CHEMISTRY

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1958

SovietRxiv

Abstract

Full Text

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STUDY OF THE CATALYTIC DEHYDROGENATION OF HYDROCARBONS AND ALCOHOLS OVER METALLIC RHENIUM

Recently, increasing attention has been devoted to the study and application of rhenium. In this connection, elucidating its catalytic properties is of great importance.

We extended to rhenium the investigations on catalytic dehydrogenation being carried out in our laboratory (for a review, see ([1])). According to the multiplet theory of catalysis, for dehydrogenation of the sextet type it is necessary ([2]) that the catalyst have a lattice of type A1 or A3 and an atomic radius r within the range 1.22–1.39 Å. It subsequently became known that metallic rhenium has an A3 lattice and an atomic radius of 1.368 Å. Thus, for it the above requirements are fulfilled and, consequently, according to the theory, it should be a catalyst for the dehydrogenation of six-membered hydrocarbons. The structure and atomic radius of rhenium also satisfy the principle of conservation of the valence angle of the multiplet theory ([3],[4]); therefore rhenium may also serve as a catalyst for the dehydrogenation of hydrocarbons and alcohols by the doublet mechanism.

Experimentally, the catalytic properties of rhenium have not yet been sufficiently studied. M. S. Platonov and his co-workers ([5]) established that rhenium is an active catalyst for the dehydrogenation of alcohols and that, as a rule, the process proceeds without side reactions. In activity, rhenium is not inferior to copper. However, the optimum dehydrogenation temperature for rhenium, according to Platonov' s data (400–450°), is 100–150° higher than for Cu ([6]), Fe, Co, and Ni ([7]). Platonov was the first to find that rhenium is capable of catalyzing the dehydrogenation of cyclohexane ([8]), thereby confirming the prediction of the multiplet theory. However, the experimental details and the method of preparing the catalyst remained unknown. Therefore, a more detailed investigation was required.

In the present work it is shown that rhenium deposited on carbon is an active catalyst for the dehydrogenation of cyclohexane and its homologs, of cumene, and for the dehydrocyclization of n-heptane. On the rhenium catalysts obtained by us, dehydrogenation of alcohols also proceeds in the temperature range 120–300°, as does the conversion of butane-1,4-diol into γ-butyrolactone.

Experimental Part

Catalysts. The rhenium catalysts were prepared by us according to a method developed as a result of a special investigation in which different methods of preparation and different supports were studied. Rhenium was deposited on activated carbon either in the form of ammonium perrhenate (from aqueous solution) or in the form of a complex of rhenium anhydride with dioxane, $Re_2O_7 \cdot xC_4H_8O_2$ ([9]) (from a solution in absolute methanol). The carbon impregnated in one or the other way was ···

with the other solution, the charcoal was charged into the catalytic tube and treated with hydrogen while the temperature was slowly raised to 500°. Reduction was carried out for 4-5 h. As was established, the most active catalyst contains about 30 wt. % Re.

The substances passed over the catalyst had constants corresponding to the literature values.

Dehydrogenation of hydrocarbons. The catalyst prepared from NH_4ReO_4, in the dehydrogenation of cyclohexane, proved to be less active and less stable than the catalyst obtained by the dioxane method. The first catalyst dehydrogenates cyclohexane at 350-450°; the activation energy is 12.8 kcal/mole; in addition to benzene, the catalyzate contains 1-1.5% cyclohexene. The second causes dehydrogenation of cyclohexane in the temperature range 250-350°, with an activation energy of 7.8 kcal/mole; the catalyzate contains no cyclohexene. On the catalyst obtained by the dioxane route, we carried out the dehydrogenation of methylcyclohexane and ethylcyclohexane. As Tables 1-3 show, the rate of hydrocarbon dehydrogenation decreases, and the activation energy increases, with increasing molecular weight of the hydrocarbon, the homologous difference being ~2.5 kcal/mole.

Table 1

Dehydrogenation of cyclohexane. Re—C. Catalyst volume 10 ml. Feed rate 0.2 ml/min. Activation energy $E = 7.8$ kcal/mole; average $k_0 = 1.7 \cdot 10^4$

Temp., °C	m*	m, calc.	Gas analysis, vol. % H_2	Gas analysis, vol. % CH_4	$E/\lg k_0$
246	0.98	0.90	88.6	11.4	2.40
272	1.35	1.29	90.0	10.0	2.40
281	1.49	1.45	88.0	12.0	2.41
284	1.50	1.48	88.2	11.8	2.46
341	2.70	2.82	86.4	13.6	2.44

* m —amount of gas in ml at NTP evolved in 1 min per 1 ml of catalyst.

The process of hydrocarbon dehydrogenation on both catalysts is accompanied by cracking of the hexamethylene ring, as evidenced by the presence of methane in the gaseous reaction products.

Dehydrogenation of alcohols was studied on the catalyst obtained from the dioxane complex. The dehydrogenation of secondary alcohols (isopropyl and sec-butyl) proceeds practically without side reactions, if one does not count some decomposition of the ketone formed, which gives small amounts of saturated hydrocarbons (1-8%) in the gas. The conversion of isopropyl alcohol to acetone at temperatures of 150-200° occurs with yields close to the thermodynamically possible ones. The activation energies for dehydrogenation of isopropyl and sec-butyl alcohols are, respectively, 4.8 and 6.5 kcal/mole. Dehydrogenation of pri-

Table 2

Dehydrogenation of methylcyclohexane. Re–C. Catalyst volume 10 ml. Feed rate 0.2 ml/min.; $E = 10.3$ kcal/mole; average $k_0 = 8.7 \cdot 10^3$

Temp., °C	m	Gas analysis, vol. % H_2	Gas analysis, vol. % CH_4	$E/\lg k_0$
267	0.59	92.4	7.6	2.62
285	0.81	88.4	11.6	2.61
302	1.08	84.2	15.8	2.61
316	1.31	52.5	17.5	2.61

Table 3

Dehydrogenation of ethylcyclohexane. Re–C. Catalyst volume 10 ml. Feed rate 0.1 ml/min; $E = 12.6$ kcal/mole; average $k_0 = 3.5 \cdot 10^4$

Temp., °C	m	Gas analysis, vol. % H_2	Gas analysis, vol. % CH_4	$E/\lg k_0$
286	0.39	91.3	8.7	2.78
322	0.80	90.0	10.0	2.77
399	1.11	86.0	14.0	2.77
388	2.23	77.7	2.23	2.79

of primary alcohols: ethyl, *n*-propyl, and *n*-butyl proceeds somewhat less readily. The process is complicated by the formation of an ester and by decarbonylation of the aldehyde formed. The activation energies for ethyl, *n*-propyl, and *n*-butyl alcohols are, respectively, 7.8, 9.5, and 11.7 kcal/mol.

From the data obtained it is evident that the rate of alcohol dehydrogenation and the activation energy depend on the structure of the alcohols. On going

from a primary alcohol to the isomeric secondary alcohol, the activation energy decreases by approximately 5 kcal/mol. In addition, with increasing molecular weight of the alcohol the rate of the process decreases somewhat, while the activation energy increases, the homologous difference amounting to approximately 2 kcal/mol.

Dehydrogenation of 1,4-butanediol leads to the formation of γ-butyrolactone and γ-hydroxybutyraldehyde. Succinic aldehyde could not be detected in the catalyzate. The results of the experiments are presented in Table 4. The activation energy of the process of formation of γ-butyrolactone is 11.5 kcal/mol, which coincides with the activation energy of *n*-butyl alcohol.

Table 4

Dehydrogenation of 1,4-butanediol. Re–K. Catalyst volume 10 ml. Feed rate 0.1 ml/min.

Temp., °C	Amount of gas, ml/min	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %	Catalyzate, wt. %	Catalyzate, wt. %
Temp., °C	Amount of gas, ml/min	H_2	CO_2	CO	unsaturates	CH_4	butyrolactone	hydroxyaldehyde
233	9.99	100	–	–	–	–	11.9	16.5
252	11.60	–	–	–	–	–	16.8	14.9
261	16.20	91.0	0.8	2.4	2.9	2.9	22.5	15.4
297	22.87	92	1.4	1.8	2.2	2.6	36.2	14.1
306	24.61	85.7	–	2.8	3.2	8.3	46.3	10.3

This makes it possible to suppose that the limiting stage of the process is the elimination of one molecule of hydrogen from 1,4-butanediol with formation of γ-hydroxybutyraldehyde. On the other hand, it is known that hydroxyaldehydes are in tautomeric equilibrium with cyclic hemiacetal forms (10):

$$\mathrm{HOCH_2CH_2CH_2CHO} \mathit{leftarrows} \mathrm{CH_2CH_2CH_2{-}C(H)(OH)}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\quad | \quad O$$

Dehydrogenation of such a cyclic form should proceed very readily and lead directly to butyrolactone.

In order to test this assumption, we synthesized γ-hydroxybutyraldehyde (12) and succinic aldehyde (13) and studied their transformations over a rhenium catalyst. It was found that γ-hydroxybutyraldehyde is readily converted into γ-butyrolactone, the degree of conversion, equal to 40–48%, depending little on

temperature in the range 230–300°, which indicates a low activation energy for this process. Succinic aldehyde was not detected among the conversion products. Succinic aldehyde, when passed over the rhenium catalyst, does not give butyrolactone. The bulk of it passes through unchanged, and part is converted into condensation products. Reppe (13) obtained the practically important γ-butyrolactone by dehydrogenation of 1,4-butanediol over Cu and considered that the reaction proceeds through succinic aldehyde. In contrast to Reppe' s assumption, the present work has shown that the intermediate product in the conversion of 1,4-butanedi-

ol into γ-butyrolactone is γ-hydroxybutyraldehyde, and not succinic aldehyde; moreover, formation of the former is the rate-limiting stage of the process.

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Received
16 VII 1958

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