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# DEPENDENCE OF THE ACTIVITY OF Ce-Zn-O CATALYSTS IN THE REACTION OF THE CONVERSION OF ETHANOL INTO ACETONE ON THE ACIDIC PROPERTIES OF THE SURFACE

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***Abstract:*** *The reaction of ethanol conversion to acetone on binary cerium-zinc oxide catalysts has been studied. It has been established that the reaction products of the conversion of ethyl alcohol on binary cerium-zinc oxide catalysts are ethylene, acetaldehyde, acetone, carbon dioxide and, at high temperatures, destructive decomposition products. The highest yield of acetone is observed on samples rich in zinc at temperatures of the order of 450-550°C, while catalysts rich in cerium are active in the reaction of dehydration of ethanol to ethylene. In this work, the acid properties of cerium-zinc oxide catalysts were evaluated by their activity in the isomerization of butene-1 to trans and cis butenes-2. It was found that cerium-rich catalysts are active in butene-1 isomerization reaction. The activities of cerium-zinc oxide catalysts in the reactions of the conversion of ethanol to acetone and the isomerization of butene-1 into trans and cis butenes-2 are compared. It was found that the reaction of the conversion of ethanol to acetone proceeds on the centers of the basic nature, and the formation of ethylene proceeds on the centers of the acidic nature.*

***Keywords:*** *Ethanol, acetone, binary catalysts, butene-1 isomerization, zinc oxide, cerium oxide.*
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## Introduction

Acetone is one of the most important monomers widely used in the chemical industry. One of the possible methods for obtaining acetone is the reaction of the vapor phase conversion of ethanol [1, 2]. The promise of this method for obtaining acetone lies in the fact that ethanol is a renewable raw material and is obtained in large quantities from vegetable raw materials [3,4]. In this regard, the creation of active and selective catalysts for this process is a very important issue for the chemical industry. It is known from periodic literature that catalysts based on zinc oxide exhibit a high activity of the reaction of the conversion of ethanol to acetone [5, 6]. In this regard, we previously studied the effect of cerium oxide on the activity of zinc oxide in the reaction of the conversion of ethanol to acetone [7]. It was found that binary cerium-zinc catalysts exhibit a fairly high activity in the reaction of the conversion of ethanol to acetone. It is known that the surface properties of the catalyst affect their catalytic activity. One of the surface properties of a catalyst that can have a strong influence on their activity is acid-base properties [8–10]. To assess the acid–base properties of a surface under conditions close to real catalytic reactions, some catalytic reactions are widely used as model ones [11–13]. Due to the ease of implementation, the measurement of the activity of catalysts for the reaction of isomerization of butene-1 to cis and trans butenes-2 is most often used for these purposes [14, 15]. Earlier, we studied the acid surface properties of binary tungsten-containing catalysts by their activity in the reaction of

isomerization of butene-1 into trans and cis butenes-2 [16]. A continuation of these studies is the present paper where, we compared the activity of cerium-zinc oxide catalysts in the reactions of the conversion of ethanol to acetone and the isomerization of butene-1 into trans and cis butenes-2.

## Experimental technique

Binary cerium-zinc oxide catalysts of various compositions were prepared by coprecipitation of aqueous solutions of cerium 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 completely released. The resulting solid mass was calcined at 700°C for 10 hours. Thus, we synthesized nine binary cerium-zinc oxide catalysts of various compositions from Ce-Zn=1-9 to Ce-Zn=9-1. The activity of the synthesized catalysts in the reaction of the conversion of ethanol to acetone was studied on a flow unit with a quartz reactor in the temperature range of 250–700°C. The volumetric feed rate of the raw material was 1800 $h^{-1}$. The ratio of ethanol : steam : nitrogen was 1:1:8. 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 yields of ethanol conversion products, as well as the amount of unreacted ethanol, were determined on a chromatograph with a flame ionization detector and a 2-m 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. The isomerization reaction of butene-1 to butene-2 was carried out at a feed space velocity of 1200 $h^{-1}$, in the temperature range of 150–400°C. The reactor was loaded with 5 ml of a catalyst with grains of 1–2 mm, and a reaction mixture of butene-1 and nitrogen was fed. The ratio of butene-1 to nitrogen was 1:9. The analysis of the mixture of unreacted butene-1 and the resulting trans and cis butenes-2 was carried out by chromatography using a 5-meter column filled with celite coated with Vaseline oil.

## Results and discussions

The results of the experiments showed that the reaction products of the conversion of ethyl alcohol on binary cerium-zinc oxide catalysts are ethylene, acetaldehyde, acetone, carbon dioxide and, at high temperatures, destructive decomposition products. We have studied the effect of temperature on the yields of reaction products. As an example, Table 1 shows the results of a study of the oxidation reaction of ethanol on the catalyst Ce-Zn=2-8. As can be seen, the conversion of ethanol on this catalyst begins at a temperature of 300°C. At this temperature, 0.8% acetaldehyde is formed. With increasing temperature, the yield of acetaldehyde increases and at 400°C reaches its maximum value of 8.8%, after which it decreases to 2.8% at 450°C. The formation of ethylene and acetone begins at 350°C, their yields at this temperature are 1.2% and 3.1%, respectively. With an increase in the reaction temperature, the yield of acetone passes through a maximum at a temperature of 500°C (63.7%). The yield of carbon dioxide increases throughout the studied temperature range and at 550°C is 9.9%. The ethanol conversion on this sample reaches 89.8% at 550°C.

**Table 1.** Conversion of ethanol to acetone on the catalyst Ce-Zn=2-8

| Temperature, °C | Yields of the reaction products, % | | | | Selectivity by acetone, % | Conversion, % |
|---|---|---|---|---|---|---|
| | $CO_2$ | $C_2H_4$ | $CH_3CHO$ | $CH_3COCH_3$ | | |
| 300 | 0 | | 0,8 | 0 | 0 | 0,8 |
| 350 | 1,2 | 0 | 6,3 | 3,1 | 29,3 | 10,6 |
| 400 | 2,5 | 1,1 | 8,8 | 13,3 | 51,8 | 25,7 |
| 450 | 8,1 | 9,9 | 2,8 | 47,5 | 69,5 | 68,3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 500 | 9,5 | 14,5 | 0 | 63,7 | 72,6 | 87,7 |
| 550 | 9,9 | 23,9 | | 55,2 | 61,5 | 89,8 |

The activity of binary cerium-zinc oxide catalysts also depends on the atomic ratio of cerium to zinc. Table 2 shows the dependences of the yields of the reaction products of the vapor phase conversion of ethanol on the Ce/Zn atomic ratio at a temperature of 350°C. As can be seen from Table 2, with an increase in the atomic ratio of cerium to zinc, the yield of acetone at first does not change, and then, starting from the Ce-Zn=6-4 sample, it begins to increase and reaches 27.3% for the Ce-Zn=8-2 sample. The yield of acetaldehyde decreases with an increase in the atomic ratio of cerium to zinc, and its formation is practically not observed on samples with a Ce/Zn atomic ratio above 4/6. The yields of carbon dioxide and ethylene increase with an increase in the atomic ratio of cerium to zinc. It can be seen from the obtained results that at 350°C the maximum yields of carbon dioxide and ethylene are 7.3 and 5%, respectively. The maximum conversion of ethanol at a given temperature is observed on a sample with a ratio of Ce-Zn=8-2 and reaches 38.3%.

**Table 2.** Dependences of the yields of the products of ethanol conversion on the atomic ratio of cerium to zinc. T= 350°C

| Atomic ratio Ce/Zn | 1:9 | 2:8 | 3-7 | 4:6 | 5:5 | 6:4 | 7:3 | 8:2 | 9:1 |
|---|---|---|---|---|---|---|---|---|---|
| Reaction products | Reaction product yields, % | | | | | | | | |
| $CO_2$ | 0 | 1,2 | 0,7 | 3,2 | 2,6 | 2,8 | 4,2 | 6,3 | 7,3 |
| $C_2H_4$ | 0 | 0 | 0 | 0 | 0 | 1,2 | 2,3 | 3,7 | 5 |
| $CH_3CHO$ | 8,9 | 6,3 | 5,5 | 0 | 0 | 0 | 0 | 0 | 0 |
| $CH_3COCH_3$ | 3,5 | 3,1 | 5,4 | 3,3 | 2,8 | 11,2 | 11,7 | 27,3 | 21,9 |
| Selectivity by acetone, % | 28,2 | 29,2 | 28,4 | 50,8 | 51,9 | 73,7 | 64,3 | 71,3 | 64,0 |
| Conversion | 12,4 | 10,6 | 11,6 | 6,5 | 5,4 | 15,2 | 18,2 | 38,3 | 34,2 |

A different picture of the dependence of the yields of ethanol conversion products on the composition of the catalysts is observed at higher temperatures. Table 3 shows the dependences of the yields of reaction products on the Ce/Zn atomic ratio in catalyst samples at 500°C. As can be seen from Figure 3, the dependences of ethanol conversion and acetone yield on the atomic ratio of cerium to zinc have two maxima on the catalysts Ce-Zn=2-8 and Ce-Zn=7-3. The maximum conversion of ethanol is observed on the sample Ce-Zn=2-8 and is 87.7%. The highest yield of acetone is also observed on the Ce-Zn=2-8 sample and is equal to 63.7%. The yield of carbon dioxide slightly increases with an increase in the atomic ratio of cerium to zinc and varies between 8.1% and 14.7. Ethylene yield tends to increase with increasing Ce/Zn atomic ratio and varies from 14.5% to 37.8%.

**Table 3.** Dependences of the yields of ethanol conversion products on the atomic ratio of cerium to zinc. T= 500°C

| Atomic ratio Ce/Zn | 1:9 | 2:8 | 3-7 | 4:6 | 5:5 | 6:4 | 7:3 | 8:2 | 9:1 |
|---|---|---|---|---|---|---|---|---|---|
| Reaction products | Reaction product yields, % | | | | | | | | |
| $CO_2$ | 8,9 | 9,5 | 8,1 | 13,1 | 9,8 | 13,4 | 14,7 | 13,7 | 12,2 |
| $C_2H_4$ | 20,3 | 14,5 | 22,1 | 30,5 | 21,9 | 34,2 | 37,8 | 36,4 | 35,5 |
| $CH_3CHO$ | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 |
| $CH_3COCH_3$ | 46,9 | 63,7 | 40,4 | 27,3 | 24,6 | 24,8 | 30,4 | 22,1 | 15,3 |
| Selectivity by acetone, % | 61,6 | 72,6 | 52,7 | 38,5 | 43,7 | 34,3 | 36,6 | 30,6 | 23,8 |
| Conversion | 76,1 | 87,7 | 76,6 | 70,9 | 56,3 | 72,4 | 82,9 | 72,2 | 64,3 |

Thus, the conducted studies have shown that the highest yield of acetone is observed on samples rich in zinc at temperatures of the order of 450-550°C. Cerium-rich catalysts are active in the dehydration of ethanol to ethylene.

It is known that the acid–base properties of solid catalysts in heterogeneous catalysis affect their activity and selectivity in many catalytic reactions [16–18]. In this regard, we evaluated the acidic properties of cerium-zinc oxide catalysts by their activity of butene-1 isomerization reaction into trans and cis butenes-2. Figure 1 shows the results of a study at a temperature of 450°C of the butene-1 isomerization reaction on the studied catalysts. It can be seen that on samples with the atomic ratio Ce-Zn=1-9 and Ce-Zn=2-8, the yields of trans and cis butenes-2 are 3.4 and 3.1%, respectively. With a further increase in the atomic ratio of cerium to zinc, the yields of trans and cis butenes-2 increase and starting from the Ce-Zn=7-3 sample, a sharp increase in the yields of butenes-2 up to almost 50% is observed. It should be noted that the ratio of the yields of trans and cis butenes-2 is approximately equal to unity.

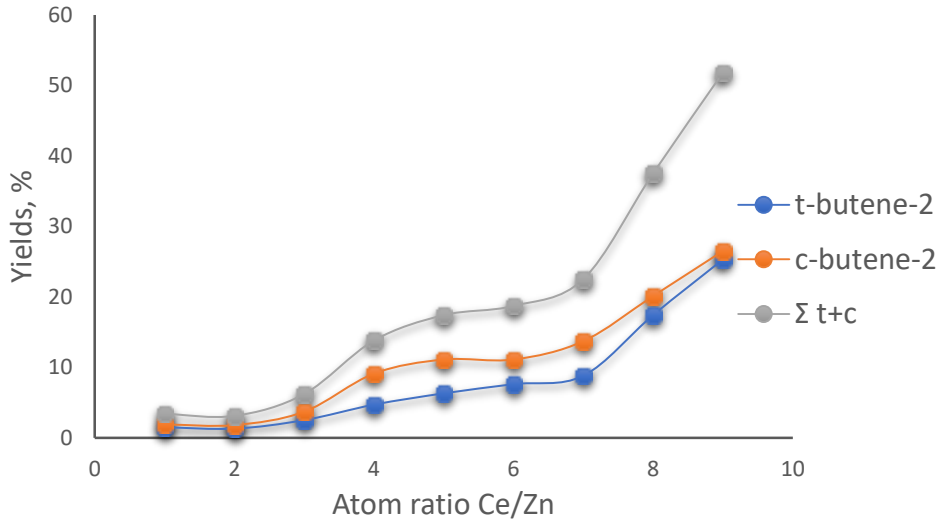


**Fig.1.** Dependences of the degree of isomerization of butene-1 to butenes-2 on the atomic ratio of cerium to zinc. T=450°C.

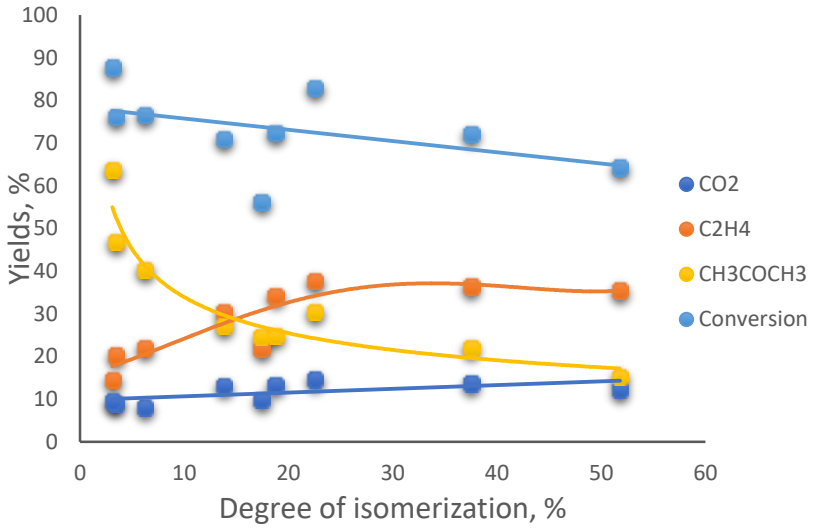


**Fig.2.** Dependences of the yields of ethanol conversion products on the degree of isomerization of butene-1 to butenes-2. T=450°C

In paper [15] it is assumed that the total surface acidity is determined by the total rate of butene-2 formation. At the same time, according to [19] the formation of trans-butene-2 occurs on the Bronsted centers, and the formation of cis-butene-2 on the Lewis acid centers. Thus, based on the results obtained we can say that the isomerization rate of butene-1 (total surface acidity) on cerium-zinc oxide catalysts with increasing atomic ratio of cerium to zinc increases and the surface has approximately the same number of Bronsted and Lewis centers (yields of trans and cis butenes-2 are approximately equal).

Dependences of yields of ethanol conversion reaction products on butene-1 isomerization degree to butenes-2, i.e. on total surface acidity of binary cerium-zinc oxide catalysts are presented in Figure 2. As can be seen from Fig. 2 increasing the activity of cerium-zinc oxide catalysts in butene-1 isomerization reaction (with increase of total acidity) ethylene yield increases, while acetone yield and total ethanol conversion decreases. This suggests that increasing surface acidity leads to a decrease in the reaction rate of vapor-phase conversion of ethanol to the target product – acetone. Based on this, we can say that the reaction of the conversion of ethanol to acetone proceeds on the centers of the basic nature, and the formation of ethylene proceeds on the centers of the acidic nature.

## Conclusions

- The highest yield of acetone is observed on samples rich in zinc at temperatures of the order of 450-550°C, while catalysts rich in cerium are active in the reaction of dehydration of ethanol to ethylene. Thus, the highest yield of acetone (63.7%) is observed on the sample Ce-Zn=2-8, while the maximum yield of ethylene (36.4%) is observed on the catalyst Ce-Zn=8-2.
- With increasing total acidity of cerium-zinc oxide catalysts (with increasing yields of trans and cis butenes-2) ethylene yield increases, while acetone yield and total ethanol conversion decreases. Based on this we can say that the reaction of conversion of ethanol to acetone proceeds on the centers of basic nature, while the formation of ethylene proceeds on the centers of acid nature.

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## Ce-Zn-O KATALİZATORLARININ AKTİVLİYİNİN ETANOLUN ASETONA ÇEVRİLMƏSİ REAKSİYASINDA SƏTHİN TURŞU XÜSUSİYYƏTLƏRİNDƏN ASILILIĞI

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**Xülasə:** Binar serium-sink oksid katalizatorları üzərində etanolun asetona çevrilməsi reaksiyası öyrənilmişdir. Müəyyən edilmişdir ki, etil spirtinin binar serium-sink oksid katalizatorları üzərində çevrilməsi reaksiyasının məhsulları etilen, sirkə aldehidi, aseton, karbon qazı və, yüksək temperaturlarda, destruktiv parçalanma məhsullarıdır. Asetonun ən yüksək çıxımı sinklə zəngin olan nümunələrdə 450-550$^{o}$C temperatur aralığında müşahidə olunur, halbuki seriumla zəngin olan katalizatorlar etanolun etilenə dehidratasiyası reaksiyasında aktivdir. Bu işdə serium-sink oksid katalizatorlarının turşu xüsusiyyətləri buten-1-in trans və sis buten-2-yə izomerləşməsi reaksiyasında aktivliyinə görə qiymətləndirilmişdir. Aşkar edilmişdir ki, seriumla zəngin

katalizatorlar buten-1-in izomerləşmə reaksiyasında aktivdir. Serium-sink oksin katalizatorlarının etanolun asetona çevrilməsi reaksiyasında və buten-1-in trans və sis buten-2-yə izomerləşməsi reaksiyasında aktivliyi müqayisə olunmuşdur. Aşkar edilmişdir ki, etanolun asetona çevrilməsi reaksiyası əsas təbiətli, etilenin alınması isə turşu təbiətli mərkəzlərdə gedir.
**Açar sözlər:** Etanol, aseton, binar katalizatorlar, buten-1-in izomerləşməsi, sink oksid, natrium oksid.

## ЗАВИСИМОСТЬ АКТИВНОСТИ Ce-Zn-O КАТАЛИЗАТОРОВ В РЕАКЦИИ ПРЕВРАЩЕНИЯ ЭТАНОЛА В АЦЕТОН ОТ КИСЛОТНЫХ СВОЙСТВ ПОВЕРХНОСТИ

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**Аннотация:** Изучена реакция превращения этанола в ацетон на бинарных церий-цинк оксидных катализаторах. Установлено, что продуктами реакции превращения этилового спирта на бинарных церий-цинк оксидных катализаторах являются этилен, уксусный альдегид, ацетон, углекислый газ и при высоких температурах продукты деструктивного разложения. Наибольший выход ацетона наблюдается на образцах, богатых цинком, при температурах порядка 450-550°C, в то время как катализаторы, богатые церием, активны в реакции дегидратации этанола в этилен. В работе оценены кислотные свойства церий-цинк оксидных катализаторов по их активности в реакции изомеризации бутена-1 в транс и цис бутены-2. Найдено, что катализаторы, богатые церием, активны в реакции изомеризации бутена-1. Сопоставлена активность церий-цинк оксидных катализаторов в реакциях превращения этанола в ацетон и изомеризации бутена-1 в транс и цис бутены-2. Найдено, что реакция превращения этанола в ацетон протекает на центрах основной природы, а образование этилена протекает на центрах кислотной природы.
**Ключевые слова:** Этанол, ацетон, бинарные катализаторы, изомеризация бутена-1, оксид цинка, оксид церия.