

## Nanosized Catalysts in the Process of Hydrogenating Acetylene

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### Abstract

Hydrogenating process of the acetylene to ethylene using automated flow catalytic installation at nanoscaled catalysts Ni, Co and carriers at a pressure of 5 atm was studied. The actions of carriers and nanosized catalysts during hydrogenation reaction of acetylene to ethylene at low temperatures in the range from 50–120 °C were analyzed. With ratio of C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> being equal to (1:2), at 80 °C the aluminum oxide carrier exhibits an activity, conversion of acetylene makes up 70%, when using zeolite 3A it is 63%. When the temperature rises to 120 °C, the aluminum activity is decreasing and conversion is 53%. However, zeolite exhibits its activity at high temperatures, at a temperature of 120 °C conversion of acetylene reaches to 73.5%. It is shown that with increasing of hydrogen ratio, the ethylene yield increases from 5 to 10.7% using catalyst 5% Ni/3A. In addition, in reaction of acetylene hydrogenation there are not formed waste products. For this process, the optimum reaction temperature is 80 °C, feedstock ratio (1:3) is positive, where the ethylene yield increased up to 16.7% and at catalyst to 5% Co/3A.

## 1. Introduction

Production of propylene and ethylene takes top-ranked places in large-scale petrochemical synthesis. The main industrial method for production of ethylene and propylene – is a pyrolysis of oil alkanes, gasoil stock and naphtha. The impurities of acetylene and diene hydrocarbons reduce the selectivity and negatively affect on catalysts of further processing of raw materials. In the CIS countries, the process of alkylation using aluminum chloride as a catalyst was most developed [1].

The impurities of acetylene and diene hydrocarbons that formed during pyrolysis reduce the selectivity and negatively affect on catalysts and further processing of raw materials. The authors [1–3] studied catalysts of selective hydrogenation of acetylene using Pd-Cu, Pd-Ga, Pd-Zn catalysts on aluminum oxide.

When hydrogenating acetylene, the authors have studied the catalysts containing precious metals, such as Pd, Pt, Au, Ag, deposited on aluminum oxide supports and different zeolites [4, 5].

Now, nanoscaled catalysts containing precious metals such as Pd, Pt, Au, Ag, are widely used in large-scale industrial processes of hydrogenating acetylene to ethylene [6, 7]. However, other active oxide catalysts supported on different carriers can be used for this process, because Pd, Pt, Au, Ag containing catalysts that more expensive than oxide catalysts [2, 4, 8]. The authors [7–9] have established the existence of Pd-Ag alloy, which surface is silver-enhanced. The formation of alloy leads to the decrease of adsorption hydrogen, hydrogen spillover as well as increasing of hydrogen. But detailed study shown that during introduction of modifiers, the conversion of acetylene and selectivity for ethylene are 70 and 50% [10].

That is why the Ni, Co containing catalysts deposited on aluminum oxide carrier and zeolite 3A are been selected.

## 2. Experimental

The paper presents the investigation results of the carriers and nanosized nickel, cobalt catalysts

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deposited at different carriers. The studies concerning selection of the carrier for nanoscaled catalysts with low dispersity and for applying of active concentration of metals were carried out. In this paper, for applying of active phase of catalyst, the 3A and  $\text{Al}_2\text{O}_3$  which have different morphological, structural and texture characteristics, and widely used in many chemical processes were chosen as carriers. Acetylene and hydrogen in different ratios: (1:1, 1:2, 1:3) ( $\text{C}_2\text{H}_2:\text{H}_2$ ) were used as initial feedstock. The catalytic activity of carriers have been studied using automated flow catalytic installation in acetylene hydrogenation reactions.

An installation includes a gas-flow regulatory control block, reactor, evaporator, switch, separator and control unit. In the installation, mass thermal regulators of gas flow rate, where the initial gases from cylinders fed at a pressure of 0.2 to 10 MPa are used. The reaction products analyzed on "CHROMOS GC-1000" using the method absolute calibration and thermal conductivity detectors.

### 3. Results and discussion

The action of temperature on catalytic activity of zeolite and aluminum oxide has investigated in the temperature range of 80–120 °C and received results presented in Table 1.

As can be seen from the table, the zeolite 3A and  $\text{Al}_2\text{O}_3$  showed catalytic activity during hydrogenation process of acetylene. The carriers 3A and  $\text{Al}_2\text{O}_3$  at reaction temperature of  $T = 100$  °C, with the ratio of acetylene and hydrogen  $\text{C}_2\text{H}_2:\text{H}_2$  (1:1), conversion of acetylene was 26%. At the temperature of 80 °C, the carriers show the same result, and conversion of acetylene is 32%. With rising of a temperature (up to 120 °C), at a ratio of 1:1, the conversion of acetylene using  $\text{Al}_2\text{O}_3$  is 34.5%, while on zeolite 3A is 26%. With a ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  (1:2) at 80 °C, the aluminum oxide carrier

exhibits an activity and acetylene conversion is 30% conversion of acetylene using zeolite 3A is 37%. During hydrogenation process of acetylene at a temperature of 120 °C, the activity of aluminum oxide rises, and conversion makes up 47.5%, but the zeolite 3A exhibits an activity at a low temperature of 80 °C at a ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  1:3, conversion of acetylene reaches 39%.

Thus, among studied carriers, the  $\text{Al}_2\text{O}_3$  actively operates at high temperatures during hydrogenation process of acetylene. Optimum temperature for aluminium oxide is 120 °C, in a ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  1:3, the conversion of acetylene is 47.5%. Zeolite 3A exhibits catalytic activity at low temperatures (80 °C), in a ratio of 1:3, conversion of acetylene was 39%.

Figures 1 and 2 shows investigation results of carriers and target product yield on zeolite.

Figure 1 shows the effect of carrier on ethylene yield of at different ratios of  $\text{C}_2\text{H}_2:\text{H}_2$ . As can be seen from Fig. 1 at a ratio of 1: 3 the ethylene yield increases up to 10%.

Investigation results showed that at a reaction temperature of  $T_p = 80$  °C, a volumetric reaction rate is  $W = 300$  h<sup>-1</sup> at a ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  (1:1), the yield of ethylene is 5%, and at the ratio of  $\text{C}_2\text{H}_4:\text{H}_2$  (1:3), is equal to 8%.

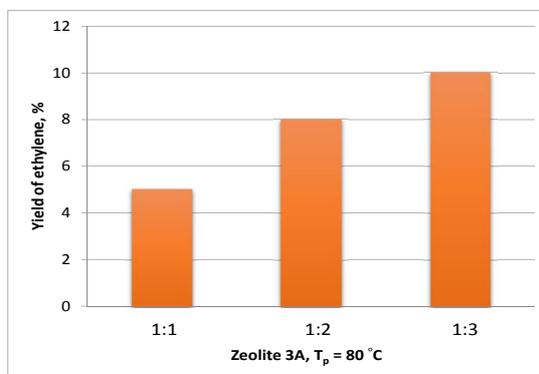


Fig. 1. The effect of zeolite 3A on the yield of ethylene ( $T_p = 80$  °C,  $W = 300$  h<sup>-1</sup>).

**Table 1**

Effect of the carriers on acetylene conversion during the hydrogenation process, (at different temperatures, volumetric rate of reaction  $W = 300$  h<sup>-1</sup>)

Carriers	Conversion of acetylene at different ratios $\text{C}_2\text{H}_2:\text{H}_2$ , %			
	Reaction temperature, °C	$\text{C}_2\text{H}_2:\text{H}_2$ (1:1)	$\text{C}_2\text{H}_2:\text{H}_2$ (1:2)	$\text{C}_2\text{H}_2:\text{H}_2$ (1:3)
$\text{Al}_2\text{O}_3$	80	32.0	30.0	24.0
	100	26.0	26.0	30.0
	120	34.5	47.0	47.5
Zeolite 3A	80	32.0	37.0	39.0
	100	26.0	27.0	28.0
	120	26.0	26.5	27.0

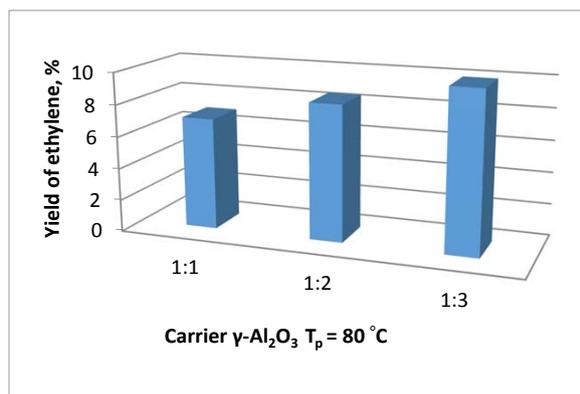


Fig. 2. The effect of carrier  $\gamma\text{-Al}_2\text{O}_3$  on the yield of ethylene ( $T_p = 80\text{ }^\circ\text{C}$ ,  $W = 300\text{ h}^{-1}$ ).

Figure 2 shows the influence results of  $\gamma\text{-Al}_2\text{O}_3$  carrier on ethylene yield at a reaction temperature of  $T_p = 800\text{ }^\circ\text{C}$ , the reaction volume rate is  $W = 300\text{ h}^{-1}$  in the ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  (1:1), the ethylene yield is 7%, and at ratios of 1: 2 – 8.5%, 1: 3 the ethylene yield has increased up to 10%.

Comparative results of carriers presented in further. The effect of carriers at temperature of  $100\text{ }^\circ\text{C}$  in the ratios 1: 2 and 1: 3 ( $\text{C}_2\text{H}_2:\text{H}_2$ ) was studied.

Figure 3 shows the results of zeolite effect 3A and aluminium oxide  $\gamma\text{-Al}_2\text{O}_3$  at ethylene yield. Temperature is  $T_p = 100\text{ }^\circ\text{C}$ , volumetric reaction rate is  $W = 300\text{ h}^{-1}$ . Zeolite sample 3A at a ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  1:2, shows the ethylene yield which is 8.3%, and aluminum oxide  $\gamma\text{-Al}_2\text{O}_3$  shows 5.8% of yield of ethylene. On the carrier  $\gamma\text{-Al}_2\text{O}_3$  in ratios of  $\text{C}_2\text{H}_2:\text{H}_2$  1:3 the yield of ethylene is 9.2%. Thus, the investigation result on the effect of carriers on the yield of ethylene shows that optimal ratio of hydrogen with acetylene 1:3 gives the yield of the target product up to 10.9% on zeolite 3A. As is seen in the Fig. 4 influence of zeolite 3A carrier on the yield of ethylene at a reaction of temperature of  $120\text{ }^\circ\text{C}$  and volumetric reaction rate

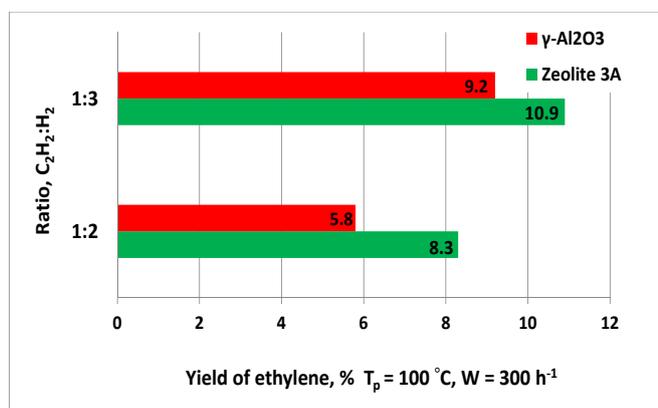


Fig. 3. The effect of carriers (zeolite 3A,  $\gamma\text{-Al}_2\text{O}_3$ ) on the yield of ethylene ( $T_p = 100\text{ }^\circ\text{C}$ ,  $W = 300\text{ h}^{-1}$ ).

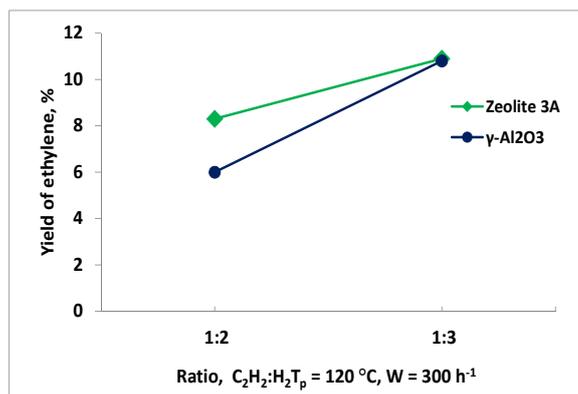


Fig. 4. The effect of carriers (zeolite 3A,  $\gamma\text{-Al}_2\text{O}_3$ ) on the yield of ethylene ( $T_p = 120\text{ }^\circ\text{C}$ ,  $W = 300\text{ h}^{-1}$ ).

$W = 300\text{ h}^{-1}$  with the ratio of 1:2 the yield of the target product is 8.3% and at the ratio 1:3 reaches 10.9%. On the carrier aluminum oxide  $\gamma\text{-Al}_2\text{O}_3$  at the ratio of  $\text{C}_2\text{H}_2:\text{H}_2$  1:2 we get ethylene in the amount of 6%, at a ratio of 1:3, the yield of ethylene increases from 6 to 10.8%.

The important characteristics of the carriers and catalysts are the value specific surface, the volume and size of pores, i.e. the porous structure. With the help of BET method, textural characteristics of carriers were studied. The results presented in Table 2.

As can be seen from Table 2 specific surface and specific volume of aluminum oxide and zeolite pores are the same, so that is why the carriers show activity during the process of hydrogenating acetylene to ethylene. Thus, in the hydrogenation reaction, the yield of ethylene was 10.9%, and on the  $\gamma\text{-Al}_2\text{O}_3$  carrier, the yield of the target product was 10.8%. After investigation of carriers, the effect of active phases has been studied.

Next, as the active component cobalt oxide and nickel were investigated. The catalysts were prepared by capillary impregnation of the carrier on the capacity. The figure shows results of influence of the content of nickel oxide on the carrier in the process of acetylene hydrogenation. The results of the study of modified  $\gamma\text{-Al}_2\text{O}_3$  with nickel oxide are presented in Figs. 4 and 5. Figure 4 shows the effect of the content of nickel oxide on the  $\gamma\text{-Al}_2\text{O}_3$  carrier on the yield of ethylene.

**Table 2**

Textural characteristics of carriers

Carriers	Specific surface, $\text{m}^2/\text{g}$	Specific pore volume, $\text{cm}^3/\text{g}$
Zeolite 3A	425.618	0.182
$\text{Al}_2\text{O}_3$	423.034	0.181

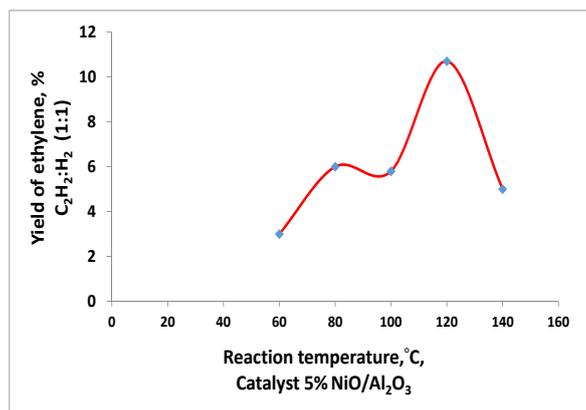


Fig. 5. The effect of catalyst 5%NiO/Al<sub>2</sub>O<sub>3</sub> on the yield of ethylene at different temperatures.

On the catalyst 5% NiO/Al<sub>2</sub>O<sub>3</sub> at 60 °C, the yield of ethylene was 3%, at the temperature increase up to 80 °C, the yield of ethylene increased from 3 to 6%. At the reaction temperature of 100 °C, the yield of ethylene decreased from 6 to 5.8%. A further increase of the reaction temperature up to 120 °C leads to increasing of the target product up to 10.7. The increasing in the reaction temperature up to 140 °C results are decreasing in the yield of ethylene to 5% (Fig. 6). Thus, on the catalyst 5%Ni/Al<sub>2</sub>O<sub>3</sub>, the optimum reaction temperature is 120 °C at ratios of (C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>) 1:1, where the yield of ethylene is 10.7%. Therefore, the investigation results on the effect of raw materials and temperature showed that at a ratio of C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> (1:1) at 120 °C, the yield of ethylene is 10.7%, and at a temperature of 80–100 °C with the ratios of C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> (1:2), (1:3), the yield of ethylene reduces up to 10%. Thus, on 5% NiO/Al<sub>2</sub>O<sub>3</sub> catalyst the optimum temperature is 120 °C, and the ratio of C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> is (1:1). To study the catalytic activity of nanoscale catalysts in hydrogenation reaction of acetylene, cobalt-containing catalysts deposited on zeolite and aluminum oxide were chosen.

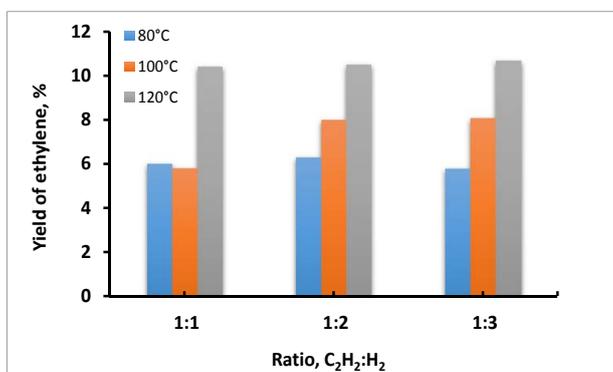


Fig. 6. The effect of catalyst 5%NiO/Al<sub>2</sub>O<sub>3</sub> on the yield of ethylene at different ratios (C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>) and different temperatures (80–120 °C). ссылка в тексте?

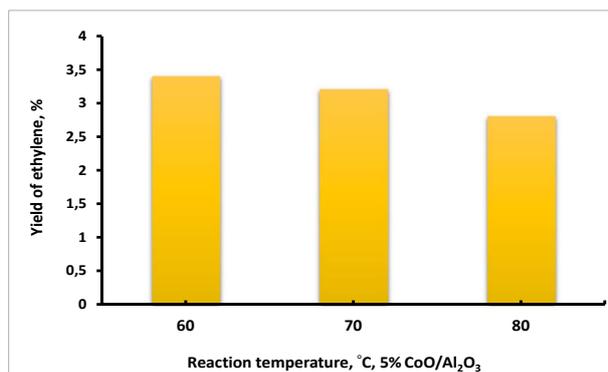


Fig. 7. Effect of catalyst 5%CoO/ Al<sub>2</sub>O<sub>3</sub> on the yield ethylene at different temperatures at ratios C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> (1:1) and different temperatures (60–80 °C).

As can be seen from Fig. 7 at a temperature of 60 °C the ethylene yield was 3.4%, further increase of a temperature leads to a decrease of the target product yield from 3.4% to 2.8%. Figure 8 shows the hydrogenation results of acetylene using cobalt-containing catalyst 5% CoO/3A. The effect of reaction temperature at different ratios of feedstock (C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>) to ethylene yield during hydrogenation process of acetylene was studied.

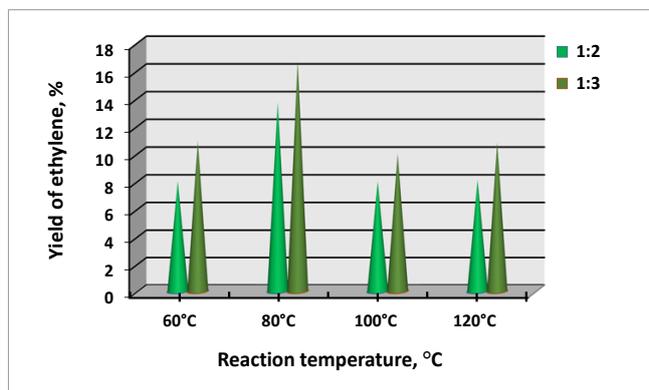


Fig. 8. Effect of catalyst 5%CoO/3A, reaction temperature and initial stock ratio (C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>) on the yield of ethylene.

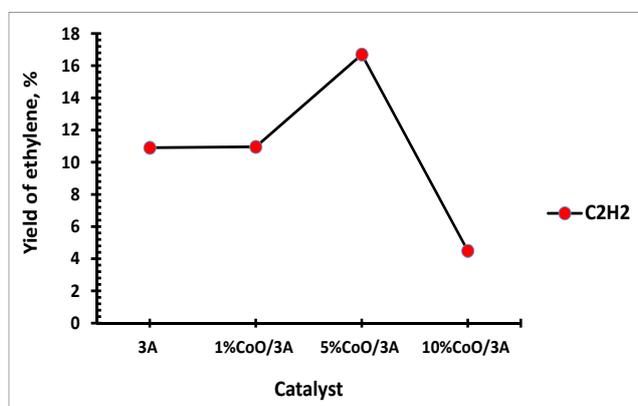


Fig. 9. Effect of the content of cobalt on the carrier on the yield of ethylene in hydrogenation reaction of acetylene at W = 300 h<sup>-1</sup>, T<sub>p</sub> = 80 °C, the ratio C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> (1:3).

Using catalyst 5% CoO/3A at the reaction temperature of 60 °C, with a ratio of C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> (1:2) the ethylene yield is 8%, in ratios of (1:3), the ethylene yield is increased up to 10.9%. When temperature increasing up to 80 °C the ratio C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub> (1:2) the ethylene yield increases to 13.7%, but with a ratio of (1:3), the ethylene yield increases to 16.7%. Increasing of reaction temperature up to 100–120 °C leads to decrease of target product from 16.7% to 8%. The results presented in Fig. 9.

The effect of cobalt using support from 1% to 10% on the yield of ethylene was studied. The investigation results showed that the optimum cobalt content is 5%. During the hydrogenation of acetylene on a 1% CoO/3A catalyst, the yield of the desired product was 10.96%, the 5% CoO/3A catalyst, the ethylene yield was 16.7%, with an increase in the cobalt content of 5% to 10%, the yield of ethylene from 16.7% to 4.5%. Thus, the optimum cobalt content is 5% for the process of hydrogenation of acetylene using zeolite.

By the method of electron microscopy there is studied a surface morphology of cobalt-containing samples on zeolite. The micrographs of catalysts are shown in Fig. 10. As can be seen from Fig. 10, there are particles of round shape with nanosize of 24–27 nm in composition of catalysts.

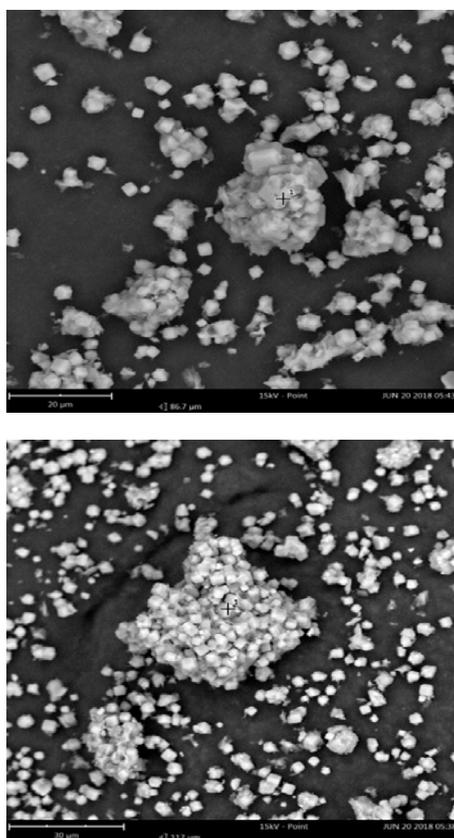
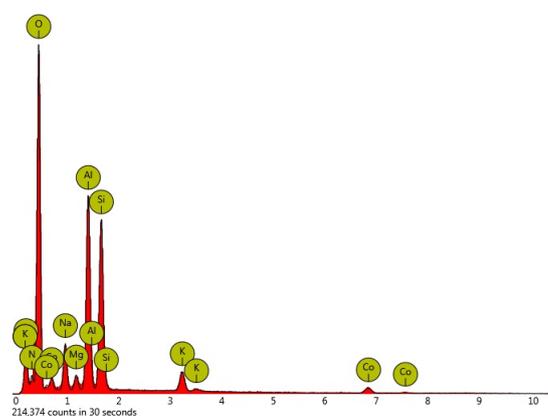


Fig. 10. Micrographs of cobalt-containing catalysts.

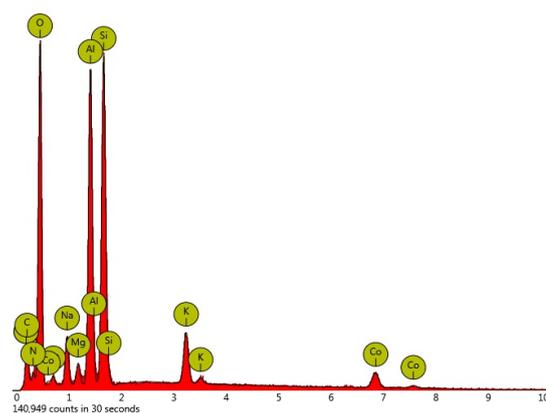
Thanks to photomicrograph is possible to see that particles are distributed evenly at the surface of catalyst before and after reaction. Also, it can be seen that the catalyst is actively operate and do not lose its activity during after hydrogenation process of acetylene to ethylene. Figure 11 shows an elemental analysis of cobalt-containing catalysts.

Spectra of elemental composition (Fig. 11) of the catalyst surface 5% CoO/3A before test reaction and after experiment shows that at the surface of granule the intensity of spectra related to cobalt is greater than in the middle of the granule. This means that distribution of active phase of cobalt occurred at the outer surface of zeolite 3A.

Thus, the cobalt-containing catalyst deposited to the carrier 3A exhibits a catalytic activity during hydrogenation process of acetylene to ethylene.



5%CoO/3A before reaction execution (surface)



5%CoO/3A after reaction execution (surface)

Fig. 11. Elemental analysis of cobalt-containing catalysts.

#### 4. Conclusions

According received results, execution of hydrogenation reaction of acetylene to ethylene in automated flowing catalytic unit under the pressure of

5 atm using different carriers (3A, Al<sub>2</sub>O<sub>3</sub>) and catalysts 5%NiO/Al<sub>2</sub>O<sub>3</sub>, 5%CoO/ Al<sub>2</sub>O<sub>3</sub>, 5%CoO/3A) at low temperatures (80 °C) allows to reach a high degree of conversion and formation of ethylene up to 16.7% without secondary products. Further increasing of target product may be associated both with modification of the catalysts and the change of reaction conditions.

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