.2	11.2	8.6	2.6	50.6	2.1	15.9
3	56.4	1.4	14.5	8.5	54.5	6.0	15.9
4	64.7	9.7	13.7	7.7	46.1	-2.4	15.0
5	62.0	7.0	14.3	8.3	46.8	-1.7	13.6
6	62.0	7.0	15.3	9.3	47.0	-1.5	14.8

summarized, characterizing the effect of the nature of the surface, which for the bond energy according to Balandin is,

$$Q_{XK} = Q^0_{XK} + \lambda_{XK} \qquad (6)$$

where Q_{XK} represents the surface bond strength value; Q^0_{XK} represents that in the bulk phase; λ_{XK} the so-called sublimation factor representing the effect of surface atoms on the bond strength.

From the data of table 7 it can be seen that though the single values of Q_{XNi} and λ_{XNi} measured over different catalysts differ considerably, the sum of λ_{XNi} values shows only small deviation, i. e. , the changes in the bond strength values compensate each other.

The appearance of this compensation confirms the fact that really the most favourable interval is chosen by the reaction because the sum of deviations from the bond energy in the bulk phase are the same with respect to all the catalysts. The selection, however, has a limit as for different atoms the sites of different activity have an optimum. As a consequence of this for some of the atoms the part of the surfaces on which the reaction takes place really differs from the optimum to some extent. Since the energy of activation for different reactions is given by various combinations of the bonding energy of HNi, ONi and CNi, so the values of energy of activation differ from each other for different catalysts.

Summarizing our investigations it can be stated that the reactions investigated above take place over that part of the surface which is less active from the point of view of adsorption, and the catalytically active surface is characterized by a weak adsorption of the participants. The method of preparation of catalysts influences the energy of activation of reactions and the bond energies of atoms taking part in the reaction, but the values of $\Sigma \lambda_{XNi}$ characterizing the activity of different catalysts from the energetical point of view change to a smaller degree which confirms the supposition, that the reaction selects the optimum interval on the surface.

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THE INVESTIGATION ON INTERMEDIATE SURFACE COMPOUNDS OCCURING IN ELEMENTARY STAGES OF HETEROGENEOUS CATALYTIC REACTIONS

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Abstract: Adsorption-chemical equilibria, para-ortho hydrogen conversion and non-gradient reaction kinetics method have been used in obtaining characteristic information on intermediate surface compounds, and in determining the effects of these on the mechanisms of heterogeneous catalytic reactions. Data have been obtained on the surface compounds on nickel catalysts with oxygen or carbon and on those yielded by chemisorption of cyclohexane on nickel, as well as on the nature of catalytic centres on the surfaces of some synthetic polymers. The nature of the surface intermediates formed by some reactions and the mechanisms of the latter are discussed. The optimum stability of the surface compounds and the problem of the optimum catalyst are considered.

1. INTRODUCTION

The regularities of heterogeneous catalytic reactions essentially depend on the type, nature and stability of the surface intermediates formed at elementary reaction steps. The specific features of reactions in real adsorption layers [1], in particular, the effect of an energetically heterogeneous surface which predominates in a number of cases should be allowed for in investigating these kinds of compounds.

As the same substance may yield different surface compounds, predominance of the desired reaction route will be a function of optimal stability of the respective compound. The rate of reaction appears to be maximum for surface compounds of medium stability ensuring sufficiently fast formation and decomposition of these.

Therefore estimation of the stability of intermediates on various sites of the catalyst surface is of great importance in understanding the reaction mechanisms. The best way to achieve it at present would be combined determination of thermodynamic functions of the surface layer formed in the course of reaction, and kinetic studies, as well as the investigations of physical properties.

The work from Professor Balandin's laboratory was concerned with the character and the stability of intermediate surface compounds. The para-ortho hydrogen conversion was used under various conditions, as well as the method of adsorption-chemical equilibria and the kinetic non-gradient methods.

aluminium fluoroborate solution [1-3]). In the temperature range 250 - 500ºC
alkylphenols with an alkylgroup higher than methyl undergo dealkylation,
isomerisation, and to some extent also disproportionation.

$$\text{(phenol with } C-R^1, R^2, CH^3) \longrightarrow \text{(phenol)} + CH_2{=}C{<}^{R^1}_{R^2} \qquad (1)$$
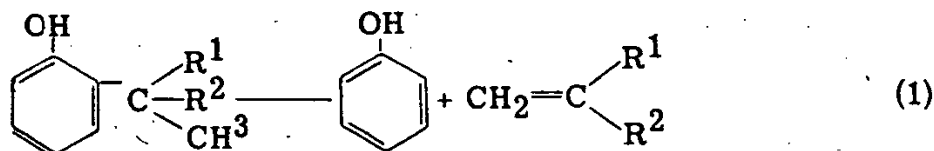
The values listed in table 1 show that the reactivity decreases in the
order ortho, meta, para. The rate of dealkylation is greater with the propyl
group than with the ethyl group but further lengthening of the chain has no
more effect. A very strong influence on the reactivity of alkylphenols is
exercised by the branching of the alkyl group. This effect is particularly
marked with ortho-substituted alkylphenols, most extremely in the case of
2-tert-butylphenol. Equality of the reactivities of 4-isopropylphenol with
4-tert-butylphenol is somewhat surprising.

Table 1
Dealkylation of alkylphenols on aluminium
fluoborate catalyst [1,2].

Alkylphenol	Activation energy (kcal/mol)	k_{rel} for 450ºC
2-ethylphenol	24.0	6.6
3-ethylphenol	22.7	3.0
4-ethylphenol	24.3	1.0
2-propylphenol	28.8	15.1
4-propylphenol	29.8	2.0
2-isopropylphenol	22.4	456
4-isopropylphenol	27.8	100
2-butylphenol	26.6	15.1
3-butylphenol	–	4.0
2-tert-butylphenol	27.9	33 000
4-tert-butylphenol	25.8	100

The results concerning the dialkylphenols are summarized in tables 2
and 3. The methyl group constitutes in these compounds a substituent non-
reactive under conditions used. The presence of a third substituent (methyl
or hydroxyl) on the benzene nucleus decreases in all cases the reaction rate.
On a nickel catalyst promoted with aluminium oxide [6,7] and in the
presence of hydrogen, the alkylphenols undergo hydrogenolytic cleavage of
the alkyl group (reaction (2)). The rates of this reaction are also dependent
on the structure of the alkyl group and on its position in respect to the hy-
droxyl group [5]). The representative values are listed in table 4. It is evident
that again the order of reactivity is ortho, meta, para. For the three mem-
bers of the homologous series the rate of hydrogenolysis decreases rapidly
with the number of carbon atoms of the alkyl group; with further members
the decrease in rate is only negligible. The branching of the side chain also
lowers the reactivity but to a small extent. Both these factors (i.e., length

Table 2
Dealkylation of some dialkylphenols on aluminium
fluoborate catalyst [3].

| Compound	k_{rel}	Ratio
2-tert-butylphenol *	2180	1.0
2-tert-butyl-4-methylphenol *	1530	0.7
2-isopropylphenol *	30	1.0
2-isopropyl-5-methylphenol *	12	0.4
2-propylphenol **	1	1.0
2-propyl-4-methylphenol **	0.5	0.5

* At 250°C.

** At 400°C.

Table 3
Effect of the methyl or hydroxyl group on the overall reactivity
of the ethyl group on an acidic catalyst at 400°C [3].

Compound	k_{rel}
2-ethylphenol	1
2-ethyl-4-methylphenol	0.86
2-ethyl-5-methylphenol	0.84
2-ethyl-6-methylphenol	0.78
2-ethyl-3-hydroxyphenol	0.56
2-ethyl-4-hydroxyphenol	0.35

Table 4
Hydrogenolysis of alkylphenols on Ni-Al$_2$O$_3$ catalyst
at 350°C [4].

Compound	Relative reaction rate
2-methylphenol	1.0
2-ethylphenol	0.52
2-propylphenol	0.22
2-isopropylphenol	0.19
2-butylphenol	0.23
2-sec-butylphenol	0.19
2-tert-butylphenol	0.14
2-methylphenol	1.0
3-methylphenol	0.31
4-methylphenol	0.0

of chain and branching) operate reversely than in dealkylation on the acidic
catalyst. Here it is worthwhile to point out the characteristic feature of this
hydrogenolytic dealkylation, namely that the fission occurs between all car-
bon atoms of the alkyl group and not only between this group and the aroma-
tic nucleus.

$$\underset{OH}{\bigcirc}\!-\!R + H_2 \longrightarrow \underset{OH}{\bigcirc}\!+ RH . \tag{2}$$
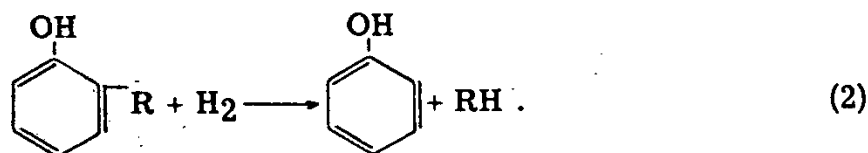
In the case of dialkylphenols it has been established (table 5) that the introduction of a further alkyl group has practically no influence on the rate irrespective of whether this second alkyl group is methyl or ethyl, and whether it is in meta or para position to the reacting group. However, if this group is in the ortho position the rate is rather strongly diminished.

Table 5

Hydrogenolysis of o-methyl group in dialkylphenols
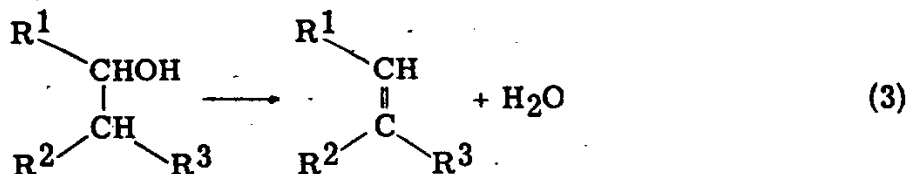on Ni-Al$_2$O$_3$ catalyst at 350°C [4).

Compound	Relative reaction rate
2-methylphenol	1
2,4-dimethylphenol	1.16
2,5-dimethylphenol	1.19
2,6-dimethylphenol	1.31
2,3-dimethylphenol	0.22
2-methyl-4-ethylphenol	1.14
2-methyl-6-ethylphenol	1.08

Table 6

Dehydration of secondary alcohols over γ-alumina [5).

Compound	Activation energy (kcal/mol)	k_{rel} for 200°C
Heptanol – (4)	1.0	33
2-methylhexanol – (3)	1.0	34
2,4-dimethylpentanol – (3)	1.3	32
Cyclopentanol	1.9	36
Cyclohexanol	1.0	35
Cycloheptanol	2.3	35
Cyclooctanol	8.6	–
2,2-dimethylcyclohexanol	0.9	34
trans-2-methylcyclohexanol	1.8	44
trans-4-methylcyclohexanol	1.9	38
trans-4-tert-butylcyclohexanol	2.1	38
cis-2-methylcyclohexanol	12.1	21
cis-2-tert-butylcyclohexanol	40.3	19
cis-4-tert-butylcyclohexanol	13.6	27

Further correlation between structure and reactivity was obtained in the study of dehydration of aliphatic and cyclic secondary alcohols on aluminium oxide (reaction (3)). It has been ascertained that with aliphatic alcohols (table 6) the branching of the chain in the neighbourhood of the

carbon bearing the hydroxyl group does not markedly affect the rate or the value of the activation energy.

$$\underset{R^2}{\overset{R^1}{\diagdown}}\underset{CH}{\overset{CHOH}{\diagup}}\underset{R^3}{\overset{|}{\diagdown}} \longrightarrow \underset{R^2}{\overset{R^1}{\diagdown}}\underset{CH}{\overset{CH}{\diagup}}\underset{R^3}{\overset{\|}{\diagdown}} + H_2O \qquad (3)$$

A more marked dependency of reaction rates may be observed with the ring size of simple secondary cyclic alcohols. However, the values of the activation energies are practically the same for all members of this group and differ only slightly from those for the aliphatic alcohols. From comparison of the value for cyclohexanol and its 2,2-dimethyl derivative it is evident that the presence of quarternary carbon atom diminishes the reactivity only slightly. Larger differences in reaction rates and activation energies were found among stereoisomeric alkylcyclohexanols. Table 6 shows that on the average the activation energies of the cis-isomers are substantially lower than that of the trans-isomers. For the aliphatic and simple cyclic alcohols this quantity has values between those for the alkylcyclohexanol stereoisomers. In the series of the trans-alkylcyclohexanols no effect of the alkyl-group structure on the rate has been detected whereas the opposite has been observed for the cis-compounds. We assume therefore that different reaction mechanisms of water elimination from these two types of compounds are operating.

3. DISCUSSION

In discussing the effect of structure on reaction rate it is convenient to consider separately the electronic and steric factors. From current experience with transformations of the type studied we could expect to find electronic effects on rate to be specially marked in these cases:

In dealkylation of alkylphenols on the acidic catalyst, the reaction rate should increase with the length and with the branching of the alkyl group, electropositive substituents on the benzene nucleus should decrease the rate, electronegative should increase it, and o- and p-alkylphenols should eliminate the alkyl group faster than m-derivatives. In hydrogenolysis of the alkylphenols a second alkyl group in dialkylphenols should influence the reaction rate of the o-alkyl group and the effect should depend on its position in respect of the reaction centre. In dehydration of secondary alcohols the exchange of the propyl group for the isopropyl group in dialkylcarbinols (heptanols) should influence the rate of the elimination of water, and the rate of dehydration of cyclohexanol and 2,2-dimethylcyclohexanol should differ.

As the results in tables 1 - 6 show of these predicted effects only the increase of the reaction rate with length and branching of the alkyl group was experimentally confirmed. The same reactivity of the isopropyl and tert-butyl group in the para position is at present difficult to explain. How-

ever, Rase and Kirk [8] have observed the same phenomenon in dealkylation of alkylbenzenes on an alumosilicate catalyst.

In all other cases the electronic effects of the structure were feeble or indistinguishable. Of special interest is the fact that in no case the transfer of the electronic charge through the aromatic system was observed. This indicates that in the reactions studied the aromatic character of the compounds was probably disturbed by chemisorption.

This absence of electronic effects could be explained in various ways. We suppose that in most cases it is due to predomination of steric effects. The important role which the steric effects play in the reactions studied is clearly seen from these findings: The reactivity of the ortho derivatives is much higher than that of meta or para isomers both in transformations of alkylphenols on the acidic and on the metallic catalysts. Extremely high reactivity of 2-tert-butylphenol in acid-catalysed dealkylation is evidently due to a combination of this ortho-effect and steric acceleration by the bulky group. The decrease of the rate of hydrogenolysis of 2,3-dialkylphenols in comparison to 2,4- and 2,5-isomers can be explained only as a steric hindrance. The rapid decrease in the hydrogenolysis rate in the series of o-alkylphenols with increasing number of carbon atoms in the chain is very probably caused also by steric hindrance. In the dehydration of cyclic alcohols the influence of the ring size conforms with generally accepted explanation which is based on steric considerations. The steric requirements of the dehydration on the solid catalyst are probably so strict that they lead to different mechanisms of the reactions of cis- and trans-alkylcyclohexanols.

The predominance of steric effects in heterogeneous catalytic reactions can be deduced also from the work of other authors. In this respect most complete data are those concerning hydrogenation of aromatic compounds on metallic catalysts as published by Lozovoj and Djakova [9], Wauquier and Jungers [10], and mainly by Smith et al. [11-18]. The order of reactivities found can be explained as increasing steric hindrance with increasing number of alkyl groups. In this way one may also understand why the reactivity of the ortho isomers is lower than that of meta and para compounds.

From the facts described here it appears that one of the main factors affecting the reactivity of organic compounds in heterogeneous catalytic reactions is the steric arrangement of the reacting molecule especially of the chemisorbed species.

It is clear that from so limited a number of experimental findings it is not possible to draw final conclusions. Further work is necessary and it is hoped that it may bring deeper understanding of the heterogeneous catalysts.

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EFFECTS OF STRUCTURE ON RATE IN REACTIONS OF ORGANIC COMPOUNDS OVER SOLID CATALYSTS

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Abstract: The effects of structure of organic compounds on the rate of their heterogeneous catalytic reactions have been studied by dealkylation of alkyl- and dialkylphenols over an acid-type catalyst, by hydrogenolysis of alkyl- and dialkylphenols over a nickel catalyst, and by dehydration of secondary alcohols over aluminium oxide. The results are discussed in terms of electronic and steric effects of the structure of the reacting substance. It was found that steric conditions are the most important factors determining the reactivity within a series of homologues and isomers over a particular type of catalyst. The work of other authors on hydrogenation of alkylaromatic compounds is interpreted in the same way.

1. INTRODUCTION

The study of effects of the structure of reacting compounds on their reaction rates represents one approach to the elucidation of mechanisms of organic reactions. Although this method has been extensively exploited for homogeneous reactions there are relatively few papers devoted to analogous studies of heterogeneous catalytic reactions. However, the work hitherto published indicates that such research may help to understand better mutual interactions between a substrate and a solid catalyst.

In recent years we were concerned with effects of structure on reactivity in acid-catalysed dealkylation of alkylphenols [1,2] and dialkylphenols [3], in hydrogenolysis of alkylphenols on a nickel catalyst [4], and in dehydration of secondary alcohols on aluminium oxide [5]. All these studies were carried out with the substrate in the gaseous phase and the kinetics of these transformations have been determined. This approach has made it possible to obtain in most cases the values of reaction rate constants which served as a basis for comparisons.

The results of this work indicate that for heterogeneous catalytic reactions different relationships are valid in comparison with homogeneous reactions. This conclusion is in agreement with the findings of other authors especially in the case of hydrogenation of aromatic compounds.

2. RESULTS

The dealkylation of alkyl- and dialkylphenols (reaction 1) was studied on an acidic catalyst which was prepared by impregnation of γ-alumina with an

## 2. METHOD OF ADSORPTION-CHEMICAL EQUILIBRIA

This is a convenient method [2] for obtaining thermodynamic character-istics for different parts of the surface layer formed on the catalyst in the course of the reaction. It involves the investigations of the equilibrium in a reaction between substance (X), adsorbed on the catalyst surface (K), and substances in the gas phase (Y and XY):

$$X(K) + Y_{(gas)} = XY_{(gas)} + (K). \qquad (1)$$
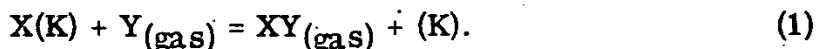
The thermodynamic functions relating to equilibrium

$$X_{(gas)} + (K) = X(K) \qquad (2)$$

at different sites of the catalyst surface may be obtained by combining equa-tion (1) with the data found for equilibrium

$$X_{(gas)} + Y_{(gas)} = XY_{(gas)}. \qquad (3)$$
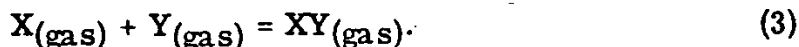
An advantage of this method is the ease of obtaining the necessary val-ues for the adsorbed layer fugitivity p solely by varying the Y to XY con-centration ratio in the gas phase. This enables studying the equilibria over a large range of p's and the degrees of coverage depending on p.

The adsorption-chemical equilibria of type (1) may set in at fast steps of the catalytic process. For instance, when reaction (3) proceeds through steps (2) and (1), the former being rate-limiting, fast step (1) can be con-sidered as an equilibrium step. The adsorption-chemical equilibrium of this step would determine the concentration and stability of the X(K) surface intermediate and may be characteristic of the slow step.
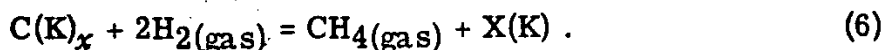
We studied the adsorption-chemical equilibria of nitrogen on an iron catalyst (2):

$$N(K) + \tfrac{3}{2}H_{2(gas)} = NH_{3(gas)} + (K) , \qquad (4)$$
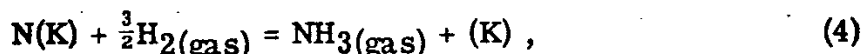
of oxygen on nickel catalysts (in both directions) [3,4]:

$$O(K) + H_{2(gas)} = H_2O_{(gas)} + (K) \qquad (5)$$
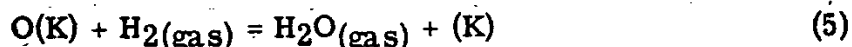
(see also refs. [5,6]), and of carbon on nickel:

$$C(K)_x + 2H_{2(gas)} = CH_{4(gas)} + X(K) . \qquad (6)$$

The study of equilibrium (5) shows that there occurs at first a regular increase in the chemical potential with the covering of nickel by oxygen [4]. After coverage of 15 to 20% of the surface the chemical potential begins to vary around a certain constant value. This is probably due to diffusion of adsorbed oxygen from sites of moderate adsorption capacity into the surface layer. The last phenomenon is due to greater stability of the bulk NiO com-pound, as compared with surface O(Ni) compound at these sites.

This interpretation is in agreement with other data [7-11]. Our study of equilibrium (5) on nickel pre-heated in vacuum at 800°C provides further support for this standpoint. In this case even the first portions of oxygen sorbed brought about chemical potential variations around a constant value, which seemed to result from disappearance of maximum activity sites.

A similar effect was observed in the study of equilibrium (6). The data
obtained by Varushchenko and the author (fig. 1) shows that at first the re-
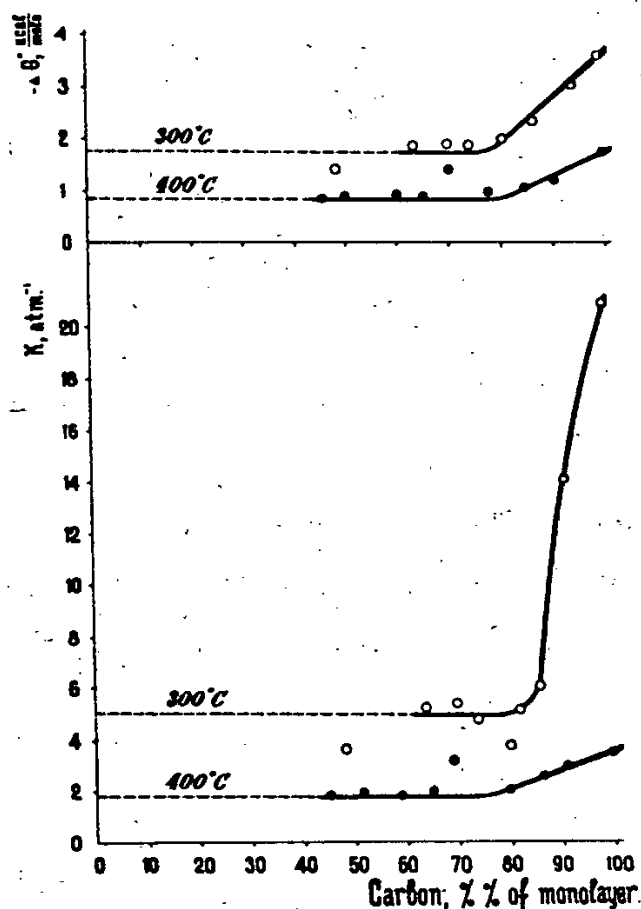

Fig. 1. Adsorption-chemical equilibrium of carbon on reduced nickel
at 300 and 400°C; Dependence of equilibrium constants and of
the standard free energy change ΔG^0 on the amount of carbon
sorbed (in %% of the monolayer).

moval of sorbed carbon causes regular changes in thermodynamic functions;
then the latter begin to vary around a certain value. Carbon seems to be
capable of penetrating from sites of moderate activity under the surface
layer in the course of adsorption. This part of sorbed carbon would be the
last to leave the catalyst, so that the change in chemical potential values
would not be regular. The penetration of some surface compounds into the
catalyst (partially or completely) might affect indirectly the reactivity of
the surface layer. This effect may be used in determining the fraction of
reactive sites in the total surface of the catalyst.

3. APPLICATION OF PARA-ORTHO HYDROGEN CONVERSION

The reaction of para-ortho hydrogen conversion

$$p\text{-}H_2 = o\text{-}H_2 \qquad (7)$$

was used by Davydova and the author in studying the effect of oxygen or
pyridine surface compounds upon the catalytic activity of reduced nickel.
The kinetic data for reaction (7) as well as for the exchange reaction:

$$H_2 + D_2 = 2HD \qquad (8)$$

after sorption of different amounts of oxygen by the catalyst are listed in
table 1. It will be seen that after coverage of about 20-30% of the surface

Table 1
The rate of reaction (7) and (8) on reduced Ni after the sorption of oxygen
(quasi-static circulating system, 0-100°C, 10 mm Hg).

Temperature of sorption °C	Oxygen sorbed (% of the monolayer)	Reaction rate at 90°C k min^{-1}.min^{-2}	Activation energy kcal/mole
Reaction (7)			
350	0	1.14	6.8
"	15	0.61	9.3
"	50	0.61	10.3
"	0	1.0	7.4
"	30	0.50	10.3
"	50	0.60	11.7
"	85	0.55	10.6
"	100	0.62	9.4
"	50 *	1.07	7.2
35-100	0	1.80	4.6
"	20	0.78	8.5
"	60	0.52	12.5
"	70	0.52	12.0
"	100	0.53	4.8
"	50 *-	1.80	
Reaction (8)			
35-100	0	2.01	8.0
"	100	0.29	20.0
"	50 *	2.0	7.8

* 50% of oxygen sorbed is removed.

further sorption of oxygen no longer alters the rate of reaction (7). Removal
of a half only of the sorbed oxygen would bring the rates of reactions (7) and
(8) to their initial values. These results confirm those obtained for equilib-
rium (5). The most probable suggestion would be that oxygen is retained only
by a certain part of the surface (varying with temperature), bonding with
the other part being but weak, and diffusing under the surface. Hence,
further sorption of oxygen at a coverage exceeding some 20-30% of the sur-
face would not change the reaction rate. The removal of a half of the sorbed
oxygen involves first of all that part of it which is bound with the surface;
this provides an explanation for the restoration of the reaction rates to
their initial values. The rate of reaction (7) per surface unit of nickelous

oxide is considerably less than that for oxygen-covered Ni. The effect of
the first portions of oxygen seems to be due to changes in the nature of sur-
face heterogeneity. After treating nickel at 800°C the sorption of oxygen,
whatever its amount, does not affect the rate of reaction (7). This is prob-
ably caused by the capacity of even the first portions of oxygen to penetrate
into the catalyst. Thermal treatment alone brings about a sharp increase
in the apparent activation energy as a result of changes in the nature of sur-
face heterogeneity.

It will be seen from table 2, that poisoning of the nickel catalyst by in-

Table 2
The influence of pyridine on the velocity of reaction (7) in the presence
of skeletal nickel in a non-gradient system.

Pyridine sorbed, %% of the monolayer	Reaction rate at 90°C, k min^{-1}.m^{-2} × 10^{-5}	Activation energy, kcal/mole
0	2.00	8.9
10	1.40	9.2
20	0.11	9.4
50	0.09	8.7
100	0.	–

creasing amounts of pyridine results in decreasing the reaction rate. Yet,
the apparent activation energy remains practically the same. A similar
effect is observed for other reactions occuring on catalysts poisoned by
sulfur compounds [13-16]. The latter was usually considered to result from
homogeneity of the catalyst surface, but it may be also interpreted by sur-
face heterogeneity. An expression of the apparent activation energy E for
reaction (7) was obtained [17]:

$$E = E^O + \alpha \, q^O + 2RT, \tag{9}$$

where E^O and q^O are the activation energy and the heat of the elementary
step of adsorption of para-H_2, related to the most active sites of the sur-
face, α is the exponent in correlating the equilibrium constant K_i for an
elementary step of formation of the surface compound and the correspond-
ing rate constant at i sites of the surface [18]:

$$\vec{k}_i = GK_i^\alpha \tag{10}$$

(G is a constant), the rate constant of the same step in the inverse direction
being:

$$\overleftarrow{k}_i = GK_i \, -(1-\alpha) \,. \tag{11}$$

Although in passing from one site to another the true activation energy
will vary, it follows from equation (10) that the sum $E + \alpha \, q$ and consequently
eq. (9) remain constant for a reaction at any site of the surface.

In order to elucidate the nature of surface compounds and the origin of
catalytically active centres of some polymers with conjugated π-bonds,
Davydova, Slinkin, Dulow and the author have studied reactions (7) and (8),

6

Table 3
The rates of reactions (7) and (12) in presence of polymers and the properties of the latters
(quasi-static circulating system, 20-200 mm Hg)

Catalyst	Temperature of the thermal treatment °C	Magnetic suscepti-bility x10^6	Electro-conductivity logarithm (log)		Electro-conductivity activation energy, eV	Spins unpaired (ESR-data)	$k \times 10^5$ (min^{-1}.m^{-2})	
			0°C	300°C			reaction (7)	reaction (12)
Poly (methyl vinyl ketone)	570	-0.5	-1.45	-5.52	0.35	3.8×10^{20}	4700	3700
	670	-0.5	1.67	0.70	0.11	6×10^{19}	850	-
	870	-0.6	2.05	1.74	0.035	4×10^{18}	70	670
	1000	-0.8	-	-	-	-	12	10
Poly (p-diethynylbenzene)	500	0.1	-0.95	-4.30	0.38	3×10^{17}	17.5	150
	600	0.1	-0.60	-2.25	0.18	-	4.3	280
Ashless charcoal	-	-0.4	-	-	-	-	-	87

I.34

and the reaction of ortho-para-conversion:

$$o\text{-}H_2 = p\text{-}H_2 \tag{12}$$
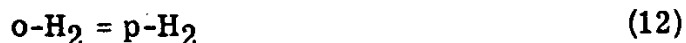
in correlation with measurements of electric and magnetic properties of polymers.

It will be seen from table 3 that changes in properties of samples subjected to different thermal treatments are consistent with those in rates of reactions (7) and (12). The maximum reaction rate is attained at the maximum number of unpaired electrons and minimum specific electroconductivity. At different pressures the rate of reaction (7) follows a first-order equation, the activation energy being 6.5 kcal/mole or more. No signs of reaction (8) or adsorption of hydrogen were observed under the same conditions. A conclusion may be drawn that a specific physical mechanism, namely, the action of the inhomogeneous magnetic field created by catalytic centres upon hydrogen molecules colliding with the surface, is characteristic of reaction (7) in this case. Such centres may be conceived as electron-transfer surface complexes. The existence of these centres was suggested as an explanation for the properties of the above-mentioned polymers [19]. The validity of the first-order equation for various pressures is in favour of the physical mechanism of the reaction; however the temperature coefficient of the reaction is abnormally high. This may be due to the energy of thermal excitation of surface sites, to the irradiation effect [20] or to excitation of π-electrons to the triplet state necessary for cis-trans-interconversions [21].

In order to determine the character of surface compounds formed by chemisorption of paraffins on metals Davydova and the author made use of reaction (12). Preadsorption of cyclohexane at 30-100°C (10% of the monolayer), was found markedly to accelerate the reaction (12) on reduced nickel at -196°C. Accelaration increased with increasing temperature of C_6H_{12} adsorption. Hence, a conclusion may be drawn that even at low temperatures the chemical adsorption of cyclohexane is accompanied by the formation of surface compounds which accelerate reaction (12) due to their radical-like nature (possibly by dissociation of initial molecules). The previous conclusions about the dissociative nature of adsorption were based on studies of reaction mechanisms or, in some cases, on experimental results [22,23]; yet, the interpretation of the latter was not always unambiguous. A similar effect might be expected for adsorption of other saturated compounds on some metals because of the small differences in energies of bonds of the same type [24]. This effect should be allowed for when considering the mechanisms of corresponding reactions on metals, in particular, those of the dehydrogenation processes.

4. NON-GRADIENT METHODS IN THE STUDY OF REACTION KINETICS AND ME-
CHANISMS

Non-gradient methods [25-27] were used along with other techniques for the study of the kinetics and the mechanisms of some reactions and for the

elucidation of the nature of surface compounds. These methods are most reliable. They permit operating directly with differential kinetic equations, thereby avoiding difficulties which arise for reactions in flow or static systems and also allow us to work with differing amounts of the catalyst. We shall report some results as obtained by using this technique.

A question arises whether the rate-determining step in hydrogenation and dehydrogenation on a skeletal nickel catalyst at low temperatures is the formation or the decomposition of the surface compound of hydrogen. Kaplan, Nikolaeva, Davydova and the author made a comparison between the rates observed for the hydrogenation of ethylene and for the dehydrogenation of alcohols in a non-gradient system [27] and the rate of reaction (7), which under these conditions was much higher. It appeared that the formation or decomposition of such surface compounds (i. e., adsorption or desorption of H_2) cannot be the rate-limiting step. The rates (ω) of hydrogenation of acetone and of dehydrogenation of isopropanol at temperatures below 100°C in the same system are described by the kinetic equation:

$$\omega = \overrightarrow{k}\, P_{C_3H_6O}\, \frac{P_{H_2}^{0.5}}{P_{C_3H_7OH}^{0.5}} - \overleftarrow{k}\, \frac{P_{C_3H_7OH}^{0.5}}{P_{H_2}^{0.5}} \tag{13}$$

It is consistent with the suggestion that the formation and the decomposition of an intermediate surface compound - adsorbed acetone - are the rate-determining steps.

The rate of dehydrogenation of formic acid on reduced skeletal nickel in the non-gradient [27] and flow systems, examined by Nagyshkina and the author over a conversion range from 0.54 to 82% and temperatures from 77 to 196°C appeared to be of zero-order. These data, as well as experiments using deuterium, provide a confirmation for the scheme implying that decomposition of the surface intermediate is the slow step, as was suggested before by Dutch scientists [28]. The bond energy of the surface compound can be estimated in this case as being about 40 kcal/g-atom for one valence for sites of the lowest activity.

Andreev and the author have used the flow-circulating method [25] in investigating the kinetics of dehydrogenation of cyclohexane in the presence of a nickel-zinc oxide catalyst at temperatures up to 300°C in a region far removed from equilibrium. At partial pressures of C_6H_{12} exceeding 100 mm Hg it will be described by a zero-order equation, below 100 mm Hg - by equation:

$$\omega = k\, P_{C_6H_{12}}^{0.5} \tag{14}$$

The change in the reaction order may be due to passage from the region of high coverage to that of medium coverage. The kinetics of the reaction may be interpreted under the assumption that the reaction proceeds via several slow steps and the fast step of formation of a radical-like compound $C_6H_{12}^*(K)$.

It was shown by Nagyshkina and the author [25], that the kinetics of

dimerisation of ethylene in a flow-circulating system at 200-300°C in the
presence of a nickel catalyst on silica-alumina follow a first-order quation.
This may be interpreted on the assumption from the standpoint that the re-
action on inhomogeneous catalyst surfaces proceeds by the formation and
decomposition of a surface compound, i.e., of adsorbed ethylene.

5. STABILITY OPTIMUM FOR INTERMEDIATE SURFACE COMPOUNDS AND THE PROBLEM OF THE OPTIMAL CATALYST

The different stabilities of surface compounds on various sites of the
surface as well as the reaction mechanism and conditions should be taken
into account in approaching the problem of the optimal catalyst (in the sense
of its highest activity). As the reaction rate for various sites of the surface
is different, attention should be paid to the problem of optimum sites where
the intermediate surface compounds would posses optimal stability. The
assumption that their stability should be neither too high nor too low, is, in
fact, a qualitative presentation of Balandin's "energy correspondence"
principle [29].

The reaction rate should be maximum at such sites of the surface,
where the possibility of formation of an intermediate equals α (see eq.
(10) [1,30]. As a rule α is close to 0.5 and consequently optimum sites
should be those where at a given fugitivity p of the adsorption layer the
coverage probability would be close to $\frac{1}{2}$; therefore, the maximum reaction
rate would correspond to medium coverages. The optimum heat of forma-
tion of the surface intermediate will be

$$q_{opt} = RT \ln \frac{B_0}{(1-\alpha)p}, \tag{15}$$

where B_0 is the reciprocal of the adsorption coefficient pre-exponential
factor. When chemical-adsorption (or adsorption) equilirbium determining
the value of p sets in at fast steps of the reaction, the optimal bond energy
of the surface intermediate $Q_{M(K)_{opt}}$ will be:

$$Q_{M(K)_{opt}} = \Sigma Q' + RT \ln \frac{B_0}{1-\alpha} \pm RT \ln \frac{KP_j'}{P_j''}, \tag{16}$$

where $\Sigma Q'$ is the sum of dissociation energies of initial bonds, P_j' and
P_j'' are the partial pressures of reactants and products of fast reaction
steps the signs + and – relate to cases when the rate-determining step is
the formation or decomposition, respectively, of the surface compound.

When no rate-determining step may be detected in a reaction (e.g., in
a region remote from equilibrium) and the reaction follows a two-step
scheme [1], the maximum rate will correspond to the equality of rates of
both steps and

$$Q_{M(K)_{opt}} = \alpha(\Sigma Q' + \frac{1-\alpha}{\alpha} \Sigma Q'') + RT \ln \frac{\alpha G_{II}(K_{II}^0)^{1-\alpha}}{(1-\alpha)G_I(K_I^0)^\alpha} + RT \ln \frac{P_{II}}{P_I}, \tag{17}$$

where Q'' is the sum of energies of the bonds formed, K_I^0 and K_{II}^0 are pre-exponential factors of the equilibrium constants for each step, G_I and G_{II} are factors of eq. (10), corresponding to stages I and II respectively, P_I and P_{II} are the partial pressures of reactants involved in steps I and II. When $\alpha = 0.5$, $G_I = G_{II}$, $K_I^0 = K_{II}^0$ and $P_I = P_{II}$, eq. (17) will coincide with the quantitative formulation of the energy correspondence principle [29], which was also obtained by Temkin [1] for "symmetric" reaction (i.e., when $G_I = G_{II}$). More complex cases may often be reduced to the two-steps scheme.

It will be seen that the optimum characteristics of the surface are functions of many factors: a change in the reaction mechanism, degree of removal from equilibrium, experimental conditions (in particular, and changes in the ratio of partial pressures of the components in the course of the reaction). Yet the above equations may be used for approximate estimations.

Thus, for reaction (7) at $300^{\circ}K$ the changes in pressure from $P = 760$ to 0.4 mm Hg would bring about changes in the optimum stability of the surface compound $Q_{H(K)_{opt}}$ from 56.5 to 60.4 kcal/g-atom, which corresponds to a shift of the optimal heat of adsorption (q) equal to 8 kcal/mole. These values lie within the range of q variations on nickel.

For ammonia synthesis we obtain from equation (17) and using the data [2] for $T = 723^{\circ}K$ and $P = 300$ atm $Q_{N(K)_{opt}} = 42.7$ kcal/g-atom (per 1 nitrogen valence) while for $P = 1$ atm $Q_{N(K)_{opt}}$ is 44.1 kcal/g-atom. This corresponds to a change q from 30.3 to 38.7 kcal/mole. The latter lies close to the middle of the range of q variations on iron and tungsten which are active catalysts for this reaction. Although tantalum adsorbs nitrogen readily, it does not show sufficient catalytic activity, the q value being considerably in excess of the optimum [31].

For hydrogenation of ethylene (using relation (17) and estimating B_0 as being about 3×10^7 atm at $T = 300^{\circ}K$) the change in $P_{C_2H_4}$ from 300 to 1 mm Hg brings about a change in $Q_{C(K)_{opt}}$ from 36.1 to 37.8 kcal/g-atom (with respect to 1 carbon valence), which corresponds to ethylene adsorption heats of 11-14 kcal/mole. The values of q on nickel are higher than the optimum value and the reaction seems to take place at high degrees of coverage, when the sites with low q values become occupied. Of the metal examined by Beeck [31] the lowest q value and the strongest catalytic activity were displayed by rhodium.

From the standpoint as discussed above, a catalyst may be regarded as optimal when its surface offers the largest number of optimal sites under given experimental conditions. For an ideal case the maximum rate would be attained for a reaction occurring on a homogeneous surface consisting of optimum sites only. However, this hypothetic catalyst with a homogeneous surface would no longer be optimum once the reaction conditions have changed, whilst with a heterogeneous surface the possibility always remains of finding a sufficient number of sites which would be optimal under new conditions. It is hardly reasonable to treat the problem of the optimal catalyst without considering specific experimental conditions.

It would be reasonable to suggest that further progress in the theory of

catalysis will largely depend on advance in new methods for the investigation of the intermediate surface compounds and the estimation of their stability.

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STAT

THE EFFECT OF ELECTRON PROPERTIES
OF SUPPORT UPON EXO-ELECTRON EMISSION
AND CATALYSIS

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Abstract: A number of supported catalysts has been investigated by the exo-electron emission method. The relationship between catalytic and exo-emission activities of catalysts on semiconductor and dielectric supports is discussed. Catalytic activity is not a simple function of exo-electron emission for supported platinum catalysts. Catalytic activity of luminophor catalysts $ZnS \cdot Cu$ and $ZnS \cdot Ag$ is a direct function of their luminescence and exo- electron emissivity. It is concluded, that (1) electron gas of support does not affect considerably the catalytic activity of supported metal catalysts and (2) electron gas of crystals is an active participant of the act of catalysis in case of crystallophosphor catalysts.

1. INTRODUCTION

The present report will deal with the discussion of relationship between catalytic and exo-electron properties of supported catalysts, particularly, platinum adsorbed on various inert carriers at various surface coverage values (α). This type of catalysts has been extensively studied in our laboratory (for reviews see refs. 1, 2). The catalysts may occur in the surface layer in form of a wide variety of aggregation states from separate atoms at very low α (ca. 10^{-3}), groups of several atoms, or "ensembles", at intermediate, and crystals with dimensions 50-100 Å at high α (ca. 1). Such aggregates can be generally formulated as Me_n ; with growing coverage n may take values from 1 to 10^4 - 10^5.

Kobozev has proposed a theory of the formation and catalytic activity of this type of adsorbed layers, known as "active ensembles theory" [3]. The data to be discussed lower were obtained with systems, involving aggregates Me_n, emerged into or in contact with the support electron gas of varying density. The study of relationship between the exo-emission and catalytic activities seems to be an advisable approach to experimental solution of the problem of electron gas of support upon the catalysis process. This was interpreted formerly in terms of rather general assumptions to lead to some discrepancy of conclusions [2, 4, 5].

The exo-electron emission phenomenon has been extensively studied during the last decade after several basic publications by Kramer [6] and is now attracting attention of many solid state physicists. Compared with the more common Richardson's emission, exo-electron emission can be ob-

electron, ultra-violet and visible light irradiation of metallic and non-metallic crystals. The decay of emission after the end of exciting action is usually fitted by the following equation:

$$J = A/t^n ,$$

where A and n are constants, and t is the time after the end of exciting action.

Emission may take place at room and lower temperatures, but sometimes heating is necessary. In the latter case, the "electron emission glow curves", similar to glow-curves from thermo-luminiscent phosphors, are to be measured. These curves show usually one or several maxima.

The firmly established low energy of exo-electrons, not exceeding tenths of an electron volt, suggests the exo-emission phenomenon to take place in only a thin surface layer.

A large number of substances which can emit exo-electrons is now available. These are metallic and non-metallic crystals, oxydes, salts and complex minerals. There has been proposed a number of theories for interpretation of the exo-electron emission phenomenon [7, 10]. Kramer's original hypothesis, based on the assumption that the energy supply of electron emission is provided by exothermal * post-excitement recrystallisation or relaxation processes is no longer considered valid. However, neither of the modern theories is sufficient.

2. EXPERIMENTAL

Supported platinum catalysts and luminophor catalysts $ZnS \cdot Ag$ and $ZnS \cdot Cu$ were investigated.

Platinum catalysts were prepared on six supports - alumina, zirconia, barium sulphate (dielectrics), and zinc oxide, chromium sesquioxyde, magnesia (semiconductors) - by adsorption of chloroplatinic acid and subsequent reduction with electrolytic hydrogen. All the supports except alumina were non-porous "analytical grade" commercial preparations. Low temperature krypton adsorption method showed the following values of surface areas: ZrO_2 - 9.6 m^2/g, ZnO - 1.9 m^2/g, MgO - 8.9 m^2/g, Cr_2O_3 - 1.5 m^2/g, and $BaSO_4$ - 5.5 m^2/g. Alumina was prepared from aluminium sulphate by precipitation with ammonia from aqueous solution; it exhibited a surface area of ca. 250 m^2/g. Hydrogen peroxyde decomposition and cyclohexene hydrogenation (in dry ethanol at 20°) served test reactions for assaying the activities of platinum catalysts. The rates of reactions were measured gasometrically.

Luminophor catalysts were prepared by impregnating zinc sulphide with cupric nitrate and silver nitrate solutions and subsequent glowing at 900°. The catalytic activities were assayed by the rate of isopropyl alcohol decomposition in a continuous-flow apparatus at $315-360^o$. Luminescence was excited with a mercury-quarz lamp, λ_{max} = 365 mμ. Intensity of lu-

* This assumption prompted the term "exo-electron emission".

minescence was measured by means of a luminescent photometer at room
temperature.

Exo-electron emission was excited with X-rays (Mo-anticathode, 30
kV, 10 mA) and measured by means of a Geiger-Müller point counter with
argon-ethanol filling, attached to a conventional radiometric instrument.
The intensity of emission J was evaluated by the number of counts per min-
ute, 5 minutes after the end of irradiation. If no emission could be obtained
at room temperature, glow-curves were measured. The temperature was
increased at a constant rate of ca. 7° per minute. The intensity of emission
was evaluated by the number of counts per minute at the temperature of the
first emission maximum.

3. RESULTS AND DISCUSSION

Exo-electron emissivity and specific activity * of platinum supported
with carriers of varying electron effinity are plotted in figs. 1-3 versus
coverage α **. Specific activity of a supported catalyst is the total activity
of layer divided by coverage, $a = A/\alpha$ *** ; it characterizes the activity of
the amount of the applied substance, equivalent with a monoatomic layer.
Comparing J and a, one can draw some conclusions concerning the effect
of weakly-bound electrons of the support (covered partially with metal cat-
alyst) upon the activity of the supported metal weight unit.

Rather obvious parallelism is observed between J and a for platinum
supported with dielectrics ZrO_2 and Al_2O_3 (fig. 1): with increasing coverage
both the emission and specific activity at first sharply drop (according to
exponential law), pass a minimum and again increase at high values.

The initial steep slope of the curve can be easily explained in terms of
active ensembles theory by decreasing amount of platinum in form of sepa-
rate atoms, which is known to be most reactive in H_2O_2 decomposition cat-
alysis [11, 12]. The decreasing exo-electron emission reveals the fact, that
separate platinum atoms are as well most effective as electron traps.

More complex catalytically active structures M_n, $n \gg 1$, appear at
high coverage ($\alpha \to 0.01$), and they as well are exo-emission centres. Anal-
ogous formation of complex emission and catalysis centrès is observed for
platinum supported with MgO and Cr_2O_3 (fig. 2). However, it appears that
with dielectric supports Al_2O_3 and ZrO_2 in the diluted layers region, con-
sumption of electrons is not related immediately to catalytical activity, as
the activity maximum is observed at $\alpha \to 0$, where both consumption of
electrons and fading of exo-emission by platinum atoms are still negligable.
Hence, the two phenomena - exo-electron emission and catalysis - are re-
lated only indirectly, through the atomic structure of the applied platinum.
A somewhat less distinct parallelism between J and a values is ob-

* In hydrogen peroxyde decomposition.
** Intensity of exo-emission was measured for aluminium, magnesium and chro-
mium oxydes and barium sulphate at room temperature, for zirconia - at 75°,
and for zinc oxyde - at 140°.
*** A is expressed in terms of first order reaction rate constant.
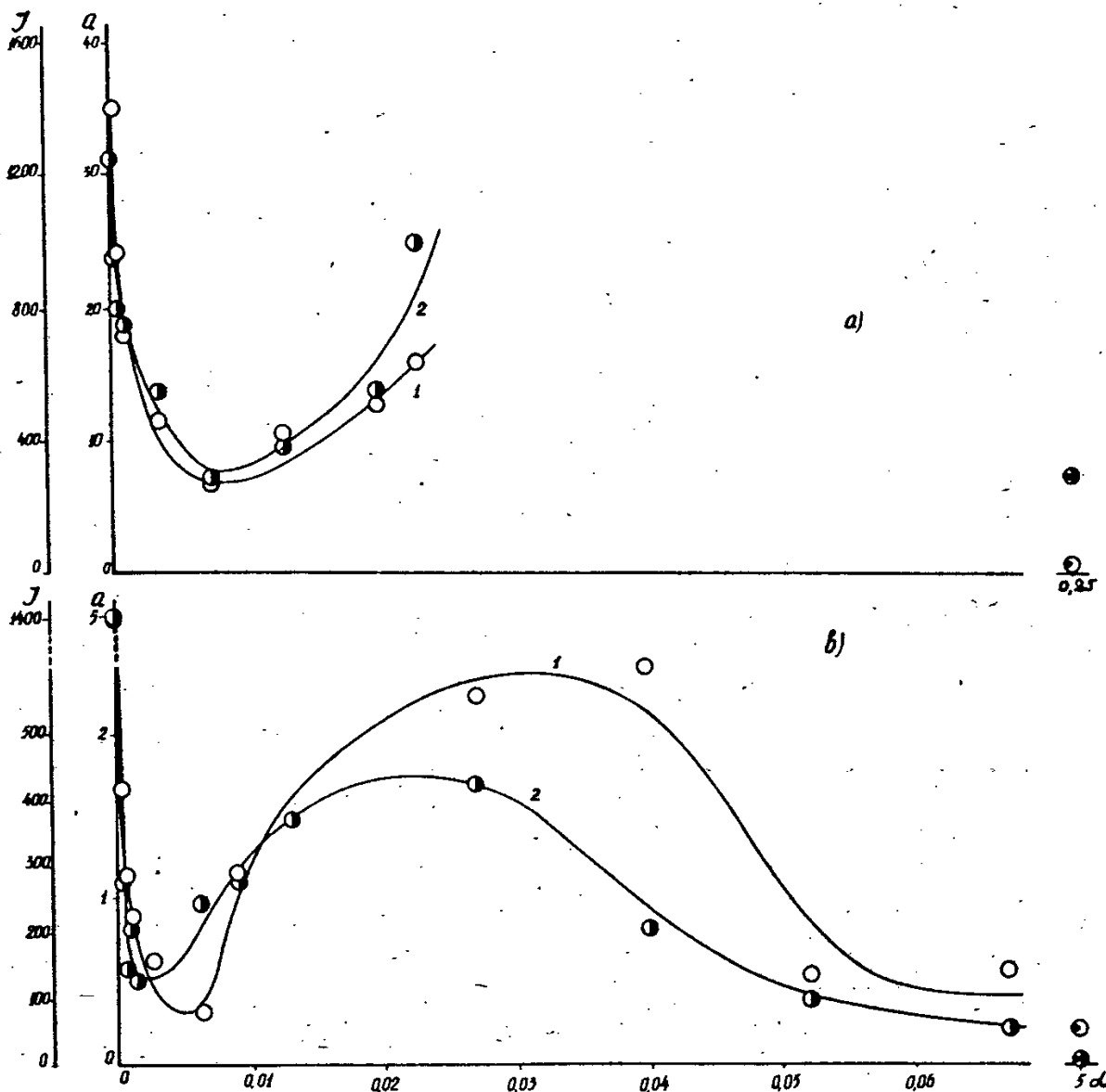
4

Fig. 1. Specific catalytic activity (1) and exo-electron emissivity
(2) of supported catalysts versus content of platinum for
Pt/Al_2O_3 (a) and Pt/ZrO_2 (b).
Points J for Pt/Al_2O_3, $\alpha = 0.25$; for Pt/ZrO_2, $\alpha = 5$.
α

served with non-typical semiconductors MgO and Cr_2O_3 (fig. 2), and the
two curves become anti-parallel for a typical n-semi-conductor ZnO (fig.
3a). No parallelism of J and a is observed with $BaSO_4$, this dielectric giving
abnormal exo-electron emission (some two-orders more intensive than
other materials investigated). Hence, it can be concluded, that coverage
functions of exo-electron and catalytical activities may be both parallel and
anti-parallel.

All the exo-electron emission curves reveal the fact that the most in-
tense drop (fig. 1a and b), or increase (fig. 3a and b) of emission takes
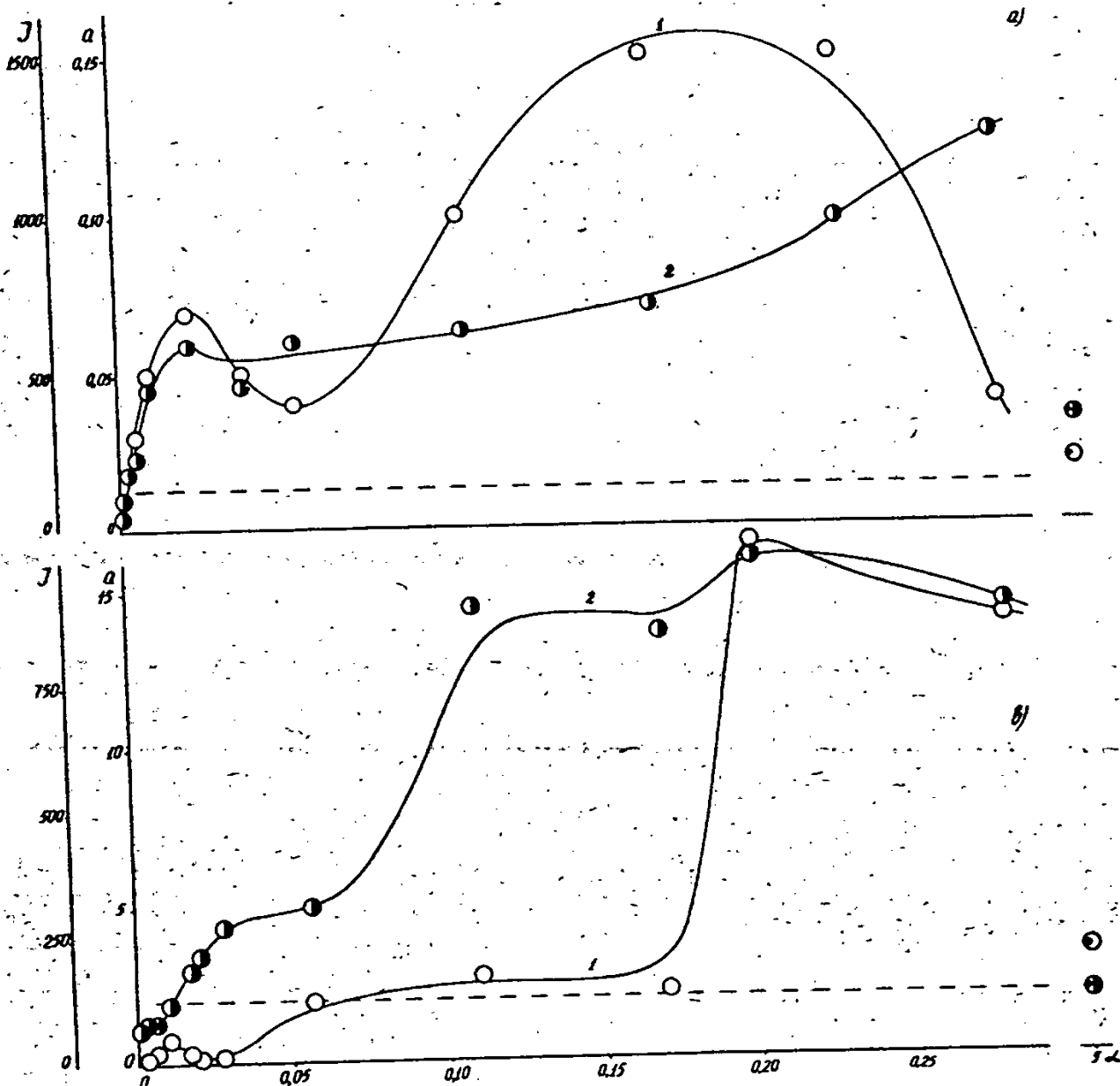place at very low coverage, when there are only separate metal atoms on

Fig. 2. Specific catalytic activity (1) and exo-electron emissivity
(2) of supported catalysts versus the content of platinum for
Pt/Cr$_2$O$_3$ (a) and Pt/MgO (b).
Points $\odot$ α for Pt/MgO and Pt/Cr$_2$O$_3$, α = 5.
$\bullet$ J

the surface of the support. Such diluted layers are at the same time the best
photon traps, as indicated by the sharp drop of reflective index at low cov-
erage, seen in fig. 4. This figure shows also parallelism of specific cata-
lytical activity a and reflective index for Pt/Al$_2$O$_3$.

The above data suggest, that platinum atoms may both increase the
number and energy depth of electron traps and reduce it subsequently by
shielding. Hence, the concentration and the state of electron gas is strongly
dependent on the nature and coverage of the support. However, these vari-
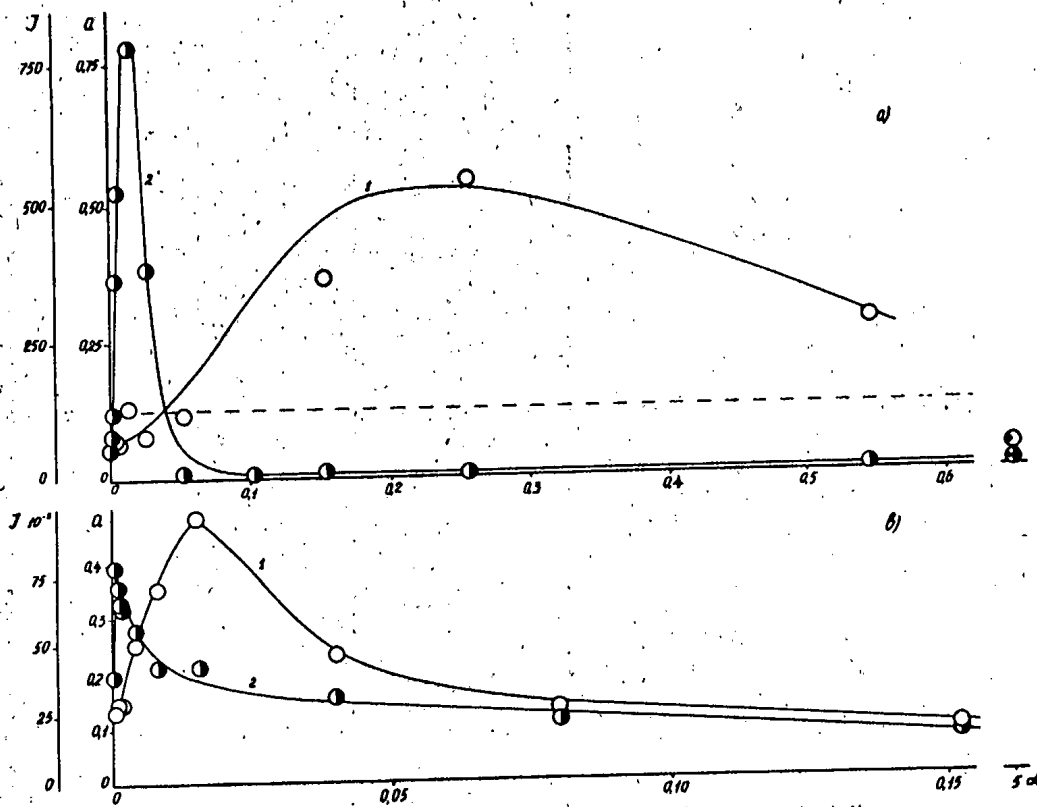ations are of no direct effect upon the catalytical activity, as it is demon-

Fig. 3. Specific catalytic activity (1) and exo-electron emissivity
(2) of supported platinum catalysts versus the content of
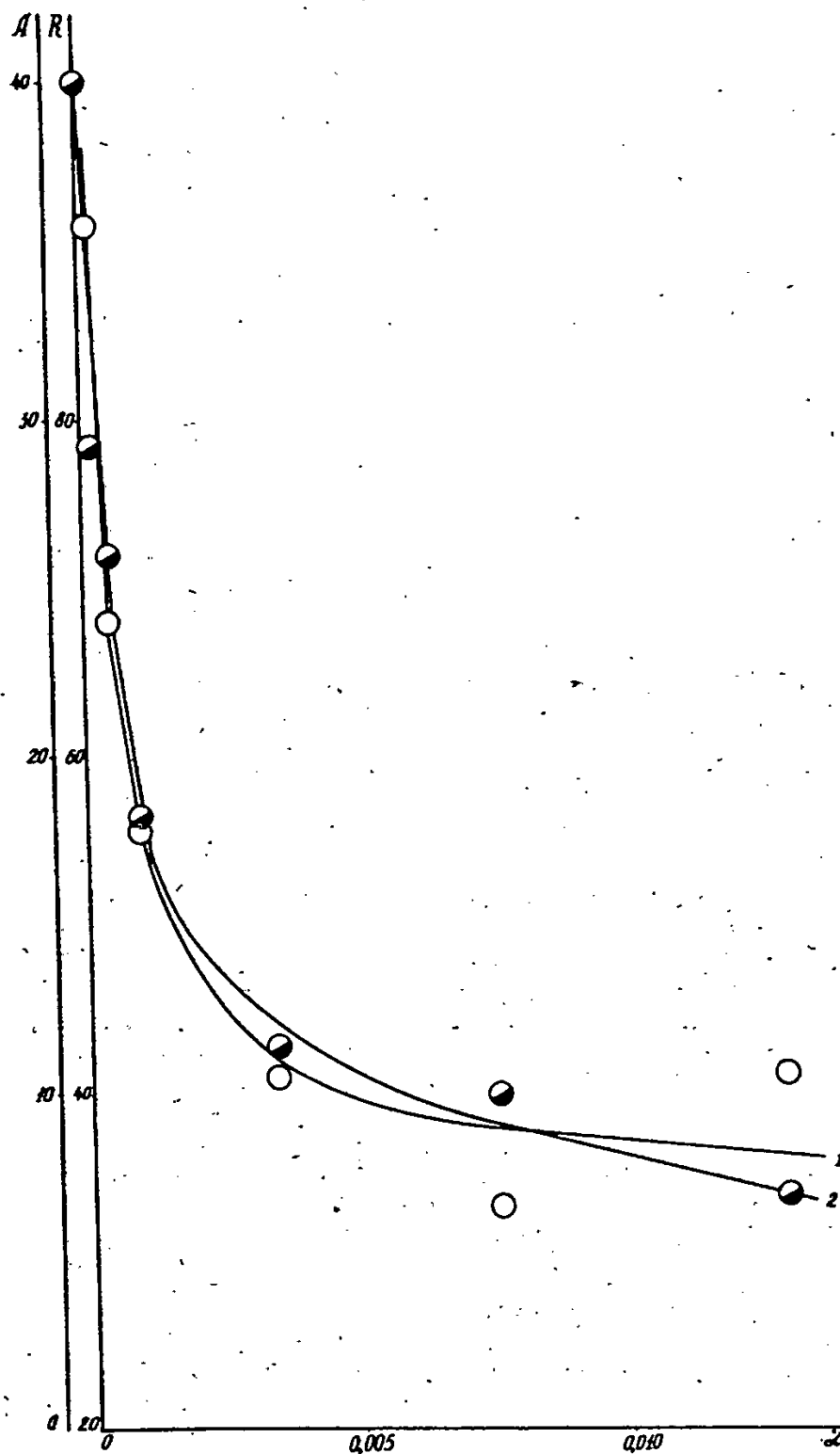platinum for Pt/ZnO (a) and Pt/BaSO₄ (b).
Points ⊖a for Pt/ZnO, α = 5.

Fig. 4. Specific catalytic activity (1) and reflective index R (2) of
Pt/Al$_2$O$_3$ catalysts versus the content of platinum.

strated in table 1, where absolute specific catalytic activities of catalysts
with various supports of different electron properties (particularly, exo-

Table 1
The effect of emissivity of carrier upon the catalytic activity
of supported platinum.

Support	Surface area of support	Emissivity of pure support	Emissivity of catalysts	Activity in H_2O_2 decomposition mole/sec	Activity in cyclohexene hydrogenation
Al_2O_3	250	1400	1400	1.5	-
MgO	8.9	1300	1000	0.4	0.14
ZrO_2	9.6	1400	1400	0.36	1.3
Cr_2O_3	1.5	3000	1000	0.14	0.5
ZnO	1.9	50	0	0.34	0.36
$BaSO_4$	5.5	40000	40000	1.35	0.48
platinum black	10	-	130	0.6	-

electron emission activity) * are surveyed.

As it is seen in this table, the maximum catalytical activity (expressed in terms of number of H_2O_2 molecules decomposed on 1 platinum atom or, for hydrogenation, H_2 molecules, consumed on 1 platinum atom, per second) is not strongly dependent on the nature of the support and exhibits no parallelism with its electron properties (column 3) and the exo-emission activity of catalysts (column 4).

This important conclusion is in accordance with the evidence, concerning the effect of the support upon the turnover of active centres, obtained in our as well as in other laboratories and surveyed in table 2. Here we can once more see that catalytic activity of the supported metal is completely independent of the nature of the support.

The presented data are a step forward in as much as they are the first attempt to make a direct comparison of the catalytic activity of the supported platinum layer with the concentration and the energy state of the surface layer electron gas. The absence of a simple relationship between the two properties is an evidence in favour of minor role of the electron gas, surrounding the platinum active centres, in their catalytical function.

The conclusion must be referred certainly to only atomic (e.g., platinum) supported catalysts. On going to ionic catalysts, and particularly, with ions involved in crystalline lattice (luminophors), the phenomena become completely different. It has been already mentioned in previous publications that the activity of ionic catalysts, in contrast to that of the atomic ones, is strongly dependent on the nature of carrier. A parallel study of catalytic, exo-electron and luminescent properties of luminophors $ZnS \cdot Cu$ and $ZnS \cdot Ag$ revealed a quantitative relationship between the catalytic and emission activities, and, consequently, confirmed direct participation of electron gas in the act of catalysis.

The curves in fig. 5 (a and b) show the catalytic activity and intensities

* Exo-electron emission intensities are given at lowest temperatures, at which they still can be measured.

Table 2
The effect of electron properties of carriers upon the catalytic
activity of supported platinum.

A. Decomposition of hydrogen peroxyde (20°).

Carrier	Type of carrier	Activity mole/sec	Authors [2]
Charcoal	semiconductor	0.58	Kobozev and Reshetovskaya
Garmanium	semiconductor	0.9	Krilova, Ogaröv, Kobozev
Metallic bismuth	cathode-polarized conductor	0.9	Krilova, Ogaröv, Kobozev
Metallic bismuth	conductor	0.3	Krilova, Ogaröv, Kobozev
Metallic cadmium	conductor	8.3	Lebedev, Trossman
Alumina	dielectric	0.9	Krilova
Silica I	dielectric	0.54	Krilova
Silica II	dielectric	0.21	Strelnikova, Lebedev

B. C = C-double bond hydrogenation (at 25° in ethanol).

| Substance for hydrogenation	Carrier	Type of carrier	Activity mole/sec	Authors
Cyclohexene, methylcyclo-hexene	Silica	dielectric	0.23	Maltsev, Kobozev et al.
1-Heptene	Silica	dielectric	0.76	Maltsev, Kobozev et al.
1-Heptene	Ni on silica	conductor + dielectric	0.2	Buchman, Sokolsky
Styrene	Raney-Ni	conductor	1.35	Stsheglov, Sokolsky
2-Methyl-4-methoxy-2,3-butene	Raney-Ni	conductor	0.14	Stsheglov, Sokolsky
Cyclohexene	ZrO_2	dielectric	1.1	Maxted [4]
Cyclohexene	ThO_2	dielectric	0.85	Maxted [4]
Cyclohexene	MgO	semicon-ductor	0.38	Maxted [4]
Cyclohexene	Cr_2O_3	semicon-ductor	0.46	Maxted [4]
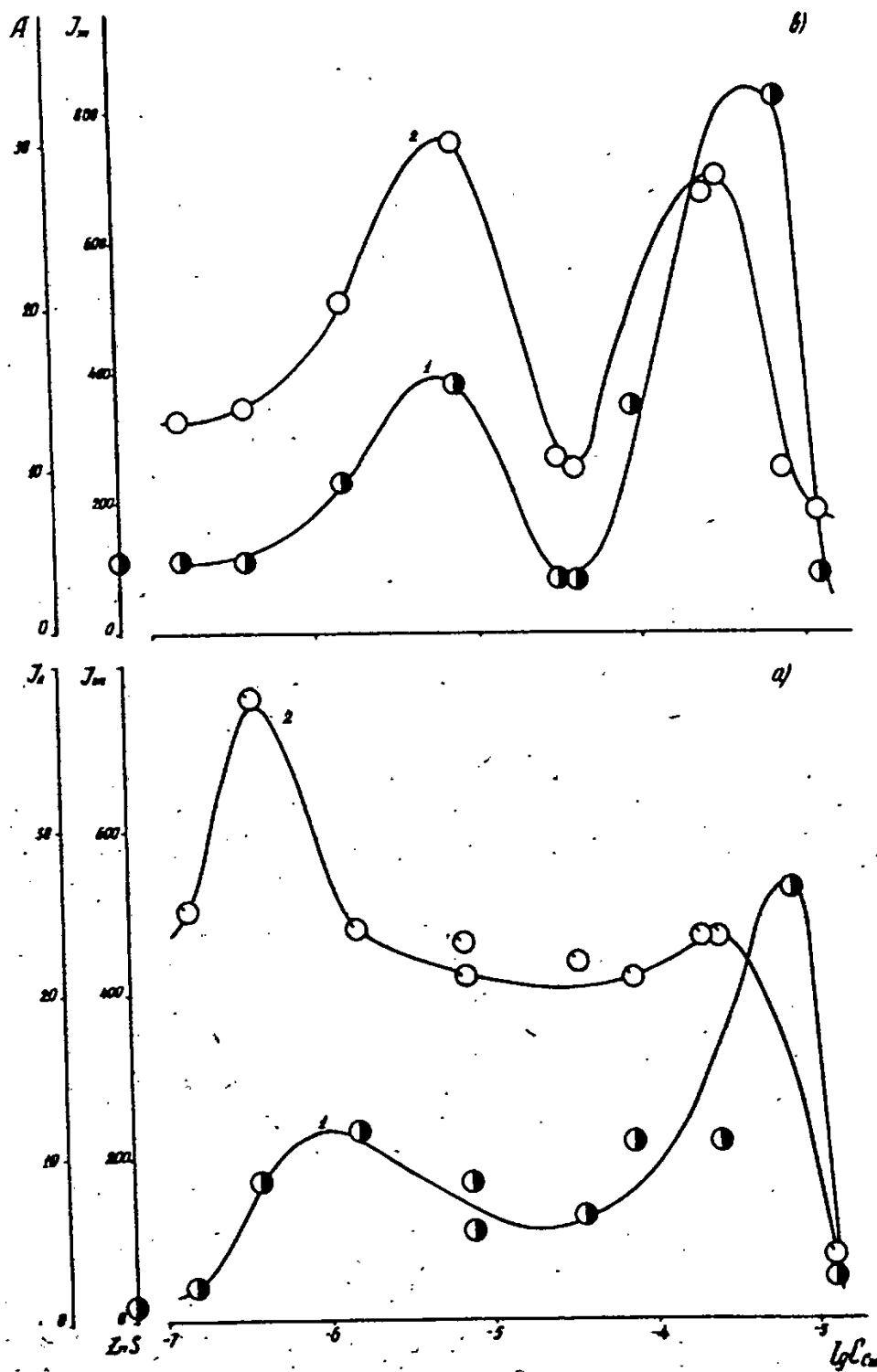
Fig. 5: (a) Catalytic activity, 330° (1), and exo-electron emissivity, 260° (2), of $ZnS \cdot Cu$, (b) Intensity of luminescence, J_{lum}, 20° (1), and exo-emissivity, J_e, 140° (2), of $ZnS \cdot Cu$, versus the content of copper.
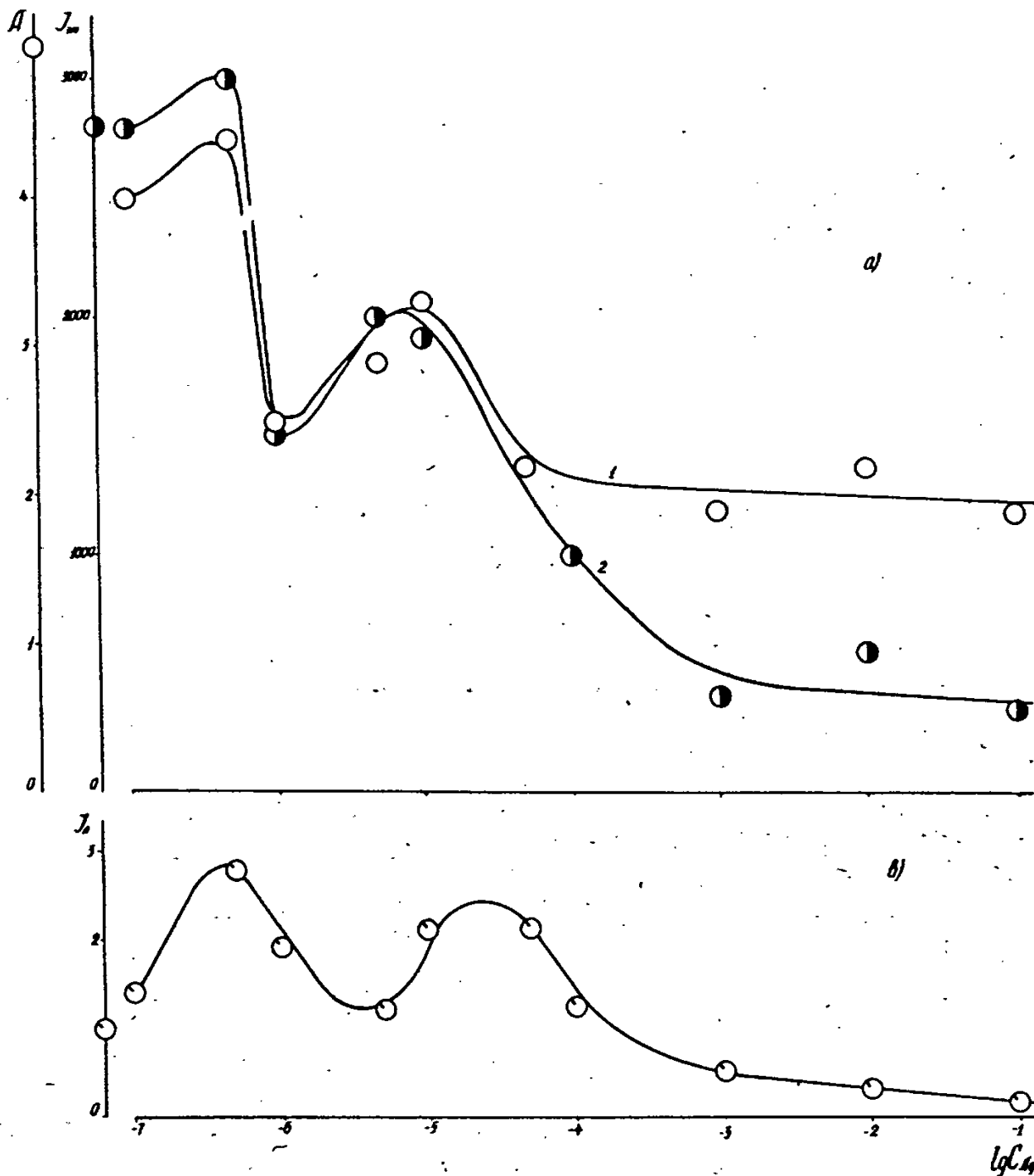
Fig. 6. (a) Catalytic activity, A, 345° (1), and exo-emissivity, J_e,
140° (2), of $ZnS \cdot Ag$, (b) Intensity of luminescence, J_{lum},
of $ZnS \cdot Ag$, versus the content of silver.

of exo-emission and luminiscence of $ZnS \cdot Cu$ to increase with increasing
concentration of copper *. Both the catalytic activity and the luminescence

* The curves in fig. 5 were obtained at close temperatures. The exo-emission curves
of $ZnS \cdot Cu$ at room temperature pass maxima at the same concentrations of copper,
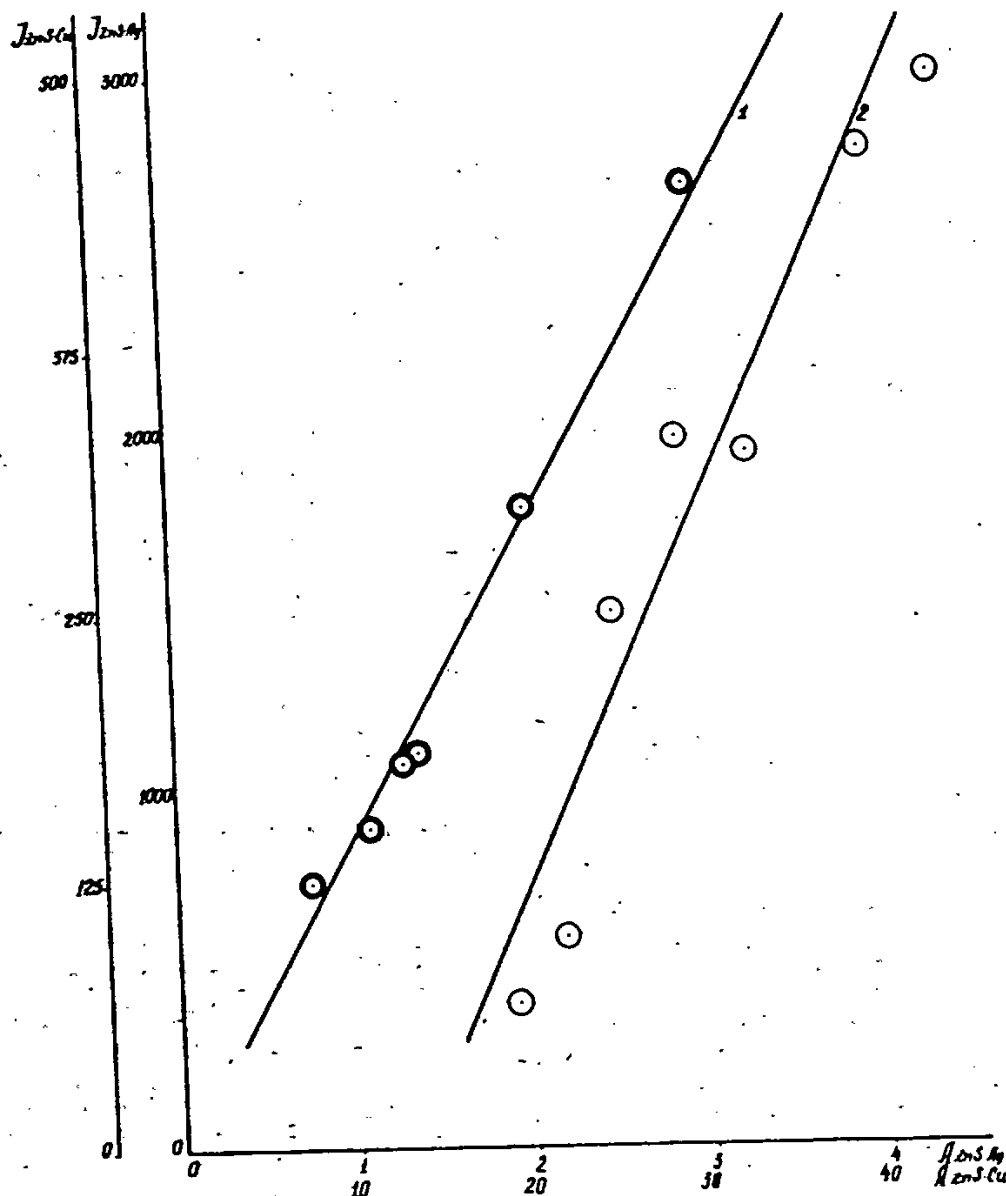but these maxima are less distinct.

Fig. 7. Catalytic activity versus intensity of exo-emission
(1) – ZnS · Cu, (2) – ZnS · Ag.

and exo-emission curves show two maxima at close concentration of copper.
Good superimposability of the two maxima will become even more evident,
if one remembers of the logarithmical scale on the abscissae axis.

Catalytic activity and luminescence and exo-emission intensities are
plotted in fig. 6 (a and b) versus silver content in ZnS · Ag samples. Silver
contamination, on the contrary with copper reduces the catalytic activity of
zinc sulphide, but there takes place a parallel decrease of exo-electron
emission. The slope of the luminescence curve is somewhat different *

* As the luminescent centres are situated in the whole volume, whereas the exo-
  emission and catalytic centres are situated in the surface layer of solid bodies,
  a somewhat better correspondence of exo-emission and catalytic activity curves
  could be anticipated. This is confirmed also by experimental evidence (see figs.
  5 and 6).

(fig. 6b), but its general character remains very similar.

Direct correspondence between the catalytic and exo-emission activities of luminofor catalysts is most distinctly seen in fig. 7, where catalytic activities a of ZnS·Ag and ZnS·Cu catalysts of various silver and copper content is plotted versus exo-electron emission J. The observed parallelism suggests the catalysis. exo-emission and luminescent centres to be common.

Hanlew and Gourgé [10] have pointed out the similarity of methods for exciting emission and luminescence. Exo-emission and luminescence exhibit usually very similar decay and temperature curves, etc. The workers proposed the observed similarity to be the consequence of the analogous character of elemental physical processes giving rise to the two phenomena.

It is known, that the blue luminescence centres of non-activated zinc sulphide are Zn^+ interstitial ions. Their concentration may increase on addition of minor activator contaminations [13]. The above data suggest the same ions to account for the increase of catalytical activity and exo-emission at low concentrations of copper (the first maxima of the curves in fig. 5).

The second maximum of luminescence curves must be due to the effect of properly the activator (separate ions, or atoms, of copper and silver), and the subsequent decrease of luminescence is due to its aggregation [14]. The coincidence of the second maxima of catalysis, emission and luminescence curves leads one to the conclusion that the active centres of the phenomena are common, and that inactivation is caused for all of them by aggregation processes.

Hence, on the contrary with supported metal catalysts luminophors ZnS·Cu and ZnS·Ag exhibit a direct relationship between the catalysis, luminescence and exo-emission phenomena. The observed parallelism suggests the presence of common active centres (isolated ions or atoms of Zn, Cu and Ag) as well as direct participation of crystal electrons in the act of catalysis.

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   E. B. Maxted and J. S. Elkins, J. Chem. Soc. (1961) 5086.
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CONCERNING THE MECHANISM OF CYCLENE ISOMERIZATION OVER ALUMINA

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Abstract: Adsorption, calorimetric, and gas-chromatographic evidence has revealed the specific behaviour of six-membered cyclenes over alumina at precatalytic temperatures. The precatalytic state of reacting molecules has enabled to predict the most likely course of the catalytic isomerization of these hydrocarbons. The study of kinetic regularities of the isomerization of cyclohexene derivatives over alumina has substantiated these suggestions and helped to elucidate the sequence of the elementary steps involved in the process.

1. INTRODUCTION

Adsorption studies, carried out up to precatalytic temperatures with different classes of hydrocarbons that are catalytically active over alumina have shown an anomaly in the behaviour of six-membered cyclenes [1]. The higher catalytic activity of this particular class of hydrocarbons toward isomerization over alumina has allowed to discover a relation between their behaviour in the precatalytic state and the subsequent catalytic conversion. The present report deals with this problem.

2. EXPERIMENTAL

The cyclic hydrocarbons with a different degree of unsaturation of the cycle such as benzene, toluene, cyclohexane, methylcyclohexane, the synthesized cyclohexene, 1-methylcyclohexene-1, 1-methylcyclohexene-3 and 1-ethylcyclopentene-1, as well as normal heptane were all carefully purified until their physical-chemical constants practically coincided with literature data. The purity of hydrocarbons was substantiated chromatographically.

Alumina, silica gel and erbia were used as contacts. The characteristics and treatment of alumina were described in ref. [2]. The granulated silica gel of the trade mark KSK had specific surface of 340 m^2/g determined by the adsorption of benzene vapours at 20° (B. E. T.). It was treated similarly to alumina. Erbia, prepared and treated following the procedure described in ref. [3] had specific surface of 55 m^2/g measured by means of gas chromatography [4].

The adsorption of vapours was investigated on an apparatus similar to Mc. Bain-Bakr balance at 20° [5]. The adsorption from solutions in an inert

solvent, n-heptane, was measured interferometrically at $0°$ through $80°$. To measure adsorption from solutions at elevated temperatures a special procedure was worked out to effect reliable separation of equilibrium solution from the adsorbent at the particular temperature of the experiment [6].

The heat of wetting of alumina by pure hydrocarbons and their solutions in n-heptane, was measured at $20°$ in a calorimeter with a permanent heat exchange of $1-5 \times 10^{-5o}$ and $2-4 \times 10^{-3}$ cal. sensibility [7]. The heats of hydrocarbon vapour adsorption under precatalytic conditions ($100°-250°$) were studied by gas chromatography [8].

Catalytic isomerization of 1-methylcyclohexene-1 over the $250° - 450°$ range was investigated in a conventional continuous flow installation. Catalytic isomerization of 1-methylcyclohexene-1, 1-methylcyclohexene-3, and 1-ethylcyclopentene-1 over the $180° - 310°$ range at various rates of the gas-carrier, helium were studied under chromatographic conditions by impulse microtechnique [9,10].

The isomerization products were analysed by means of gas chromatography. The overall catalysate was separated on a column filled with diatomite bricks impregnated with the liquid OP-7 [11] at $68°$. The combined peak of 1,2-dimethylcyclopentene-1, 1-ethylcyclopentene-1, and 1-methylcyclohexene-3 was frozen out and separated on a second column filled with "Inzen" bricks impregnated with a saturated solution of silver nitrate in ethylene glycol at $50°$.

Detection was effected by a katharometer with helium used as gas-carrier, passing through the first column at a rate of 40 ml/min and through the second 30 ml/min. The reproducibility of results amounted to $\pm 5\%$.

3. RESULTS AND DISCUSSION

The comparison of adsorption properties of six-membered cyclic hydrocarbons and their methyl derivatives with a different degree of the unsaturation of the cycle has shown an anomalous behaviour on the surface of alumina.

The calculation of the isotherms of cyclohexene vapours over alumina at $20°$ gave a higher total volume of adsorbent pores than that calculated in terms of benzene vapour adsorption. Such a result was accounted for by closer packing of cyclohexene molecules in the monolayer due to their double bond orientation to the surface of the adsorbent on chemisorption [5].

The arrangement of cyclohexene molecules on the surface of alumina was determined by measuring adsorption from solutions. Isotherms of cyclohexene adsorption from solutions in n-heptane over alumina at $0°$, $20°$ and $30°$, are given in fig. 1. The shape of isotherms at $20°$ and $30°$ having curve bends reminds of stepped isotherms of alcohol adsorption known in the literature, with their molecules being reoriented on the surface of the adsorbent from a planar to a more inclined position [12]. The calculation of isotherms by conventional methods [13] shows, that the area occupied by the molecule of cyclohexene in a dense monolayer (about 30 $Å^2$) is about twice smaller than it is at the point of the bending of the isotherms.
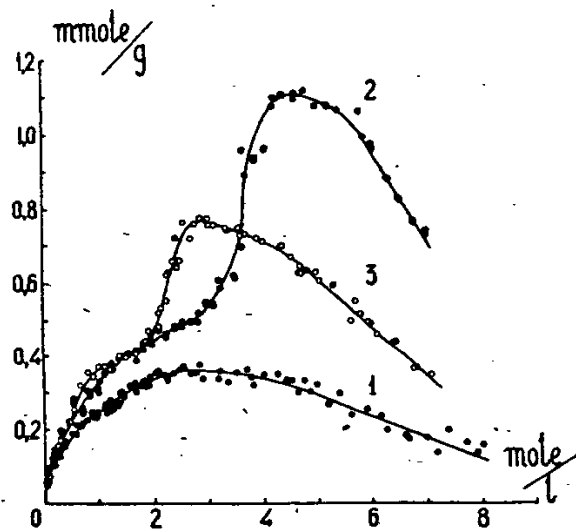
Fig. 1. Adsorption isotherms of cyclo-
hexene from solutions in n-hep-
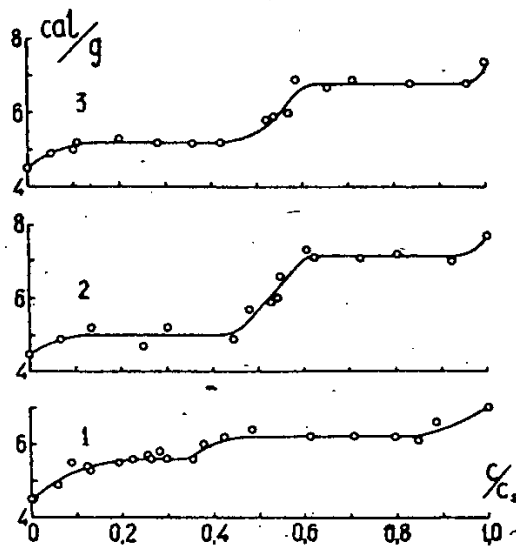tane over alumina at 0° (1), 20°
(2), and 30° (3).

Fig. 2. Isotherms of heats of wetting of
alumina by solutions of cyclo-
hexene (1), 1-methylcyclohex-
ene-1 (2), and 1-methylcyclo-
hexene-3 (3), in n-heptane at 20°.

It is evident that cyclohexene molecules are first adsorbed by the main
plane of the cycle parallel to the surface of alumina with increase in cyclo-
hexene concentration; in the process of adsorption they acquire a "rib"-
orientation remaining as a double bond at the surface [1]. With methylcyclo-
hexenes adsorbed from solutions under similar conditions the bend on the
isotherm is scarcely noticeable. Only at a much higher temperature (80°
for 1-methylcyclohexene-1) does the isotherm reveal a pronounced band
corresponding to the reorientation of molecules to an inclined position, be-
cause the transition to the "rib"-orientation is hindered for these cyclenes
owing to a methyl radical introduced in the molecule. The introduction of a
methyl radical lowers also adsorption, the maximum adsorption of 1-methyl-
cyclohexene-1 at 20° being four times lower than that of cyclohexene [6].

The reorientation of cyclohexene molecules over alumina is substantiat-
ed by calorimetric measurements of heats of wetting [7].

The isotherms of heats of wetting of alumina by cyclohexene and methyl-
cyclohexenes in n-heptane over the whole range of concentrations at 20° are
given in fig. 2. Their shape corresponds to that of adsorption isotherms of
the cyclenes studied and the band on the isotherms of heats of wetting is in
accordance with the picture of reorientation of molecules on adsorption.
The introduction of the methyl radical in the cyclohexene molecule increases
the difference in the energies of interaction with the surface of differently
orientated molecules.

In table 1 the heats of wetting of alumina by cyclohexenes are compared
with heats of adsorption of respective cyclenes measured by gas chromato-
graphy (Q_R) under conditions rather similar to those of catalytic isomeri-
zation in the flow. It is to be noted that the values of heats of wetting and
adsorption of cyclohexenes and their methyl derivatives are lower than the

Table 1
Heats of wetting and adsorption of six-membered
cyclenes over alumina.

	Heats	
	of wetting (cal/g)	of adsorption (cal/mole)
Cyclohexene	7.0	7.0
1-methylcyclohexene-1	7.7	8.3
1-methylcyclohexene-3	7.4	7.5

corresponding ones found for hydrocarbons of a similar structure but with another degree of the unsaturation of the cycle [7, 8]. This also speaks for the specific behaviour of cyclohexene molecules on the surface of alumina.

Cyclenes that are more catalytically active to isomerization over alumina have lower values of energetic characteristics. From the hydrocarbons under investigation the most active one proved to be cyclohexene that was found to isomerize over alumina already at the liquid phase at 40°. At precatalytic temperature (30°) the adsorption isotherm (fig. 1) has shown the greater part of cyclohexene molecules on the surface of the catalyst to have a "rib" orientation, or a double bond orientation to the surface. On going over to 0°, or to a temperature that is not as near to the initiation of the catalytic conversion of cyclohexene, the adsorption isotherm shows that practically no reorientation of cyclohexene molecules takes place. Thus, the "rib"-orientation of cyclohexene molecules seems to precede catalytic conversion.

Another proof of such a relation is afforded by the study of the behaviour of cyclohexene on adsorption over catalysts that do not cause isomerization. To this end we have measured adsorption isotherms of cyclohexene from solutions in n-heptane at 20° over silica gel that was found to initiate isomerization of cyclohexene at 250° only, and over erbia with no skeleton isomerization even at 500°. With these catalysts no reorientation of cyclohexene molecules is to be observed.

For methyl derivatives of cyclohexene of a similar importance on transition to precatalytic state is the reorientation of their molecules on the surface of alumina to an inclined position. The peculiarity in the reorientation of methylcyclohexene molecules is displayed by a higher temperature of their catalytic isomerization. 1-Methylcyclohexene-1 does not undergo catalytic conversion in the liquid phase even at 100°.

We believe that the "rib"-orientation of the molecules of six-membered cyclenes on the surface of the catalyst in the precatalytic state that we have demonstrated should govern their further catalytic conversion. With a "rib"-orientation of the cyclene molecule the most polarized hydrocarbon atoms would be those that are nearer to the surface of the catalyst and this should favour the breaking of their bonds. Therefore, the behaviour of molecules of 1-methylcyclohexene-1 and 1-methylcyclohexene-3 during the elementary catalytic event of skeleton isomerization should be different. Isomerization of 1-methylcyclohexene-1 must lead to 1-ethylcyclopentene-1
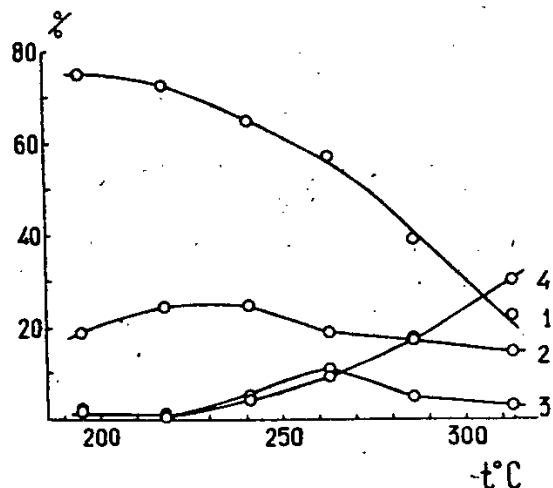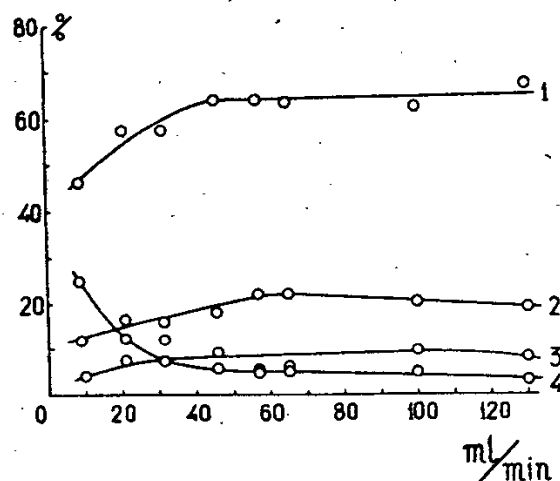
Fig. 3. Percentage of 1-methylcyclo-
hexene-1 (1), 1-methylcyclo-
hexene-3 (2), 1-ethylcyclopen-
tene-1 (3), and 1,2-dimethyl-
cyclopentene-1 (4) in the cata-
lysate, depending on the tem-
perature, at the rate of gas-
carrier of 60 ml/min.

Fig. 4. Percentage of 1-methylcyclo-
hexene-1 (1), 1-methylcyclo-
hexene-3 (2), 1-ethylcyclopen-
tene-1 (3), and 1,2-dimethyl-
cyclopentene-1 (4) in the cata-
lysate, depending on the rate
of gas-carrier at 268°.

as one of the products, whereas the skeleton isomerization of 1-methyl-
cyclohexene-3 should give no such product.

To check this suggestion we have studied kinetic regularities of cataly-
tic isomerization over alumina of both methylcyclohexenes and 1-ethyl-
cyclopentene-1. The catalytic runs were carried out under chromatographic
conditions with the gas-carrier rate 60 ml/min over 180° - 310° range, and
also at several temperatures and changing rates of gas-carrier from 10 to
150 ml/min. Fig. 3 shows temperature dependences of isomerization of
1-methylcyclohexene-1 over alumina. It will be seen that with rising tem-
perature and decreasing percentage of 1-methylcyclohexene-1 in the catalys-
ate the amount of 1-ethylcyclopentene-1 in the products of catalytic conver-
sion passes through a maximum just as does the amount of 1-methylcyclo-
hexene-3 formed. The maximum on kinetic curves points to the fact that the
products formed are intermediates.

Carrying out isomerization of 1-methylcyclohexene-1 in a continuous
flow installation over a broad range of temperatures led to similar results.
The dependence of catalytic isomerization of 1-methylcyclohexene-1 on the
rate of gas-carrier at 268° is exemplified in fig. 4. The study of the in-
fluence of the rate of gas-carrier at several different temperatures has
also shown that 1-ethylcyclopentene-1 and 1-methylcyclohexene-3 are form-
ed as intermediates.

Kinetic investigations of isomerization of 1-methylcyclohexene-3 have
demonstrated that this cyclene is converted essentially to 1-methylcyclo-
hexene-1 (up to 70%) and also to 1,2-dimethylcyclopentene-1 (up to 20%).
Experiments on catalytic isomerization of 1-ethylcyclopentene-1 have
shown that the catalysate consists mainly of 1-methylcyclohexene-1 (up to
50%) and dimethylcyclopentenes

As a result of our investigation the catalytic isomerization of 1-methyl-cyclohexene-1 may be pictured as follows: the molecule of 1-methylcyclo-hexene-1, chemisorbed by the double bond on the surface of the catalyst undergoes the breaking of the cycle to form 1-ethylcyclopentene-1 that is then converted to one of dimethylcyclopentenes. 1-Methylcyclohexene-1 can also give 1,2-dimethylcyclopentene-1 or undergo isomerization with the transfer of the double bond to 1-methylcyclohexene-3 that leads to 1,2-dimethylcyclopentene-1 directly, without intermediate formation of 1-ethyl-cyclopentene-1
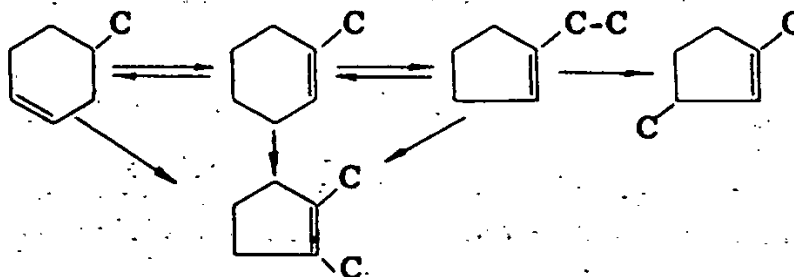
The formation of 1-ethylcyclopentene-1 as one of intermediates of catalytic isomerization confirms our suggestion about the specific behaviour of six-membered cyclenes on the surface of alumina. At the same time a more detailed information, provided by the investigation, on the sequence of elementary steps involved in catalytic isomerization must contribute to the elucidation of the mechanism of the process.

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