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PRODUCTION OF HIGH-ACTIVITY CATALYSTS FOR OBTAINING LIQUID HYDROCARBONS FROM NATURAL GAS

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Abstract

The article presents the use of highly catalytically active catalysts in industrial processes of petrochemistry and oil refining, mainly for converting low-molecular hydrocarbons to obtain liquid hydrocarbons from natural gas. It also describes the stages of developing modern processes for obtaining environmentally friendly liquid fuels, with a minimum amount of harmful impurities, and a group composition that meets the requirements for motor fuels.

Keywords: *Catalyst, methods, hydrocarbon, zeolite, Fisher-Tropsch-Synthesis, gas, stage*

Introduction

Catalytic reforming is one of the main technological processes in petrochemical synthesis, which serves to obtain high-octane gasolines, which are important for internal combustion engine fuels. Fischer-Tropsch synthesis (FTS) is the main stage of the technology for producing high-quality liquid fuels from low-molecular hydrocarbon feedstocks. This is a heterogeneous catalytic process for converting a mixture of CO and H_2 (synthesis gas) into organic substances, which can be widely used as fuel and raw material for organic synthesis. The relevance of developing technologies based on FISHER-TROPCH SYNTHESIS is currently determined by a number of factors, primarily the need to use natural resources with unconventional hydrocarbon content and increasing requirements for the properties of motor fuels. The most acute problem is the utilization of tail gas (TSG). (Kuybokarov O. et al., 2024).

Catalysts considered for Fischer-Tropsch synthesis are based on transition metals of iron, cobalt, nickel and ruthenium. FT catalyst development has largely been focused on the preference for high molecular weight linear alkanes and diesel fuels production. Among these catalysts, it is generally known that:

- Nickel (Ni) tends to promote methane formation, as in a **methanation process;** thus generally it is not desirableIron (Fe) is relatively low cost and has a higher water-gas-shift activity, and is therefore more suitable for a lower hydrogen/carbon monoxide ratio (H_2/CO) syngas such as those derived from coal gasification;
- Cobalt (Co) is more active, and generally preferred over ruthenium (Ru)

because of the prohibitively high cost of Ru;

- In comparison to iron, Co has much less water-gas-shift activity, and is much more costly. (Mark Crocker, 2010).

Catalysts with high catalytic activity for the production of liquid hydrocarbons from natural gas were prepared by two-stage impregnation of composite supports with a 75% aqueous solution of cobalt nitrate (Rahimov G. et al., 2024).

Materials and methods

Catalysts with high catalytic activity for the production of liquid hydrocarbons from natural gas were prepared by two-stage impregnation of composite supports with a 75% aqueous solution of cobalt nitrate.

The mechanical strength of the granules was determined by the impact force required to break and crush the granules under compression between two parallel planes. The strength of a catalyst with high catalytic activity intended for the production of liquid hydrocarbons from natural gas was calculated as the average value of the breaking force based on a sufficient number of tests.

The crushing (crushing) force of the granules was measured using the Vollstadt Diamant Diatest-S device. The force required for radial crushing (kilogram-force expended per granule) was determined. The result was obtained as an average value for 20 granules.

The device was equipped with a special pneumatic and hydraulic system, which allowed the possibility of adjusting the rate of load generation on the granules, which did not require the participation of the experimental scientist in the process (Murtazayev F. et al., 2024).

Composite supports are prepared in stages:

Stage 1 – preparation of the binder.

In a glass container, a solution of nitric acid, 0.45 ml of HNO_3 (64%) and 7 ml of distilled water were prepared. In a porcelain container, 2 g of beechmite and 1 g of zeolite with high sorption and catalytic properties were thoroughly mixed and the resulting acid solution was added. The resulting mixture was mixed until a homogeneous gel-like mass was formed.

Stage 2 – preparation of aluminum metal powders. Simultaneously with stage 2, 4 g of aluminum metal powder with an average particle size of 20 μm was weighed in a separate container. 1.13 g of TEG and 2.25 g of ethyl alcohol were added to the resulting mixture (strictly in this order). The aluminum was mixed gently, without force, so that it was evenly moistened with a mixture of alcohol and TEG.

Stage 3 – preparation of the carrier composition (paste). The mixture prepared in step 3 was added to the mixture obtained in step 2 and mixed thoroughly until a uniform consistency of soft and plastic dough was obtained.

Stage 4 – molding. The dough was transferred to an extruder and pressed onto trays through a die with a diameter of 2.5 mm. The extrudates were placed on trays so that they did not obstruct the air flow and were kept in the air for at least 15 hours.

Step 5 – drying and polishing the carrier. The extrudates stored in air were annealed in a muffle furnace at temperatures from 60 to 450 degrees Celsius for 20 to 480 minutes as follows:

The extrudates were cooled to room temperature, removed from the muffle furnace, and ground to 2.5 × 2.0 mm.

The amount of components for the preparation of cobalt nitrate solution was calculated as follows:

The amount of cobalt required to obtain 10 g of a highly catalytically active catalyst for the production of liquid hydrocarbons from natural gas containing 20 wt. % cobalt.

The second impregnation and final annealing were carried out in a manner similar to the first impregnation and intermediate annealing.

To study the effect of the degree of cationization, zeolites with different K cations content and high sorption and catalytic properties were prepared. KHB and HKA zeolites with high sorption and catalytic properties were prepared by the following methods for cationization and decationization of HB and KA zeolites with high sorption and catalytic properties, respectively. (Togayev A, 2023).

Method for cationization of HB zeolite with high sorption and catalytic properties:

Initial components:

15 gr of HB zeolite with high sorption and catalytic properties

150 ml of 0.1 N KNO_3

15 gr of HB zeolite with high sorption and catalytic properties were added to 150 ml of 0.1 N KNO_3 solution and stirred with a magnetic stirrer without heating for 2 hours, after which it was kept at room temperature for at least 12 hours. Then the resulting solution was washed to a neutral pH in a Buchner funnel and dried at

120 °C for two hours. Decatation procedure of zeolite KA with high sorption and catalytic properties

Initial components:

15 gr of highly sorption and catalytic zeolite KA

300 ml of 0.5 n NH_4NO_3

The highly sorption and catalytic zeolite KA was kept in a drying oven at 120 °C for 2 hours. Then, the highly sorption and catalytic zeolite KA was added to the 0.5 n NH_4NO_3 solution and stirred with a magnetic stirrer for 5 hours at 60–70 °C. Then, it was kept overnight and then washed with hot distilled water in a Buchner funnel to a neutral pH value. Subsequently, the resulting zeolite, which has high sorption and catalytic properties, is annealed in the following mode:

Heating to –120 °C

- 2 hours isotherm 120 °C
- 1 hour heating to 220 °C
- 2 hours isotherm 220 °C
- 1 hour heating to 550 °C
- 4 hours isotherm 550 °C

The whole process was repeated 3 times.

Results and discussion

Sorption volume analyzers are usually used to analyze the specific surface area of nanoporous materials (pore sizes from 0.4 to 500 nm). The method consists in saturating the pre-cleaned surface of the tested substance with adsorbate gas at a constant negative temperature with a gradual increase in pressure. The specific surface area of the catalytic system can be calculated based on the amount of adsorbate gas used to form a single layer. With further increase in pressure, the specific surface of the catalyst with high catalytic activity for the recovery of liquid hydrocarbons from natural gas continues to be filled with adsorbate molecules until all the pores of the solid are completely filled. In this way, the pore volume and pore volume distribution on the surface of the catalyst with high catalytic activity for the recovery of liquid hydrocarbons from natural gas are calculated.

The BET method can be used to determine the specific surface area with an accuracy of 5–10% in the range of $p/p_0 = 0.05–$ $–0.35$. Additional computational models are required to determine the volume of pores of different diameters in the total pore volume for determining the fraction from adsorption isotherms.

The process of catalytic synthesis of high molecular weight synthetic hydrocarbons from natural gas, from pentane to pentadecane, was carried out in a flow reactor operating in differential mode.

The reactor for obtaining high molecular weight synthetic hydrocarbons from natural gas, from pentane to pentadecane, in the form of a steel tube with an internal diameter of 20 mm, contains an immobile bed of a catalyst selected for obtaining high molecular weight synthetic hydrocarbons from pentane to pentadecane from 5 synthesis gases, i.e., a mixture consisting of carbon monoxide and hydrogen.

The catalytic activity per unit volume of the catalyst selected for obtaining high molecular weight synthetic hydrocarbons from pentane to pentadecane from synthesis gases, i.e., a mixture consisting of carbon monoxide and hydrogen, was determined by the following formula:

$$\mathbf{W=A\times S\times \eta.}$$

Here, W – is the catalytic activity per unit volume of the catalyst;

A – is the relative activity of the catalyst,

S – is the surface area of the catalyst;

η – is the utilization rate of the selected catalyst.

The reactor for the production of high molecular weight synthetic hydrocarbons from natural gas, from pentane to pentadecane, is placed in a cylindrical electric furnace. The temperature in the furnace is controlled. The temperature in the furnace is measured thermocouple, and in the reactor for the production of high molecular weight synthetic hydrocarbons from natural gas, from pentane to pentadecane. Both thermocouples are made of chromel wires. The temperature in the reactor for the production of high molecular weight synthetic hydrocarbons from natural gas, from pentane to pentadecane, is maintained with an accuracy of +10 °C.

Conclusion

1. It was found that granular cobalt catalysts containing cationic zeolites allow the production of synthetic oil with a final boiling point of up to 360 °C from CO and H_2 in one step.

2. In this work, it was shown that the use of zeolites cationized with alkali and alkaline earth metals allows the production of liquid hydrocarbons containing more than 40% of the C_{11}–C_{15} fraction, suitable for the production of high-quality diesel fuel.

3. It is shown that the degree of cationization of the zeolite affects the main characteristics of the process and the composition of synthetic oil.

4. It was confirmed that secondary transformations of hydrocarbons with the participation of composite cobalt catalysts based on zeolites cationized with alkali and alkaline earth metals proceed mainly by a monomolecular mechanism.

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