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Dependence of the activity of copper-tungsten oxide catalysts in the ethanol oxidation reaction on their acidic properties

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Abstract: The reaction of ethanol oxidation on copper-tungsten oxide catalysts has been studied. It has been shown that the main products of ethanol oxidation reaction on tungsten-copper oxide catalysts are acetaldehyde, ethylene, and carbon dioxide. It has been found that with an increase in the reaction temperature, the yields of acetaldehyde and acetone pass through a maximum, while the yields of ethylene and carbon dioxide increase over the entire temperature range studied, reaching their maximum value at 500°C. It has been shown that, on the studied copper-tungsten oxide catalysts, the dependences of the yields of acetaldehyde on the composition of the catalyst have the form of curves with two maxima. In order to characterize the acidic properties of the surface of the studied catalysts, their activity was studied in the isomerization of butene-1 to butenes-2. It was found that when copper is introduced into the composition of the tungsten oxide catalyst, the total yield of butenes-2 passes through a maximum on samples rich in tungsten. It is shown that an increase in the degree of isomerization of binary copper-tungsten oxide catalysts leads to a rise in the yields of ethanol partial oxidation products and a decrease in the yield of carbon dioxide.

Keywords: Ethanol oxidation; butene-1 isomerization; tungsten oxide; copper oxide; binary catalysts.

1. Introduction

Our previous studies have shown that copper–tungsten oxide catalysts are highly active in ethanol conversion reactions [1]. It has also been shown that the activity of copper-tungsten oxide catalysts depends on their composition. In heterogeneous catalysis, solid catalysts' acid-base properties affect the activity and selectivity of many catalytic reactions [2-4]. The acid-base properties of solid catalysts have been correlated with their catalytic properties for many years; however, clear and generalized correlations with catalytic properties have not been unequivocally established. The main reason was that the acid-base properties were determined mainly at room temperature, i.e., under conditions far from catalytic. In this regard, some catalytic reactions were often used as model ones to characterize the acid-base properties under conditions close to real catalytic reactions [5,6]. In recent years, due to the ease of implementation, the acid-base properties of oxide catalysts are often characterized by measuring their activity in the reaction of isomerization of butene-1 to cis and trans-2-butenes [7-9]. In this regard, in this work, in order to assess the effect of the acidic properties of the surface on the activity of copper–tungsten oxide catalysts, we compared their activities in butene-1 isomerization and ethanol oxidation.

2. Experimental

Copper-tungsten oxide catalysts were prepared by coprecipitation from aqueous solutions of copper nitrate and ammonium tungsten. The obtained mixture was evaporated, dried at 95-100°C, and decomposed until the complete release of nitrogen oxides at a temperature of 250-300°C. The solid mass was calcined at a temperature of 600°C for 10 hours. Thus, 9 catalysts were synthesized with an atomic ratio of elements from Cu:W=1:9 up to Cu:W=9:1. The reaction of ethanol oxidation over synthesized binary tungsten containing catalysts was studied on a flow unit with a tubular reactor in the temperature range of 250–700°C. 5 ml of the studied catalyst with a grain size of 1.0–2.0 mm was loaded into a quartz reactor, and its activity in the ethanol oxidation reaction was studied at a volumetric feed rate of 1200 h^{-1}. The molar ratio of ethanol: water vapor: air was 1:4:5. The ethyl alcohol, acetaldehyde, acetone, and ethylene analysis was carried out on a chromatograph with a 2 meter long column filled with separon sorbent. Carbon dioxide was analyzed using a 6-meter-long column filled with celite coated with vaseline oil. The isomerization reaction of butene-1 into butenes-2 was carried out under the same conditions as the oxidation of ethanol, namely, at a space feed rate of 1200 h^{-1}, in the temperature range of 150–500°C.

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3. Results and Discussion

Conducted studies have shown that the reaction products of ethanol conversion on Cu-W-O catalysts are acetaldehyde, acetone, ethylene, and carbon dioxide. It has been established that the yield and distribution of ethanol conversion products strongly depend on the reaction temperature and the atomic ratio of copper to tungsten in the catalyst composition. For example, Figure 1 shows the effect of the reaction temperature on the yields of ethanol oxidation reaction products on the Cu:W=3:7 catalyst, on which the highest acetaldehyde yield is observed.

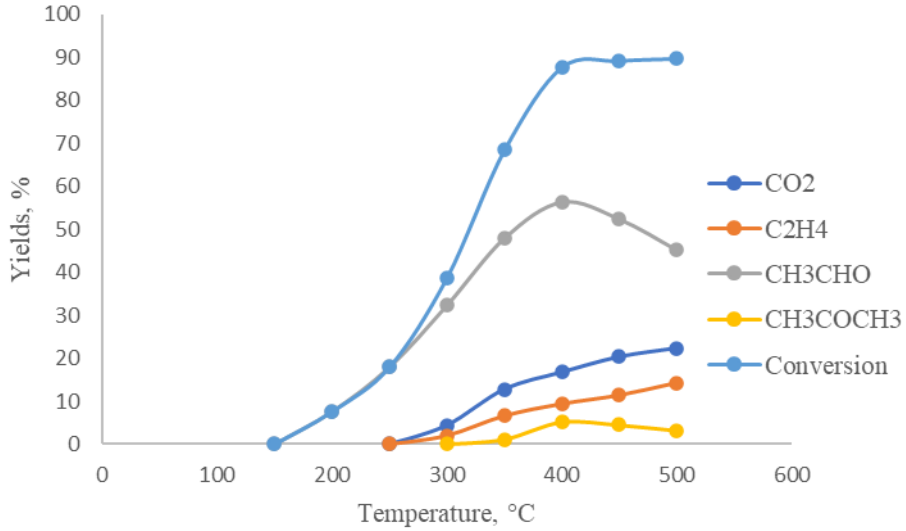

Figure 1. Effect of temperature on the yields of ethanol oxidation products over the Cu-W=3-7 catalyst.

Figure 1 shows that the ethanol conversion reaction on the studied catalyst begins at a temperature of 200°C with the formation of 7.6% acetaldehyde. A subsequent increase in the reaction temperature leads to the formation of other reaction products. As seen in Figure 1, the acetaldehyde yield passes through a maximum at 350°C. At this temperature, 56.4% acetaldehyde is formed. The yield of acetone also gives to a maximum with increasing reaction temperature. The ethylene and carbon dioxide yields rise over the studied temperature range, reaching their maximum value at 500°C. At low temperatures, the ethanol oxidation reaction proceeds in parallel; at higher temperatures, the oxidation of reaction products such as acetaldehyde and acetone also begin, so a further increase in temperature leads to a decrease in their yields. The yield of carbon dioxide naturally increases with an increase in the reaction temperature since it is the final product of the reaction. Sequential oxidation of ethylene is not observed in our case; therefore, its yield constantly increases with increasing temperature. Figure 1 also shows that the ethanol conversion on the Cu:W=3:7 catalyst reaches about 90%.

Table 1 shows the dependence of the yields of ethanol oxidation reaction products at 400°C on the atomic ratio of copper to tungsten in the composition of Cu-W-O catalysts. It can be seen that with an increase in the catalyst's copper content, the acetaldehyde yield passes through a maximum on the Cu-W=3:7 (52.4%) samples and then slowly decreases to 32.6% on the Cu-W=9-1 catalyst.

Table 1. Dependences of the yields of ethanol conversion reaction products at 400°C on the atomic ratio of copper to tungsten in the catalyst composition.

Reaction products	**Yields, %**								
Ratio of copper to tungsten	1-9	2-8	3-7	4-6	5:5	6-4	7-3	8-2	9-1
Carbon dioxide	21,6	19,7	16,8	17,8	20,4	19,8	23,2	20,3	24,6
Ethylene	18	13	9,4	5,4	4,8	4,3	0	0	0
Acetaldehyde	32,2	50,8	56,4	52,4	44,4	52,6	45,6	40,4	37,4
Acetone	0	6	5,2	0	0	6,2	1,5	1,2	0
Ethanol conversion	71,8	89,5	87,8	75,9	69,9	83	70,3	66,3	63,5

The ethylene yield decreases with an increase in the copper content in the composition of the catalyst, and on samples rich in copper, it is practically equal to zero. On the other hand, the yield of the product of deep oxidation of ethanol of carbon dioxide with an increase in the content of copper in the composition of the catalyst first slightly decreases and then practically does not change. As seen in Table 1, the dependence of ethanol conversion on the composition of the catalyst has the form of a curve with two maxima, and the highest conversion of ethanol reaches 90.8%. The obtained results show that, on the studied copper-tungsten oxide catalysts, the dependences of the yields of acetaldehyde and acetone on the composition of the catalyst have the form of curves with two maxima.

In order to assess the acid properties of the surface of copper-tungsten oxide catalysts, their activity in the isomerization of butene-1 to trans and cis butenes-2 was studied. The results obtained at a temperature of 400°C are shown in Figure 2. As seen in Figure 2, the dependence of the yields of butenes-2 on the atomic ratio of copper to tungsten has the form of a curve with a maximum on the Ti-W=3-7 sample. In this sample, the maximum yield of butenes-2 reaches 57%.

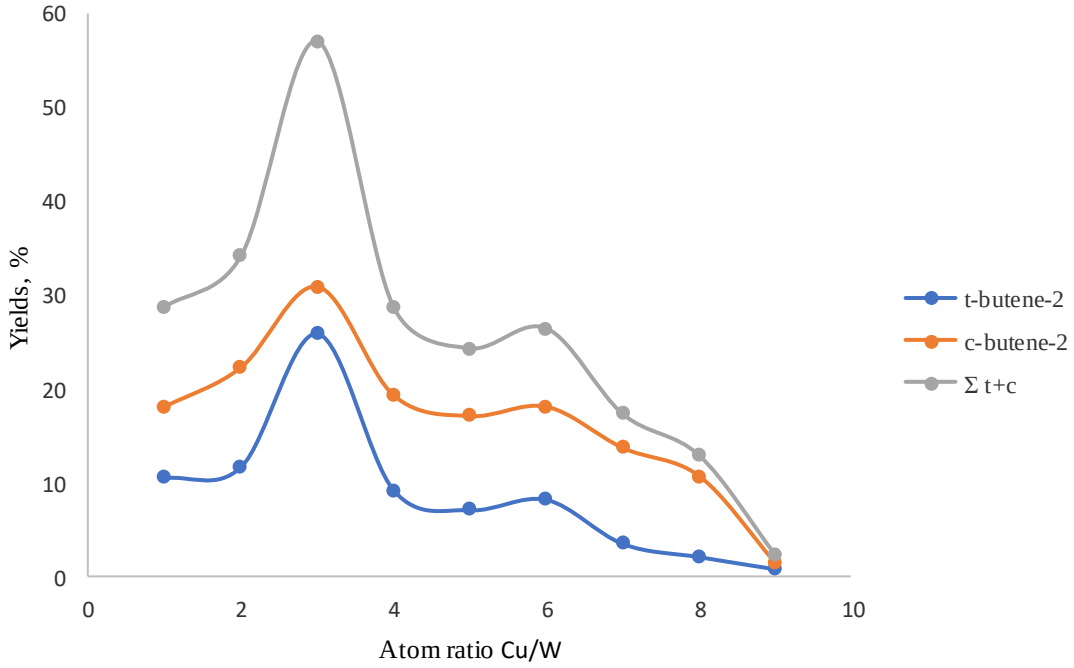

Figure 2. Dependence of the yields of trans and cis butenes-2 in the butene-1 isomerization reaction on the atomic ratio of copper to tungsten. T = 400°C .

Based on the obtained results, it can be said that when copper is introduced into the composition of the tungsten oxide catalyst, the total yield of butenes-2 passes through a maximum on samples rich in tungsten.

To assess the effect of the acidic properties of the surface of copper–tungsten oxide catalysts on their activity in the ethanol oxidation reaction, we compared their activities in the reactions of ethanol oxidation and the isomerization of butene-1 to butenes-2. The dependence of the yields of ethanol conversion reaction products on the degree of butene-1 isomerization of binary copper-tungsten oxide catalysts is shown in Figure 3.

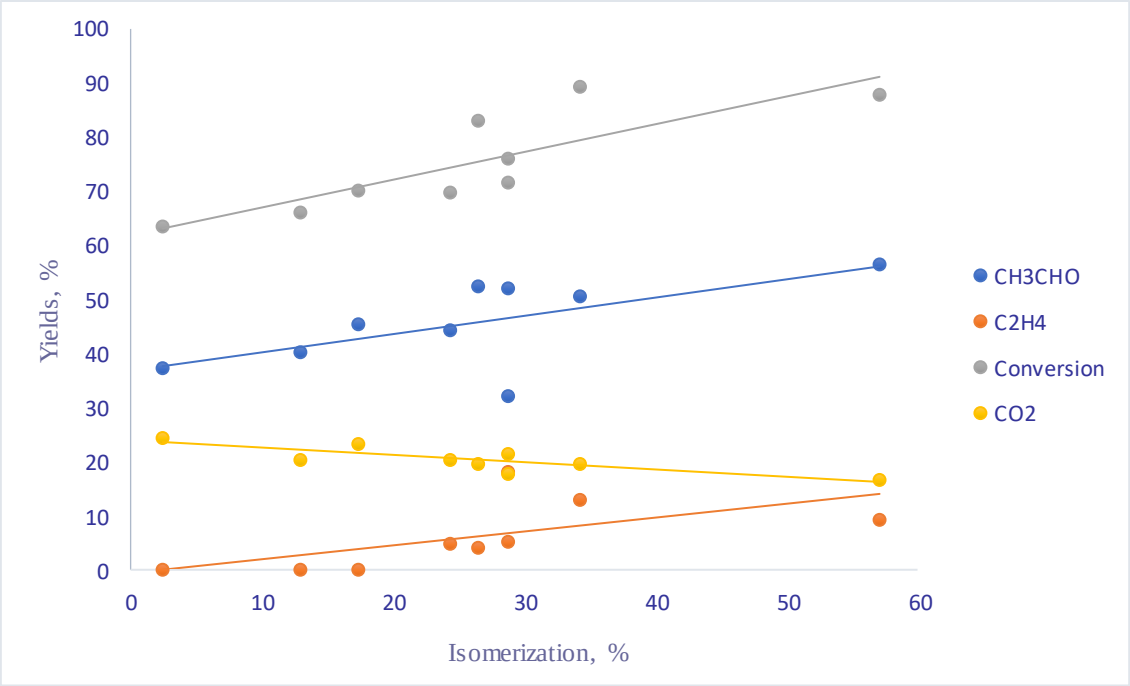

Figure 3. Dependence of the yields of ethanol oxidation reaction products on binary copper-tungsten oxide catalysts on the degree of butene-1 isomerization.

As seen in Figure 3, with an increase in the degree of butene-1 isomerization, the yields of acetaldehyde and ethylene increase, while the yield of carbon dioxide decreases. Figure 3 also shows that the conversion of ethanol also increases with an increase in the isomerization of butene-1.

4. Conclusion

1. The main products of ethanol oxidation reaction on tungsten-copper oxide catalysts are acetaldehyde, ethylene, and carbon dioxide.
2. On the studied copper-tungsten oxide catalysts, the dependences of the yields of acetaldehyde on the composition of the catalyst have the form of curves with two maxima.
3. An increase in the degree of isomerization of binary copper-tungsten oxide catalysts leads to an increase in the yields of products of the partial oxidation of ethanol and a decrease in carbon dioxide yield.

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