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OPTIMIZATION OF TECHNOLOGICAL PARAMETERS OF HYDRAGENERATION PROCESS OF ACETYLENE USING A PILOT CATALYTIC PLANT

Abstracts. A pilot plant was launched and the modes of acetylene hydrogenation on cobalt catalysts were worked out. It has been found that the modified 7% Co/ SiAl cobalt catalyst is active in the process of hydrogenating acetylene into ethylene. Optimal conditions of acetylene hydrogenation on 7% Co/ SiAl catalyst were determined. The effects of temperature, space velocity and the ratio of initial components in the hydrogenation of acetylene to ethylene were investigated.

The textural characteristics of cobalt catalysts before and after the hydrogenation of acetylene were investigated by the SEM method. The structure of cobalt catalysts after the hydrogenation of acetylene does not lose catalytic activity and selectivity. It has been found that catalyst samples have channels of different sizes, flaky particles and fibers located in the gaps between large aggregates are also present on the surface.

The optimum temperature was 180 °C in the hydrogenation of acetylene into ethylene at conversion 73.0%. Conversion of acetylene increases to 81.2% when temperature rises to 200°C, acetylene conversion decreases to 68% with further temperature exceeding to 220°C. Acetylene conversion again increases from 68 to 73.6% at 140°C in the ratio of acetylene to hydrogen 1:2. The selectivity of the catalyst 7%Co/SiAl to ethylene was studied depending on the temperature in the acetylene hydrogenation reaction. The selectivity to ethylene decreases with increasing temperature, since an increase in temperature activates side reactions.

Key words: catalytic unit, hydrogenation, acetylene, ethylene, catalysts.

Introduction. The main factor of large-scale production of light unsaturated compounds such as ethylene, propylene, butenes and other aromatic compounds (benzene, toluene, xenones etc.) is a pyrolysis of petrol content such as naphtha and liquefied petroleum gases, at thermal conversion with olefins forms acetylene and diene hydrocarbons in small amounts. Their selection is often economically ineffective. Their presence as an impurity in product disable further use of olefins for polymerization processes [1-4]. Thus, acetylene hydrocarbons have a poison effect on polymerization catalysts of ethylene, and their content in ethylene fraction supplied to polymerization should be below 1 ppm. In this regard, one of the most important tasks when preparing raw materials in order to produce various polymers is a hydrogenation of diene and acetylene hydrocarbons without complete hydrogenation of olefins, which contain only one double bond in their composition to alkanes. In industry, for selective hydrogenation, there are used precious metal based catalysts, predominantly palladium. The price of such catalysts has been high for a long time due to significant metal content (1-5%). At present, it has been shown that it is possible to create heterogeneous catalysts for selective hydrogenation of diene and acetylene hydrocarbons with a low metal content and a narrow distribution in size [5, 6].
Experimental part. The basic process flow diagram of the plant for hydrogenation of acetylene is shown in figure 1. The plant for hydrogenation of acetylene includes a stainless steel reactor; reactor heating system (oven with thermo regulator), gas supply unit, gas supply system and measurement of gas consumption; means of regulation and control of pressure, made in the form of solenoid valve, a gas pressure guard and a pressure gauge; gas mixer (evaporator) and heater with thermostat, separator with cold water circulation system and gas chromatograph.

![Figure 1 - Scheme of catalytic plant for selective hydrogenation of acetylene](image)

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

The plant for study of hydrogenation of acetylene to ethylene contains a gas supply unit, consisting of cylinders with argon, hydrogen and acetylene (1-3), gas pipelines (4), needle valves (5), flowmeter (6), supply system and gas flow metering containing of IRG-3 (7), units for regulation and pressure control, like a solenoid valve (8), a gas pressure regulator (9), manometer (10), gas mixer (vaporization device) heater (11), with thermostat (12), catalytic reactor (13), with a heating system, consisting of furnace and thermocontroller (14), thermocouple (15), container for a catalyst (16), a separator (17), with circulation system of cold water (a), (b) dump cock and condensate collection (18), gas chromatograph (19).

The plant has 3 independent channels for measuring of flow rate by means of rotameters (6) that determines the current volumetric flow rate, which is important to maintain the performance and efficiency for further usage. The flow rate measurement can be carried out simultaneously using all three channels. The measurement data for each channel is given in digital form with reduction to standard conditions.

Results and discussions. A certain sample of catalyst is loaded into container and placed to the reactor. The temperature of reaction zone is measured using a chromel-alumel thermocouple which was placed to catalyst layer, and target temperature with accuracy of ± 1 ° is kept due to temperature controller.

In order to reach a temperature, the developed catalysts are purged with argon. Heat treatment is carried out at a temperature of 100-120 ° C for 60 minutes under argon (10 ml / min), after that the catalyst is restored with hydrogen (10 ml / min) for 60 minutes. When target temperature is reaching reactor, a reaction mixture flow with different ratios is fed into reactor using IRG-3 flowmeter through a mixer (evaporator), and during passing there is formed uniformly mixed gas. Acetylene and hydrogen were used as reaction raw materials in a volume ratio of 1: 3. The setting and maintenance of gas flow rate is carried out in automatic mode using computer. In mixer there is occurred a heating of gas mixtures to a temperature of 200 ° C. Then the gas-vapor steam came from outlet of the reactor and directed to the
separator. In separator, the hot flow of gas-vapor steam is initially cooled up to operating temperature, and after that the liquid reaction products enter the condensate collector, but gaseous products are analyzing using a gas chromatograph «Chrome-3700» and Gas Chromatography with mass spectrometric detection (Agilent 7890A / 5975C).

The separator is connected to chromatograph through a pipeline where a needle valve is installed. Helium was used as a gas carrier. Reaction products were identified by comparing of their retention time and reference substances in the same conditions, increasing the corresponding picking intensity with addition of reference substances to reaction product mixture. Almost all studies have shown a relative error of chromatographic analysis which is no more than 3%.

By using proposed plant, there is a possibility to carry out various sample tests with catalysts keeping operating conditions such as (temperature from 25 to 500 °C, pressure from 0 to 10 atm, gas consumption from 5 to 2500 cm³/min) in order to produce hydrogenation of hydrocarbon, the yield of target products and selectivity of technological parameters.

In this work, a cobalt catalyst 7% Co/SiAl was chosen in order to optimize the technological parameters of hydrogenation process of acetylene using a pilot catalytic plant.

The study of volumetric velocity effect was carried out at different temperatures from 180 to 220 °C and ratio of C₂H₂:H₂=1:2. Figure 2 shows the effect of volumetric reaction rate to ethylene yield during hydrogenation process of acetylene using 7% Co/SiAl catalyst.

From figure 2 it can be seen that best results in formation of target products when output from reactor are equal to the volumetric velocity and corresponding to 216 h⁻¹, at a temperature of 220 °C, it reaches the maximum value. At this rate, the ethylene yield increases from 48.37 to 52.38%. A further increase in volumetric velocity leads to decrease in ethylene yield. From obtained data it can be seen that the optimal volumetric flow rate of ethylene formation is 220 hours⁻¹.

There was studied an effect of reaction temperature and raw material ratio on ethylene yield in the process of acetylene hydrogenation using cobalt-containing catalyst 7% Co/SiAl. Figure 3 shows the results of ethylene yield depending on reaction temperature.

On cobalt-containing catalyst 7% Co/SiAl at reaction temperature of 180 °C, the ratio C₂H₂:H₂(1: 2), and ethylene yield is 42.9%, but at a ratio of (1:3), the ethylene yield increases to 66.7%. A further increase of a temperature up to 200 °C at a ratio of C₂H₂:H₂ (1:2), the ethylene yield increases from 42.9 to 62.2%, but at a ratio (1:3), the ethylene yield increases to 62.9%. An increase of reaction temperature up to 100-120 °C leads to a decrease in target product from 62.9 to 52.9%.
Thus, for this process, an optimal reaction temperature is 180°C in a ratio of raw material (1:3) is positive, where the ethylene yield is 62.9%.

With an increase of hydrogen flow during hydrogenation process of acetylene 1:3 at reaction temperature of 180°C, the conversion of acetylene was 73.0%, at increasing of a temperature up to 200°C, the conversion of acetylene has increased to 81.2%, with a further increase in temperature to 220°C, the conversion of acetylene is reduced to 68%. At 140°C in the ratio of acetylene to hydrogen 1:3, the conversion of acetylene increases again from 68 to 73.6%.

Figure 4 shows the selectivity data during hydrogenation process of acetylene to ethylene using 7% Co/SiAl catalyst. The selectivity of catalyst 7% Co/SiAl catalyst was studied depending on temperature in acetylene hydrogenation reaction.

As can be seen from Figure 4, with increasing of temperature the selectivity of ethylene decreased, because increase of a temperature activates side reactions.

The properties of applied catalysts are determined not only by composition and nature, but also by texture features of a carrier and the particle size of active component. The most important strategic factor is a choice of carrier and method of catalyst preparation. Although the clays do not possess a large amount of acidic centers, but due to resistance to high temperatures and ease of surface modification, it is possible to enhance the catalytic properties [5].
The texture and morphological characteristics of obtained catalysts were studied by employees of Xinjiang University, Institute of Chemistry and Chemical Engineering (Ürümqi city, PRC), using scanning electron microscope JEOL JSM-6390 LA with an energy dispersive X-ray detector JED 2300. figure 5 shows SEM photomicrographs on 7% Co / SiAl cobalt catalysts.

![SEM micrographs of 7% Co / SiAl cobalt catalysts](image)

**Figure 5 - Micrographs of 7% Co / SiAl cobalt catalysts**

According to electron microscopy data, in samples 7% Co/SiAl there are presented microparticles of different sizes, moreover, with an increase of it up to 1000 times, a lot of scaled particles and fibers are becoming visible, that located in spaces between large areas (figure 5 (a, b)). The structure of samples before (5b) and after (5g) hydrogenation of acetylene does not change and not lose catalytic and selective activity. Samples of catalysts have channels of different sizes, and there are also scaly particles and fibers at the surface, located in the intervals between large aggregates.

According to elemental analysis results, there is no any change in composition of 7% Co/SiAl catalyst; this catalyst worked for 62 hours without losing a catalytic activity in the process of acetylene hydrogenation.

**Conclusions.** As the results of experiments there are obtained following results:

1. A pilot plant was launched and the modes of acetylene hydrogenation using cobalt catalysts were tested;
2. When studying the effect of volumetric velocity at different temperatures, a ratio is $\text{C}_2\text{H}_2:\text{H}_2=1:2$ on 7% Co/SiAl catalyst, it can be seen that best results on target products formation are equal to volumetric velocity and corresponds to 216 h$^{-1}$, at the temperature of 220°C and reaches maximum value. At this rate, the ethylene yield rises from 48.37 to 52.38%;
3. The study of cobalt catalysts 7% Co / SiAl on scanning electron microscope - JEOL JSM-6390LA have shown that in sample 7% Co / SiAl there are presented microparticles with different sizes, when
Increasing 1000 times there are appeared many scaled particles and microfibers located in spaces between large aggregates. The structure of samples before (5c) and after (5d) hydrogenation of acetylene does not change and not lose catalytic activity and selectivity. Samples of catalysts have channels with different sizes; there are also scaly particles and fibers at the surface that located in the spaces between large aggregates.

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**ОПТИМИЗАЦИЯ ТЕХНОЛОГИЧЕСКИХ ПАРАМЕТРОВ ПРОЦЕССА ГИДРИРОВАНИЯ АЦЕТИЛЕНА НА ПИЛОТНОЙ КАТАЛИТИЧЕСКОЙ УСТАНОВКЕ**

**Аннотация.** Была запущена пилотная установка и отработаны режимы гидрирования ацетилена на кобальтовых катализаторах. Установлено, что модифицированный 7%Co /SiAl кобальтовый катализатор является активным в процессе гидрирования ацетилена в этилен. Определены оптимальные условия гидрирования ацетилена на 7%Co /SiAl катализаторе. Исследованы влияния температуры, объемной скорости и соотношение исходных компонентов в гидрировании ацетилена в этилен.

Методом СЭМ исследованы текстурные характеристики кобальтовых катализаторов после гидрирования ацетилена. Структура кобальтовых катализаторов после гидрирования ацетилена не теряет каталитическую активность и селективность. Обнаружено, что образцы катализаторов обладают каналами
разных размеров, также присутствуют на поверхности чешуйчатые частицы и волокна, расположенные в промежутках между крупными агрегатами.

Оптимальная температура процесса гидрирования ацетилена в этилен составляет 180°C, конверсия ацетилена — 73,0 %. При повышении температуры до 200°C конверсия ацетилена увеличивается до 81,2 %; при дальнейшем превышении температуры до 220°C конверсия ацетилена уменьшается до 68 %. При 140°C в соотношении ацетилена и водорода 1:2 конверсия ацетилена снова увеличивается от 68 до 73,6 %.

Изучена селективность 7%Co/SiAl катализатора по этилену в зависимости от температуры в реакции гидрирования ацетилена. Селективность по этилену с повышением температуры падает, так как повышение температуры активизирует побочные реакции.

**Ключевые слова:** каталитическая установка, гидрирование, ацетилен, этилен, катализаторы.

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**REFERENCE**