CATALYTIC EFFECT OF COBALT CATALYSTS IN THE REACTION OF HYDROGENATION OF ETHYLENE-CONTAINING ACETYLENE TO ETHYLENE

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Abstract. The results of the study on physicochemical and catalytic properties of cobalt catalysts during hydrogenation of acetylene mixed with ethylene are presented. The process of hydrogenation of ethylene-containing acetylene to ethylene on 5% and 7% cobalt catalysts has been studied. The catalytic activity of a palladium catalyst is compared with a cobalt that of one. It is shown that a 7% cobalt catalyst develops a high catalytic selectivity in the hydrogenation reaction of ethylene-containing acetylene without loss of ethylene. Comparative tests of the palladium catalyst and 7% cobalt catalyst in the hydrogenation process of ethylene-containing acetylene have been carried out. It is found that an increase in temperature to 180 ° C in the hydrogenation reaction of ethylene-containing acetylene leads to a decrease in the yield of ethylene.

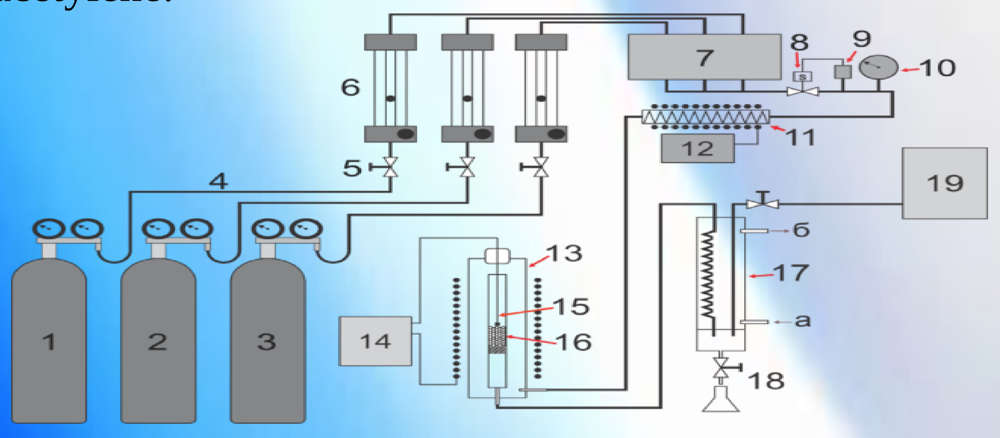
Introduction

The petrochemical potential of industrialized countries is determined by the volume of production of lower olefins. It is these products that form the raw material base of the organic synthesis industry. The main method for production of lower olefins (ethylene, propylene) is pyrolysis of hydrocarbons [1, 2]. Both liquid and gaseous pyrolysis products require the so-called hydrostabilization. It is a process for removing highly unsaturated impurities by catalytic hydrogenation. Purification of ethane-ethylene and propane-propylene fractions from impurities of acetylene and diene compounds is carried out under mild conditions in the presence of palladium catalysts [3, 4].

EXPERIMENTAL PART

In this work, we have developed methods for modifying the carrier of cobalt catalysts and for applying active components. The conditions for hydrogenation of ethylene-containing acetylene on the developed cobalt catalysts were optimized in a pilot plant.

Chemically pure ethylene, acetylene and hydrogen were used as initial reagents. Before use, the carrier is activated with nitric acid and modified with aluminum nitrate to improve structural performance. The synthesis of cobalt catalysts was carried out according to the previously described method [7]. The elemental composition of the surface of the samples was determined using a JED 2300 energy-dispersive X-ray detector (resolution 133 eV). The microstructures of the samples were studied using Quanta 200i 3D scanning electron microscopy. The pictures were taken at voltage from 200 V to 30 kV and resolution of 2.5 nm. The catalytic activity of the samples of the cobalt catalyst was tested in the selective hydrogenation of ethylene-containing acetylene.



1, 2, 3 - gas balloons; 4 - gas pipelines; 5 - a needle valve; 6 - gas rotameters; 7 - gas flow meter IRG; 8 - solenoid valve; 9 - gas pressure cut-out; 10 - gauges; 11 - gas mixer (evaporator) and heater; 12 - thermostat; 13 - reactor; 14 - thermocontroller, 15 - thermocouple; 16 - container for the catalyst; 17 - separator (a, b - cooling water); 18 - tap for draining and condensate collection; 19 - chromatograph

Fig. 1. Scheme of a catalytic plant for selective hydrogenation of acetylene

RESULTS AND DISCUSSION

Optimization of conditions for hydrogenation of ethylene-containing acetylene was carried out on previously tested cobalt catalysts (5 - 7% of the active component), which showed catalytic activity in the hydrogenation process of acetylene. In the first stage, the parameters of hydrogenation in the reactor were optimized by varying the feed rate and the molar ratio of hydrogen and acetylene [11]. To achieve the selective conversion of ethylene-containing acetylene with the maximum yield of ethylene, the hydrogenation conditions, temperature conditions, and molar ratios of the reactants have been worked out.

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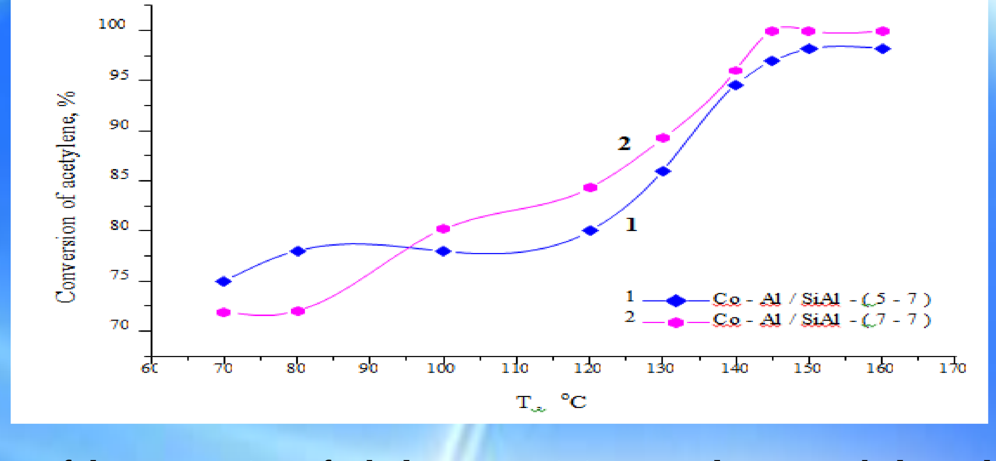


Fig. 2. Dependence of the conversion of ethylene-containing acetylene on cobalt catalysts on temperature

Fig. 2 shows the results of hydrogenation of ethylene-containing acetylene on cobalt catalysts as a function of temperature. When ethylene is mixed in the acetylene hydrogenation reaction at a molar ratio of $C_2H_2/C_2H_4/H_2$ = 1: 0.2: 2.0; no abrupt changes are observed. No by-products were formed in the reaction products. The selectivity over ethylene in the hydrogenation process of acetylene in a mixture with ethylene is 100% on a 7% cobalt catalyst, and 94.5% on a 5% cobalt catalyst.

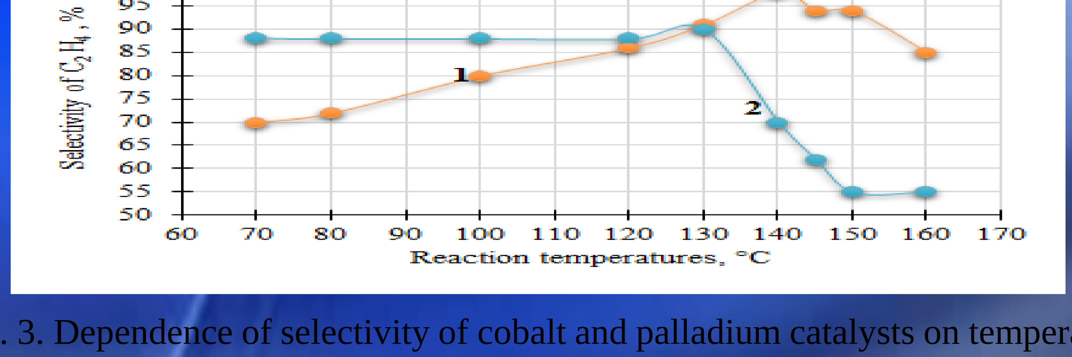
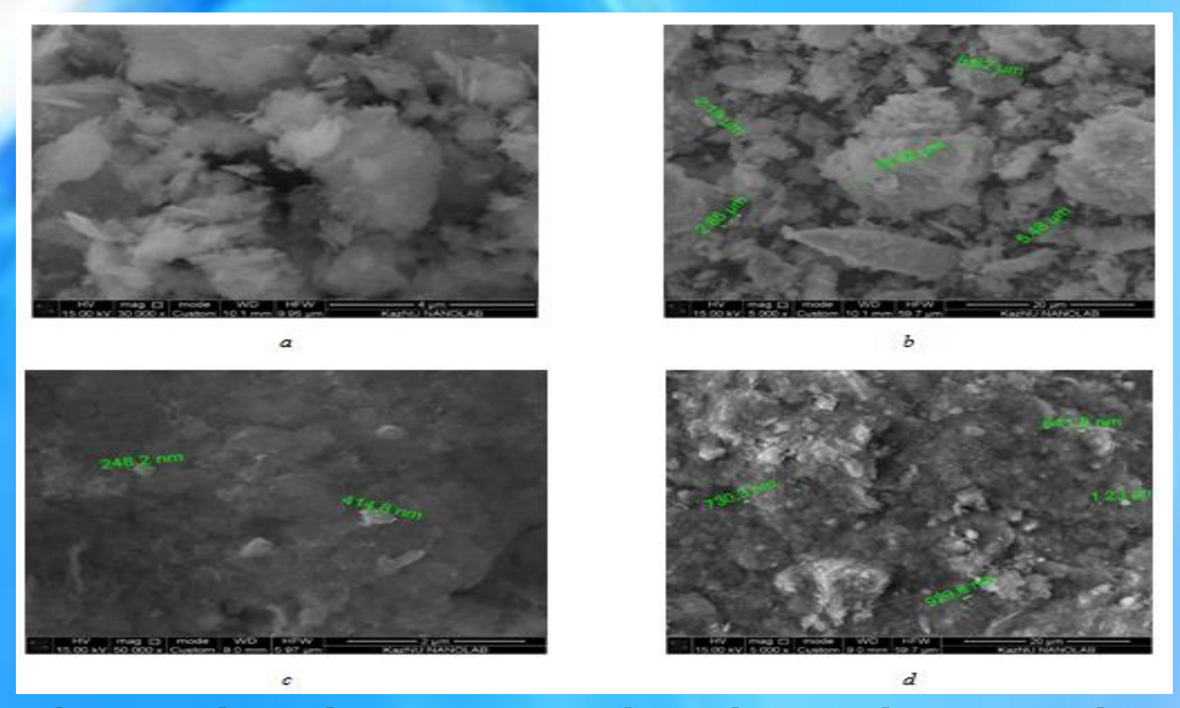


Fig. 3. Dependence of selectivity of cobalt and palladium catalysts on temperature

The catalytic activity and selectivity of the cobalt catalyst were compared with those of the palladium catalyst. As seen in Fig. 3, on a cobalt catalyst at a temperature of 140 ° C and a molar ratio of 1: 2, the ethylene yield is 92%. Based on the data obtained, a feed rate of 450 h -1 was selected, at which a high conversion of acetylene is observed. As it was previously determined, on a cobalt catalyst with an increase in temperature to 140 ° C, the ethylene yield increases. In this case, in the temperature range 180-240 ° C, the ethylene yield decreases, since an increase in temperature activates side reactions. With an excess of hydrogen, ethane, methane are formed, and traces of butadiene are found in small amounts.

Further, the ratio of a mixture of ethylene-containing acetylene and hydrogen ($C_2H_2/C_2H_4/H_2$ = 1: 0.2: 2.0) depending on the feed rate at an optimum temperature of 140 ° C was investigated. An increase in the temperature in the reactor from 120 to 140 ° C at a molar ratio of acetylene and hydrogen of 1: 2 leads to an increase in the conversion of acetylene to 92% and an increase in the yield of ethylene by 0.45 vol. %. The ethylene selectivity increases by 23.8% (from 71.6 to 91.4%).

According to the results of XRD, the main phases in the samples, depending on the modification, are quartz, aluminum oxide, reduced cobalt, in a small amount Co_3O_4, $Na(Si_3O_8)$, KSi_3AlO_8.



a, b – Co Al/ SiAl (5-7); c – Co Al/ SiAl (7-7); d – Co / SiAl

Fig. 4. Electron microscopic images of cobalt catalysts

According to SEM data (Fig. 4 a, d) prepared cobalt samples give a set of deposited cobalt particles differing in their morphology. Sample (4 b) contains cobalt particles with sizes of 8.82 and 19.92 μm and aggregates consisting of several particles. Samples (4 c, d) contain cobalt particles with sizes of 248.2 and 641.8 nm. For measurements, 0.5 mg of the catalyst was placed in 1 ml of isopropanol and dispersed by ultrasound, then the resulting suspension was applied to a copper grid coated with a layer of amorphous carbon and dried in air at room temperature for 20 minutes. The analysis of the elemental composition by the EDAX method was carried out by identifying the positions on the energy scale of the characteristic lines of the elements in the secondary X-ray spectrum obtained at a given point (area) and comparing them with the tabular data.

CONCLUSIONS

Based on the obtained results of physicochemical methods of analysis, cobalt acts as an active component of the catalyst in the hydrogenation reaction of acetylene. The effect of the composition of cobalt catalysts on the catalytic properties in the hydrogenation reaction of ethylene-containing acetylene to ethylene has been studied. The XRD results show that aluminosilicate phases, cobalt oxide and cobalt are formed in the structure of cobalt catalysts. The catalytic selectivity to ethylene of the modified cobalt catalysts in the hydrogenation of ethylene-containing acetylene is 92.5%.

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