Section 3. Chemistry

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ETHANOL CONVERSION TO ACETONE ON BINARY ZR-ZN-O CATALYSTS

Abstract. The effect of zirconium oxide additives on the activity of zinc oxide in the reaction of ethanol conversion to acetone has been studied. It is shown that the highest yield of acetone is observed on samples rich in zinc at temperatures about 450–550 °C. It was found that the dependences of the yield of acetone and the conversion of ethanol on the atomic ratio of cerium to zinc have the form of a curve with two maxima.

Keywords: Ethanol, acetone, binary catalysts, zinc oxides, zirconium oxides.

Introduction

In regards with the transition to the use of renewable sources of raw materials, interest is growing in ethanol conversion reactions to obtain substances valuable for industry. Thus, ethanol is obtained in large quantities from plant raw materials [1; 2]. One of the interesting reactions of ethanol conversion is the obtaining of acetone [3; 4]. Acetone is one of the most important monomers widely used in the petrochemical industry. 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 show a high activity of the reaction of the ethanol conversion to acetone [5; 6]. It is also known that zirconium-based catalysts are often used as catalysts for various reactions [7; 8]. In this regard, in this work, the effect of zirconium additives on the activity of zinc oxide in the reaction of the conversion of ethanol to acetone was studied.

Experimental technique

Binary zirconium-zinc oxide catalysts of various compositions were prepared by coprecipitation of 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 completely released. The resulting solid mass was calcined at 700 °C for 10 hours. The activity of the synthesized catalysts was studied on a flow unit with a quartz reactor in the temperature range of 250–700 °C. Thus, nine binary cerium-zinc oxide catalysts of various compositions from Z_r–Z_n = 1–9 to Z_r–Z_n = 9–1 were synthesized. Five ml of the studied catalyst 1.0––2.0 mm in size was loaded into the reactor, and its activity in the ethanol steam conversion 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.

Results and discussion

Our preliminary studies have established that the reaction products of the conversion of ethyl alcohol on binary zirconium-zinc oxide catalysts are ethylene, acetaldehyde, acetone, carbon dioxide, as well as destructive decomposition products at high temperatures.

The results of study of ethanol conversion on a catalyst with the atomic ratio $\frac{Z_r}{Z_n} = \frac{1}{9}$ are shown in Figure 1. As can be seen from the figure, the ethanol conversion reaction starts at the temperature of 300 °C with the formation of acetaldehyde in the amount of 1.2%. With a further increase in temperature, the yield of acetaldehyde passes through a maximum at 400 °C equal to 12.6%. An increase in the reaction temperature leads to the formation of other reaction products. Thus, the formation of another main reaction product, acetone, begins at 350 °C, and its yield at this temperature is 1.2%. Carbon dioxide also begins to form at 350 °C, and as the temperature rises to 500 °C, its yield increases from 0.9% to 9.9%. Ethylene also begins to form at 350 °C in an amount of 0.3%, and its yield increases with increasing temperature and reaches 4.1% at 550 °C. The highest conversion of ethanol on this sample reaches 37.3% at a temperature of 550 °C.

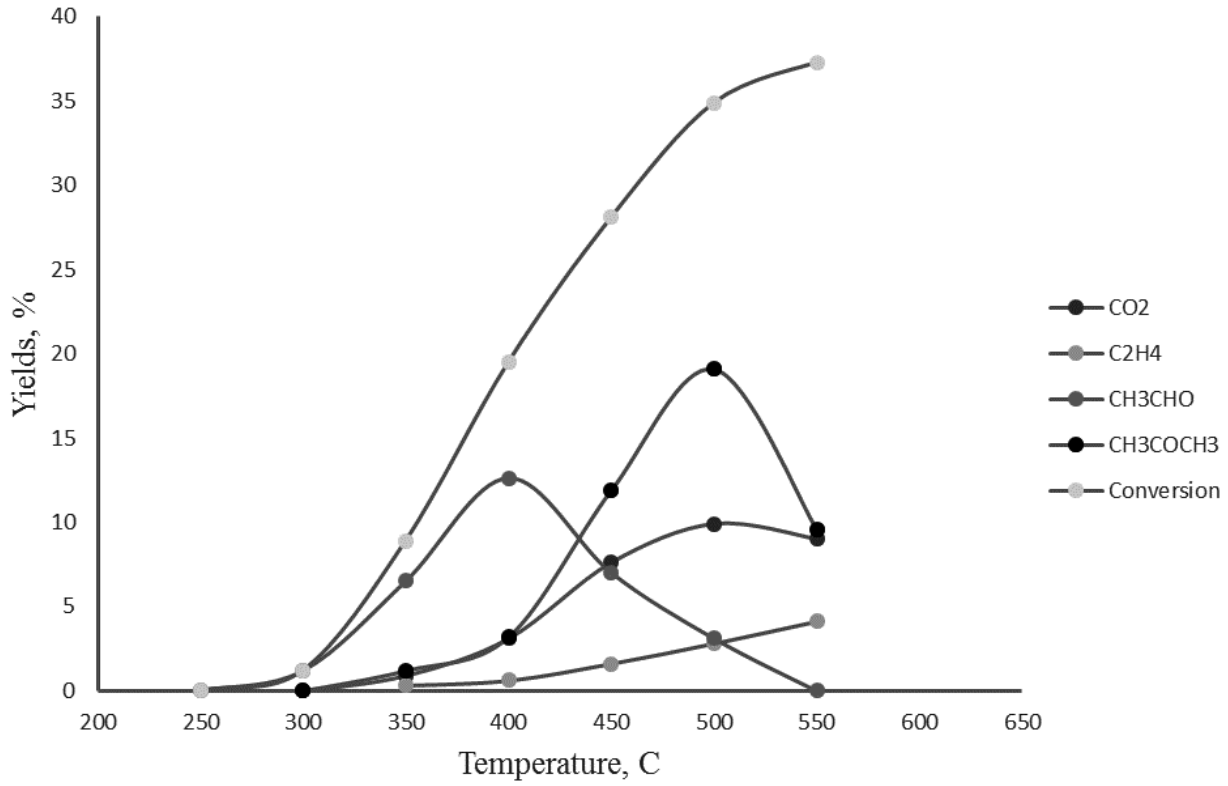

Figure 1. Dependence of the yields of reaction products on temperature on the catalyst with an atomic ratio $\frac{Z_r}{Z_n} = \frac{1}{9}$

The composition of the binary Z_r–Z_n–O catalyst also significantly affects the yield and distribution of ethanol conversion reaction products. Figure 2 shows the dependences of the yields of ethanol conversion reaction products on the $\frac{Z_r}{Z_n}$ atomic ratio at a reaction temperature of 350 °C. As can be seen from Figure 2, with an increase in the $\frac{Z_r}{Z_n}$ atomic ratio, the yield of acetaldehyde passes through two maxima on samples Z_r–Z_n = 2–8 and Z_r–Z_n = 7–3. The highest yield of acetaldehyde is observed on the $\frac{Z_r}{Z_n} = \frac{2}{8}$ sample and is equal to 22.6%. The yield of another target product of the reaction, acetone, increases with an increase in the atomic ratio of zirconium to zinc in the composition of the catalyst. The maximum yield of acetone is observed on the Z_r–Z_n=9–1 catalyst and is equal to 24.5%. It can be seen from the data obtained that carbon dioxide and ethylene are practically not formed at a temperature of 350 °C. The maximum conversion of ethanol at this temperature does not exceed 40%.

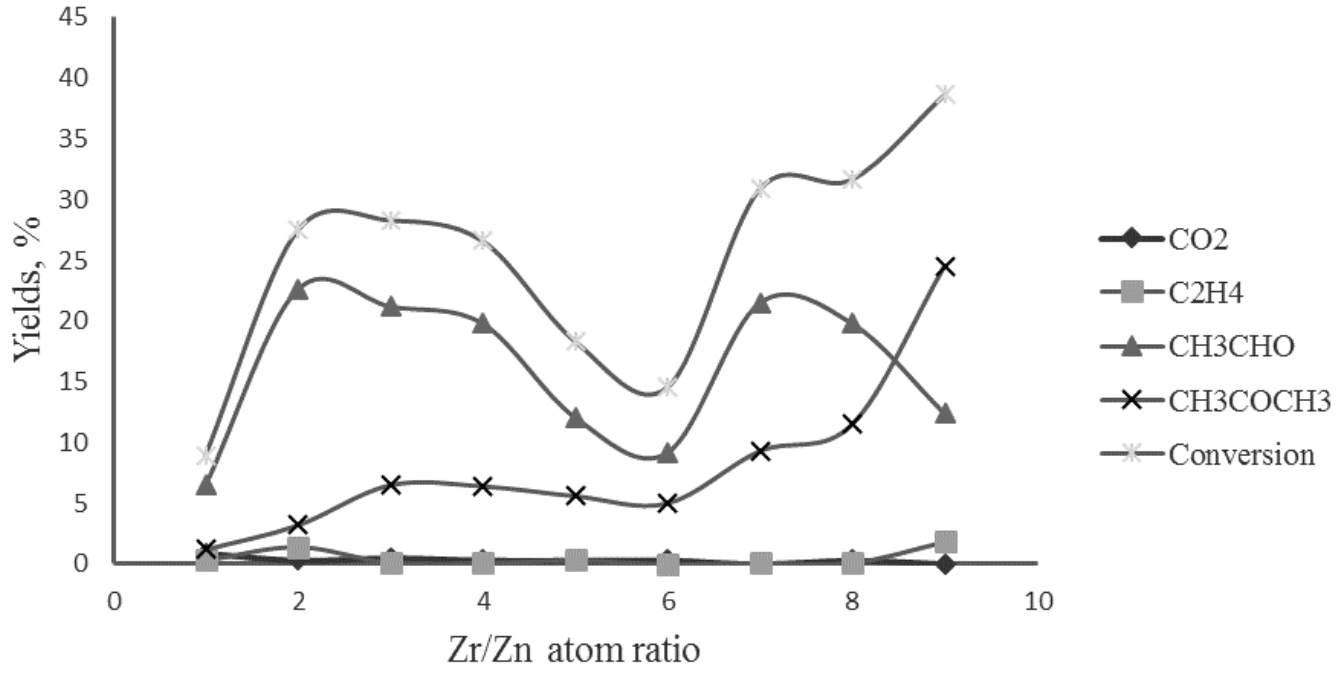

Figure 2. Dependence of yields of reaction products on the atomic ratio of $\frac{Z_r}{Z_n}$ at 350 °C

At higher temperatures, different picture of the dependence of the yields of reaction products on the $\frac{Z_r}{Z_n}$ atomic ratio is observed. The results of studying the dependence of the reaction product yields on the $\frac{Z_r}{Z_n}$ atomic ratio at 500 °C are shown in Figure 3. It can be seen from the figure that at this temperature, the dependence of the acetone yield and ethanol conversion on the $\frac{Z_r}{Z_n}$ atomic ratio has the form of a curve with two maxima on the samples Z_r–Z_n = 3–7 and Z_r–Z_n = 8–2. The highest acetone yield and ethanol conversion are observed on the Z_r–Z_n = 8–2 catalyst and are 58.2 and 84.9%, respectively. The yields of acetaldehyde, ethylene, and carbon dioxide slightly depend on the atomic ratio of zirconium to zinc and do not exceed 14.5%.

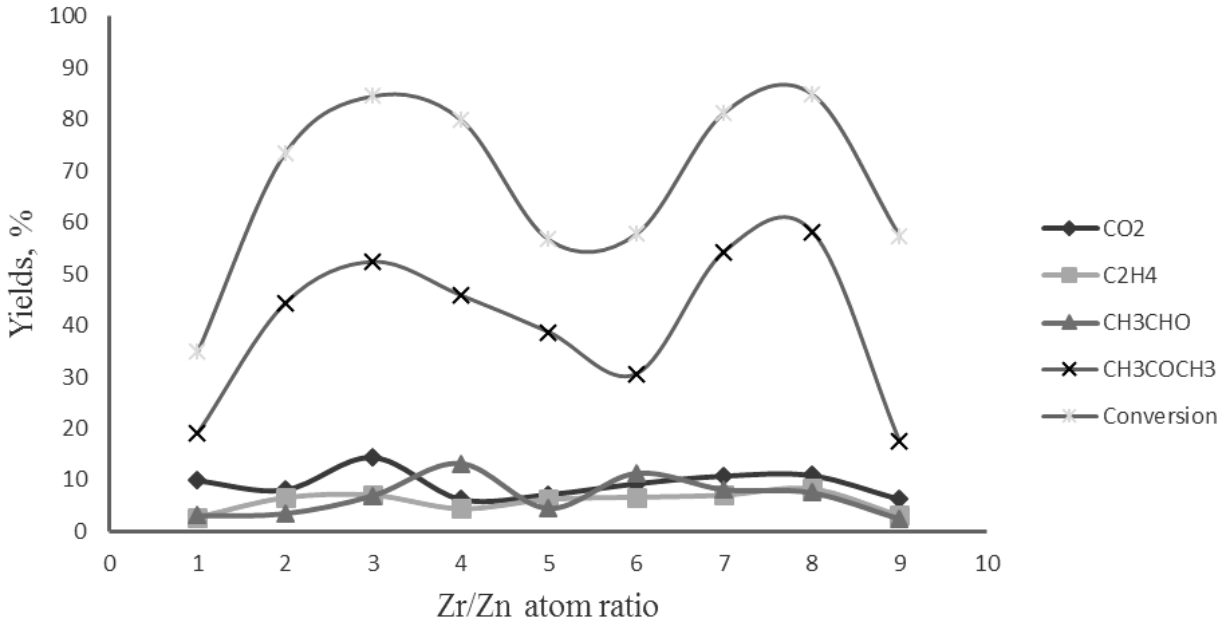

Figure 3. Dependence of yields of reaction products on atomic ratio $\frac{Z_r}{Z_n}$ at 500 °C

Based on the conducted studies, it can be said that catalysts with a predominance of zirconium or zinc at temperatures about 450–550 °C exhibit high activity in the reaction of acetone formation. The maximum yield of acetone on Z_r–Z_n–O catalysts reaches 58.2%.

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