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

Abstract. The effect of cerium oxide additives on the activity of zinc oxide in the reaction of ethanol conversion to acetone has been studied. 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 oxide, cerium oxide.

Introduction

Acetone is one of the most important monomers widely used in the petrochemical industry. One of the interesting methods for obtaining acetone is 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, in this work, we studied the effect of cerium oxide on the activity of zinc oxide in the reaction of the ethanol conversion to acetone.

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. 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 Ce-Zn=1–9 to Ce-Zn=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

The conducted studies have shown that the reaction products of ethyl alcohol conversion on binary cerium-zinc oxide catalysts are ethylene, acetaldehyde, acetone, carbon dioxide, and, at high temperatures – destructive decomposition products. Figure 1 shows the results of a study of the reaction of the conversion of ethyl alcohol on the catalyst Ce-Zn=1–9. As can be seen from Figure 1, the ethyl alcohol conversion reaction starts at a temperature of 300 °C and only acetaldehyde is formed in an amount of 5.5%. As the reaction temperature increases, the yield of acetaldehyde passes through a maximum, and the
reaction selectivity for acetaldehyde decreases from 100% to 2.9%. As can be seen from the data obtained (Figure 1), the maximum yield of acetaldehyde is 10% with a selectivity of 40.8%. An increase in the reaction temperature leads to the formation of other reaction products. The formation of ethylene and carbon dioxide begins at a temperature of 400 °C and with increase in temperature their yields increase, reaching 33.4% and 12.2%, respectively, at 500 °C. The formation of acetone begins at a temperature of 350 °C, while its yield is 3.5%. Figure 1 shows that the yield of acetone passes through a maximum at a temperature of 500 °C (46.9%). With an increase in the reaction temperature, the yield of carbon dioxide, a product of the deep oxidation of ethyl alcohol, increases over the entire temperature range studied. Thus, the maximum yield of carbon dioxide on cerium oxide at 550 °C is 12.2%. The selectivity of the conversion of ethanol to acetone decreases with increasing reaction temperature from 55% at 350 °C to 15% at 550 °C. The maximum conversion of ethanol on this catalyst reaches 79.4% at 550 °C. Similar results were obtained for other binary cerium-zinc oxide catalysts.

Preliminary experiments showed that the activity of binary cerium-zinc oxide catalysts, in addition to the reaction temperature, also depends on the atomic ratio of cerium to zinc.

![Figure 1. Dependence of the yields of reaction products on temperature on a catalyst with an atomic ratio Ce-Zn=1–9](image)

Figure 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. The target product of the reaction, acetone, is formed on all the studied samples. As can be seen from Figure 1, 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% on 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 not observed on samples with a Ce/Zn atomic ratio above 4/6.

It can be seen from the figure that, in all the samples studied, the yields of carbon dioxide and ethylene increase with an increase in the atomic ratio of cerium to zinc. The formation of carbon dioxide is not observed on the sample Ce-Zn=1–9. This amount increases with increasing cerium content in the sample and reaches 9.1% for a sample with a ratio of Ce/Zn=9/1. It can be
seen from the results obtained that at 350°C ethylene is not formed on the first five samples. The maximum yields of carbon dioxide and ethylene at 35 °C 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%.

A different picture of the dependence of the yields of ethanol conversion products on the composition of the catalysts is observed at higher temperatures. Figure 3 shows the dependences of the reaction product yields on the Ce/Zn ratio in the 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 the form of a curve with 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 within 8.1% (for the sample Ce/Zn=3/7) and 14.7 (for the sample Ce/Zn=7/3). The yield of ethylene tends to increase with increasing atomic ratio Ce/Zn and varies from 14.5% (on the sample Ce/Zn=2/8) to 37.8% (on the sample Ce/Zn=7/3).

Thus, based on the studies carried out, it can be said that the highest yield of acetone is observed on samples rich in zinc at temperatures about 450–550 °C. Cerium-rich catalysts are active in the dehydration of ethanol to ethylene. 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.

References: