HETEROGENE-CATALYTIC SYNTHESIS OF BUTYNE-2-DIOL-1,4

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Abstract: *the results of the preparation of butyne-2 diol 1,4 in the reaction with acetylene and formaldehyde with a heterogeneous catalytic method are reported. A reaction mechanism is proposed for the synthesis of acetylene glycol. The influence of the composition, nature and amount of catalyst on the yield of the product was analyzed. The activity of the available catalytic properties of the compounds copper, bismuth, nickel, cobalt, properties of kaolin, bentonite, silica gel, zeolite was used as the carrier and efficiency of peptizators. The influence of different temperatures on the synthesis of butyne-2-diol-1,4 is shown. The influence of the duration of the reactions is given.*
Keywords: *acetylene, formaldehyde, acetylene alcohols, catalyst, butyn-2-diol-1,4, product efficiency.*

ГЕТЕРОГЕН-КАТАЛИТИЧЕСКИЙ СИНТЕЗ БУТИН-2-ДИОЛ-1,4

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Аннотация: *приведены результаты получения бутин-2-диол 1,4 при реакции с ацетиленом и формальдегидом гетерогенно-каталитическим методом. Предложен механизм реакции процесса синтеза ацетиленгликола. Анализируется влияние состава, характера и количества катализатора на выход продукта. Изучена активность имеющегося каталитического свойства соединений меди, висмута, никеля, кобальта, свойства каолина, бентонита, силикагеля, цеолита, использовано как носитель, и эффективность пептизаторов. Показано влияние разных температур на синтез бутин-2-диол-1,4. Приведено влияние продолжительности реакций.*
Ключевые слова: *ацетилен, формальдегид, ацетиленовые спирты, катализатор, бутин-2-диол-1,4, эффективность продукта.*

Introduction: One of the relatively inexpensive and easy-to-use substances in organic synthesis, which is effectively used in many ways, is acetylene and its various derivatives. As a result of the coupling reaction between acetylene and carbonyl compounds, a new substance that stores the -C≡C- bond is of particular importance. Synthesis of acetyl alcohol can be synthesized by a heterocyclic catalytic method, and the synthesis of vinyl derivatives has been poorly studied. The use of various selective catalysts in these processes is one of the topical problems in the chemistry of acetylene compounds [1].

Acetylene and carbonyl compounds have relatively low-temperature acetylated alcohols, while a rise in temperature increases the production of acetylene diols [2-4].

Methodology:A sample of 100 g of the finished catalyst is placed in the reactor. The gas line is introduced into the reactor, then 500 ml of formaldehyde are added dropwise. The test is carried out at a temperature of 105-110°C. The mixture of reaction gases is removed from the upper outlet of the reactor. The synthesized product and the reactive compounds are extracted through the lower outlet of the reactor and collected in a collector. After the reaction ceases, the nitrogen currents generate additional gases from the reaction medium. The reaction mixture is then left to stand for 12 hours. The obtained organic phase is separated by distilling off 300-350 ml of distilled water and the aqueous portion is extracted 3-4 times in diethyl ether, filtered and transferred to a dosing device. The catalyst dries using $CaCl_2$.

Results: In this work, formaldehyde acetylene as a result of interaction with butyne-2-diol-1,4 in a heterogeneous catalytic method, that is, the synthesis of butyne-2-diol-1,4 based on copper-bismuth-nickel-kaolin catalysts (CBNK), copper-bismuth-nickel-silicagel catalysts (CBNS), copper-bismuth-nickel-bentonyte catalysts (CBNB), copper-bismuth-nickel-zeolite catalysts (CBNZ), pressure 0,1-0,5 MPa, and the effect of temperature effects on the yield of the product. The influence of active components on the properties of the product of catalysts based on kaolin, bentonite, silica gel and zeolite rods is determined. Technical parameters and properties of catalysts (porosity, strength, etc.) were analyzed. The recommended service life of the catalyst is 72-84 hours.

Mechanism of process:

$$HC \equiv CH + K \longrightarrow K*HC \equiv CH$$

$$HC \equiv CH + 2H\text{-}\underset{\underset{O}{\|}}{C}\text{-}H \xrightarrow{\text{кат, } ^0t} H_2\underset{\underset{OH}{|}}{C} - C \equiv C - \underset{\underset{OH}{|}}{CH_2}$$

The results of the effect of temperature in the reaction of formaldehyde with acetylene in the range of 75-115°C are shown in Table 1.

Table 1. Effect of temperature on the product of butyne-2-diol-1,4 (peptizer: HNO_3, NH_4OH, methylcellulose)

Conventional symbol of the catalyst	**Temperature,^{0}C**	**Efficiency of product, %**
CBNK-3	75	52,4
	85	55,3
	95	58,1
	105	60,2
	115	57,3
CBNK-5	75	59,2
	85	62,8
	95	65,7
	105	67,4
	115	64,3
CBNK-7	75	53,1
	85	56,3
	95	59,4
	105	61,2
	115	58,6

An analysis of the results shows that an increase in temperature increases the production of butyne-2-diol-1,4 (Table 1). When the temperature rises from 75-115°C, the yield of acetylene diol increases from 59,2 to 67,4% when the CBNK-5 catalyst is used. The optimum temperature for the synthesis of butyne-2-diol-1,4 was 105°C.

With a further increase in temperature, the yield of the product falls. The reason for this is the starting and synthesized substances in triglycerides, vinyls, oligomerization and polymerization reactions due to the presence of three groups and hydroxyl groups.

The effect of butyne-2-diol-1,4 also affects the reaction time. The results are shown in Fig. 1.

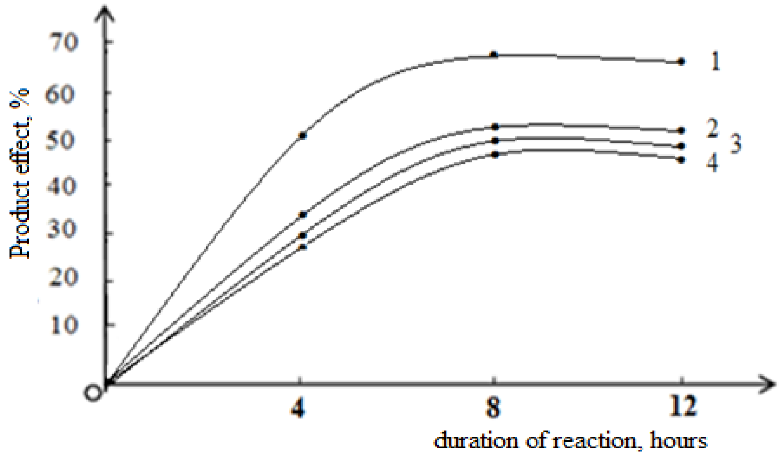

Fig 1. Influence of temperature to efficiency of prduct1-CBNK-5; 2-CBNB-5; 3-CBNZ-5; 4-CBNS-5

Analysis of the results shows that the optimal time for this process, that is, the product, is a maximum of 8 hours. With increasing duration of time, the main taste of the product falls due to the formation of various lubricants from the starting and forming substances.

As you know, the nature of the product depends on the nature and amount of the catalyst. The results of the experiments are shown in Table 2.

Table 2 shows that Butin-2-diol-1,4 depends on the amount of the active component of the catalyst. For example, the increase in the amount of copper oxide increases with the correct yield.

Catalysts produced by catalysts also significantly affect (Table 2). Analysis of the results shows that when using kaolin, it was determined that a product with a high content of bentonite, silica gel and zeolite was detected. The main reason for this is that the active surface of the catalyst in the presence of kaolin is larger in size than the pores.

In the study, the three-dimensional structure of synthesized compounds, atomic charge, and electron density distribution were performed by quantum chemical calculations using the RMZ method.

Table 2. Effect of properties and composition of catalyst on the product of butyne-2-diol-1,4 (peptizer: HNO_3, NH_4OH, methylcellulose)

№	Conventional symbol of the catalyst	Catalyst composition (%)	Efficiency for producing butyne-2-diol-1,4, %
1	CBNK-1	CuO-20; Bi_2O_3- 4; NiO-1; Каолин-75	42,3
2	CBNK-2	CuO-25; Bi_2O_3- 5; NiO-1,3; Kaolin -68,7	49,2
3	CBNK-3	CuO-30; Bi_2O_3-6; NiO-1,5; Kaolin -62,5	56,4
4	CBNK-4	CuO-35; Bi_2O_3- 7; NiO-1,7; Kaolin -56,3	60,3
5	CBNK-5	CuO-40, Bi_2O_3- 8, NiO-2, Kaolin-50	67,4
6	CBNK-5	CuO-40, Bi_2O_3- 8, CoO -2, Kaolin-50	64,2
7	CBNS-5	CuO-40, Bi_2O_3- 8, NiO-2, Silica Gel -50	48,6
8	CBNS-5	CuO-40, Bi_2O_3- 8, CoO -2, Silica Gel -50	46,6
9	CBNB-5	CuO-40, Bi_2O_3- 8, NiO-2, Bentonyte-50	52,3
10	CBNB-5	CuO-40, Bi_2O_3- 8, CoO – 2, Bentonyte-50	48,9
11	CBNZ-5	CuO-40, Bi_2O_3- 8, NiO-2, zeolite-50	50,1
12	CBNZ-5	CuO-40, Bi_2O_3- 8, CoO – 2, zeolite-50	47,3
13	CBNK-6	CuO-45; Bi_2O_3- 9; NiO-2,3; Kaolin -43,7	59,2
14	CBNK-7	CuO-50; Bi_2O_3-10; NiO-2,5; Kaolin -37,5	52,1

Table 3. Quantum-chemical calculations of primary and synthesized substances

Properties of substance	Total energy, kkal/mol	Energy of formation, kkal/mol	Teperature of formation, kkal/mol	Electron energy, eV	Nuclear energy, kkal/mol	Dipole moment (D)
Primary substance						
Acetylene	-6489.10	-391.22	54.76	-12975.65	6486.55	0.0173

Formaldehyde	-1068.62	-1057.67	-1.94	-67991.31	46922.70	1.809
Synthesized substances						
propyn-2-ol-1	-6349.92	-776.28	4.35438	-45683.35	29333.42	1.571
butyne-2-diol-1,4	-6574.12	-1159.93	-44.6479	-88186.91	61612.78	2.656

The distribution of electron density and electron density of synthesized substances is studied on the basis of quantum chemical calculations. The results showed that the process of catalytic vinylation, as well as the processes of oxygenation and polymerization are determined because the oxygen atom is the reaction center.

Conclusion: Synthesized by butyne-2-diol-1,4 by a heterogeneous catalytic method based on acetylene and formaldehyde. The effect of catalysts on the synthesis process, the basis of catalyst preparation, the amount of active ingredients, the temperature and the reaction time were studied. In addition, the copolymerization of reactions with a copper catalyst prevents polymerization. The compounds of bismuth, nickel and cobalt, which increase the activity of the catalyst, reduce the process of adhesion, vinylation, oligomerization and polymerization of starting materials and acetylene. Quantum-chemical calculations of the first and synthesized substances were also performed. It was found that the maximum yield of butyne-2-diol-1,4 is 67,4%.

References / Список литературы

1. *Temkin O.N.* Chemistry of acetylene. "Acetylene tree" in organic chemistry of the XXI century. // Soros Educational Journal. Vol. 7. № 6, 2001.
2. *Vapoev Kh.M., Nurmanov S.E, Umarova Zh.R., Mukhiddinov B.F.* Technological parameters of syntheses based on butin-1-ol-3 // Journal of Chemical Industry today. M., 2009. № 6. FROM. 12-16.
3. *Vapoev Kh.M., Sirliboev T.S., Mukhiddinov B.F., Nurmonov S.E.* Kinetics of synthesis of vinyl ester of butin-1-ol-3 // Proceedings of the scientific-practical conference of professors and teachers of young scientists of the National University of Uzbekistan. Tashkent, 2008. B. 58-59.
4. Patent 3572 (RUz). Method for the preparation of butyne-2-diol-1,4 / D.Yusupov, A.U. Karimov, H.Sh.Shirinov and others. 05/29/1995. № IHDP 9500512.1. Opubl. in the BI. № 2, 1996.