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# CATALYTIC CONVERSION OF BIO-ETHANOL TO ETHYLENE

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**Abstract**

*Catalytic conversion of ethanol to ethylene on Cu-, Cr- and Ce- containing catalysts supported on alumina was investigated.Cerium-containing catalysts were studied by electron microscopy and defined phases and particle sizes.Optimal conditions (W = 6000 $h^{-1}$, $C_{ethanol}$ = 19.7 $g/m^3$ and T = 400°C) of the catalytic conversion of ethanol into ethylene in 82% yield with 94% ethanol conversion with 87.2% selectivity were found.*

**Key words:** *ethanol, dehydration, ethylene, catalyst*

## 1. INTRODUCTION

The intensive use of fossil hydrocarbon energy sources leads to a gradual depletion of our planet.Therefore, the search for alternative sources of raw materials is the most urgent task of the modern science and industry [1-3]. Bioethanol is the most promising renewable raw materials with almost unlimited reserves which meet modern environmental standards for chemical raw materials and from which receive the broad spectrum of intermediate and target products of large-scale petrochemical and fine chemicals. Plants containing starch (potatoes, wheat, corn, etc.), as well as waste of wood, pulp and paper industry, field crops and livestock can be the raw material for the production of bioethanol [4].

The use of bioethanol as a motor fuel is complicated by the limited use in cold regions. In this regard, the researchers focused on creating of technological bases of the catalytic conversion of bioethanol to produce hydrocarbons of gasoline range, aromatic hydrocarbons, hydrogen containing gasand olefins (ethylene, propylene, etc.) [5, 6].

Olefins are widely used in industry [7, 8]. Due to the presence of double bond the olefins are reactive which makes them important product in the various processes of organic chemistry. For example, ethylene is the most demanded intermediate chemicals. Petrochemical potential of individual countries is assessed in terms of production of lower olefins - ethylene and propylene, which are the basic chemical raw materials for the production of polyethylene, polypropylene, plastics, styrene and other products.According to forecasts of Nexant Inc. consultancy world consumption of ethylene in the next 10 years will increase from 100 million tons to 160 million tons per year.Demand for polyethylene will increase from 60 million tons to 100 million tons, and for polypropylene - from 40 million tons to 60 million tons a year.

At present, almost all ethylene produced by the pyrolysis of naphtha and liquefied petroleum gas (propane-butane fraction).This process is endothermic and requires a high temperature reaction - 780-1200°C.Water vapor in the ratio of 1:1 is used as a coolant.Evaluation of industrial emissions has shown [9] that the 180 million tons of carbon dioxide $CO_2$ is released into the atmosphere during the production of ethylene by such technology.Therefore, the problem of obtaining of the $C_2$-$C_4$ olefins

from $C_1$-$C_4$ alcohols becomes relevant due to the high price of crude oil, because of environmental concerns and the decline of natural resources and their uneven distribution in the different regions.

## 2. EXPERIMENTAL

In this work was studied the catalytic conversion of ethanol on flow installation. The experimental setup is shown in Fig. 1. To study the activity of the synthesized catalysts a portion of catalyst (4 ml) was loaded into the reactor. The upper and lower part of the reactor was filled with quartz particles.

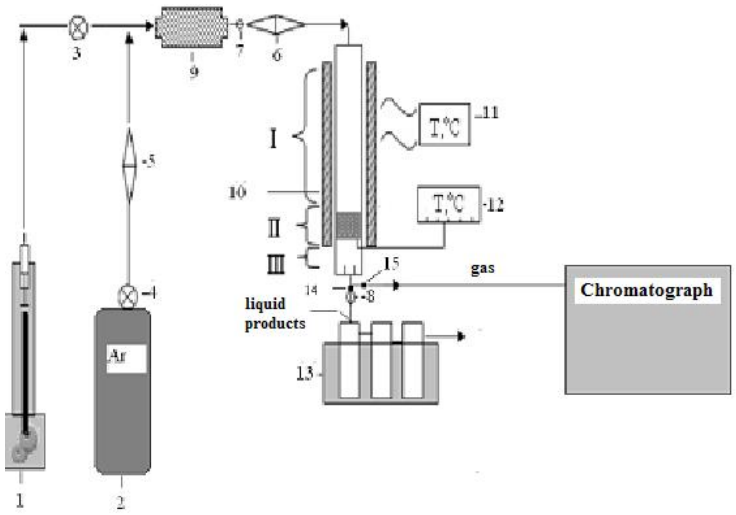


**Fig. 1.** Diagram of flow installation of dehydration of ethanol.1 - batcher for supply of ethanol, 2 - cylinder with an inert gas, 3.4 - taps, 5.6 - rheometers, 7.8 - samplers, 9 - mixer, 10 - quartz reactor with electric heating, 11 - temperature control, 12 - unit temperature measuring, 13 - bubblers, 14.15 - clamps; I - area of preheating mixture; II - reaction zone; III - refrigerator.

The gaseous reaction products (ethylene, propylene, butylene, etc.) were analyzed on chromatograph "Chromatek-Crystal 5000M" with a capillary column CP-Sil 5 CB. Analysis of the liquid products of the reaction and the initial mixture was carried out on a column filled with sorbent DB-1 № 128-1052.

Dehydration of ethanol was studied on supported Cu -, Cr -, and Ce – containing catalysts as well as on Ce-containing catalyst modified by lanthanum.The catalysts were prepared by incipient wetness impregnation of the support, followed by drying at room temperature and at 300°C and calcination at 500°C for three hours.The catalysts were reduced in a flow of hydrogen at 500°C for 60 minutes.

## 3. RESULTS AND DISCUSSION

The conversion of ethanol into ethylene was studied on 3% Cu catalyst supported on carriers (CL > 70%), CaA and $\gamma$-$Al_2O_3$ in the temperature range from 250 to 450°C and the space velocity 3000 $h^{-1}$. On the whole temperature range during dehydration of ethanol on all catalytic systems is formed ethylene. The results of these experiments are shown in Fig. 2. The figure shows that the variation of reaction temperature increases the activity of catalyst regardless of the nature of carrier; the maximum

yield of the main product is observed at 400°C. The increase of reaction temperature from 250 to 400°C increases the yield of desired product on all catalysts. Further increase of reaction temperature on 50°C reduces the activity of catalyst with respect to ethylene. Supporting of copper oxide on clinoptilolite (CL > 70%) reduces the activity of carrier; ethylene yield decreases from 20 to 10%. The activity of copper oxide on CaA slightly increased; the yield of ethylene is increased from 28 to 35% compared to pure support without the active phase. The positive effect is observed at supporting of copper oxide on γ-$Al_2O_3$; ethylene yield increases from 35 to 75%, the selectivity of ethylene was 94.9% for the conversion of ethanol 79%.

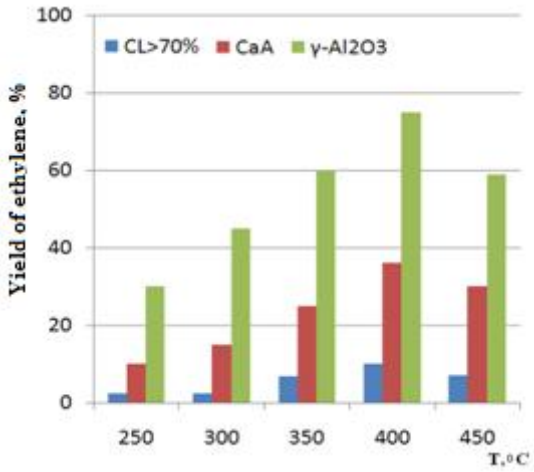


**Fig. 2.** Effect of reaction temperature on the yield of ethylene.

We have also studied the activity of other transition metals such as chromium and cerium on the formation of products in the dehydration reaction of ethanol on the best carrier γ-$Al_2O_3$.

Effect of the nature of 3% Cr/γ-$Al_2O_3$ catalyst on formation of products in the dehydration reaction of ethanol were carried out in the temperature range from 250 to 450°C and space velocity of reaction mixture 3000 $h^{-1}$.The experimental results are shown in Table 1 which shows that with increasing reaction temperature from 250 to 450°C the conversion of ethanol increases from 13 to 86%.Ethylene is produced at a reaction temperature 250°C on the 3% Cr/γ-$Al_2O_3$ catalyst with yield 10.4% at 13% ethanol conversion and selectivity of 80%. Increasing the reaction temperature on the 50°C increases the yield of the desired product ethylene is almost 4 times.Ethylene yield reached 49.3% with selectivity of 91.3% and 54% ethanol conversion. Propylene is produced in the reaction products in small amounts (0.74%).Methane and ethane are formed in the reaction products other than ethylene and propylene at 350°C with yield 0.44% and 0.40%, respectively. At this temperature the conversion of ethanol is 71%, yield of ethylene - 66%, propylene - 2.5% with selectivity of 92.3% and 3.5%, respectively.The highest yield of the desired product ethylene (76.3%) was observed with increasing the reaction temperature to 400°C; the conversion of ethanol is 83%, the selectivity by ethylene - 91.9% which is slightly lower than the selectivity at 350°C.

**Table 1.** Effect of reaction temperature on the yield of products of dehydration of ethanol on the catalyst 3% Cr/γ-$Al_2O_3$.

| T | $X_{EtOH}$,% | Concentration of the products ,% | | | | | Selectivity ,% | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ |
| 250 | 13 | - | 10,4 | - | - | - | - | 80,0 | - | - | - |
| 300 | 54 | - | 49,3 | - | 0,74 | - | - | 91,3 | - | 1,4 | - |
| 350 | 71 | 0,44 | 66,0 | 0,4 | 2,5 | - | 0,62 | 92,3 | 0,6 | 3,5 | - |
| 400 | 83 | 0,87 | 76,3 | 0,69 | 3,4 | - | 1,0 | 91,9 | 0,83 | 4,1 | - |
| 450 | 86 | - | 69,5 | 4,4 | 5,5 | 0,55 | - | 80,8 | 5,1 | 6,4 | 0,6 |

Propane is formed with increasing temperature up to 450 ° C in small amounts (0.55%).Ethanol conversion reaches 86%, the yield of ethylene as well as the selectivity decreases, reaching 69.5% and 80.8%, respectively.

Activity of the 3% Ce/γ-$Al_2O_3$catalyst in dehydration of ethanol in the temperature range from 250 to 450°C has been studied.The results show (Table 2) that ethylene is formed in products at the reaction temperature 250°C with yield 39.9% and selectivity of 95% while the conversion of ethanol is 42%.Propylene (0.70%) appears in the reaction products other than ethylene with increasing the reaction temperature up to 300°C.The conversion of ethanol increased to 59%, the yield of ethylene reaches 56%.Ethylene (67%) and propylene (4.5%) are formed at the reaction temperature 350°C in the reaction products.The highest yield of ethylene - 80% is observed at reaction temperature of 400°C, the selectivity by ethylene was 91.9% at the conversion of ethanol 87%.Starting from 400°C, except for ethylene and propylene in the small quantities (0.38%) produced ethane.A further increase in the reaction temperature up to 450°C leads to decrease in product yield to 75%, the conversion of ethanol is 90%.The data show that 400°C is the best temperature on studied catalysts for dehydration of ethanol.

**Table 2.** Effect of reaction temperature on the yield of products of dehydration of ethanol on the catalyst 3% Ce/γ-$Al_2O_3$.

| T | $X_{EtOH}$,% | Concentration of the products,% | | | | | Selectivity,% | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ |
| 250 | 42 | - | 39,9 | - | - | - | - | 95 | - | - | - |
| 300 | 59 | - | 56 | - | 0,70 | - | - | 95 | - | 1,2 | - |
| 350 | 75 | - | 67 | - | 4,5 | - | - | 89,3 | - | 0,6 | - |
| 400 | 87 | - | 80 | 0,38 | 3,8 | - | - | 91,9 | 0,4 | 4,4 | - |
| 450 | 90 | 1,0 | 75 | 0,62 | 3,3 | - | 1,11 | 83,3 | 0,7 | 3,7 | - |

The effect of 1% lanthanum on activity of 3% Ce/γ-$Al_2O_3$ catalyst in the temperature range 250 450°C and space velocity 1500-13500 $h^{-1}$ (Fig. 3) was investigated.As can be seen from the figure, at reaction temperatures of 250 and 300°C the space velocity effect on activity of catalyst is low; the yield of the

main product is about the same for all space velocities.At 250°C the yield of ethylene from 5 to 8%; at the reaction temperature 300°C the main product yield from 28 to 32%.With increasing of reaction temperature on the 50°C the effect of space velocity is more significant at 1500 $h^{-1}$. Ethylene yield is 43%, the highest yield of the main product - 65% at reaction temperature of 350°C and space velocity - 13500 $h^{-1}$.

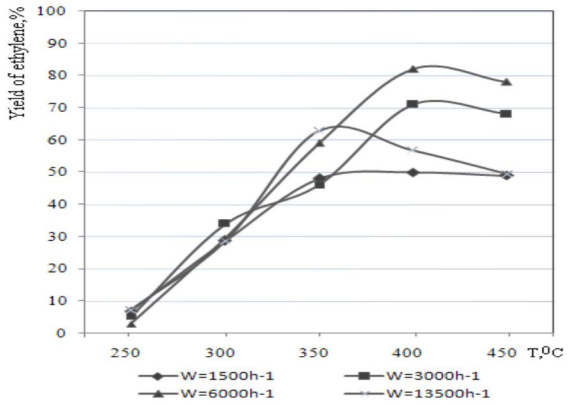


**Fig. 3.** Effect of temperature and space velocity of reaction on the yield of ethylene.

The optimum space velocity increases from 3000 to 6000 $h^{-1}$ with the introduction of lanthanum into the 3% Ce/γ-$Al_2O_3$ catalyst. At the reaction temperature 400°C and W-6000 $h^{-1}$ experienced the highest yield of ethylene - 82%.

Ce-containing catalysts were studied by transmission electron microscopy.Activity of the Ce-containing catalysts, probably, due to the formation of dispersed particles of 2-10 nm (Fig. 4, 5). Thus, the concentration of particles with size of 5-10 nm can be seen in Fig. 4 at low magnification; micro diffraction picture from them can be attributed to mixture of $Ce_6O_4$ (JCPDS, 32-196) and $AlCe_3$ (JCPDS, 9-260)phases.

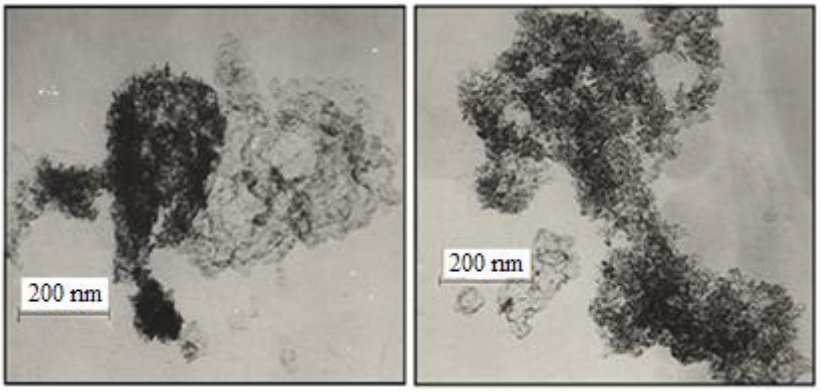


**Fig.4**.TEM image of 3% Ce/γ-$Al_2O_3$ catalyst.

Modification of Ce/γ-$Al_2O_3$ by 3% lanthanum increases the dispersion of catalyst. Accumulations of small particles with size of 2 nm are observed; particles with size of 10 nm are present sometimes in clusters.Microdiffraction pattern (Fig. 5) is represented by small set of rings and can be attributed to mixture of phases -α-La (JCPDS, 2-618), $Ce_2O_3$ (JCPDS,23-1048),$La_2O_3$ (JCPDS, 22-269), $La_2O_3$ (JCPDS, 24-554),as well as the metalloclusters - $Al_3La$ (JCPDS, 19-25), $AlCe_3$ (JCPDS,9-269), $AlLa_3$ (JCPDS, 25-1131).

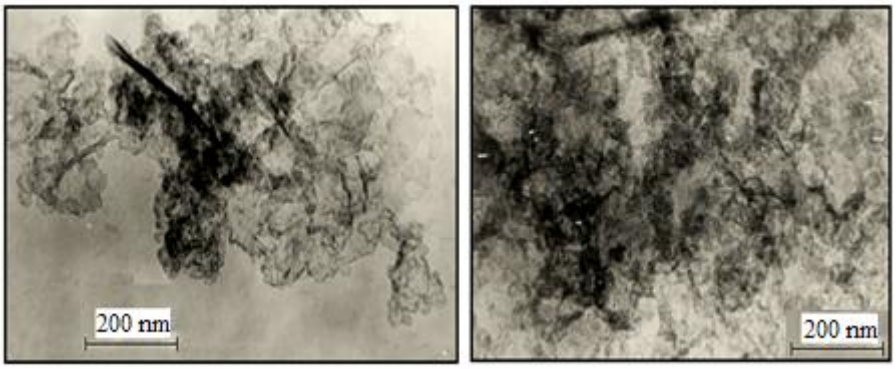


**Fig.5**.TEM image of 3% Ce +1% La/γ-$Al_2O_3$ catalyst.

## 4. CONCLUSION

Thus, on the basis of the experimental results were determined the optimum temperature of dehydration of ethanol, the yields of the reaction products depend on the composition of catalyst and the reaction temperature. Most important characteristic of developed Ce-containing catalysts is high selectivity by ethylene and low - by-products. Have been experimentally determined the optimal conditions (W = 6000 $h^{-1}$, $C_{ethanol}$ = 19.7 g/$m^3$ and T = 400°C) of catalytic conversion of ethanol on the 3% Ce+1% La/γ-$Al_2O_3$catalyst where the yield of ethylene of 82% at 94% ethanol conversion and selectivity of 87.2%.

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