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Heterogeneous-Catalytic Synthesis 3, 6-Dimethylol-4-Diol-3, 6

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ABSTRACT: Acetylene and its derivatives have a higher reactivity. Chemistry of acetylene continues to seek new methods of reactions with the formation of various hetero- and carbo-compounds as a result of the accumulation of various nucleophiles in its molecule and the formation of a $-C\equiv C$ bond. Especially practical is the formation of a new bond $-C\equiv C$ - in the interaction of acetylene and a combination of various carbonyl compounds.

KEYWORDS: Acetylene, methyl ethyl ketone, 3,6-dimethylol-4-diol-3,6, homogeneous and heterogeneous catalysis, acetylenic alcohols, kaolin, methylcellulose, peptizator, concentration, reaction time, yield.

I. INTRODUCTION

The presence in the molecule of acetylenic alcohols of the triple bond and hydroxyl group gives them peculiar characteristic properties. These compounds are widely used as raw materials for the production of various polymers in the production of monomers, trapping agents, agricultural defoliants, pesticides, stimulants, raw materials for paint, glue and plasticizers, derivatives in the leather and textile industries and pharmaceuticals. Higher acetylene alcohols (C_{15} - C_{20} carbon bonds) are used as semi-finished products in the production of vitamins A, E and K.

Diols are mainly synthesized using various reactions (Favorsky, Grinyar-Iochitsch, Reppe) based on carbonyl and acetylene compounds. In the beginning, acetyl alcohol is formed, followed by acetylene glycol. In addition, processes of isomerization, vinylation, polymerization, and others occur in parallel.

The synthesis of acetylenic alcohols by a homogeneous-catalytic method and the study of the properties of vinyl derivatives have been studied in several publications [1-4], and the use of various selective-action catalysts in these processes is one of the topical problems in the chemistry of acetylene compounds. Synthesis and properties of acetylene alcohol based on aldehydes and ketones are one of the urgent problems of today and the purpose of our research.

II. OBJECTS AND METHODS OF THE RESEARCH

The preparation of the acetylene alcohol depends on the temperature, the reaction medium, the nature and amount of the catalyst and the rate of acetylene release. Increasing the supply of acetylene at high temperatures leads to an increase in the synthesis of diols.

The formation of 3,6-dimethylol-4-diol-3,6 with a heterogeneously catalytic method was studied by the interaction of acetylene and methyl ethyl ketone. The reaction mechanism, the composition and nature of the catalyst, the duration of the synthesis time of 3,6-dimethylol-4-diol-3,6 were studied. Numerous empirical quantum chemical calculations of the RMZ for 3,6-dimethylol-4-diol-3,6 using the HyperChem program were performed.

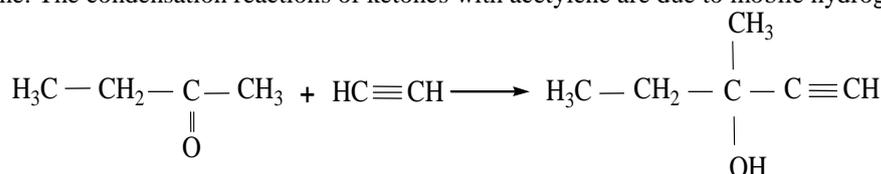
The synthesis was carried out for 12 hours at a pressure of 0.1-0.5 MPa in a reactor with bubbling between methyl ethyl ketone and acetylene in the presence of a newly prepared catalyst.

There was studied the heterogeneous catalytic method for the reaction of methyl ethyl ketone and acetylene at a pressure of 0.1-0.5 MPa in the presence of copper-bismuth-nickel-kaolin (CBNK) catalysts, copper-bismuth-cobalt-kaolin (CBCK), copper-bismuth-nickel bentonite (CBNB), copper-bismuth-cobalt-bentonite (CBCB), copper-bismuth-nickel-silica gel (CBNS), copper-bismuth-cobalt-silica gel (CBCS), copper-bismuth-nickel zeolite (CBNZ) and copper-bismuth-cobalt-zeolite (CBCZ) with the preparation and synthesis of 3,6-dimethyloctin-4-diol, and the effect of the amount of catalyst on the duration of time synthesis of acetylene alcohol.

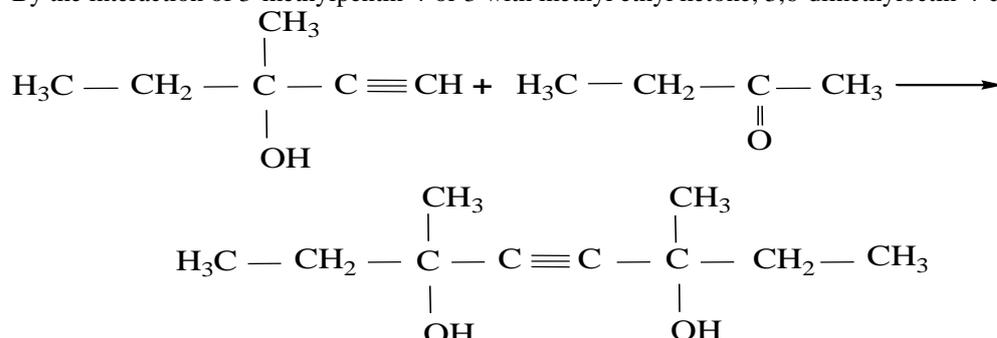
Temperature, density and refractive index of products (n, d) of synthesized compounds were determined, kinetic parameters based on kinetic constants, spectra and chromatograms were calculated using appropriate devices.

III. RESULTS AND DISCUSSION

The catalysts used in the synthesis of acetylene alcohol should be multifunctional. Active components of the catalyst are compounds of copper, silver, mercury, zinc, cobalt, cadmium and nickel. The atoms of these elements form π -complexes on the basis of d-orbitals. Therefore, the catalysts obtained on their basis are widely used in the chemistry of acetylene. The condensation reactions of ketones with acetylene are due to mobile hydrogen as follows:



By the interaction of 3-methylpentin-4-ol-3 with methyl ethyl ketone, 3,6-dimethyloctin-4-diol-3,6 is formed.



The effect of the chemical process in the order of increasing the number of active components in the composition of the catalyst was studied. The results of the study show that the activity of the new catalysts in the synthesis of the product was arranged in the following order:

CBCZ<CBCS<CBNZ<CBNS<CBNB<CBCK<CBNK

The results of the dependence of the productivity of 3,6-dimethyloctin-4-diol-3,6 on the nature and amount of the catalyst are given in Table 1.

Table 1

Influence of the nature and amount of the catalyst in the synthesis of 3,6-dimethyloctin-4-diol-3,6

№	Catalyst	Peptizator	Composition of catalyst (%)	Product yield, %
1	CBNK-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ -5,63; NiO-1,87; Kaolin-62,5	76,25
2	CBNK-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ - 8, NiO-2, Kaolin-50	79,18
3	CBNK-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ - 9,37; NiO-3,12; Kaolin-37,5	73,43
4	CBCK-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ - 5,63; CoO -1,87; Kaolin-62,5	73,24
5	CBCK-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ - 8; CoO -2; Kaolin-50	76,17
6	CBCK-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ - 9,375; CoO-3,125; Kaolin-37,5	71,46
7	CBNB-3	HNO ₃ , NH ₄ OH,	CuO-30; Bi ₂ O ₃ - 5,63; NiO-1,87;	74,74

		methylcellulose	Bentonite-62,5	
8	CBNB-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ - 8; NiO-2; Bentonite-50	76,63
9	CBNB-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ - 9,375; NiO-3,125; Bentonite-37,5	71,34
10	CBCB-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ - 5,63; CoO -1,87; Bentonite-62,5	69,57
11	CBCB-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ - 8; CoO-2; Bentonite-50	73,27
12	CBCB-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ - 9,375; CoO-3,125; Bentonite-37,5	68,12
13	CBNS-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ - 5,63; NiO-1,87; Silica gel-62,5	69,23
14	CBNS-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ - 8; NiO-2; Silica gel -50	72,37
15	CBNS-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ -9,375; NiO-3,125; Silica gel-37,5	67,53
16	CBCS-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ -5,63; CoO -1,87; Silica gel -62,5	66,47
17	CBCS-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ - 8; CoO -2; Silica gel -50	69,33
18	CBCS-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ - 9,375; CoO-3,125; Silica gel -37,5	65,74
19	CBNZ-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ - 5,63; NiO-1,87; Zeolite-62,5	67,46
20	CBNZ-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ -8; NiO-2; Zeolite-50	70,74
21	CBNZ-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ -9,375; NiO-3,125; Zeolite -37,5	66,74
22	CBCZ-3	HNO ₃ , NH ₄ OH, methylcellulose	CuO-30; Bi ₂ O ₃ -5,63; CoO-1,87; Zeolite -62,5	64,53
23	CBCZ-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40; Bi ₂ O ₃ -8; CoO-2; Zeolite -50	67,45
24	CBCZ-7	HNO ₃ , NH ₄ OH, methylcellulose	CuO-50; Bi ₂ O ₃ -9,375; CoO-3,125; Zeolite -37,5	62,64

The output of the product was the most effective option 2 (CBNK-5), which increased the yield of the product by 79.18%. The remaining options for productivity are much inferior to this option.

These catalysts prepared on the basis of kaolin have a good effect on reaction performance than catalysts prepared on the basis of bentonite, silica gel and zeolite.

Table 2

The effect of various peptizators on the activity of the catalyst

№	Catalyst	Peptizator	Composition of catalyst (%)	Product yield, %
1	CBNK-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Kaolin-50	79,18
2	CBNK-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Kaolin-50	76,65
3	CBNK-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Kaolin-50	75,14
4	CBCK-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Kaolin-50	76,17
5	CBCK-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Kaolin-50	73,12
6	CBCK-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Kaolin-50	71,65
7	CBNB-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Bentonite-50	76,63
8	CBNB-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Bentonite -50	73,24
9	CBNB-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Bentonite -50	70,82
10	CBCB-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Bentonite -50	73,27
11	CBCB-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Bentonite -50	70,14
12	CBCB-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Bentonite -50	68,54
13	CBNS-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Silica gel-50	72,37
14	CBNS-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Silica gel-50	69,73
15	CBNS-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Silica gel-50	67,47
16	CBCS-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Silica gel-50	69,33
17	CBCS-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Silica gel-50	65,87
18	CBCS-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Silica gel-50	63,47

19	CBNZ-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Zeolite-50	70,74
20	CBNZ-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Zeolite-50	67,57
21	CBNZ-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, NiO-2, Zeolite-50	65,04
22	CBCZ-5	HNO ₃ , NH ₄ OH, methylcellulose	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Zeolite-50	67,45
23	CBCZ-5	HNO ₃ , NH ₄ OH, CH ₃ COOH	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Zeolite-50	64,15
24	CBCZ-5	HNO ₃ , NH ₄ OH, polyacrylic salts	CuO-40, Bi ₂ O ₃ - 8, CoO-2, Zeolite -50	62,04

To increase the degree of binding of the compounds, various kinds of methylcellulose peptizing agents, acetic acid, polyacrylic salts were added to the catalyst.

In case of using the peptizator, Table 2.in the form of methylcellulose, good performance is observed for 3,6-dimethyloctin-4-diol-3,6. At the same time, the degree of increase in the activity of the catalyst reaches 79.18%.

In addition, the dependence of the yield of the product on the ratio of kaolin to methylcellulose was studied in time, as shown in Fig. 1.

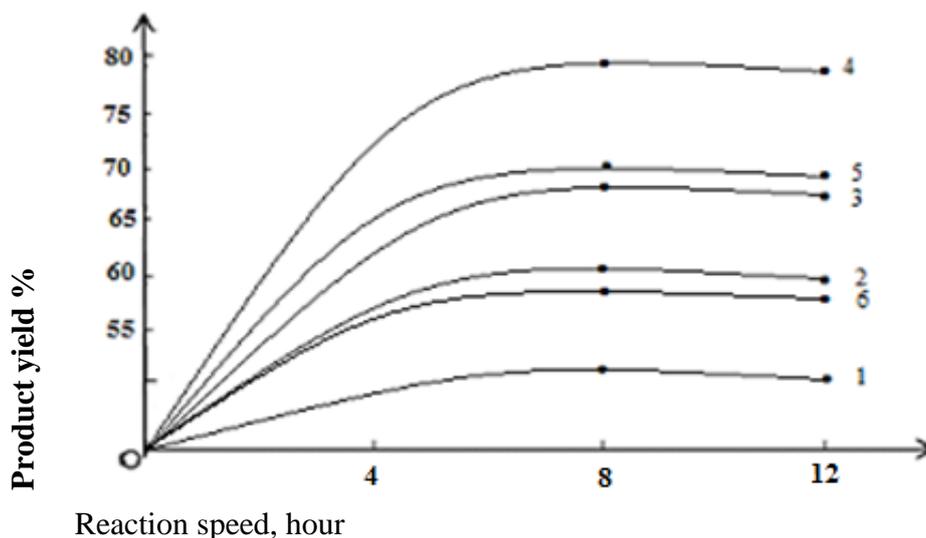


Figure 1. Dependence of the product yield on the ratio of kaolin to methyl cellulose in time.

1-CBNK-5 (K:CZ = 2:0,25); 2-CBNK-5 (K:CZ= 2:0,5); 3-CBNK-5 (K:CZ= 2:0,75); 4-CBNK-5(K:CZ= 2:1); 5-CBNK-5 (K:CZ= 2:1,025); 6-CBNK-5 (K:CZ= 2:1,5)

As it is clear from Fig.1. the yield of the product is greater (79.18%) with a ratio of 2: 1 kaolin-methylcellulose. With an increase in the concentration of methylcellulose, the pores of kaolin are saturated excessively, this leads to incomplete combustion. As a result, during the preparation of the catalyst, this leads to its brittleness, as well as incomplete absorption of CBN in kaolin.

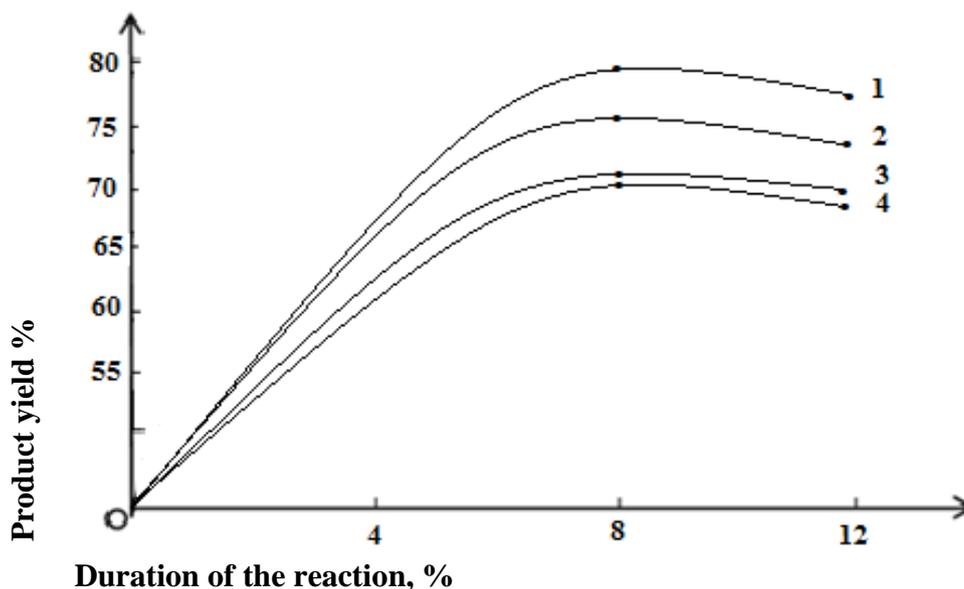


Figure 2. Dependence of the synthesis of 3,6-dimethyloctin-4-diol-3,6 on the duration of time. 1-CBNK-5, 2-CBNB-5, 3-CBNS-5, 4-CBNZ-5

As can be seen from Fig. 2, the synthesis of 3,6-dimethyloctin-4-diol-3,6 depends on the length of time. In this case, the yield of the product passes through a maximum of 8 hours. In other cases, the yield remains practically constant. Based on IR spectroscopic analysis, the following results are revealed. IR spectra of hydroxyl groups were in the region of absorption bands from 3700 to 3500 cm^{-1} . The valent oscillations in the $\sigma\text{-OH}$ state correspond to the absorption band of 1400 cm^{-1} . The value of methylene groups is 2850 cm^{-1} . At the same time, in the form of symmetrical arrangements, the displacement of molecules of deformation vibrations is observed for weak bands in the region of 2500 cm^{-1} . This indicates the presence of a hydrogen bond between the hydrogen atoms in the hydroxyl group and the content of the tertiary bond. The absorption band in the 1110 cm^{-1} region is a typical feature for the deformation vibrations of C-O.

As a result of this research, quantum chemical calculations of the substance were also determined:

The total energy, the energy of formation, the heat of formation, the energy of the electron, nuclear energy, the dipole moment, the charge of the oxygen atom of acetylene and the target product.

Table 3

Quantum-chemical calculations of the used substances

Quantum-chemical parameters	Nature of compounds	
	acetylene	3,6-dimethyloctin-4-diol-3,6
Total energy, kcal / mol	-6489,10351	-40371,10938
Energy generation, kcal / mol	-391,2214355	-2284,808105
Heat of education, kcal / mol	54,76256943	-69,14212799
The electron energy, eV	-12975,6523	-203224,5156
Nuclear energy, kcal / mol	6486,549316	162853,4063
The dipole moment (D)	0,01728	2,356
Oxygen charge	-	-0,315



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IV.CONCLUSION

The productivity of producing acetylenic alcohols in the presence of higher-base systems in a heterogeneously-catalytic homogeneous process is higher than in a homogeneous process. The presence of a copper catalyst prevents the polymerization of certain reactions.

Quantum-chemical calculations have shown that carbon atoms in hydrocarbons containing a triple bond are more active, have been studying the characteristics of OH groups. Thus, summarizing the foregoing, it is possible to point out the effectiveness of the heterogeneously catalytic method, in which the maximum yield of the product occurs with the use of anCBNK-5 catalyst (79.18%)

REFERENCES

- [1] Temkin O.N. Chemistry of acetylene. "Acetylene tree" in organic chemistry of the XXI century. // Soros Educational Journal., Vol. 7, No. 6. 2001
- [2] VapoevKh.M., Nurmanov S.E., Umarova J.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] Yusupov D., Karimov A.U., Tirkashev I., Korotaev A.V. Preparation of butyne-2-diol-1,4 from acetylene and formaldehyde at atmospheric pressure. // Chem. prom. 1998, №7.p. 387-390
- [4] Pat. 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. No. IHDP 9500512.1.Opubl.in the BI. №2, 1996