HYDROGENATION OF 2,3-DIHYDROPYRAN TO TETRAHYDROPYRAN

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The optimum conditions for the hydrogenation of 2,3-dihydropyran to tetrahydropyran on an industrial nickel—chromium catalyst under flow and periodic conditions were found. A regression model for the process was found. The results of hydrogenation of 2,3-dihydropyran by means of a flow reactor and an autoclave of the Vishnevskii type are compared.

Tetrahydropyran, which is an intermediate in the synthesis of physiologically active substances, including prostaglandins, is obtained by cyclization of 1,5-pentanediol [1-5], by pyrolysis of ammonium salts $Me_3N^+(CH_2)_5OH$ [6], by cyclization of 1-bromo-5-methoxypentane in the presence of $FeCl_3$ [7], by catalytic hydrogenation of 2,3-dihydropyran [8-11], and by other methods.

Methods for the hydrogenation of 2,3-dihydropyran are of great practical value, since the latter can be obtained catalytically in rather high yield (80-87%) from tetrahydrofurfuryl alcohol [11-13]. The hydrogenation of 2,3-dihydropyran is accomplished on platinum [9], rhodium [10], and Raney nickel [8, 14, 15].

When a Pt catalyst is used, in addition to the formation of tetrahydropyran, one observes the hydrogenolysis of 2,3-dihydropyran to give amyl alcohol. Prolonged activation by leaching out of the aluminum from the alloy is required in the hydrogenation of 2,3-dihydropyran on Raney nickel.

Applied Ni catalysts are highly selective. Nickel on diatomaceous earth [8] has a number of advantages as compared with Raney nickel. (The catalyst is not pyrophoric, and side condensation processes play a lesser role.) However, Ni on diatomaceous earth has a relatively low efficiency and requires complex prior treatment at a high temperature. Aniline, dibutylamine, and piperidine [16], which, however, complicate the purification of tetrahydropyran, are added to the reaction mixture in this case to prevent hydrogenolysis.

The aim of the present research was to develop the optimal variant for the hydrogenation of 2,3-dihydropyran on an industrial nickel—chromium catalyst (OST 6-03-314-75). The experiments were performed by means of a UOSUG-12M flow autoclave with periodic operation with Teflon coating of the inner surface, a flow reactor with continuous operation of the OL-105/01 type (Hungary), and a reactor of the Vishnevskii type.

2,3-Dihydropyran obtained from tetrahydrofurfuryl alcohol, which was purified by rectification until it was 99% [17], was used in the investigation. The unchanged 2,3-dihydropyran and tetrahydropyran were determined by gas—liquid chromatogrpahy (GLC) with a Khrom-3 chromatograph with a flame-ionization detector; the column was 200-300 cm long with an inner diameter of 2-4 mm and was made of glass or stainless steel, the vaporizer temperature was 240°C, the column temperature was 100°C, and the carrier-gas (helium) pressure was 1 atm with 15% Apiezon and 3% KOH on Chromosorb HP as the stationary phase.

The yield of tetrahydropyran was 98-99% when the UOSUG-12M flow autoclave with periodic operation was used at 131-135°C and a hydrogen pressure of 21-24 atm for reaction times of 3-4 h; the amount of unchanged 2,3-dihydropyran was 0.7-2.2% (Table 1).

To find the optimum conditions for the hydrogenation of 2,3-dihydropyran under flow conditions we used mathematical planning of the experiment [18]. A half replica of the 2^{3-1} type (experiments 1-4) with subsequent steep ascent (experiments 5-8) was realized in the experiments with the OL-105/01 flow apparatus. The plan of the experiment and the results obtained

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TABLE 1. Average Results of Hydrogenation of 2,3-Dihydropyran to Tetrahydropyran with a UOSUG-12M Apparatus (nickel–chromium catalyst, 11% of the weight of the 2,3-dihydropyran; the catalyst was used in the form of a powder with d $\leqslant 0.1$ mm)

Amount of 2,3-dihydropyran, g	Temp., °C	Pressure, mm	Exptl. time, h	Yield of tetrahydropyran, %	Unchanged raw material, %
73,8	137	18	1,1	80,2	19,5
55,4	135	24	2,7	97,0	2,2
55,4	131	21	3,2	98,0	1,1
92,3	131	22	4,0	99,0	0,7

TABLE 2. Optimization of the Hydrogenation of 2,3-Dihydropyran to Tetrahydropyran with an OL-105/01 Apparatus (nickel–chromium catalyst, 200 ml of the catalyst, pellet size 5 × 5 mm)

	x_1, T, °C	x_2, p, atm	$x_3 = x_1x_2$, G, ml/h	Yield of tetrahydropyran, V, %
Center of interval 0	135	20	100	
Interval Δ	15	5	20	
1	+	+	+	96,7
2	+	−	−	93,9
3	−	+	−	80,4
4	−	−	+	81,5
b_i	8,15	1,40	0,55	$b_0=87,7$
$b_i \cdot \Delta$	122,25	7,0	11,0	
Δ'	5	0,3	0,5	
5	140	20,3	100,5	...
6	145	20,6	101	96,4
7	160	21,5	102,5	98,2
8	170	21,8	103,5	98,5

TABLE 3. Average Results of the Hydrogenation of 2,3-Dihydropyran to Tetrahydropyran with an Apparatus of the OL-105/01 Type (hydrogen space velocity 50 h^{-1})

Temp., °C	Space velocity, h^{-1}	Pressure, atm	Yield of tetrahydropyran, %	Unchanged 2,3-dihydropyran, %	Efficiency, g/liter$_{cat}$-h
151	0,77	25	95,0	...	660
144	0,56	25	97,8	2,2	495
170	0,53	22	98,5	1,4	476
171	0,50	25	98,0	...	451
172	0,43	26	98,0	...	388
160	0,40	26	99,0	0,97	364
164	0,40	25	99,5	...	366

are presented in Table 2. The optimum hydrogenation conditions were found to be as follows: a temperature of 170°C, a pressure of 22 atm, a 2,3-dihydropyran feed rate of 100-104 ml/h per 200 ml of the catalyst, and hydrogen circulation rate of 10 liters$_{eff}$/h in all of the experiments. The yield of tetrahydropyran was 98%, and the amount of unchanged 2,3-dihydropyran was ~1.5%. The efficiency was 364-660 g/liter-h under conditions that were close to optimum (Table 3).

As compared with Raney nickel [8], the hydrogenation of 2,3-dihydropyran on the nickel–chromium catalyst is characterized by a fourfold to fivefold increased efficiency. The nickel–chromium catalyst does not lose its activity when it has been in operation for 150 h.

To obtain a mathematical model for the hydrogenation process under periodic conditions we realized a second-order orthogonal central composition plan (OCCP) [18]. An autoclave of the Vishnevskii type, in which ideal mixing (Reynolds number 44,000) is realized, was used

TABLE 4. Results of the Hydrogenation of 2,3-Dihydropyran to Tetrahydropyran with a Vishnevskii Reactor (nickel—chromium catalyst, powder, d ≤ 0.1 mm; orthogonal central composition plan (OCCP), α = 1.215)

	x_1, T, °C	x_2, P, atm	x_3, amount of catalyst, %	y_1, time, min	y_2, yield, %
Center of interval 0	130	20	10		
Interval Δ	10	5	5		
1	+	+	+	165	97,8
2	+	+	−	200	98,2
3	−	+	+	185	98,2
4	−	+	−	1300	98,0
5	+	−	+	185	98,1
6	+	−	−	200	98,4
7	−	−	+	245	98,3
8	−	−	−	345	97,0
9	0	0	α	195	99,5
10	0	0	−α	225	98,3
11	α	0	0	185	98,6
12	−α	0	0	315	98,2
13	0	α	0	180	100
14	0	−α	0	270	98,8
15	0	0	0	225	97,4

TABLE 5. Average Rates of Hydrogenation of 2,3-Dihydropyran with a Reactor of the Vishnevskii Type and a Flow Reactor

Temp., °C	Pressure, atm	Av. reaction rate, mole/h·g_{cat}	
		Vishnevskii reactor	OL-105/01 flow reactor
118	20	0,0201	0,0028
120	15	0,0110	0,0027
120	25	0,0330	0,0029
130	20	0,0311	0,0037
130	25	0,0389	0,0039
140	20	0,0421	0,0041
140	25	0,0503	0,0047
160	20	0,0680	0,0048

in the experiment. Each experiment was carried out with 300 ml of 2,3-dihydropyran and a fresh portion of previously powdered catalyst until hydrogen absorption ceased. The experimental conditions and results are presented in Table 4. A second-order equation that describes the dependence of the overall hydrogenation time (y, minutes) on the encoded variables, viz., the temperature (x_1), pressure (x_2), and amount of catalyst (x_3), was found on the basis of the results obtained:

$$y=226.77-44.09x_1-21.40x_2-27.52x_3+15.26x_1^2-1.70x_2^2-11.88x_3^2+ \\ +10.63x_1x_2+20.63x_1x_3-4.38x_2x_3.$$

It is apparent from this equation that in the selected experimental region the temperature (coefficient $b_1 = -44.09$) has the greatest effect on the dihydropyran hydrogenation time (i.e., on the average reaction rate). The quadratic term for the x_2 factor (the pressure) is virtually insignificant, and the x_2x_3 interaction is also small. The acceptable hydrogenation time, viz., 3-3.5 h, is reached at 140°C and 25 atm with 5% of the catalyst.

The rates of hydrogenation of 2,3-dihydropyran when a flow reactor and an autoclave of the Vishnevskii type were used were compared (Table 5). It was established that for other comparable conditions the rate of hydrogenation of 2,3-dihydropyran is an order of magnitude higher when an autoclave of the Vishnevskii type is used than the rates observed when the reaction is carried out in a flow reactor. This is explained by an increase in the specific area of the nickel—chromium catalyst in the powdered state as compared with the catalyst in the form of pellets. It may be assumed that the process is retarded appreciably under flow conditions by diffusion of the hydrogen.

Thus, the results of this study show that the nickel–chromium catalyst is an extremely selective catalyst in the hydrogenation of 2,3-dihydropyran to tetrahydropyran and is characterized by high efficiency and a satisfactory operational lifetime. It is expedient to realize the process by means of reactors of the Vishnevskii type.

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