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Abstract

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CHEMISTRY

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STUDY OF THE INFLUENCE OF GENESIS ON THE ACTIVITY OF NICKEL CATALYSTS

(Presented by Academician A. A. Balandin, 31 V 1962)

The influence of genesis on the activity of catalysts of identical chemical composition has been studied by many authors ($^{1-9}$). However, the number of investigations of this kind with unsupported metallic catalysts is small. In these investigations, only a single reaction was used as a model for comparing the catalytic activity of different samples.

In the present work, the influence of genesis on the catalytic activity of metallic nickel was investigated. The catalytic activity of 10 nickel samples prepared by different methods was studied. The model reactions were the dehydrogenation of cyclohexane and isopropyl alcohol and the dehydration of tertiary butyl alcohol. The apparent activation energy of the indicated reactions was taken as the measure of catalytic activity—a quantity independent of the specific surface area of the catalyst. It should be borne in mind, however, that, owing to the presence of a compensation effect between the constants of the Arrhenius equation, the actual course of catalytic activity may be quite different from what might be expected from the values of the activation energy. Nevertheless, analysis of the dependence of the activation-energy values of reactions on the genesis of the catalyst is of great interest, since it is precisely in this way that one can obtain an answer to the question of the influence of genesis on the energy of interaction of the catalyst with the reacting substances, and on the energy barrier of the reactions studied.

Catalysts Investigated

Catalyst No. 1 was obtained from $Ni(NO_3)_2$ by precipitating $Ni(OH)_2$ from solution with ammonia, decomposing the hydroxide, and reducing the oxide in a stream of hydrogen at 400°. **Catalyst No. 2** was obtained from $Ni(NO_3)_2$ by calcination in air and subsequent reduction of nickel oxide in a stream of hydrogen at 400°. **Catalyst No. 3** was obtained by decomposing $Ni(NO_3)_2$ in

Fig. 1. Arrhenius straight lines characterizing the dehydrogenation of C_6H_{12} and the dehydration of tert.-C_4H_9OH over catalyst No. 8

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a stream of argon and in a stream of hydrogen at 400°. **Catalyst No. 4** was obtained from nickel oxalate (precipitated from a solution of $NiSO_4$ with ammonium oxalate) by calcination in a stream of hydrogen at 400°. **Catalyst No. 5** was skeletal nickel of the firm "Chinoin." **Catalyst No. 6** was an industrial catalyst of the "Schuchardt" grade, obtained from nickel carbonyl. **Catalyst No. 7** –radioactive nickel (^{63}Ni) with a specific activity of $\sim$ 1 mCi/g–was dissolved in nitric acid. From the $Ni(NO_3)_2$ solution a metallic catalyst was obtained by the same method as catalyst No. 1. **Catalyst No. 8** was obtained by decomposition of nickel formate in a stream of hydrogen at 400°. **Catalyst No. 9** was obtained by decomposition of nickel carbonate in a stream of hydrogen at 400°. The decomposition temperature of nickel carbonate is not given in the literature; therefore a thermogram of its decomposition was recorded, from which it can be established that nickel carbonate loses crystalline water at about 140—150° and decomposes at 350°.

Catalyst No. 10–from a solution of $NiCl_2$, $Ni(OH)_2$ was precipitated with ammonia, which was subsequently treated as in the case of catalyst No. 1.

All the catalysts (except radioactive nickel) were subjected to X-ray structural analysis: the diameters of the primary particles were determined and, for most of them, the value of the crystal-lattice parameter. The diameter of the primary particles was determined on the basis of analysis of the broadening of the interference rings. The values of the crystal-lattice parameters were determined by the powder method using a diffractometer, by comparison with an internal standard.

Fig. 1. Arrhenius straight lines characterizing the dehydrogenation of C_6H_{12} and the dehydration of tert.-C_4H_9OH over catalyst No. 8

Kinetic experiments were carried out in a flow system. The apparatus for measurement and the procedure for carrying out the experiments are described in (10). All catalysts for study were taken in the same amount (1 g). The rate of passage of the starting substances was 0.1-0.2 ml/min. In the dehydrogenation of isopropyl alcohol, the conversion was determined from the rate of hydrogen evolution. In the dehydrogenation of cyclohexane and in the dehydration of tert-butyl alcohol, the conversion was determined from the refractive index of the liquid catalyzate with a refractometer with an immersion prism, with an accuracy of $±0.00002.*Bygaschromatographyitwasestablishedthatcyclohexane*, *onallcatalysts*(*exceptskeletalnickel*), *isse*
99*{3}H*{7}*OH*, 150–200°; *inthecaseofcyclohexane*, 270–330°; *inthecaseoftert.*–
C{4}H{9}$OH, 200-360° (depending on the activity of the catalyst).

Fig. 2. Change in the values of the apparent activation energy of the reactions studied for nickel catalysts of various preparation

Figure 2: Fig. 2. Change in the values of the apparent activation energy of the reactions studied for nickel catalysts of various preparation

The values of the apparent activation energy of the reactions studied were calculated from the dependence of the logarithm of the conversion on the reciprocal tem-

temperatures from Arrhenius straight lines (see Fig. 1). The values obtained are contained in Table 1. The same table gives the results of X-ray analysis of various samples.

The results of the study presented in Table 1 show that the catalytic properties of nickel—the energy barrier of the reactions occurring on it—change significantly depending on the method of its preparation. From these data it is evident that there is no parallelism between the course of the activation-energy values for the different reactions: for example, in going from catalyst No. 1 to No. 4, the activation energy for the dehydrogenation of cyclohexane decreases from 12.4 to 4.6, whereas for isopropyl alcohol it increases from 7.1 to 11.8 kcal/mol.

Table 1

Values of the apparent activation energy and crystalline parameters of nickel catalysts of various preparation

Catalyst No.	Dehydrogenation ε, kcal/mol: C_6H_{12}	Dehydrogenation ε, kcal/mol: iso-C_3H_7OH	Dehydrogenation ε, kcal/mol: tert.-C_4H_9OH	Diameter of primary particles, Å	Lattice constant, Å
1	12.4	7.1	18.5	193	3.530
2	13.2	9.3	16.2	264	3.528
3	8.3	4.6	25.5	83	3.532
4	4.6	11.8	19.2	133	3.526
5	4.3	4.4	21.4	68	—
6	8.5	6.1	31.1	350	3.527
7	15.2	14.0	26.9	—	—
8	13.9	12.7	20.8	77	—
9	10.8	7.6	29.4	59	3.529
10	12.5	—	—	220	—

The differences in the course of the activation-energy values of the various reactions when going from one catalyst to another are illustrated by the graph shown in Fig. 2.

Fig. 2. Change in the values of the apparent activation energy of the reactions studied for nickel catalysts of various preparation

From the X-ray structural analysis data it is evident that the method of preparation has practically no effect on the value of the crystal-lattice parameter, but the diameter of the primary particles, the dispersity of the catalyst, changes significantly. However, we were unable to detect the presence of an unambiguous dependence between dispersity and the catalytic activity of the samples studied.

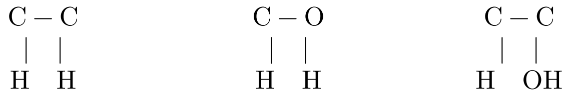
Changes in the catalytic activity of nickel cannot be explained solely by geometrical causes, since the crystal-lattice parameters of the various samples have practically the same value. The genesis of the catalysts apparently affects the bonding energy of the atoms of the catalytic surface with the atoms of the reacting molecules. It is known ([11]) that the energy of the bond between the atoms of the reacting molecule and the atoms of the catalyst surface is expressed by the equation:

$$Q_{AK} = Q^0_{AK} + \lambda_A,$$

where Q^0_{AK} is the energy of the A—K bond inside the lattice, and λ_A is a quantity expressing the influence of neighboring atoms on the energy state of the surface atom forming the given bond with the molecule being transformed. In view of the constancy of the lattice parameter in the cases we investigated, the influence of genesis must be attributed to a change in the values of λ_A.

The different influence of genesis on the energy barrier of different catalytic reactions is apparently the result of the fact that in the indicated

different index groups participate in the reactions in question[12]:



$$\begin{array}{ccc} \mathrm{C-C} & \mathrm{C-O} & \mathrm{C-C} \\ |\quad| & |\quad| & |\quad| \\ \mathrm{H\quad H} & \mathrm{H\quad H} & \mathrm{H\quad OH} \end{array}$$

dehydrogenation	dehydrogenation	dehydration
C_6H_{12}	*iso*-C_3H_7OH	tert.-C_4H_9OH

Thus, the magnitude of the energy barrier, which includes the bond energies of the reacting atoms with the catalyst, must depend differently on the genesis of the catalyst for different reactions; consequently, the influence of genesis affects the values of bond energies in different ways, and the energy barriers of the above-mentioned reactions turn out to be different combinations of these quantities.

It should be noted that the data presented above on the influence of genesis on the catalytic activity of metallic nickel should be regarded as a first approximation, since so far only the influence on the energy barrier of model reactions has been studied, and only the magnitudes of the apparent activation energy of these reactions have been determined.

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