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# Effect of specific surface on the activities of binary Zr-Zn-O catalysts in the reaction of ethanol conversion

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**Abstract**: The activities of binary zirconium-zinc oxide catalysts in the reaction of ethanol conversion to acetone were studied. It has been established that with an increase in the reaction temperature, the yields of acetone, carbon dioxide, and acetaldehyde pass through a maximum. In contrast, the yield of ethylene increases over the entire temperature range studied. It was found that the dependences of the acetone yield and the ethanol conversion on the atomic ratio of zirconium to zinc have the form of a curve with two maxima. A maximal yield of acetone 58.2% was observed over catalyst Zr-Zn=8-2 at a temperature of 500°C. The specific surfaces of zirconium-zinc oxide catalysts have been studied. It has been established that the specific surface area of zirconium-zinc oxide catalysts varies in the ra.8 $m^2/g$. The effect of the surface on the yields of ethanol conversion products has been studied. It has been shown that with an increase in the specific surface area of zirconium-zinc oxide catalysts, the yield of acetone passes through a maximum. In contrast, the yields of acetaldehyde, carbon dioxide, and ethylene practically do not change.

**Keywords**: Ethanol; acetone; binary catalysts; zinc oxide; zirconium oxide; specific surface.

## 1. Introduction

Acetone is one of the most important monomers widely used in the chemical industry. Various methods can obtain acetone. A promising approach for obtaining acetone is the conversion of ethanol in the presence of steam [1,2]. This production method is important because ethanol is obtained from bio-feedstock and is considered a renewable feedstock [3,4]. It is known from periodical literature that catalysts based on zinc oxide exhibit high activity in the reaction of ethanol conversion to acetone [5,6]. We have previously shown that on binary zirconium–zinc oxide catalysts, ethanol is converted to acetone at a reasonably high rate [7]. X-ray studies of our catalysts showed that they contain phases of zirconium and zinc oxides [8]. The process of acetone obtained from ethanol occur according to the reaction:

$$2C_2H_5OH + H_2O \quad CH_3COCH_3 + CO_2 + 4H_2$$

As is known in heterogeneous catalysis, the reactions of transformation of raw materials into reaction products take place on the catalyst's surface. Therefore, the size of the developed surface of the catalyst has a significant effect on its activity and is one of its important properties [9-11]. In this regard, we studied the impact of the specific surface area of the catalysts synthesized by us on their activity in the reaction of the vapor phase transformation of ethanol.

## 2. Experimental

Binary zirconium-zinc oxide catalysts were prepared by precipitating aqueous solutions of zirconyl and zinc nitrates. The resulting mixture was evaporated at 95–100°C, dried at 100–120°C, and calcined at 250–350°C until nitrogen oxides were wholly released. The resulting solid mass was calcined at 700°C for 10 hours. Thus, we synthesized nine binary zirconium-zinc oxide catalysts of various compositions from Zr-Zn=1-9 to Zr-Zn=9-1. The specific surface area of the studied catalysts was determined by the chromatographic method with thermal desorption of nitrogen. The activity of the synthesized catalysts in converting ethanol to acetone was studied on a flow unit with a quartz reactor in the temperature range of 250–700°C. The reactor was loaded with 5 ml of the studied catalyst 1.0–2.0 mm in size, and its activity in the ethanol steam reforming reaction was studied. The volumetric feed rate of raw materials was 1800 $h^{-1}$. The molar ratio of ethanol: water vapor: the air was 1:4:10.

The reaction products' yields and feedstock were determined on a chromatograph with a flame ionization detector and a 2-meter column filled with a specially treated Polysorb-1 sorbent. The amount of carbon dioxide formed was determined on a chromatograph with a 6-meter column filled with a Celite sorbent coated with Vaseline oil.

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## 3. Results and Discussion

Our studies have shown that the products of the reaction of the conversion of ethyl alcohol on binary zirconium-zinc oxide catalysts are ethylene, acetaldehyde, acetone, and carbon dioxide, as well as products of destructive decomposition at high temperatures. So, Figure 1 shows the results of a study of the ethanol conversion reaction on the most active catalyst with the atomic ratio Zr/Zn=3/7. It can be seen from the figure that the ethanol conversion reaction starts at a temperature of 300°C with the formation of 2.1% acetaldehyde. With a further temperature increase, acetaldehyde's yield passes through a maximum at a temperature of 400°C with the formation of 32.5%. As the reaction temperature rises, other reaction products begin to form. With increasing the reaction temperature, the yield of the main reaction product, acetone, also passes through a maximum. The highest yield of acetone is observed at 500°C, equal to 52.3%. Figure 1 also shows that ethylene and carbon dioxide yields increase with increasing reaction temperature, reaching their maximum value. The highest ethylene and carbon dioxide yields are 7.3 and 14.6%, respectively. The highest ethanol conversion on this sample reaches 85.0% at a temperature of 550°C.

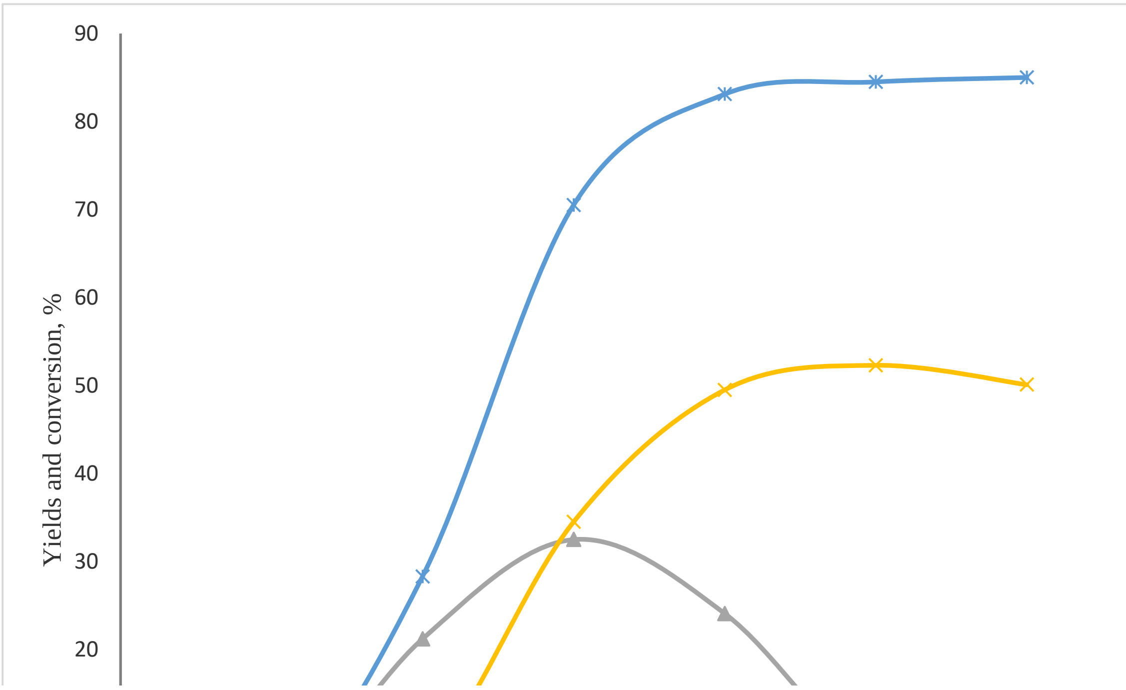


**Figure 1**. The dependence of the yields of the reaction products on the temperature over the catalyst with the atomic ratio Zr/Zn=3/7

The composition of the binary Zr-Zn-O catalyst also significantly affects the yield and distribution of ethanol conversion reaction products. Table 1 shows the dependences of the yields of ethanol conversion reaction products on the Zr/Zn atomic ratio at a reaction temperature of 450°C. As seen from Table 1, with an increase in the Zr/Zn atomic ratio, the acetaldehyde yield passes through two maxima on samples Zr-Zn=4-6 and Zr-Zn=8-2. The highest yield of acetaldehyde is observed on the Zr/Zn=4-6 sample and is equal to 40.5%. Similar dependences are also observed for the acetone reaction's yield of another target product. The maximum yield of acetone is observed on the Zr-Zn=3-7 catalyst and is equal to 49.5%. However, the sample shows the highest ethanol conversion, equivalent to 83.1%.

**Table 1**. Dependence of the activity of Zr-Zn-O catalysts in ethanol conversion reaction on atomic ratio Zr/Zn. T=450°C.

| Atomic ratio Zr/Zn | 1:9 | 2:8 | 3-7 | 4:6 | 5:5 | 6:4 | 7:3 | 8:2 | 9:1 |
|---|---|---|---|---|---|---|---|---|---|
| Reaction products | Yields of reaction products, % | | | | | | | | |
| $CO_2$ | 7.6 | 7.1 | 5.7 | 3.5 | 4.8 | 6 | 6.5 | 3.5 | 2.3 |
| $C_2H_4$ | 1.6 | 5.5 | 3.8 | 4.1 | 4.3 | 3.8 | 3.9 | 3.2 | 2.9 |
| $CH_3CHO$ | 7 | 15 | 24.1 | 40.5 | 13,2 | 16 | 13.6 | 38.1 | 5.4 |
| $CH_3COOH$ | 11.9 | 41.1 | 49.5 | 27.8 | 26 | 21.6 | 41.2 | 29.1 | 23.2 |
| Conversion | 28.1 | 68.9 | 83.1 | 75.9 | 48.3 | 48.4 | 65.2 | 73.9 | 56.1 |

As is known in heterogeneous catalysis, the reactions of conversion of raw materials into reaction products take place on the surface of the catalyst. The specific surface area of complex catalysts depends on their composition and preparation conditions. The results of the study of the specific surface of binary zirconium zinc oxide catalysts are presented in Table 2. As seen from Table 2, with a change in the content of zirconium in the composition of the binary catalyst, the specific surface varies in the range from 1.5 to 11.8 $m^2$/q.

**Table 2**. Specific surfaces of Zr-Zn-O catalysts of various compositions, $m^2$/g.

| Atomic ratio of Zr/Zn | $ZrO_2$ | 1-9 | 2-8 | 3-7 | 4-6 | 5-5 | 6-4 | 7-3 | 8-2 | 9-1 | ZnO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Specific surface, $m^2$/q | 35.2 | 2.8 | 11.8 | 6.4 | 3.8 | 1.5 | 3.3 | 4.2 | 3.1 | 2.5 | 4.5 |

The developed surface of a catalyst has a significant effect on its activity and is one of its very important properties. Therefore, we studied the impact of the specific surface of the synthesized catalysts on their activities in the ethanol vapor phase conversion reaction.

Figure 2 shows the dependences of the yields of carbon dioxide, ethylene, acetaldehyde, acetone, and ethanol conversion on the specific surface area of zirconium-zinc oxide catalysts. As seen from Figure 2, with an increase in the specific surface area, the conversion of ethanol and the yield of acetone pass through a maximum (58.2%). In contrast, the yields of carbon dioxide, ethylene, and acetaldehyde practically do not change with an increase in the specific surface area.

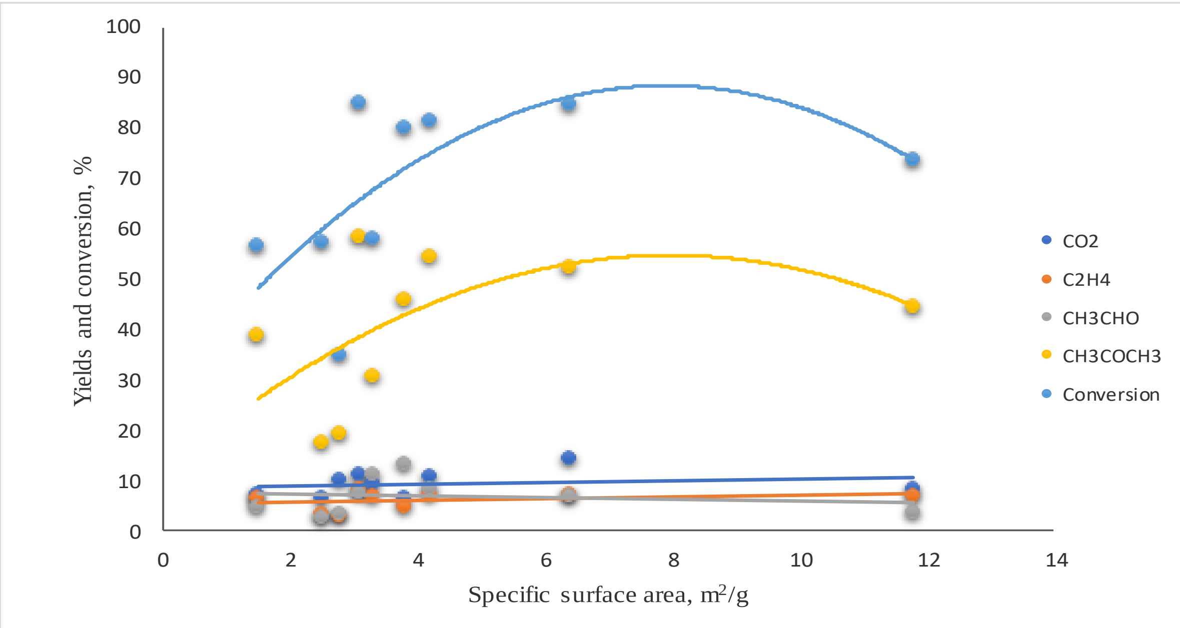


**Figure 2**. Dependence of the activity of zirconium-zinc oxide catalysts in the ethanol conversion reaction on the specific surface

## 4. Conclusion

1. The catalysts show high activity in the formation reaction of acetone with a predominance of zirconium or zinc at temperatures of 450-550°C. The maximum yield of acetone on Zr-Zn-O catalysts reaches 58.2%.

2. The dependence of butene-2 yields on the catalyst composition has the form of a curve with two maxima on samples with the ratio

Zr-Zn=2-8 and Zr-Zn=8-2.

3. With an increase in the specific surface area of zirconium-zinc oxide catalysts, the yield of acetone passes through a maximum. In contrast, the yields of acetaldehyde, carbon dioxide, and ethylene practically do not change.

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