Physical Chemistry

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Abstract

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DEHYDROGENATION OF CYCLOHEXANE ON CERTAIN CARBIDES, BORIDES, AND SILICIDES

As is known, characteristic catalysts for reactions of the oxidation-reduction class are solids with electronic conductivity (1). These regularities, found for metal, oxide, and sulfide catalysts, have recently also been extended to new semiconductors—isoelectronic analogues of the simple bodies of the 4th period (2).

At present, compounds of transition metals with such metalloids as nitrogen, carbon, silicon, and boron are being intensively studied and used as electrical-engineering materials and abrasives (3). It was of interest to determine whether the above-mentioned regularity could be extended to this group of materials as well. The corresponding carbides and borides are closest to metals in their properties, whereas certain silicides (of chromium, manganese, rhenium) exhibit semiconductor properties (4); some nitride phases are also semiconductors (5), especially alloys of metals with nitrogen in the homogeneity range of the corresponding nitride phases.

Until recently, carbides, silicides, borides, and nitrides of transition metals had scarcely been studied in this respect. Exceptions are works on carbides and nitrides of iron and cobalt (6), connected with the study of ammonia synthesis and hydrocarbon synthesis by Fischer–Tropsch. Dowden (7) believes that carbides, nitrides, and also carbonitrides should be less active than the corresponding transition metals, since, according to his conception of the role of unfilled *d*-shells in catalysis, the latter become filled in this process.

As a model reaction, the reaction of cyclohexane dehydrogenation was chosen, as one characteristic of transition metals. It is also known (8) that it proceeds on certain oxides of transition metals, but at higher temperatures and with a higher activation energy. For a rapid test, the chromatographic method was selected. Its essence is as follows. A dynamic tube filled with catalyst is continuously swept with a carrier gas (Ar) and is maintained at the reaction temperature. A sample of unsaturated cyclohexane vapors in argon is introduced by means of a syringe into the upper part of the catalytic tube. Immediately after the catalytic tube there are placed a chromatographic column 2.5 m long, filled

Fig. 1. Schematic of the apparatus for pulse testing of catalysts.

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with firebrick (grain diameter 1 mm) impregnated (15% by weight) with dinonyl phthalate, and an ionization detector using promethium-147. The outlet curves of the chromatographic analysis were recorded on an EPPV-51 self-recording potentiometer with an input resistance of 1.5 gigaohms. A diagram of the apparatus is shown in Fig. 1. The pulsed chromatographic method for studying catalytic reactions makes it possible to carry out a quantitative analysis of the reaction of dehydrogenation of cyclohexane to benzene.

As was shown (^{13,14}), experimental data * on the linear dependence

$$\ln \frac{1}{1-x} \text{ on } \frac{P_{\text{in}}}{W}$$

confirm the first order of the reaction (x is the fraction of conversion— ···conversion, W is the gas-flow rate, P_{in} is the pressure at the inlet to the catalytic column). The dependence of $\ln\ln\frac{1}{1-x}$ on $\frac{1}{T}$ makes it possible to calculate the apparent activation energies. The specific surface area of the catalysts was determined by the chromatographic method (^{9}). The surface area of ZrB_2, checked by the volumetric method using krypton adsorption, was 2.4 m^2/g, and, by heptane adsorption, the surface area of CaO was 48 m^2/g, which agrees well with the surface-area value obtained by the chromatographic method (respectively 2.4 m^2/g and 42 m^2/g).

Fig. 1. Schematic of the apparatus for pulse testing of catalysts. **1** –cylinder with carrier gas, **2, 15, 16** –fine-control valves, **3** –mercury manometer, **4** –catalytic column, **5** –Dewar vessel, **6, 8** –four-way stopcocks, **7** –chromatographic column, **9** –ionization detector on promethium-147, **10** –proportional counter for determining the radioactivity of substances, **11** –drying column ($CaCl_2$), **12, 13, 14** –flowmeters.

The dehydrogenation of cyclohexane under static conditions in vacuum was also studied on some samples. The initial pressure was 1.5 mm Hg, the catalyst charge was 2 g, and the system volume was 200 ml. During dehydrogenation of C_6H_{12}, the pressure increased in the course of the reaction. In the reaction products, gases not condensed in liquid air were recorded, and hydrogen was recorded separately (as a gas passing through a heated palladium capillary).

Table 1 gives the results of tests, by the chromatographic method, of certain borides, carbides, and molybdenum silicides. The electrical resistivity of these

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* Part of the measurements was carried out by I. G. Galkina and Liu Chzhunkhue, to whom the authors express their gratitude.

samples according to data ([1]) is also indicated here.

Figures 2a, b show chromatograms of the dehydrogenation of cyclohexane at 486 and 530° on Mo_2C. The degree of conversion was determined from the chromatogram

Table 1

Sample	Specific surface area, m^2/g	Weight of sample in catalytic column, g	E, kcal/mol	X^* at 500°	t, °C, reaction onset	Resistivity ρ, $\mu\Omega\cdot$cm	Sample	Specific surface area, m^2/g	Weight of sample in catalytic column, g	E, kcal/mol	X^* at 500°	t, °C, reaction onset	Resistivity ρ, $\mu\Omega\cdot$cm
TiB_2	0.6	5.8	–	–	600	14.4	W_2C	1.1	9.7	–	–	650	–
ZrB_2	2.4	13.4	–	–	650	16.6	WC	0.4	11.5	–	0.10	400	19.2
CrB_2	2.9	1.4	–	–	600	56	$MoSi_2$	1.7	8.6	18.7	0.65	300	21.6
W_2B_5	1.4	3.5	–	–	650	43	V_3Si	0.2**	1.8	9.7	0.25	300	–
LaB_6	0.5	8.4	–	0.09	400	16.1	Mo_3Si	–	1.2	19.8	0.076	400	–
GdB_6	1.4	3.0	–	–	600	140	CaO	42	1.3	11.2	0.08	450	–
TiC	1.2	5.5	4.0	0.16	350	52.5	Aluminosilicate catalyst	>260***	1.5	21.6	0.12	400	–
ZrC	1.1	7.5	8.9	0.17	450	50.0							
Mo_2C	2.2	5.8	10.5	0.52	300	71.0							

* X corresponds to one and the same argon flow rate, equal to 20 cm^3/min.
** By krypton adsorption.
*** Under static conditions, by heptane adsorption.

by the ratio of the benzene peak area to the sum of the areas of the benzene and cyclohexane peaks.

As specially performed experiments show, cyclohexene is absent from the reaction products.*

* Cyclohexene was kindly provided by G. V. Isagulyants, for which we express our gratitude.

Experiments on the dehydrogenation of cyclohexane under vacuum static conditions show satisfactory agreement with chromatographic tests. Figure 3 presents kinetic curves for the dehydrogenation of C_6H_{12} on Mo_2C at an initial pressure

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

of 1.4-1.8 mm Hg and temperatures of 350-500°. As the figure shows, these curves are satisfactorily straightened in the coordinates $\ln\left(P_0 - \frac{p}{3}\right) - t$, which indicates that the kinetics of the reaction obey a first-order equation.

Fig. 2. Chromatograms of the products after passage of C_6H_{12} vapors in a stream of argon over Mo_2C, *(a)*—486°, *(b)*—530°. Flow rate of Ar: 20 cm^3/min

According to these data, an Arrhenius straight line was constructed in Fig. 4, the slope of which shows that the activation energy is 14.2 kcal/mol. An analogous calculation for ZrC gave a value of 11 kcal/mol. As is evident from comparison of these figures with the data in Table 1, these figures are somewhat (by 2.5–3.0 kcal) greater than the corresponding values in Table 1, but their relative magnitudes are in approximately the same ratio. The rate constant of a first-order reaction at 500° is $1.6 \cdot 10^{-2}$ min^{-1} for Mo_2C, $2.3 \cdot 10^{-3}$ for ZrC, and $1 \cdot 10^{-4}$ min^{-1} for TiB_2. Thus, the order of activities in tests by both methods is the same.

Fig. 3. Kinetic curves for the dehydrogenation of C_6H_{12} on Mo_2C at an initial pressure of 1.4–1.8 mm Hg.

The data on the composition of the reaction products differ somewhat. Thus, for example, after analysis of the reaction products in experiments at low pressure on Mo_2C, the following amounts of gases remained unfrozen in liquid air after passage through a Pd capillary: at 350°—0.8%, at 400°—1.5%, at 500°—14.8%, and at 550°—16.1%; i.e., at low temperature dehydrogenation of cyclohexane to benzene proceeds practically entirely, whereas at high temperature part of the cyclohexane cracks, possibly to CH_4, C_2H_4. According to chromatographic data, on the contrary, the fraction of C_1—C_2, amounting at 460° to about 5% of the total yield, decreases only slightly with increasing temperature.

On TiB_2, after the reaction was carried out, partial sintering and a change in the electron-diffraction structure of the surface layer were observed, while the X-ray structure of TiB_2 was preserved.

As the data obtained show, the series of tested catalysts possesses high activity for the dehydrogenation of cyclohexane, comparable with the activity of transition metals. The reaction proceeds in the same region

temperatures and with approximately the same rate. As on metals, dehydrogenation proceeds to benzene, whereas on certain oxides, according to Balandin^(10), cyclohexene may be formed. Their electrical conductivity, and in a

Fig. 4. Dependence of the logarithm of the first-order rate constant on reciprocal temperature for the dehydrogenation of C_6H_{12} on Mo_2C

Figure 4: Fig. 4. Dependence of the logarithm of the first-order rate constant on reciprocal temperature for the dehydrogenation of C_6H_{12} on Mo_2C

number of cases also their crystal lattices, are close to those of transition metals. The activation energy of the dehydrogenation of C_6H_{12} has low values (4.0–18.7 kcal/mole), which is likewise characteristic of metals. For oxides, considerably higher activation energies are observed: 25–40 kcal/mole^(8, 10, 11). Experiments carried out under chromatographic conditions on 0.5% Pt deposited on Al_2O_3 showed the higher activity of the Pt catalyst and the possibility of carrying out the reaction already at 80°.

Fig. 4. Dependence of the logarithm of the first-order rate constant on reciprocal temperature for the dehydrogenation of C_6H_{12} on Mo_2C

When comparing the activity data for the substances studied, attention is drawn to the high activity of the carbides and molybdenum silicide and the low activity of the borides. The latter may be explained by statistical filling of the *d*-electron levels of transition metals by electrons of the readily ionized boron atom^(12); in the case of carbides, the higher ionization potential of carbon leads to a decrease in the degree of filling of the *d*-levels of the transition metals, and this decreasing effect is manifested to a greater extent the smaller the incompleteness of the *d*-level, characterized by the ratio $1/Nn$, where N is the principal quantum number of the *d*-level and n is the number of electrons at this level^(12). In this sense, the sharp increase in the degree of conversion of cyclohexane x upon passing from TiC and ZrC ($1/Nn = 0.167$–0.125) to Mo_2C ($1/Nn = 0.050$) is characteristic. The further increase in activity for molybdenum disilicide may be associated with the appearance of a considerable fraction of covalent Si–Si bonds and a corresponding decrease in the probability of filling the *d*-electron levels of molybdenum. Upon going from $MoSi_2$ to Mo_3Si, the fraction of conversion x of cyclohexane decreases sharply owing to the decrease in the fraction of silicon, Si–Si bonds, and the consequent stronger acceptance of valence electrons. In the case of V_3Si, the V atom has a high degree of incompleteness of the *d*-shells and, as a result, gives a relatively high degree of conversion.

A possible reason for such a relation between activity and the electronic properties of the solid may be the transfer by hydrogen atoms of their 1*s*-electron to the vacant electronic levels of the exposed layers.

Special experiments carried out by the authors showed that Mo_2C, ZrC, WC, and $MoSi_2$ are also active catalysts for the dehydrogenation of alcohols.

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