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DEPENDENCE OF THE ACTIVITY OF BINARY ZINC - COPPER OXIDE CATALYSTS ON THEIR STRUCTURAL PROPERTIES

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Abstract. In the paper it has been studied the reaction of ethanol conversion over binary zinc-copper oxide catalysts. It was found that on Zn-Cu-O catalysts ethanol is converted mainly into acetaldehyde, acetone, and carbon dioxide. It has been shown that binary zinc-copper oxide catalysts consist of phases of zinc and copper oxides, and their degree of crystallinity varies from 42.9% to 93.8%. It was found that in the reaction of the conversion of ethanol over zinc-copper oxide catalysts with an increase in the crystallinity of the catalyst, the yield of acetaldehyde and the selectivity of the reaction of dehydrogenation of ethanol to acetaldehyde pass through a minimum.

Keywords: *ethanol, dehydrogenation, acetaldehyde, copper oxide, binary catalysts, crystallinity.*

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1. Introduction

Bioethanol of the second-generation is one of the promising raw materials for the production of various chemical compounds (Inaba *et al.*, 2006; Wang *et al.*, 2002; Liu *et al.*, 2016). By the ethanol conversion reaction can produce several chemicals such as acetaldehyde, acetic acid, diethyl ether and etc. (Men'shchikov *et al.*, 2014; Novikova *et al.*, 2018; Takei *et al.*, 2011). We have previously shown that ethanol is converted at a high rate into acetone, acetic acid over various binary zinc-copper catalysts (Mammadova & Aghayeva, 2020).

It is known that the phase composition of a catalyst and, accordingly, its structural properties can strongly affect its activity (Kushal *et al.*, 2017; Baranova *et al.*, 2012; Knyazeva *et al.*, 2019). One of the structural properties of a catalyst is its crystallinity, which depends both on the initial compounds used for its preparation and on the conditions under which it is prepared. In this regard, we investigated the dependence of the activity of the synthesized catalysts in the reaction of ethanol dehydrogenation on their phase composition.

2. Experimental part

Binary zinc-copper oxide catalysts of various compositions were prepared by coprecipitation from aqueous solutions of zinc and copper nitrate. The obtained mixture was sequentially evaporated and dried at 100-120°C, decomposed until nitrogen oxides were completely liberated at 250°C, and then calcined at 600°C for 10 hours. Thus, 9 catalysts were synthesized with an atomic ratio of elements from Zn: Cu = 1: 9 to Zn: Cu = 9: 1. The activity of the synthesized catalysts in the ethanol dehydrogenation reaction was studied in a flow-through unit with a tubular reactor in the temperature range 100-500°C. The reactor was loaded with 5 ml of the studied catalyst with a grain size of 1.0–2.0 mm, and its activity in the reaction of ethanol dehydrogenation was studied. The activity of the synthesized catalysts in the reaction of ethanol conversion was studied on a flow-through unit at a volumetric feed rate of 1200 h^{-1} in the temperature range 100-500°C. The ethanol dehydrogenation reaction was carried out in a stream of nitrogen. The conversion of ethanol and the yields of its conversion products were determined by chromatography. The yields of acetaldehyde, acetone, and other organic compounds were determined on a chromatograph with a flame ionization detector on a 2 m column filled with a Polysorb-1 sorbent. Carbon dioxide yields were determined on a chromatograph with a column 6 m long filled with sorbent celite with petroleum jelly applied to it. X-ray studies of binary zinc-copper oxide catalysts were carried out on an automatic powder diffractometer Bruker D2 Phaser (CuKα-radiation, Ni-filter, $3 \leq 2\theta \geq 80°$).

3. Results and discussion

Studies have shown that the products of the reaction of ethanol conversion over zinc-copper oxide catalysts are acetaldehyde, acetone, carbon dioxide, ethylene, ethyl acetate and, in small amounts, organic decomposition products of the initial alcohol. The data on the study of the activity of the catalyst Zn-Cu=1-9 in the ethanol conversion reaction is shown in Figure 1. As can be seen from figure 1, the ethanol conversion reaction begins at 150°C. At this temperature, the formation of 9.6% of acetaldehyde is observed. With an increase in temperature, the yield of acetaldehyde passes through a maximum at 300°C (38.4%). A further increase in temperature leads to the formation of carbon dioxide, acetone, ethyleneand ethyl acetate.

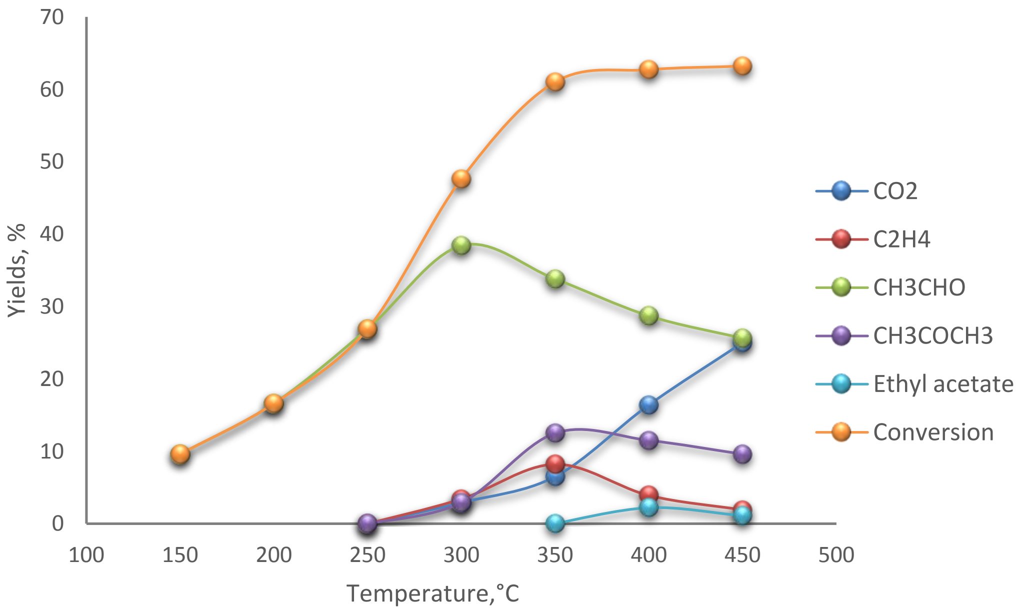

Fig. 1. Dehydrogenation of ethanol over the catalyst Zn-Cu=1-9

The formation of ethyl acetate is observed only at temperatures of 400°C and 450°C and its yield, as seen from Figure 1, does not exceed 2.2%. Provided researches show that the reaction of the formation of acetone begins at a temperature of 300°C and, with increasing temperature, passes through a maximum (12.5%) at 350°C. The yield of ethylene with an increase in the reaction temperature also passes through a maximum and its highest yield is 8.2% at 350°C. The reaction of the formation of carbon dioxide begins at 300°C and its yield increases with an increase in the reaction temperature over the entire temperature range studied. The maximum carbon dioxide yield is 25% at 450°C. Table 1 also shows that the conversion of ethanol on the studied catalyst reaches 63.2% at 450°C.

It is known that the phase composition of the catalyst, i.e. its structural properties can strongly influence its activity. One of the structural properties of a catalyst is its crystallinity, which depends both on the initial compounds used for its preparation and on the conditions for its preparation. In this regard, we investigated the dependence of the activity of the zinc-copper oxide catalysts synthesized by us in the reaction of ethanol dehydrogenation on the degree of their crystallinity. X-ray studies of binary zinc-copper oxide catalysts have shown that phases of two initial oxides are formed in this catalytic system. The crystallographic characteristics of the identified phases are shown in Table 1.

Table 1. Crystallographic properties of the phases formed in the catalytic system Zn-Cu-O

Chemical compound	Syngonia	Space group	Lattice parameters				Z, number of molecules
			a, Å	в, Å	c, Å	angle	
CuO	Monoclinic	Cc	4.692	3.428	5.137	99.54	4
ZnO	Hexagonal	$P6_3mc$	3.248	-	5.204	-	2

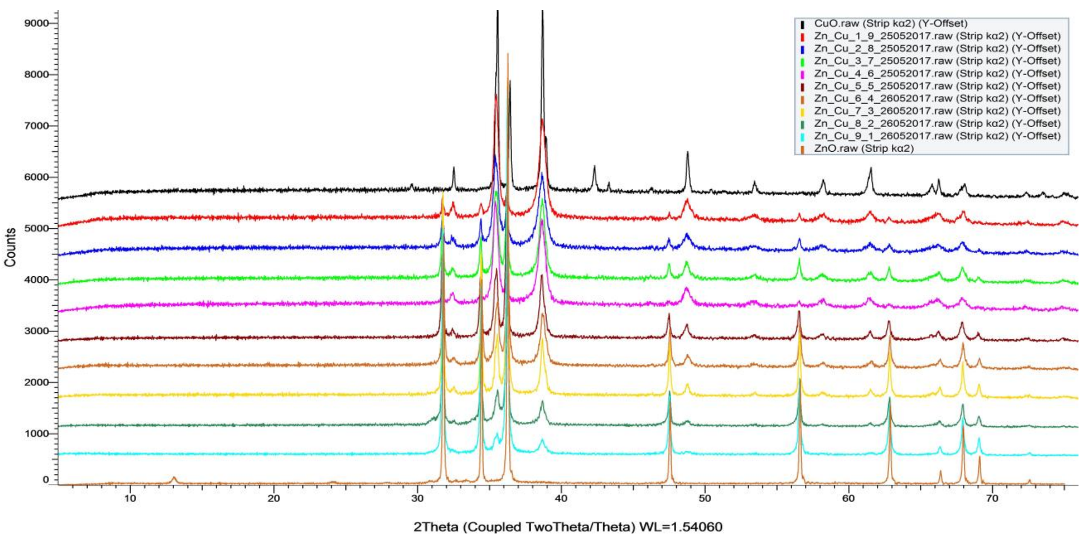

Fig. 2. Diffraction curves of zinc and copper oxides, as well as all 9 samples of the Zn-Cu-O catalytic system

In fig. 2 shows the diffraction curves brought together for all nine ratios (mZn/nCu). For comparative analysis, the diffraction curves of oxides ZnO and CuO are shown at the beginning and at the end of the diffraction curves. Analysis of diffraction curves in the Zn-Cu-O system shows the formation of two phases ZnO and CuO in all samples. A regular change in the intensity of diffraction reflections indicates the retention of the phase ratio of both components in the catalyst composition.

We also calculated the crystallinity of all samples using the DIFFRAC.EVA program. The obtained results are presented in table 2. As can be seen from table 2, the degree of crystallinity of the investigated catalytic system increases with decreasing copper content. Thus, with an increase in the zinc content in the Zn-Cu-O catalytic system, the degree of crystallinity increases from 42.9% to 93.8%.The dropout of the crystallinity value of the sample Zn-Cu=4:6 is apparently due to the formation of a solid solution.

Table 2. The degree of crystallinity of the samples of the catalytic system Zn-Cu-O

Atomic ratioZn:Cu	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Crystallinity, %	42.9	43.9	54.9	44.2	71.3	75.3	78.1	81.3	93.8

In fig. 3 have shown the dependence of the yield of acetaldehyde, the selectivity of the process for acetaldehyde and the conversion of ethanol on the degree of crystallinity of binary catalysts based on zinc oxide and copper. As can be seen from the figure, with an increase in the crystallinity of the catalyst, the yield of acetaldehyde and the selectivity of the reaction of ethanol dehydrogenation to acetaldehyde change symmetrically and pass through a minimum. Figure 3 also shows that with an increase in the degree of crystallization of the catalyst, the yield of carbon dioxide passes through a maximum, and the total conversion of ethanol slightly decreases.

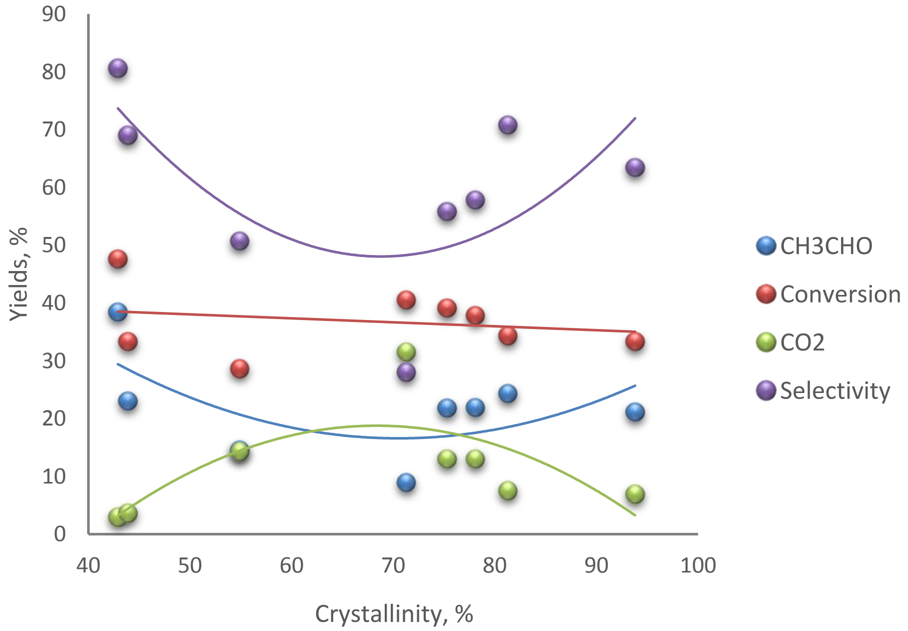

Fig. 3. Dependence of the activity of zinc-copper catalysts in the reaction of ethanol dehydrogenation on the degree of crystallization. T = 300°C

4. Conclusion

- The products of the reaction of the conversion of ethanol on zinc-copper oxide catalysts are acetaldehyde, ethyl acetate, acetone, ethylene and carbon dioxide.
- Binary zinc-copper oxide catalysts consist of phases of zinc and copper oxides, and their degree of crystallinity varies from 42.9% to 93.8%.
- In the reaction of ethanol conversion on zinc-copper oxide catalysts with an increase in the crystallinity of the catalyst, the yield of acetaldehyde and the selectivity of the reaction of ethanol dehydrogenation to acetaldehyde pass through a minimum

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