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Modern Concepts of the Ways of Forming the Active State in Cobalt Catalysts of the Fisher-Tropsch Synthesis

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Abstract:

One of the technologies for obtaining hydrocarbons from natural gas is the gas-to-liquid (GTL) technology, based on the catalytic Fischer-Tropsch synthesis (FTS). Cobalt-supported catalysts, in particular Co/Al_2O_3, are used to synthesize predominantly linear high-molecular hydrocarbons at low temperatures and pressures. The active component of the catalyst is metal particles with sizes from 6 to 10 nm, formed during the reduction of the oxide precursor of the catalyst in a hydrogen-containing environment. The temperature of the reductive activation depends on the degree of interaction of cobalt with the oxide carrier. In the case of Al_2O_3, the interaction of the carrier with cobalt cations leads to the formation of joint Co-Al oxides, which are reduced at a temperature of 500 °C and above. Such a high temperature of reductive activation creates significant difficulties in the industrial use of these catalysts. On the other hand, some interaction between the support and the metal is welcomed, as it ensures high particle dispersion by fixing the active component, preventing migration and sintering during FTS, and thus contributes to high catalyst activity and stability. It is possible to lower the activation temperature by introducing structural modifiers into the carrier, in particular oxide compounds of Zr and P, which help to reduce the degree of interaction during catalyst preparation, or by introducing a small amount of noble metals (promoters), in particular Ru, into the finished catalyst. The relevance of the work lies in the need to conduct comprehensive studies of the influence of the chemical composition, methods of obtaining and activating Co- Al_2O_3 catalysts of the SFT on the nature and character of the formation of the active state of the catalyst surface.

At present and in the near future, due to the depletion of developed resources of traditional oil and the tightening of requirements for the environmental characteristics of oil refining products, more and more attention is being paid to the development of technologies for the production of synthetic hydrocarbons. The production of synthetic hydrocarbons from a mixture of carbon monoxide and hydrogen ("syngas") is carried out through the conversion of various carbon-containing raw materials (gas, coal, biomass) using XTL technologies [1]. XTL technologies include GTL (gas-to-liquid) [2], CTL (coal-to-liquid), BTL (biomass-to-liquid) [3].

In general, the XTL process includes the following steps:

1) production of synthesis gas from natural gas, coal or biomass;

2) catalytic conversion of synthesis gas into hydrocarbons by Fischer-Tropsch synthesis;

3) separation of products into straight-run fractions: naphtha, kerosene, diesel distillate, waxes with their subsequent refinement and processing (catalytic cracking of naphtha, hydrocracking of waxes).

The process of converting carbon monoxide and hydrogen into liquid hydrocarbons was invented by Franz Fischer and Hans Tropsch in the 1920s in Germany for the production of liquid fuel from coal [4, 5]. It is a catalytic process carried out at temperatures of 150–350 °C under atmospheric or elevated pressures on Co, Fe, Ni or Ru catalysts. Iron- or cobalt-containing catalysts are widely used in industry.

The main products of SFT are aliphatic hydrocarbons, including unsaturated ones:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O,$$

$$nCO + (2n)H_2 \rightarrow C_nH_{2n} + nH_2O.$$

The value of ΔHº298 for reaction (1) in the case of methane formation is equal to – 205 kJ/mol, when $n\rightarrow\infty$ the values of {ΔHº298/n} for reactions (1) and (2) tend to the value of – 150 kJ/mol. In addition to aliphatic hydrocarbons, alcohols, carboxylic acids and aldehydes are formed:

$$nCO + (2n)H_2 \rightarrow C_2H_{2n+1}OH + (n-1)H_2O$$

$$nCO + 2nH_2 \rightarrow C_{n-1}H_{2n-1}COOH + (n-2)H_2O$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n}O + (n-1)H_2O.$$

From the point of view of thermodynamics, it is possible to form hydrocarbons of any molecular weight, type and structure, except acetylene. One of the products of the Fischer-Tropsch synthesis is water, which interacts with CO according to the water-gas-shift reaction (WGSR), ΔHo 298 = – 42 kJ/mol:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Currently, two main methods of conducting SFT are implemented in industry: low-temperature SFT (LTFT, low temperature Fischer-Tropsch) and high-temperature SFT (HTFT, high temperature Fischer-Tropsch) [6]. Table 1 presents the compositions of the products of straight-run synthetic oil fractions in mass %, obtained in various industrial processes of Fischer-Tropsch synthesis (SAS – Sasol Advanced Synthol, SSBP – Sasol Slurry Bed Process) on iron and cobalt catalysts according to the data given in the dissertation [7].

Table 1. – Composition of the products of the C5–C12 naphtha fractions and C10–C20 distillate (in mass %) obtained by the SAS and SSBP processes according to the work data.

process	Fe-HTFT, SAS		Fe-LTFT, SSBP		Co-LTFT, SSBP	
fraction	naphtha	distillate	naphtha	distillate	naphtha	distillate
olefins	70 (49)	60 (34)	64 (61)	50 (47)	35 (32)	15 (14)

(proportion of α-olefins)						
Paraffins (proportion of n-paraffins)	13 (8)	15 (9)	29 (28)	44 (42)	54 (49)	80 (76)
arenes	5	15	0	0	0	0
Oxygen-containing	12	10	7	6	11	5

Both types of catalysts: iron-containing and cobalt-containing, can be used in low-temperature FTS at T = 190–240 °C, pressure of 1–20 bar and H_2/CO ratio = 2. For low-temperature FTS, the industry uses a slurry reactor (slurry reactor, SASOL Chevron Oryx GTL (Qatar), single reactor capacity up to 700 thousand t/y) or a fixed-bed reactor (fixed-bed reactor, Shell Pearl GTL (Qatar), single reactor capacity up to 220 thousand t/y) [8]. In February 2017, the first GTL process using a microchannel reactor from Velocys (ENVIA process, USA) was put into operation [9]. Such reactors are aimed at small-tonnage production of synthetic hydrocarbons (up to 50 thousand t/y).

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