SINGLE-STAGE VAPOR-PHASE HYDROGENATION OF CROTONALDEHYDE TO n-BUTYL ALCOHOL

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The commercial hydrogenation of crotonaldehyde to n-butyl alcohol is conducted in two stages. First the feedstock is 90-95% hydrogenated, then the product is rehydrogenated. Supported copper and nickel oxide catalysts are used [1-4]. The two-stage process is required because of the inadequate hydrogenation activity of the catalyst. The most widely used catalyst is a material consisting of copper oxides deposited on diatomaceous earth, prepared by a method described in [4].

With this catalyst, hydrogenation is performed at 180°C with a 0.3 h^{-1} feedstock space velocity and a 1/10 ratio of crotonaldehyde to hydrogen, which corresponds to a hydrogen space velocity of 2000 h^{-1}. The catalyst is relatively low in activity (yield of n-butyl alcohol no more than 92%) and poor in mechanical strength.

In order to carry out the single-stage vapor-phase hydrogenation of crotonaldehyde, work was performed on the preparation of a new, active catalyst with good mechanical strength; this was obtained by coprecipitation of copper compounds with other added metals from solutions of their salts, together with silica gel. The resulting catalyst mass was subjected to further treatment, including stages of syneresis, washing, drying, pelletizing, and activation.

The catalyst was activated with a 4/1 mixture of nitrogen and hydrogen for 16h at 180-200°C. After reducing the catalyst, it was operated for 4-6 h at 180-200°C with a liquid feedstock space velocity of 1.2 h^{-1} and a hydrogen space velocity of 2000 h^{-1}. In the subsequent test runs, crotonaldehyde was hydrogenated on several catalyst specimens differing in chemical composition. These hydrogenations were performed at temperatures of 160, 180, and 200°C, liquid feedstock space velocities of 1.2-2.4 h^{-1}, and hydrogen space velocities of 1000 and 2000 h^{-1}.

The composition of the liquid reaction products was determined by gas–liquid chromatography in an LKhM-8M chromatograph with a column 5 m in length and 4 mm in diameter. The stationary phase was PEG-1500, the carrier gas was helium, and the column thermostat temperature was 87°C.

Test results are presented in Table 1 for one of the catalyst specimens, MINKh-r.

TABLE 1. Test Results on MINKh-4 Catalyst in Hydrogenation of Crotonaldehyde

Process conditions			Product composition, wt.%		
temperature, °C	feedstock space velocity, h^{-1}	hydrogen space velocity, h^{-1}	crotonaldehyde	iso-C_4H_9OH	n-C_4H_9OH
160	2,4	2000	13,1	2,0	84,9
180	1,2	1000	9,3	1,1	89,5
180	1,2	2000	1,1	0,4	98,5
200	2,4	2000	2,3	1,1	96,6

I. M. Gubkin Moscow Institute of the Petrochemical and Gas Industry (MINKh i GP). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 4, pp. 7-8, April, 1974.

TABLE 2. Influence of Linear Flow Velocity on Results in Crotonaldehyde Hydrogenation (temperature 180°C, crotonaldehyde space velocity 1.2 h^{-1}, ratio of hydrogen to feedstock 10 moles/mole)

Component	Composition of hydrogenated products (wt. %) at indicated linear gas flow velocity		
	33 m/sec	16 m/sec	8 m/sec
n-Butyl alcohol	98,2	92,8	87,9
Isobutyl alcohol	—	0,9	2,1
Crotonaldehyde	1,8	6,3	10,0

TABLE 3. Thermodynamic Characteristics of Hydrogenation Reactions of C_4 Aldehydes

Reaction	Temp., °K	Heat of reaction, kcal/mole	Maximum work of reac., kcal/mole	Equilibrium constant
$C_4H_6O + H_2 \rightleftarrows C_4H_8O$ (I)	298	—28,0	—18,97	$7{,}0\cdot10^{13}$
	500	—28,1	—12,70	$3{,}5\cdot10^{5}$
	700	—29,3	—5,68	$1{,}3\cdot10^{1}$
$C_4H_6O + 2H_2 \rightleftarrows C_4H_9OH$ (II)	298	—41,2	—24,95	$1{,}6\cdot10^{18}$
	500	—41,0	—13,76	$1{,}0\cdot10^{6}$
	700	—40,0	—3,03	8,8

TABLE 4. Results in Hydrogenation of Technical Crotonaldehyde on Commercial Catalyst and MINKh-r Catalyst

Catalyst	Product composition, wt. %		
	crotonaldehyde	iso-C_4H_9OH	n-C_4H_9OH
Commercial	33,0	1,24	65,7
MINKh-r	1,2	0,4	98,4

Note. Catalyst tests conducted at 180°C, liquid feedstock space velocity 2.4 h^{-1}.

It will be noted that the optimal conditions for this catalyst are a temperature of 180°C, a liquid feedstock space velocity of 1.2 h^{-1}, and a hydrogen space velocity of 2000 h^{-1}. When the hydrogen space velocity is decreased to 1000 h^{-1}, the yield of n-butyl alcohol drops to 96.6%. The yield of n-butyl alcohol also drops when the temperature is lowered to 160°C or increased to 200°C. An increase in the liquid feedstock space velocity to 2.4 h^{-1} does not have any appreciable effect on the n-butyl alcohol yield.

It was established that the process is influenced by the linear gas flow velocity, thus indicating the possibility of a weak external-diffusion retardation. It will be noted from Table 2 that the hydrogenation rate increases with increasing linear gas flow velocity.

In line with the data of Table 2, the linear gas flow velocity must not be less than 33 m/sec.

When the temperature is increased from 180 to 200°C, the degree of hydrogenation decreases (see Table 1), even though from thermodynamic calculations (Table 3) essentially complete hydrogenation should be obtained at

200°C. To explain this phenomenon, the thermal desorption of hydrogen from the catalyst surface was investigated; it was found that, at temperatures above 100°C, hydrogen is desorbed from the catalyst surface, and the bulk of the "mobile" hydrogen is removed at 200°C. Thus, the degree of hydrogenation is determined both by kinetic factors and by the content of adsorbed "mobile" hydrogen on the catalyst surface. At temperatures above 180°C, the content of adsorbed "mobile" hydrogen is very small, and the extent of hydrogenation is severely reduced.

Comparative results are shown in Table 4 for tests on MINKh-r catalyst prepared under laboratory conditions and a commercial catalyst prepared by the method of [4]. It will be seen that, under comparable conditions, the MINKh-r catalyst proved to be far more active than the commercial catalyst. This MINKh-r catalyst as prepared by the authors proved to have approximately twice the mechanical strength of the commercial catalyst.

LITERATURE CITED

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