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COBALT CATALYST ON THE BASIS OF THE KENDYRLIK SHALE AND ITS APPROBATION IN FISHER-TROPSH SYNTHESIS

Abstract. The method of preparation of the cobalt catalyst and the results of the Fischer-Tropsch synthesis on the resulting catalyst, in which the shale of the Kendyrlik deposit was used as the support, zirconia was used as the promoter. The shale was pretreated by carbonization in an inert argon medium in the temperature range of 25-700°C and activation by steam at 850-900°C for 60 minutes. The catalyst (composition of 10%Co/1%ZrO_2/89%slate) in a volume of 100 ml was prepared by double impregnation, wherein salts hexahydrate of cobalt nitrate $Co(NO_3)2{\cdot}6H_2O$ and zirconium oxonitrateZrO $(NO_3)_3{\cdot}2H_2O$ were used. Further, the resulting catalyst was tested in Fischer-Tropsch synthesis in order to produce synthetic hydrocarbons. The catalyst was preliminarily reduced in a hydrogen atmosphere at 350°C for 1 hour, at a hydrogen space velocity of 1000 h-1 and a pressure of 0.2 MPa. The synthesis was carried out (at a molar ratio of $H_2/CO/N_2$ = 2/1/0.2) in the temperature range 160-220°C, at a space velocity of 500 h-1, and a pressure of 1.0 MPa. Chromatographic analysis of the hydrocarbons C_6-C_{21} obtained showed that mainly alkanes and arenesare formed during the synthesis.

Keywords: catalyst, cobalt,shale, Kendyrlyk, activation, Fisher-Tropschsynthesis, hydrocarbons.

Introduction. At present, much attention is paid to the implementation of selective Fischer-Tropsch synthesis (FT synthesis), in particular, to the synthesis of linear alkanes C_{11}-C_{18}, C_5-C_{10} isoalkanes, solid linear paraffins [1]. This catalytic process occurs by hydrogenation the carbon monoxide with hydrogen and includes the steps of polymerization, oligomerization, alkylation.

In FT synthesis, iron-containing and cobalt-containing catalysts are commonly used. In addition, Ni and Ru catalysts are also active, but their use seems ineffective due to low selectivity to higher hydrocarbons (Ni) and higher costs (Ru) [2].

To maintain high activity and selectivity of FT synthesis catalysts, in addition to varying the composition and conditions of preparation, a special organization of the catalytic layer is necessary in order to reduce the probability of overheating and reduce the gas-dynamic resistance. Particularly negatively affect the catalyst overheating, accompanied by coking and deactivation of the catalyst [3].

The main requirements for the organization of the catalytic layer for FT synthesis are: high concentration of the catalytically active component in the reaction volume, small characteristic particle size of the catalyst, high effective thermal conductivity of the catalyst layer, thermal stability and high mechanical strength of the catalyst, low hydraulic resistance [4].

However, these requirements do not always correspond to the requirements of existing process schemes using conventional catalysts in a suspended, fixed or fluidized bed [5]. In this regard, increasing the efficiency of the process of obtaining hydrocarbons from synthesis gas requires the development of new catalysts.

Products of FT-synthesis are of great practical importance as carbon-chemical raw materials, especially in connection with the fact that they contain many olefins, mainly of normal structure. The development of catalysts with improved catalytic properties and directional selectivity is of particular practical

interest and includes the study of new supports, catalytic compositions, and the conditions for their formation. Promising catalysts for the synthesis of hydrocarbons from CO and H_2 include cobalt systems that allow selective production of linear alkanes [1]:

$$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O$$

Usually, Al_2O_3, SiO_2, TiO_2 are used as support for cobalt catalysts [6]. Their main disadvantage is the intensive interaction with the metal, leading to the formation of mixed compounds, which lose the active phase and have a very high reduction temperature. One way to solve this problem is to use carbon supports that have little interaction with metal catalysts. Carbon supports have a number of unique structural properties and are of interest for catalysts in heterogeneous catalysis [6]. Carbon materials used as supports can be divided into several groups: activated carbon, carbon black, graphite, carbon nanotubes [7].

Especially it is necessary to allocate catalysts on cement (alumo-calcium) basis, which are characterized by high activity and productivity, mechanical strength, and also the ability to prevent them from carbonization [8].

The source of carbonaceous catalyst carriers can be shale rocks, which are available in Kazakhstan in sufficient quantities for their industrial use. Thus, the creation of fundamental and technological fundamentals for the production of new materials for gas-phase synthesis becomes particularly relevant.

The aim of this work is to prepare Co catalysts in which the shale of the Kendyrlik deposit was used as the support, followed by their testing in the Fischer-Tropsch synthesis to produce liquid hydrocarbons.

Experimental part. For the catalyst preparation (10%Co/1%ZrO_2/89%shale), the following reagents were used: cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ six-water salt, zirconium oxonitrate $ZrO(NO_3)_3 \cdot 2H_2O$. Table 1 shows the main characteristics of the reagents.

Table 1 – Characteristics of reagents

Reagents	Content, %
$Co(NO_3)_2 \cdot 6H_2O$	Co……..99.000not less Ni ……..0.010 not more Sulfates…….....0.003 not more Chlorides……..0.001 not more
$ZrO(NO_3)_3 \cdot 2H_2O$	99.95
CO	99.999
H_2	99.95

To use Kendyrlyk shale as a carrier, it was preliminarily ground on a hammer mill (Molot-200) to a fraction of 0.1 mm and granulated samples with a diameter of 0.8 cm were obtained from the obtained powder on a tablet press (model 1000).The samples were then subjected to processes of carbonization in an inert argon medium in the temperature range 25-700 ° C and then activation by steam at 850-900 ° C for 60 minutes.

The quantity of ingredients for the preparation of catalysts in a volume of 100 ml (weight 77 g) was: shale support– 68,53 g, metal Co - 7.7 g, zirconium Zr - 0.77 g, salt (for dissolution with water) - 2.22 g, distilled water - 13,23 ml.

The catalysts were prepared by the double impregnation method as follows. The metal salts of $ZrO(NO_3)_2 \cdot 2H_2O$, Co $(NO_3)_2 \cdot 6H_2O$ were dissolved in distilled water in a certain proportion. The concentration of solutions was selected based on the desired content of the active metal and the promoter in the catalyst. The resulting solution was gradually added to the support, continuously mixing it. Then, it was left at room temperature for 1 hour, so that the solution completely absorbed onto the support. The sample was then dried at 100 °C for 12 hours, followed by calcination in a Thermogravimetric Analyzer "ThermosterEltra" at 350 °C for 1 hour in an inert argon medium. The prepared catalysts were stored in desiccators.

Catalytic tests of the obtained Co catalyst were carried out in a laboratory flow-through installation with a tubular reactor with a fixed catalyst bed at atmospheric pressure (figure 1). For the synthesis, cylinders with gases (CO, H_2, N_2) were used, the degree of purity was not less than 99%.