Study of the process of obtaining hydrocarbons on the basis of synthesis gas and the fischer-tropsch synthesis reaction

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Abstract. The Fischer–Tropsch process is a collection of chemical reactions that converts a mixture of carbon monoxide and hydrogen, known as syngas, into liquid hydrocarbons. These reactions occur in the presence of metal catalysts, typically at temperatures of 150–300°C (302–572°F) and pressures of one to several tens of atmospheres. The Fischer–Tropsch process is an important reaction in both coal liquefaction and gas to liquids technology for producing liquid hydrocarbons. In the usual implementation, carbon monoxide and hydrogen, the feedstocks for FT, are produced from coal, natural gas, or biomass in a process known as gasification. The process then converts these gases into synthetic lubrication oil and synthetic fuel. This process has received intermittent attention as a source of low-sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons. Fischer-Tropsch process is discussed as a step of producing carbon-neutral liquid hydrocarbon fuels from CO2 and hydrogen. The article is devoted to the use of synthesis gas as an alternative petroleum raw material for obtaining artificial liquid fuels, hydrocarbons (Fisher-Tropsch synthesis) and aldehydes (hydroformylation or oxo-synthesis). The mechanisms of the considered reactions are discussed.

1 Introduction

History knows a lot of examples, because of an urgent need, new original methods to solving life trouble that have existed for a long time appeared. Thus, in pre-war Germany, deprived of oil resources, there was an acute shortage of fuel necessary for the operation of powerful military equipment. Germany, which has large reserves of coal, was must to look for ways to convert it into liquid fuel. This problem was successfully solved by the efforts of good chemists, about whom we should first mention Franz Fischer, director of the Kaiser Wilhelm Institute for Coal Research [1].

In 1926, F. Fisher and G.Tropsch's work "On the direct synthesis petroleum of hydrocarbons at medium pressure" was published, in which it was reported that various substances are involved in the reaction of carbon monoxide with hydrogen at atmospheric

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pressure catalysts (iron - zinc oxide or cobalt - chromium oxide) at 270°C, liquid and even solid homologues of methane are obtained.

So, the famous synthesis of hydrocarbons from carbon monoxide and hydrogen showed, which was later called the Fischer-Tropsch synthesis. A mixture of CO and H_2 in various proportions, called synthesis gas, can be easily obtained from carbonaceous or other coal raw materials [2].

It may be noted that by the time Fischer-Tropsch synthesis was developed, there was another method to obtain liquid fuel - not from synthesis gas, but directly from coal -by direct hydrogenation. In this field, the German chemist F. Bergius also achieved considerable success, he obtained gasoline from coal in 1911. To be honest, we emphasize that the Fischer-Tropsch synthesis did not appear from scratch - by that time there were scientific conditions based on the achievements of heterogeneous catalysis and organic chemistry. In 1902, J. Sanderan and P. Sabatier were the first to obtain methane from H_2 and CO. In 1908, E. Orlov discovered that ethylene was formed when carbon monoxide and hydrogen were passed through a palladium deposited and catalyst consisting of nickel on coal [3].

The manmade liquid fuel industry its peak reached during World War II. Suffice it to say that synthetic fuel almost completely covered Germany's aviation gasoline needs. After 1945, due to the rapid development of oil production and the decrease in oil prices, there was no need to synthesize liquid fuels from H_2 and CO. The petrochemical boom has arrived. But, in 1973, the oil crisis began - the OPEC (Organization of the Petroleum Exporting Countries) oil-producing countries sharply increased the price of crude oil, and the world community was forced to understand the real threat of oil depletion in the cheap oil and near future cheap resources. The energy shock of the 70s revived the interest of scientists and industrialists in the use of alternative raw materials to oil, and the first place here undoubtedly belongs to coal. The world's reserves coal are huge, according to various estimates, they are 50 times more than oil resources, and they can last for hundreds of years. There is no doubt that the use of synthesis gas in the near future is not only important in the production of "coal" fuels (where it is still difficult to compete with petroleum fuels), but primarily for the purposes of organic synthesis. Currently, the industrial scale Fischer-Tropsch process produces gasoline, kerosene and paraffins only in South Africa. Sasol plants produce about 5 million tons of liquid hydrocarbons per year [4].

CO and H_2-based syntheses is a sharp increase in publications devoted to the chemistry of single-carbon molecules (so-called C 1 chemistry). The international journal "C1-Molecule Chemistry" has been published since 1984 [5]. Thus we are witnessing a coming renaissance in the history of coal chemistry. Let 's take a look at some of the ways syngas can be converted to produce hydrocarbons and some valuable oxygen compounds. The most important role in the transformation of CO belongs to heterogeneous and homogeneous catalysis [6].

Hydrocarbons are a class of organic compounds whose molecules consist only of carbon and hydrogen atoms. According to its structure, it is divided into acyclic or aliphatic (the carbon atoms in the molecule are connected to each other in a linear or branched chain), isocyclic or carbocyclic (the molecule consists of a ring of 3 or more carbon atoms - a cycle) [7] This group consists of U.acyclic and aromatic hydrocarbons (see also Aromatic compounds). Acyclic it is composed of saturated hydrocarbons and unsaturated hydrocarbons. Alicyclic U. can be both saturated and unsaturated. U. forms homologous groups (see also Organic chemistry). It consists of oil, natural gas, some industrial gases and tar [8].

2 Materials and methods

The first method of producing synthesis gas was the gasification of coal, which was carried out in England in the 1930s to obtain combustible gases: hydrogen, methane, carbon monoxide. This process was widely used in many countries until the mid-1950s, when it was replaced by methods based on natural gas and oil. However, due to the reduction of oil resources, the importance of the gasification process began to increase again [9].

Nowadays, there are 3 main available industrial ways for obtaining synthesis gas.

1. Coal gasification. The process is the interaction of coal based on with water vapour:

$$C + H_2O \backslash u003d H_2 + CO.$$
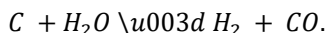
This reaction is equilibrium, and the endothermic shifts to the right at a temperature of 900-1000°C. Developed technological processes, using steam-oxygen explosion, in which, in addition to the high reaction, an exothermic reaction of coal combustion happens, which provides the necessary heat balance:

$$C + 1/2O_2 = CO.$$
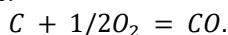
2. Conversion of methane. The reaction of the interaction of methane with water vapour is carried out at high temperature (800-900 ° C) and pressure in the presence of nickel catalysts (Ni-Al$_2$O$_3$):

$$CH_4 + H_2O \backslash u003d CO + 3H_2.$$

Any hydrocarbon feedstock can be used instead of methane as feedstock.

3. Partial oxidation of hydrocarbons. The process consists of incomplete thermal of oxidation hydrocarbons at temperatures high 1300°C [10]:

$$C_n H_{2n} + 2 + 1/2nO_2 = nCO + (n + 1) H_2.$$
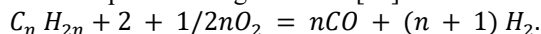
The method is applicable to any hydrocarbon raw material, but the high-boiling fraction of oil most used in industry is fuel oil. The ratio of CO: H$_2$ depends significantly on the approach used to obtain synthesis gas. In coal gasification and partial oxidation, this ratio is near to 1:1, while in methane conversion, the CO: H$_2$ ratio is 1:3. Nowadays, underground gasification, that is, direct coal Deep-sea gasification projects are being developed. Interestingly, this idea was expressed by D.I. Mendeleev 100 years ago. In the future, synthesis gas will be obtained by gasifying not only coal, but also other carbon sources, including municipal and agricultural waste.

3 Metal carbonyls and the 18-electron rule

Many syntheses based on carbon dioxide and hydrogen are of great practical and theoretical interest because they allow obtaining the most valuable organic compounds from two simple substances. And here the decisive role is played by catalysis by transition metals, which are able to activate inert CO and H$_2$ molecules. Activation of molecules is their transition to a more reactive state. In particular, it should be noted that a new type of catalysis, i.e. transition metal complexes or metal complex catalysis, has been widely developed in synthesis gas transformation [11].

CO molecule so inert? Ideas about the inertness of carbon monoxide are conditional. In 1890, Mond obtained the first carbonyl compound of a metal from nickel metal and carbon oxide, a volatile liquid with a boiling point of 43°C - Ni(CO)$_4$. The history of this discovery, which may have been accidental, is interesting. Mond studied the causes of rapid corrosion of nickel reactors in the production of soda from NaCl, ammonia and CO$_2$ and determined that the cause of corrosion is the presence of carbon monoxide compounds that react with nickel in CO$_2$ to form tetracarbonyl Ni. (CO)$_4$. This discovery allowed Mond to further develop nickel purification methods by capturing volatile nickel carbonyl and then thermally decomposing it back into nickel and CO. After 25 years, iron carbonyl - Fe (CO)$_5$ was also accidentally discovered. When a long-forgotten steel CO cylinder was opened at BASF, a

yellow liquid - iron pentacarbonyl - was found at the bottom, which was slowly formed as a result of the reaction of metallic iron with CO under high pressure. Since metal carbonyls are very toxic compounds, at first the reaction of chemists to them was very cold, but later amazing properties, including catalytic properties, were discovered, which determined their widespread use, especially in the chemistry of carbon monoxide. Note that many metals in finely dispersed state can react directly with carbon monoxide, but only nickel and iron carbonyls are obtained in this way. Carbonyls of other metals are obtained by reducing their compounds in the presence of CO at high pressures [12].

The composition of transition metal carbonyl complexes can be predicted based on the 18-electron rule, according to which the complex is stable if the valence electrons of the metal and the electrons provided by the ligand, in our case CO, are present equal to 18, because in this case the electronic configuration corresponds to the stable configuration of noble atomic gases (krypton) [13].

A carbon dioxide molecule has a lone pair of electrons, while a pair of electrons in carbon can be provided to form a donor-acceptor bond with the metal. As an example, we consider the structure of iron and nickel carbonyls $Fe(CO)_5$ and $Ni(CO)_4$. Iron and nickel atoms have 8 and 10 valence electrons, respectively, and are missing 10 and 8 electrons to fill the atom's electron shell to the krypton noble gas atom configuration, thus forming carbonyls. , the iron atom must be provided with electron pairs of five CO molecules, and the nickel atom - four.

Transition metals with an odd number of valence electrons form dinuclear carbonyl complexes. Thus, for cobalt, which has nine valence electrons, nine electrons are not enough to achieve a stable electron configuration. Uninuclear complexes have unpaired electrons due to the acceptance of four pairs from CO molecules, and such radical particles interact with each other to form a metal-metal bond, resulting in the formation of a dimeric complex CO_2. (CO)8 is formed.

The interaction or coordination of carbon oxide with the metal leads to a redistribution of electron density not only to CO, but also to the metal, which significantly affects the reactivity of the carbonyl complex. The most common linear type of CO coordination:

In this case, the interaction is not only due to the free pair of carbon electrons, but also due to the energetic transfer of electrons from the d-orbital of the metal an interaction also occurs due to the transition to the available empty carbon orbitals:

4 Concepts of basic reactions in catalysis

Let us note some important basic reactions in metal complex catalysis. These are primarily oxidative addition and reductive elimination reactions. Oxidative addition is a reaction in which neutral AB molecules, such as H_2 or halogen, are added to the metal center of the complex. In this case, the metal is oxidized, which is accompanied by an increase in its coordination number: where L is the ligand.
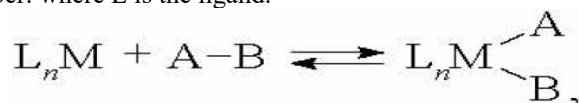
$$L_nM + A-B \rightleftharpoons L_nM \overset{\displaystyle A}{\underset{\displaystyle B,}{<}}$$

Fig. 1. This joining is accompanied by the separation of the AB bond.

The reaction of the oxidative addition of the hydrogen molecule is very important, as a result of which it is activated. [8] The oxidative addition of hydrogen to a square planar complex of monovalent iridium, discovered by Vasco and Dilucio, is well known. As a result, the oxidation state of iridium increases from I to III:
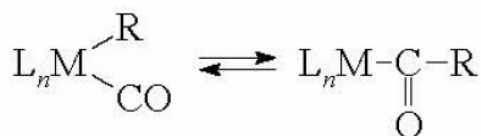
Fig. 2. Oxidative addition reaction of hydrogen to a square planar complex of monovalent iridium discovered by Vasco and Dilucio.

The reverse reaction of oxidation addition is called reductive elimination, in which the oxidation state and the coordination number of the metal are reduced by two.

Also note the migration insertion reaction, which is the introduction of unsaturated compounds through metal-carbon and metal-hydrogen bonds. The CO insertion reaction is fundamental to many processes related to gas synthesis:
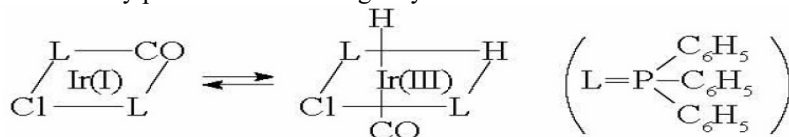

Fig. 3. Olefin introduction is the most important reaction among catalytic transformations of olefins: hydrogenation, hydroformylation, etc.

5 Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis can be viewed as a carbon monoxide-reducing oligomerization reaction in which carbon-carbon bonds are formed, and in general, it is a complex combination of a number of heterogeneous reactions that can be represented by general equations:

$$nCO + 2nH_2 = (CH_2)\,n + nH_2O,$$
$$2nCO + nH_2 = (CH_2)\,n + nCO_2.$$
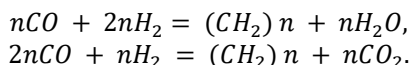
The reaction products are alkanes, alkenes and oxygen compounds, that is, a complex mixture of products characteristic of the polymerization reaction is formed. The main products of the Fischer-Tropsch synthesis are α- and β-olefins, which are converted into alkanes by subsequent hydrogenation. The nature of the catalyst used, the temperature, the ratio of CO and H_2 significantly affect the distribution of products. Thus, when iron catalysts are used, the percentage of olefins is high, while cobalt catalysts with hydrogenating activity mainly produce saturated hydrocarbons.

Currently, depending on the tasks (increasing the yield of gasoline fraction, increasing the yield of lower olefins, etc.), highly dispersed iron catalysts and bimetallic catalysts reinforced with aluminum, silicon and magnesium oxides are used as catalysts. Fischer-Tropsch synthesis: iron-manganese, iron-molybdenum, etc.

6 Conclusion

In terms of chemical properties, benzene and other aromatic hydrocarbons are saturated and is different from unsaturated hydrocarbons. Typical reactions for them are benzene are reactions of replacement of hydrogen atoms in the nucleus. These reactions are saturated it happens more easily than in hydrocarbons. Most of the organic compounds obtained in this way.

Currently as a solvent in catalytic reforming and pyrolysis devices commodity aromatic, which is used and expensive chemical raw material hydrocarbons are produced. These are benzene, toluene, technical petroleum xylene, n–, m– and o– xylols, pseudocumol. In

addition, green oil is obtained during pyrolysis. She is It is a mixture of high molecular, mostly polycyclic hydrocarbons used as a raw material in the production of carbon.

The mechanism of chemical reactions during pyrolysis is sufficient level of complexity and their degree of complexity, obtained for pyrolysis with an increase in the molecular weight of hydrocarbons and the degree of conversion, increases.

Pyrolysis reaction products are divided into pyrogas and pyrocondensate. Pyrogas is sold as a secondary product after it is separated from hydrogen, cleaned of sour components, and sent to polymerization after drying.

The amount of pyrocondensate formed depends on the type of raw material and its use 2 ÷ 25% of pyrolysis products according to constructive solutions of technology constitutes Pyrolysis distillate and pyrolysis oil, which make up pyrolysis condensate, are used in industry important naphthalene, aromatic hydrocarbons, indene, phthalic anhydride and potential raw materials for the production of other chemical products.

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