

REACTION STOICHIOMETRY IN THE SYNTHESIS OF HYDROCARBONS BY THE FISHER-TROPSCH METHOD

Suxrob Ro'ziyev

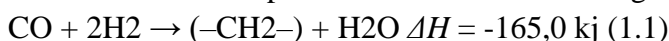
Master, Karshi Engineering and Economic Institute,
Republic of Uzbekistan, Karshi

Abstract

The synthesis of hydrocarbons from CO and H₂ in the Fischer-Tropsch method is a complex system of chemical reactions that take place in series and in parallel with the presence of a catalyst.

Introduction

The main synthesis reaction is the hydrogenation of carbon monoxide [14] (the thermal effect of reactions at a temperature of 227 °C according to [15]):

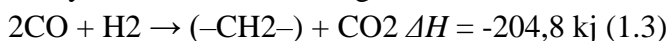


Equation (1.1) best describes the formation of hydrocarbons in the presence of cobalt catalysts.

The water formed according to the three equations can participate in the water gas reaction according to the equation (1.2), which is more typical for iron catalysts:



In this case, the general equation for the synthesis of hydrocarbons in the presence of iron catalysts takes the following form:



In general, the equation for the synthesis of hydrocarbons looks like this:

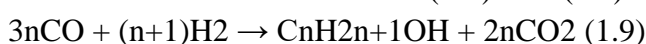
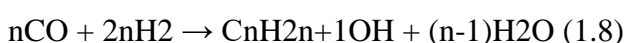
For the synthesis of paraffins



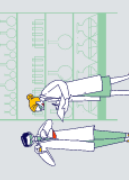
For the synthesis of olefins



In the process of synthesis, oxygen-containing compounds can also be formed: Formation of alcohols



Formation of aldehydes



In addition to the main synthesis reactions, the following side processes can occur:

- hydrogenation of CO to methane, which actively occurs at temperatures above 200 ° C in the presence of cobalt and nickel catalysts [8, 16]:



- carbon formation due to CO disequilibrium (BU-Duara reaction) leads to blocking of the active surface of the catalyst [17]:



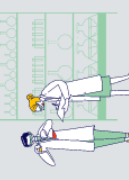
In addition to the above reactions, in the conditions of hydrocarbon synthesis, the processes of secondary transformation of the product can be observed: hydrogenation, cracking, isomerization.

Mechanism of Hydrocarbon Synthesis

A large amount of work has been devoted to the study of the mechanism of hydrocarbon synthesis by the Fischer-Tropsch method [1].

The mechanism of synthesis is reflected in several basic assumptions, the essence of which can be reduced to the following basic rules:

- hydrogen is chemisorbed in the form of atoms;
- carbon oxide is chemisorbed on the surface of metal atoms when a bond is formed in metal carbonyls;
- chain growth reactions proceed in two ways: addition to extreme carbon atoms and addition to carbon atoms adjacent to extremes;
- during the reaction between adsorbed hydrogen and carbon monoxide, intermediate compounds are formed, which are carbides, carbonyls, formaldehydes, on the basis of which hydrocarbon chains are already growing. The considered mechanisms can be summarized in two main groups: associative [2] and dissociative theory [3]. A variant of the dissociative theory of the carbide mechanism for iron catalysts (carbides as intermediate surface compounds) seems justified. The generally accepted mechanism for cobalt catalysts involves the presence of a bifunctional active site where associative adsorption of CO and polymerization of intermediates occurs [4]. Within the framework of known mechanisms, the main primary products of synthesis are mainly aliphatic hydrocarbons of normal structure. The formation of branched hydrocarbons is facilitated by secondary transformations: isomerization, cracking, entering a growing chain, etc. Attention is paid to the review of the mechanisms of secondary transformation of hydrocarbons. To date, many details of the mechanisms proposed for the synthesis of hydrocarbons remain unclear, and the mechanisms themselves are controversial for well-studied catalytic systems. However, almost everyone recognizes that FT synthesis is relevant to polymerization reactions, and this approach is widely used to characterize the molecular weight distribution (MWD) of products that obey formal kinetics. To describe the composition of FT synthesis products, it is now customary to use the Anderson-Schulz-Flory (ASF) distribution, a combination of the equations derived by Schulz and Flory for analysis. MWD of linear radical polymerization and polycondensation polymers used by Anderson in his work.



The Schulz and Flory equation looks like this:

$$g_n = (\alpha^n - \alpha) n \alpha^{n-1} \quad (1.14)$$

$$m_n = (1 - \alpha) \alpha^{n-1} \quad (1.15)$$

Here, g_n and m_n are the mass and molar fractions of FT synthesis products, n is the number of carbon atoms, α is the chain growth probability, and the ratio of growth (k_1) and termination (k_2) rate constants. hydrocarbon chain = $\frac{k_1}{k_1 + k_2}$.

The distribution of ACF corresponds to the composition of hydrocarbon synthesis products. For them, the relationship $\lg(g_n/n) - n$ is a straight line. Sometimes there may be deviations or inconsistencies in the molecular weight distribution, which may be due to the presence of two or more active centers on the surface, the reduction of the amount of C2-C4 hydrocarbons due to their participation in secondary reactions. The amount of hydrocarbon fractions formed depends on the probability of chain growth (Fig. 1.1). α values of 0.2-0.6 are typical for products consisting mainly of C1-C4 hydrocarbons. When α values approach 1, the composition of the products is mainly represented by C19+ hydrocarbons. Only methane or high molecular weight paraffins (waxes) can be obtained with 100% selectivity.

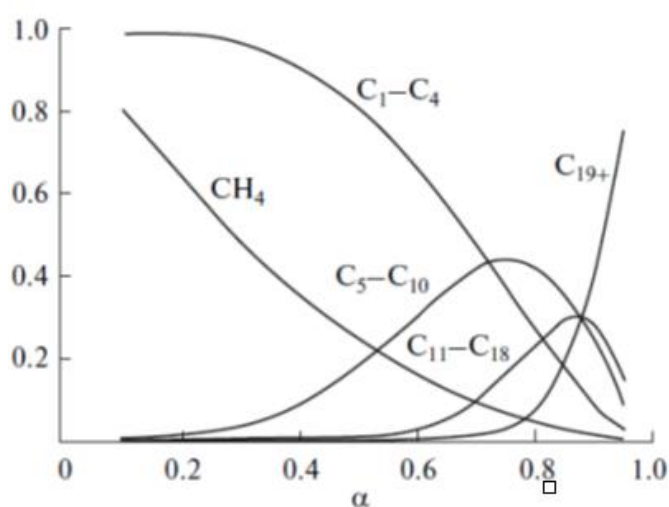


Figure 1 - The dependence of the distribution of Fischer-Tropsch fusion products on the probability of chain growth [5]

Thus, the main products of the Fischer-Tropsch synthesis are straight-chain hydrocarbons, and the formation of branched products is facilitated by secondary processes. The selectivity of the formation of liquid hydrocarbons (C5-C18) is limited according to the distribution of ASHF, characterized by a value of 45 and equal for the fractions of gasoline (C5-C11) and diesel (C10-C18). 30% respectively.

Cobalt Catalysts

Among known catalysts for FT synthesis, the most promising are cobalt catalytic systems, which are characterized by: operation at relatively low temperatures; Predominant formation of n-paraffins; negligible activity in water gas conversion, as well as in the Bell-Boudoir reaction (due to the low temperatures of the process). When preparing catalysts, it should be taken into account that FT synthesis is a structure-sensitive process, therefore selectivity and catalytic activity for C5+ hydrocarbons are affected by the size and structure of active component particles. Cobalt particles smaller than 5 nm in size are known to be active centers for the hydrogenation of CO to methane, with reduced selectivity and catalytic activity in the formation of C5+ hydrocarbons. Optimal selectivity and the highest specific activity are achieved for catalysts whose particles of the active component are dispersed in the size range from 6 to 10 nm. The formation of the active component of cobalt catalysts is influenced by the method of preparation, the mode of heat treatment, the choice of carrier, and the state of promotion and reduction. According to the methods of preparation, the following groups of cobalt catalysts are distinguished. The method of introducing the active metal is the most important component of the preparation method, because it determines both the composition of the main component and the state of the active surface of the catalyst. Supported catalysts are the most common, and the method of impregnating carriers with cobalt precursors is widely used for their preparation [6]. The final stage of preparation for supported catalysts is heat treatment (drying, calcination) of impregnated granules. During the drying stage, due to the removal of the solvent, the applied substance settles in the pores of the carrier. Obtaining the oxidized form of the catalyst is carried out by calcining the granules, which should be carried out at temperatures that do not lead to the formation of difficult-to-regenerate compounds of the active component and the support, as well as during sintering of the active catalyst. stage. As a rule, supports with a high specific surface area (oxides of aluminum, silicon, titanium, etc.) are used for the preparation of catalysts, which meet the following requirements: stabilization of the active component, formation. porous structure of the catalyst, ensuring thermal stability, etc. The most common carrier for cobalt catalysts is silica. Such catalytic systems are characterized by a relatively weak interaction between the carrier and the active component, as a result of which dispersion in such systems reaches small values [7]. Catalysts based on γ -Al₂O₃ are characterized by a strong interaction between cobalt oxide and the support to form compounds of cobalt and aluminum, which significantly affects the fineness of the active component and makes it difficult to transfer the catalyst to the metallic state (with hydrogen return). This feature is common for catalysts in this carrier. Therefore, a higher reduction temperature is required to achieve a higher degree of catalyst conversion to the metallic state. An important moment in the formation of the active component of the catalyst is stimulation. Promoters weaken the interaction between cobalt and the support, increase the active surface area of the metal, which leads to increased catalytic activity and, in some cases, better stability. The most common promoters are noble metals [8] (Pt, Ru, Re, etc.), oxide additives (Al₂O₃, MgO, ZrO, etc.), as well as transitions and alkalis. metals. The choice of the mode of transition of the catalyst to the metallic state has a significant effect on the distribution

of the active component. It is known that high temperature causes agglomeration of cobalt particles, which leads to a decrease in catalytic activity. At the same time, it is desirable to carry out the reduction of catalysts before transferring 40-60% cobalt to the metallic state. According to the literature, in the temperature range of 300-350 °C, cobalt oxide Co_3O_4 is easily reduced to CoO , and then to metallic cobalt. As a result of the reduction of CoO , pyrophoric metals with high catalytic activity are obtained. Thus, it is recommended to carry out the process of reduction of cobalt catalysts at a temperature of 350-450 °C. In industrial practice, it is technologically justified to carry out catalyst reduction processes in a separate apparatus, after which the returned catalyst is unloaded and loaded into the synthesis reactor. The recovered catalyst is pyrophoric, so it must be passivated before transport for safety reasons. Passivation is the formation of a protective film on the metal surface that prevents oxidation. The catalyst in this form remains in the air for a long time without losing activity

REFERENCES

1. Kuyboqarov O., Anvarova I., Abdullayev B. RESEARCH OF THE CATALYTIC PROPERTIES OF A CATALYST SELECTED FOR THE PRODUCTION OF HIGH-MOLECULAR WEIGHT LIQUID SYNTHETIC HYDROCARBONS FROM SYNTHESIS GAS //Universum: технические науки. – 2023. – №. 10-7 (115). – С. 28-32.
2. Kuyboqarov O., Egamnazarova F., Jumaboyev B. STUDYING THE ACTIVITY OF THE CATALYST DURING THE PRODUCTION PROCESS OF SYNTHETIC LIQUID HYDROCARBONS //Universum: технические науки. – 2023. – №. 11-7 (116). – С. 41-45.
3. Муртазаев Ф.И., Неъматов Х.И., Бойтемиров О.Э., Куйбакаров О.Э., & Каршиев М.Т. (2019). ПОЛУЧЕНИЕ КОМПОЗИЦИЙ НА ОСНОВЕ СЕРЫ И НИЗКОМОЛЕКУЛЯРНОГО ПОЛИЭТИЛЕНА ДЛЯ ДОРОЖНЫХ И СТРОИТЕЛЬНЫХ МАТЕРИАЛОВ. *Международный академический вестник*, (10), 102-105.
4. Муртазаев Ф.И., Неъматов Х.И., Бойтемиров О.Э., Куйбакаров О.Э., & Каршиев М.Т. (2019). ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА СИНТЕЗИРОВАННЫХ ОЛИГОМЕРОВ ДЛЯ ОБЕССЕРИВАНИЯ ПРИРОДНОГО ГАЗА ОТ СЕРОВОДОРОДА. *Международный академический вестник*, (10), 105-107.
5. Boytemirov O., Shukurov A., Ne'matov X., & Qo'yboqarov O. (2020). Styrene-based organic substances, chemistry of polymers and their technology. *Результаты научных исследований в условиях пандемии (COVID-19)*, 1(06), 157-160.
6. Куйбокаров О., Бозоров О., Файзуллаев Н., Хайитов Ж., & Худойбердиев И.А. (2022, June). Кобальтовые катализаторы синтеза Фишера-Тропша, нанесенные на Al_2O_3 различных полиморфных модификаций. In *E Conference Zone* (pp. 349-351).
7. Куйбокаров О.Э., Бозоров О.Н., Файзуллаев Н.И., & Нуруллаев А.Ф.У. (2022). КАТАЛИТИЧЕСКИЙ СИНТЕЗ ВЫСОКОМОЛЕКУЛЯРНЫХ УГЛЕВОДОРОДОВ ИЗ СИНТЕЗ-ГАЗА В ПОЛИФУНКЦИОНАЛЬНОМ КАТАЛИЗАТОРЕ. *Universum: технические науки*, (1-2 (94)), 93-103.
8. Куйбокаров О.Э., Бозоров О.Н., Файзуллаев Н.И., & Хайдаров О.У.У. (2021). СИНТЕЗ ВЫСОКОМОЛЕКУЛЯРНЫХ УГЛЕРОДОВ ИЗ СИНТЕТИЧЕСКОГО ГАЗА ПРИ

УЧАСТИИ СО-FE-NIZRO2/ВКЦ (ВЕРХНИЙ КРЫМСКИЙ ЦЕОЛИТ). *Universum: технические науки*, (12-4 (93)), 72-79.

9. Куйбоқаров О.Э., Шобердиев О.А., Рахматуллаев К.С., & Муродуллаева Ш. (2022). ПОЛИОКСИДНЫЕ КАТАЛИЗАТОРЫ ПЕРЕРАБОТКИ МЕТАНА В СИНТЕЗ ГАЗ. *Central Asian Research Journal for Interdisciplinary Studies (CARJIS)*, 2(5), 679-685.

10. Rustamovich O.N., Ergashovich K.O., Khujanazarovna K.Y., Ruzimurodovich K.D., & Ibodullaevich F.N. (2021). Physical-Chemical and Texture Characteristics of Coate-Fe-Ni-ZrO₂/YuKS+ Fe₃O₄+ d-FeOON. *Turkish Online Journal of Qualitative Inquiry*, 12(3).

11. О.Э.Куйбоқаров.,Т.Х.Сайфуллаев Конверсия метана в карбонат на молибденовых и цирконийных катализаторах *Universum: технические науки*. Выпуск: 12(117) Декабрь 2023 год.

12. О.Э.Куйбоқаров. Контроль качества препарата самарий153sm-оксобифор *Universum: технические науки*. Выпуск: 3 (120) март 2024 год.

13. Qo'yoqarov O.E. Metanni karbonatli konversiyalanishi Sanoatda raqamli texnologiyalar 2(1). (2024).

14. Oybek Kuybokarov, Muradulla Karshiyev, Ganisher Rakhimov, Research of the catalytic properties of a catalyst selected for the production of high-molecular weight liquid synthetic hydrocarbons from synthesis gas E3S Web Conf. III International Conference on Actual Problems of the Energy Complex: Mining, Production, Transmission, Processing and Environmental Protection (ICAPE2024) Volume 498, 2024.

