

## PHYSICAL AND CHEMICAL CHARACTERISTICS OF SYNTHESIS GAS MOLECULAR HYDROCARBONS

**N.R. Ortiqov**

Karshi Institute of Engineering Economics.

### ABSTRACT

*The article studies the reaction of obtaining high molecular weight hydrocarbons from the synthesis gas and the physicochemical characteristics of the catalyst containing Co-Fe-Ni-ZrO<sub>2</sub>/YuKTs used in this process. The increase in selectivity in methane formation is due, on the one hand, to the acceleration of the hydrogenation reaction of CO at the methane formation centers due to the increase in synthesis temperature and the diffusion of CO and H<sub>2</sub> at different rates through zeolite pores. All fractions of hydrocarbons synthesized in the presence of hybrid catalysts contain large amounts of products of secondary conversion (cracking, isomerization) - isoparaffins and olefins. The high content of isoparaffins is recorded for the composite catalyst - the iso / n parameter is 0.6, which indicates an increase in its activity relative to the catalysts absorbed in the hydro-improvement reactions.*

**Keywords:** synthesis gas, high molecular weight hydrocarbons, catalyst, IR spectrum, diffractogram

### АННОТАЦИЯ

*В статье исследована реакция получения высокомолекулярных углеводородов из синтез-газа и физико-химические характеристики катализатора, содержащего Co-Fe-Ni-ZrO<sub>2</sub>/ЮКЦ, используемого в этом процессе. Повышение селективности метанообразования обусловлено, с одной стороны, ускорением реакции гидрирования СО в центрах метанообразования за счет повышения температуры синтеза и диффузии СО и Н<sub>2</sub> с разной скоростью через поры цеолита. Все фракции углеводородов, синтезированные в присутствии гибридных катализаторов, содержат большое количество продуктов вторичной конверсии (крекинга, изомеризации) - изопарафинов и олефинов. Высокое содержание изопарафинов зафиксировано для композиционного катализатора - параметр изо/п равен 0,6, что свидетельствует о повышении его активности по отношению к катализаторам, абсорбированным в реакциях гидрооблагораживания.*

**Ключевые слова:** синтез-газ, высокомолекулярные углеводороды, катализатор, ИК спектр, дифрактограмма

## **INTRODUCTION**

One of the most promising ways to obtain motor fuel from carbon-containing sources that are an alternative to oil is GTL technology. Unlike petroleum products, synthetic fuels in practice do not contain aromatic mono- and polycyclic compounds, organic sulfur and nitrogen compounds, and are environmentally friendly and high-quality consumer fuels [1-5]. In nature, the raw material base of synthetic fuels is widespread, consisting of carbon-containing materials - natural, petroleum gases, coal, biomass. GTL technology involves the following steps: obtaining synthetic gas (a mixture of CO<sub>2</sub> and H<sub>2</sub>); catalytic conversion of synthesis gas to hydrocarbons by the Fisher-Tropsh method; separation of products into fractions of gasoline (S<sub>5</sub>-S<sub>10</sub>), diesel (S<sub>11</sub>-S<sub>18</sub>), wax (S<sub>19+</sub>).

The main stage of GTL technology is the catalytic conversion of synthesis gas to hydrocarbons by the Fisher-Tropsh method (FT-synthesis). In the catalytic conversion of synthesis gas to hydrocarbons, cobalt, nickel, ruthenium, iron, etc., from group VIII metals with variable valence, show catalytic activity. Cr, Mo, W, Mb, Te, Re from group VI metals, Cu, Ag, Au from group IV metals increase the activity of the catalyst to some extent .

## **DISCUSSION AND RESULTS**

In practice, two types of FT-synthesis are used in industry: low-temperature and high-temperature variants. Low temperature synthesis (LTFT) is carried out in cobalt or iron catalysts at temperatures below 300°C. It mainly produces high molecular weight n-paraffins, n-olnifins and oxygen-containing components. High temperature synthesis (NTFT) is carried out in an iron catalyst at temperatures above 300°C. The product is mainly a mixture of hydrocarbons with a high content of olefins, which are used as the main raw material for many chemical processes. FT is characterized by a relative lack of isoparaffins for synthesis products, so the hydrocarbons being synthesized have a low octane number. The turbidity temperature and filtration temperature of the diesel fraction are not very high, which makes it difficult to use these components as fuel. Therefore, in both options it is necessary to change the composition of raw materials obtained in the production of motor fuel, which are combined and hydraulified using cracking, isomerization and other processes according to the technological scheme.

It is advisable to intensify the process of each stage in order to demonstrate the competitiveness of GTL technology for the production of motor fuel in the traditional way. One solution to this problem is to combine hydrocarbon synthesis with

hydrocarbon synthesis in a single reactor. This requires the development of new effect hybrid catalysts. Block-modular mobile technology implemented in the GTL technological process allows the use of simple equipment in the processing of petroleum gases and low-pressure gases from used gas fields in mining conditions. GTL technologies and equipment on such a relatively small scale have been developed by Compact GTL, Velocys, Chevron, Infratechnology, Gazoxim Techno.

In the synthesis of hydrocarbons from CO and H<sub>2</sub>, the catalytic properties of the catalysts were tested in a flow isothermal reactor filled with 30 cm<sup>3</sup> of quartz (catalyst layer 10 cm<sup>3</sup>) under the following optimal conditions: temperature range 280-300 ° C, 0.5 MPa and gas flow rate (GHT) 1000 hour<sup>-1</sup>. Balanced experiments were performed for at least 150 h, the incoming and outgoing gas composition was analyzed, and the amount of hydrocarbons and reaction water obtained was recorded.

The activity of hydrocarbon synthesis catalysts was evaluated on the following indicators: CO conversion, selectivity and efficiency for hydrocarbons. The calculation error did not exceed 2.5%. CO conversion was calculated according to the following formula:

$$X_{CO} = \frac{V_{vx} \cdot c(CO)_{vix} - V_{vix} \cdot c(CO)_{vix}}{V_{vx} \cdot c(CO)_{vix}} \cdot 100\%$$

Where V<sub>kir</sub>, V<sub>chiq</sub> - gas consumption at the entrance to the reactor and at the exit from the reactor, dm<sup>3</sup> / h;

c (CO) input, c (CO) output - CO concentration at the inlet and outlet of the reactor, unit percentage.

Methane selectivity was calculated according to the following formula:

$$S_{CH_4} = \frac{V(CO)_{CH_4}}{V(CO)_{np}} \cdot 100\%$$

where V (CO) CH<sub>4</sub> - volume of CO used to produce methane, dm<sup>3</sup>; V (CO) ma - volume of CO converted to methane, dm<sup>3</sup>.

Selectivity for C<sub>5+</sub> hydrocarbons was calculated using the formula:

$$S_{C_{5+}} = \frac{V(CO)_{C_{5+}}}{V(CO)_{np}} \cdot 100\%$$

where V (CO) is the volume of CO used to form C<sub>5</sub> + - C<sub>5</sub> + hydrocarbons, dm<sup>3</sup>.

Productivity for C<sub>5</sub> + hydrocarbons was calculated according to the following formula:

$$G_{C_{5+}} = \frac{m_{C_{5+}}}{V_{kat} \cdot \tau}$$

where m<sub>C<sub>5</sub> +</sub> is the mass of C<sub>5</sub> + hydrocarbons, kg; V<sub>kat</sub> - catalyst volume, m<sup>3</sup>; τ - time, hour.

The composition of gaseous synthesis products was analyzed on a chromatograph "Crystal 5000" (Chromatek, Russia) equipped with a thermal conductivity detector with gas adsorption chromatography and two columns with active Haysep R phase and NaX molecular sieves. Analysis mode The temperature can be programmed with a heating rate of 8° C / min.

The composition of C<sub>5</sub> + hydrocarbons was determined by capillary gas-liquid chromium-mass spectrometry on a gas chromatograph (Agilent, USA) equipped with a mass-selective detector MSD 5975C.

The study of the catalytic properties of the samples during the synthesis of hydrocarbons from CO and H<sub>2</sub> was carried out at a temperature of 290 ° C, a pressure of 0.5 MPa, a volumetric velocity of the gas at 1000 h<sup>-1</sup> and a ratio of H<sub>2</sub> / CO = 2. High silicon zeolite derived from Navbahor bentonite was used as a catalyst retainer. The experimental data obtained are presented in Table 1.

## CONCLUSION

Analysis of the dependence of the conversion rate of CO on the synthesis temperature shows that the composite catalyst exhibits higher activity in FT-synthesis than the absorption catalysts. Despite a 3-fold decrease in cobalt concentration, an increase in FT-synthesis temperature to 290 ° C in the presence of a composite catalyst allows to achieve CO conversion rates of 74.2% and a hydrocarbon C<sub>5+</sub> yield of 91.7 kg / m<sup>3</sup>kat · h. The FT-synthesis catalyst is comparable to similar values for Co-Fe-Ni-ZrO<sub>2</sub> / YuKTs.

## REFERENCES.

1. Li, X. One-step synthesis of H $\beta$  zeolite-enwrapped Co/Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalyst with high spatial selectivity / X. Li, J. He, M. Meng, Y. Yoneyama, N. Tsubaki // Journal of Catalysis. 2009. T. 265. P. 26-34.
2. Yang, G. Tandem catalytic synthesis of light isoparaffin from syngas via Fischer-Tropsch synthesis by newly developed core-shell-like zeolite capsule catalysts / G. Yang, C. Xing, W. Hirohama, Y. Jin, C. Zenga, Y. Suehiro, T. Wang, Y. Yoneyama, N. Tsubaki // Catalysis Today. 2013. T. 215. P. 29-35.
3. Yang, G. Preparation, characterization and reaction performance of H-ZSM-5/cobalt/silica capsule catalysts with different sizes for direct synthesis of isoparaffins / G. Yang, J. He, Y. Yoneyama, Y. Tan, Y. Han, N. Tsubaki // Applied Catalysis A: General. 2007. V. 329. P. 99-105.

- 
4. Huang, X. CoZr/H-ZSM-5 hybrid catalysts for synthesis of gasoline-range isoparaffins from syngas / X. Huang, B. Hou, J. Wang, D. Li, L. Jia, J. Chen, Y. Sun // Applied Catalysis A: General. 2011. V. 408. P. 38-46.
  5. Mazonde, B. A solvent-free strategy for in-situ synthesis of hierarchical Co-based zeolite catalyst and its application in tuning Fischer-Tropsch product selectivity / B. Mazonde, S. Cheng, G. Zhang, M. Javed, W. Gao, Y. Zhang, M. Tao, C. Lu, C. Xing // Catalysis Science & Technology. 2018. V. 8. P. 2802-2808.