Catalytic Dehydrogenation of Cyclohexanol

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Abstract

Full Text

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In previous communications ([1]), results were presented from a study of the dehydrogenation of a series of aliphatic alcohols of various structures over a mixed oxide catalyst, which, as was shown, carries out the dehydrogenation of alcohols without appreciable formation of side products of decomposition and dehydration. In the present work it is shown that the same oxide catalyst is active for the dehydrogenation of cyclohexanol. The reaction of dehydrogenation of cyclohexanol to cyclohexanone, which is widely used for the production of polyamide fiber and is employed as a good solvent, has been studied by many authors. Tur, Anisimov, and Platonov ([2]) studied the dehydrogenation of cyclohexanol over finely dispersed rhenium and found that at 350° the yield of cyclohexanone reaches 25.3%. Benzene, cyclohexane, and other hydrocarbons are formed as by-products. In the dehydrogenation of cyclohexanol over the Zelinskii–Komarevskii nickel–aluminum catalyst at 380°, cyclohexanone is formed in a yield of about 37% ([3]); along with this, large amounts of benzene ($\sim$ 48%), phenol, cyclohexene, and polymeric products are obtained. On zinc and copper catalysts, the dehydrogenation of cyclohexanol is carried out at 400–600° ([4]). Treshchanovich ([5]) compared the rate of dehydrogenation of cyclohexanol over iron–zinc catalysts of various compositions and found that on the catalyst with the lower iron content (12.5%) the reaction rate is higher. According to data of Japanese investigators ([6]), when cyclohexanol is passed over a granulated alloy catalyst of the Raney-catalyst type, of composition Cu—Al—Ni (58 : 40 : 2), at 350°, the cyclohexanone content in the catalyzate reaches 85%. However, according to data of the same investigators ([7]), the activity of the catalyst after several hours decreases by half and after 400 hr amounts to only 20—30% of the initial value.

In the present work the kinetics of the dehydrogenation of cyclohexanol was investigated. The relative adsorption coefficients of cyclohexanone, the reaction-rate constants were determined, and from the experimental data the activation energy, changes in free energy, heat content, and entropy upon adsorption displacement of alcohol molecules by cyclohexanone from the active centers of dehydrogenation were found. In addition, conditions were found for the dehydrogenation of cyclohexanol with the aim of obtaining high yields of cyclohexanone.

Experimental Method

The experiments were carried out by the flow method in an apparatus described earlier ([8]), on the same sample of oxide catalyst. The catalyst, in an amount

of 11 ml, was placed in a quartz tube 16 mm in diameter. The alcohol was fed by means of an automatic device. Before the experiment cyclohexanol was distilled; b.p. 160.5°, d_4^{24} 0.9458, n_D^{22} 1.4660; literature data ([9]): b.p. 160.5–161°, d_4^{30} 0.94155, n_D^{25} 1.4677.

Cyclohexanone for the experiments on determining adsorption coefficients was isolated from the catalyst obtained in the dehydrogenation of cyclohexanol and distilled; b.p. 155.2–156°, d_4^{20}0.9463, n_D^{20}1.4545; literature data: b.p. 155.7°, d_4^{20}0.9465, n_D^{19}1.4503. The catalyst was analyzed for cyclohexanone content by reaction with hydrochloric-acid hydroxylamine. The contact gas consisted of pure hydrogen. Close agreement was observed between the amounts of ketone found and the hydrogen formed. The reaction rate was determined from the amount of hydrogen evolved. Experiments with cyclohexanol were carried out in the temperature range 264–336° at alcohol feed rates $v = 1.2$ and 1.4 ml in 5 min. The degree of conversion of the alcohol to cyclohexanone was from 16 to 75.8% of theory (Table 1).

Table 1

Catalytic dehydrogenation of cyclohexanol

T, °C	H_2 obtained (n.t.p.), in 5 min/ml	Degree of dehydrogenation, %	T, °C	H_2 obtained (n.t.p.), in 5 min/ml	Degree of dehydrogenation, %
$v = 1.2$ ml per 5 min., theoretical amount H_2: 256.6 ml per 5 min.	$v = 1.2$ ml per 5 min., theoretical amount H_2: 256.6 ml per 5 min.	$v = 1.2$ ml per 5 min., theoretical amount H_2: 256.6 ml per 5 min.	$v = 1.4$ ml per 5 min., theoretical amount H_2: 297 ml per 5 min.	$v = 1.4$ ml per 5 min., theoretical amount H_2: 297 ml per 5 min.	$v = 1.4$ ml per 5 min., theoretical amount H_2: 297 ml per 5 min.
264	20.0	7.9	269	24	8.1
269	28.0	11.0	281	42.8	14.4
281	48.1	18.9	300	82	27.6
297	72.5	28.4	317	123	41.5
302	85.0	33.4	322	140	47.2
313	108	42.4			
320	130	51.0			
330	160	62.9			

To determine the relative adsorption coefficients of cyclohexanone, the dehydrogenation rates of binary mixtures, cyclohexanol–cyclohexanone, containing 24.6 mol. % cyclohexanone, were measured. The experiments were conducted in the same temperature interval and at the same rates as the experiments with pure cyclohexanol. It is seen from Table 2 that the relative adsorption coefficient

Fig. 1. Dependence of $\lg z_2$ on reciprocal temperature

Figure 1: Fig. 1. Dependence of $\lg z_2$ on reciprocal temperature

Fig. 2. Dependence of $\lg k_c$ on reciprocal temperature

Figure 2: Fig. 2. Dependence of $\lg k_c$ on reciprocal temperature

of cyclohexanone at 281° is 3.03 and, with an increase in temperature to 336°, decreases to 0.91.

Fig. 1. Dependence of $\lg z_2$ on reciprocal temperature

Fig. 2. Dependence of $\lg k_c$ on reciprocal temperature

There is a logarithmic relationship between z_2 and the reciprocal absolute temperature. As is seen from Fig. 1, the points lie on a straight line. The values of the relative adsorption coefficients of cyclohexanone, found from experiments carried out at the same temperatures and different feed rates of the mixtures, retain their value (Table 2).

The rate constants of the cyclohexanol dehydrogenation reaction were calculated from the experimental data using the equation for monomolecular catalytic reactions in a flow system given earlier (10). The numerical values of the reaction rate constants are placed in Table 3. When the logarithm of the rate constant is plotted as a function of the reciprocal absolute temperature, the points fall on a straight line; the Arrhenius equation is fulfilled (Fig. 2). The activation energy, calculated from the experimentally found reaction rate constants, is 18.2 kcal/mol, and the logarithm of the pre-exponential factor $\lg k_0$ is 7.24.

The thermodynamic functions of adsorption displacement—the changes in free energy, enthalpy, and entropy—were calculated from the found—

the obtained values of the relative adsorption coefficients according to the known formulas (8) (Table 2). Experiments with cyclohexanol, carried out at higher temperatures, showed that with an increase in temperature from 333° to 360° and with an increase in the rate of passage of the alcohol to 3.1–3.94 l per 1 l of catalyst per hour, the degree of conversion of the alcohol increases from 67.9%

Table 2

Thermodynamic functions of adsorption displacement

T-ure, °C	Relative adsorp. coeff. $= x_2^a n_1^2 / x_1^2 n_2^a$, $v = 1.2$ l/5 min	ΔF, cal	ΔH, kcal	ΔS, cal/degree · mol
281	3.03	−1218		31.3

T-ure, °C	Relative adsorp. coeff. $= x_2^a n_1^2 / x_1^2 n_2^a$, $v = 1.2$ l/5 min	ΔF, cal	ΔH, kcal	ΔS, cal/degree · mol
300	1.75	−638.6	16.1	29.1
317	1.3	−214.6		27.5
320	1.2			
336	0.91			

Table 3

Reaction-rate constant and activation energy

T-ure, °C	$v =$ ml per 5 min	k_c, ml · min	ε, kcal/mol	$\lg k_0$
281	1.2	1.16		
302	1.2	2.13		
320	1.2	3.5	18.2	7.24
300	1.4	9.62		
317	1.4	15.4		

to 88.2%. The yields of cyclohexanone in this case are, respectively, 97.4 and 94.4% based on reacted alcohol. Simultaneously, 1-cyclohexylidene-cyclohexanone is formed in an amount from 1.7 wt.% to 3.3 wt.% (Table 4). The catalyst from the experiments was subjected to distillation and the content of cyclohexanone was determined. 1-Cyclohexylidene-cyclohexanone was characterized by obtaining the oxime with m.p. 146–147°.

Table 4

Yields of cyclohexanone and composition of the catalyzate

T-ure, °C	v, ml · h	Catalyst composition, wt.%: fraction to 100°	Catalyst composition, wt.%: cyclohexanone	Catalyst composition, wt.%: cyclohexanol	Catalyst composition, wt.%: dimer	Degree of conversion of alcohol, wt.%	Yield of cyclohexanone based on decomposed alcohol, wt.%
333	3180	–	66.2	32.1	1.7	67.9	97.4
342.5	3940	1.15	75.1	21.7	2.3	78.3	95.6
353	3940	1.7	79.0	16.5	2.8	83.5	94.4
360	3940	1.6	83.0	11.8	3.3	88.2	94.4

Found, %: C 74.3; H 9.91
$C_{12}H_{18}NOH$. Calculated, %: C 74.6; H 9.94

Thus, in the dehydrogenation of cyclohexanol on an oxide catalyst at elevated temperatures and high rates of passage of the alcohol, cyclohexanone can be obtained in good yields, which may be of practical interest as a method for producing cyclohexanone.

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