DEPENDENCE OF THE DIVINYL YIELD IN THE SYNTHESIS OF DIVINYL FROM ETHYL ALCOHOL ON THE CATALYST COMPOSITION

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Butadiene-1,3 is an important product in petrochemical synthesis. It is used as a monomer for the production of synthetic rubber and other types of plastics. Butadiene is mainly used in the production of polybutadiene and styrene-butadiene rubbers, which are the main raw materials for the production of automobile tires, mechanical protective coatings, and various types of plastic materials. In 2024, the global production capacity of butadiene exceeded 20 million tons, with an annual growth rate of about 5%. This reflects the high global demand and the important role of butadiene in the petrochemical industry. Currently, the main production technology is to obtain ethylene by pyrolysis of naphtha, with butadiene being obtained as a by-product in this process. Two approaches have been used to study the reduction reaction of crotonaldehyde to 1-hydroxy-2-butylene. The first approach was to attempt the selective reduction of crotonaldehyde with hydrogen using catalysts containing various metals, which have high catalytic activity and yield, and were selected for the process. The second involved the use of ethyl alcohol as a reducing agent, according to the Meyerschein-Ponndorff-Wehrle-Oppenauer reaction.

Catalysts with high catalytic activity and productivity for the hydrogenation of crotonaldehyde were selected for the process. In the reduction of crotonaldehyde to 1-hydroxy-2-butylene, catalysts based on precious metals and metals from Group IB of the Periodic Table, supported by silicon and lanthanum oxides, were selected for the process, which had high catalytic activity and productivity. The studied catalysts with high catalytic activity and productivity, selected for the implementation of the process, are listed in Table 1.

Table 1. Properties of catalysts with high catalytic activity and productivity used for the hydrogenation of crotonaldehyde, selected for the process

A catalyst of choice for process implementation with high catalytic activity and performance	Metal content,%	Used salts
$5MgO*FeO*ZnO/SiO_2$	5.0	$Mg(NO_3)_2\cdot6H_2O$
$5La_2O_3*FeO*ZnO/SiO_2$	5.2	$La(NO_3)_3\cdot6H_2O$
$5ZrO_2*FeO*ZnO/SiO_2$	5.4	$ZrCl_4$
$5ZrO_2*FeO*ZnO/SiO_2$	5.0	$ZrO(NO_3)_2\cdot2H_2O$
$5Al_2O_3*FeO*ZnO/SiO_2$	5.2	$Al(NO_3)_3\cdot6H_2O$

All catalysts selected for the process, which have high catalytic activity and productivity, were prepared by moisture absorption from solutions of the corresponding precursors until the required concentration was reached. The metal content determined by atomic emission spectroscopy agrees well with the calculated one.

Main products and reaction scheme. In all the catalysts studied, which have high catalytic activity and yield, and which were selected for the process, crotonaldehyde undergoes reduction with the formation of a mixture of products: in addition to 1-hydroxy-2-butylene, acetaldehyde, methyl ethyl ketone, butanal and butanol are observed. Acetaldehyde can be formed by the aldol condensation of crotonaldehyde in the presence of water. The formation of methyl ethyl ketone continues with the subsequent reduction of the C=C bond by the isomerization of crotonaldehyde to form methyl vinyl ketone. Butanal is formed as a result of the selective non-reactive hydrogenation of crotonaldehyde at the carbon-carbon double bond. Butanol-1 is a complete hydrogenation product and can be formed by the reduction of 1-hydroxy-2-butylene or butanal:

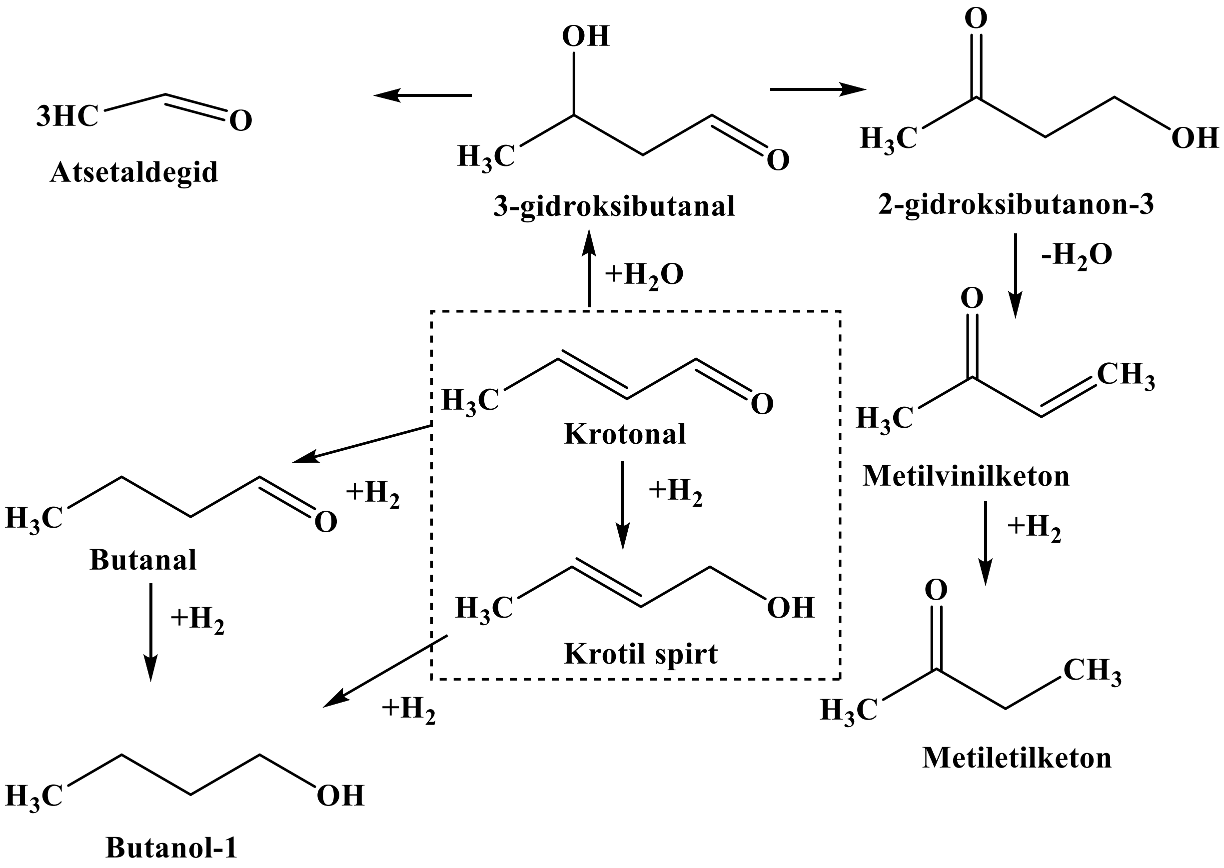

Figure 1. Scheme of the transformation of crotonaldehyde upon reduction with hydrogen.

The data presented show that the catalysts selected for the process, which have high catalytic activity and productivity based on activated metals, have a selectivity of no more than 5% in the reduction reaction of crotonaldehyde with hydrogen. In addition, all the catalysts selected for the process, which have high catalytic activity and productivity, and contain Mg, Zr and La, have a high catalytic activity and productivity, and the conversion of crotonaldehyde for the selected catalyst samples for the production of divinyl from ethyl alcohol is more than 80%. The main hydrogenation product is butanal, in addition, the complete hydrogenation product butanol-1 is formed in significant amounts. Thus, the reduction of crotonaldehyde with hydrogen on catalysts selected for the process, which contain a metal with specific hydrogenating functions and have high catalytic activity and productivity, does not allow achieving satisfactory results in terms of selectivity for crotonaldehyde. This is due to the non-selective hydrogenation of the C=C bond in metal systems.

In the reduction of crotonaldehyde to 1-hydroxy-2-butylene using the Meyerschein-Ponndorff-Wehrle-Oppenauer reaction, catalysts based on zirconium oxide activated on SiO_2, ZrO_2 and La_2O_3, as well as molecular sieves containing Zr, with high catalytic activity and yield, were studied, as well as selected for the process. The oxide catalysts with high catalytic activity and yield, selected for the process, were synthesized by precipitation of the corresponding salts from solutions, followed by filtration, drying and calcination at 673K.

For the Zr catalyst samples, the isotherm is of type IV with a narrow distribution of pores with a diameter of about 30 Å, with a relative pressure P/P0 increasing in the region of 0.35. The catalysts selected for the process, which have high activated catalytic activity and productivity, have a surface area of 80-270 m2/g, typical of amorphous materials. The average pore volume determined by the BJH method is 100 Å for silica and 50 Å for lanthanum and zirconium oxide. Pure zirconium oxide has a highly developed surface area (230 m2/g), which is comparable to ZrO_2*FeO*ZnO/SiO_2.

Table 2. Characteristics of catalysts selected for the process of reducing crotonaldehyde with ethyl alcohol, with high catalytic activity and productivity

Catalyst samples	Chemical composition		Density area, m^2/g	Porosity volume, cm^3/g	Micropore size, cm^3/g	Average pore diameter, Å
	rO_2	Si/Zr				
Zr-HSZs	1.52	134	470	0.29	0.20	7
Zr catalyst	1.07	184	870	1.1	-	30
ZrO_2*FeO*ZnO/SiO_2	1.90	105	270	0.70	-	100
ZrO_2/ZrO_2	1.85	-	80	0.08	-	50
ZrO_2/La_2O_3	2.02	-	80	0.08	-	50

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