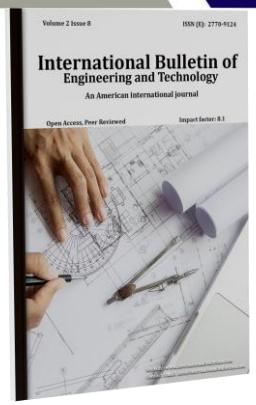

STUDY OF PALLADIUM CATALYST IN THE PROCESS OF ACETYLENE HYDROGENATION IN THE ETHANE-ETHYLENE FRACTION

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ABSTRACT
To purify the ethane-ethylene fraction from acetylene impurities, it is subjected to catalytic hydrogenation. The process of purification of the ethane-ethylene fraction (EEF) of pyrogas from the admixture of acetylenic hydrocarbons is based on the reaction of catalytic hydrogenation of alkynes. The hydrogenation reaction proceeds in the presence of metal or oxide catalysts. To study the kinetics of acetylene hydrogenation, a contact containing 0.04 wt % palladium on α-alumina with a specific surface area of 9 m^2/g was used as a catalyst. Tests of the finished catalyst were carried out at temperatures of 40 - 60 ^0C, a pressure of 2.3-2.5 MPa and a molar ratio of hydrogen and acetylene 1.6-1.9. The selectivity of acetylenic hydrogenation on this catalyst was 90%.
Keywords: industrial catalyst, acetylene hydrogenation, ethane-ethylene fraction, hydrogen conversion, acetylene conversion, pilot plant.
Pyrolysis remains the main way to obtain lower olefins - ethylene and propylene. The existing capacity of pyrolysis plants is 113 million tons/year for ethylene or 100% of the world production and 38.6 million tons/year for propylene or just over 65% of the world production. The modern world structure of pyrolysis raw materials is as follows: ethane - 27.6% (mass.), liquefied gases - 14.0% (mass.), straight-run gasoline (naphtha) - 53.1% (mass.), hydrotreated kerosene-gas oil fractions - 5.3% (mass.). Separation of the hydrocarbon stream into fractions: methane - hydrogen, ethane - ethylene, propane-propylene, etc. occurs during cooling at temperatures from 110 - to -130 ° C and pressure from 0.5 to 5.0 MPa .. To purify the ethane-ethylene fraction from acetylene impurities, it is subjected to catalytic hydrogenation.
Experimental part: An important stage in the development and implementation of a new type of catalyst is the verification of its main characteristics under conditions that are as comparable as possible with real industrial ones. This approach is necessary to predict the stability of its operational properties: activity and selectivity, service life, which is of particular importance in the case of the use of an expensive metal - palladium.
The task was solved on the basis of an assessment of the values of activity and selectivity of prototypes and their comparison with industrial catalysts during tests in reactors of four levels: laboratory, pilot, experimental and industrial. Comparative tests of prototypes and industrial catalyst G-58I on laboratory, pilot and pilot plants were carried out on a real industrial gas mixture - ethane-ethylene fraction of the composition: ethylene, approximately - 55%, ethane - 43%, acetylene - 0.3%, hydrogen - 0.9%, the rest - methane, propylene, propane, carbon monoxide, etc. The acetylene content in the contact gas should not exceed 10 ppm. We carried out comparative tests of 32 prototypes and industrial catalyst G-58I: the

minimum temperatures of the acetylene hydrogenation process at which its complete elimination (up to 1 ppm), hydrogen conversion and selectivity corresponding to these temperatures, the formation of green oil as a result of side reactions of ethylene and acetylene oligomerization on the acid centers of the inner surface of the support. Hydrogen conversion and selectivity for reactions and was calculated by the following formulas.

$K = \{ [H_2]_0 - [H_2] \} / [H_2]_0 * 100\ \%$

$S = [H_2]_{acet} / \{[H_2]_0 - [H_2] \} * 100\ \%$

where $[H_2]_0$ - hydrogen content in the initial mixture, $[H_2]$ - hydrogen content in contact gas, $[H_2]_{acet}$ - the fraction of hydrogen used for the hydrogenation of acetylene to ethylene (according to stoichiometry), i.e. in this case, it is 0.3%. The conversion of acetylene was calculated using the formula:

$$K = \{ [C_2H_2]_0 - [C_2H_2] \} / [C_2H_2]_0 * 100\ \%$$

where $[C_2H_2]_0$ - acetylene content in the original EEF, $[C_2H_2]$ - acetylene content in the contact gas.

According to the results of comparative tests, the optimal content of palladium in the catalyst was taken to be 0.2%; above this value, the catalyst is characterized by high activity at the expense of selectivity; below this value, the catalyst is characterized by instability during long-term tests. As the temperature and time dependences of selectivity, hydrogen and acetylene conversions for prototype No. 8 are the most optimal (high activity and selectivity, stability of operation over a long period of testing and changes in process temperature), in comparison with other prototypes and industrial catalyst G-58I. The lowest values of selectivity were noted for sample No. 30, after 700 hours of testing, a decrease in selectivity was observed, and with an increase in temperature from 65 ^{0}C to 75 0C, an increase in the proportion of converted hydrogen was noted. It is most likely that the activity and selectivity of the test samples is related to the size of the inner surface of both the carrier and the metal itself in the pores of the granules.

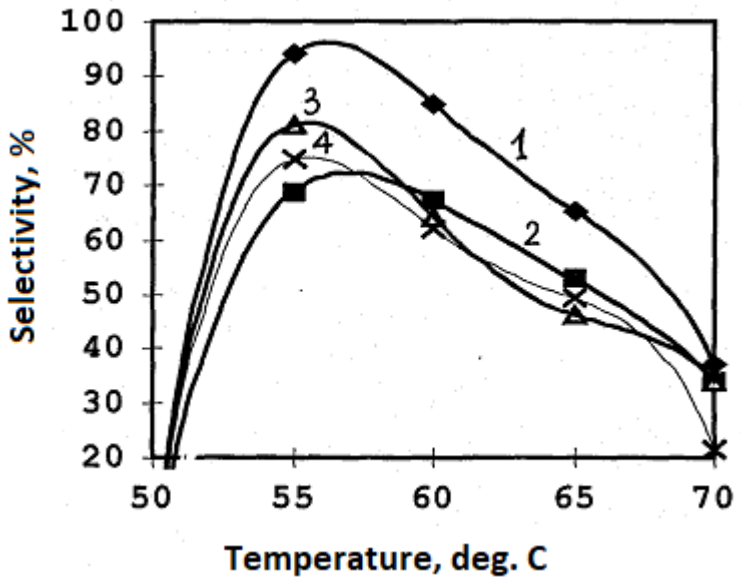

Fig. Selectivity as a function of temperature

The results obtained on prototypes confirm the presence of two types of active centers on the inner surface of the supported palladium catalyst, one of which is responsible for the hydrogenation of acetylene and is present on the fresh catalyst, the second is for the hydrogenation of ethylene, its share on the surface increases during operation, i.e. e. the

selectivity of the hydrogenation process decreases. According to the results of testing prototypes on different grades of corundum carrier with a content of 0.2% palladium, prepared according to different recipes, one was selected - No. 8, as it showed high selectivity, activity and stability in the process of acetylene hydrogenation in the ethane-ethylene fraction . On prototypes with a palladium content of 0.1 - 0.5%, the rate of hydrogenation of acetylene is higher than on the industrial catalyst G-58I.

- acetylene hydrogenation reaction has the first order in acetylene, zero in hydrogen; ethylene hydrogenation reaction - first order in hydrogen and zero in ethylene;
- the rate of acetylene and ethylene hydrogenation reactions depends on the content of palladium in the catalyst; for prototypes, it was found that the optimal content is 0.2 - 0.3 wt. %, over 0.5 wt. % it has little effect on the rate of reactions;
- additives of sodium sulfide and sodium formate help to reduce the rate of acetylene hydrogenation reaction, practically without affecting the rate of ethylene hydrogenation, which explains the decrease in the selectivity of "sulfurized" prototypes;

Results and its discussion: Comparative tests of prototypes and industrial catalyst G-58I on laboratory, pilot and pilot plants were carried out on a real industrial gas mixture - ethane-ethylene fraction of the composition: ethylene, approximately - 55%, ethane - 43%, acetylene - 0.3%, hydrogen - 0.9%, the rest - methane, propylene, propane, carbon monoxide, etc. The acetylene content in the contact gas must not exceed 10 ppm. Then we carried out kinetic studies of the process of hydrogenation of acetylene and ethylene in a laboratory facility. The temperature dependences of the rate constants of the reactions of hydrogenation of acetylene and ethylene for experimental samples and industrial catalyst G-58I are presented. From the results of comparative tests on a pilot plant and kinetic studies on a laboratory plant, it can be concluded that:

- acetylene hydrogenation reaction has the first order in acetylene, zero in hydrogen; ethylene hydrogenation reaction - first order in hydrogen and zero in ethylene;
- the rate of hydrogenation reactions of acetylene and ethylene depends on the content of palladium in the catalyst; for prototypes, it was found that the optimal content is 0.2 - 0.3 wt. %, over 0.5 wt. % it has little effect on the rate of reactions;
-additives of sodium sulfide and sodium formate help to reduce the rate of the acetylene hydrogenation reaction, practically without affecting the rate of ethylene hydrogenation, which explains the decrease in the selectivity of "sulphurized" prototypes.

Conclusion: It has been studied that the reaction of acetylene hydrogenation on a palladium catalyst has the first order in acetylene, the order in hydrogen is equal to zero; the order of the hydrogenation reaction of ethylene for hydrogen is equal to one, for ethylene - zero. The reaction proceeds in the kinetic region at temperatures of 50 - 70 ^{0} C. The characteristics of the corundum carrier are determined by the service life of the catalyst, its selectivity, the occurrence of side processes (oligomerization of acetylene and ethylene with the formation of green oil), and its mechanical strength. The content of palladium in the hydrogenation carrier catalyst affects the selectivity, the overall catalytic activity and the duration of the catalyst, the optimal content of palladium is 0.2 - 0.3%. The introduction of alkali and alkaline earth elements into the composition of the catalyst does not have a noticeable effect on its properties. The addition of sulfur compounds to the composition of the catalyst leads to a decrease in its activity in the process of hydrogenation of acetylene, without affecting the activity in the hydrogenation of ethylene.

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