

CO-Based SHS-Catalysts for the Fisher-Tropsch Process

V.N. Sanin^{1*}, V.N. Borshch¹, D.E. Andreev¹, D.M. Ikornikov¹, V.I. Yukhvid¹,
S.Ya. Zhuk¹, N.V. Sachkova¹, A.L. Lapidus², O.L. Eliseev²

¹ *Merzhanov Institute of Structural Macrokineics and Materials Sciences of Russian Academy of Sciences,
Scientific Center in Chernogolovka, 8, Academician Osipyan St., Chernogolovka, Moscow Region, 142432, Russia;*

² *N.D. Zelinsky Institute of Organic Chemistry, RAS; 47, Leninsky Pr., Moscow, 119991, Russia*

* Corresponding author: * Tel.: +7 (496) 524 65 10; fax: +7 (496) 524 6255. E-mail: svn@ism.ac.ru

Abstract

The Fischer-Tropsch (FT) process occurring only in the presence of catalysts is the most optimal for production of synthetic hydrocarbon raw materials. The use of the FT process makes it possible to diversify the raw material base of petrochemicals by processing coal, gas, coal duns and other carbon-containing raw materials into synthesis gas, and then converting it into higher hydrocarbons. A common disadvantage of modern catalysts for the FT process is the complexity and energy intensity of the preparation process. Development of original catalysts for the FT synthesis and new technologies for their preparation is urgent for further development of effective methods for synthesis of hydrocarbon raw materials of high practical value.

For the first time, new polymetallic cobalt-based catalysts with a nanostructured surface and promoting additives have been obtained by the method of centrifugal SHS metallurgy. These catalysts do not contain noble metals and have high activity in the FT process. The phase composition, microstructure and morphology of the surface of synthesized polymetallic alloys before and after chemical activation (leaching of aluminum) of synthesized alloys were studied. Investigations of the microstructure of catalyst granules after chemical activation have shown that complex two-level nanostructures are formed on their surface; apparently, they determine the high activity and selectivity of the catalysts obtained in the FT process.

Keywords

Centrifugal SHS-metallurgy; Fischer-Tropsch (FT) process; FT process catalysts; polymetallic catalysts; production of synthetic hydrocarbon raw materials.

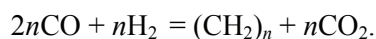
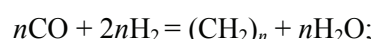
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Introduction

Up to now, oil has been the only global raw material for the production of motor fuels, and it remains crucial for chemical synthesis. However, the situation is gradually changing. The deficiency of world oil reserves forces to use other sources of hydrocarbon raw materials, the most significant of which are coal and natural gas.

The first stage of conversion of natural gas and coal into chemical products and liquid fuels is their conversion to synthesis gas – a mixture of CO and H₂. Further, among the main directions of synthesis gas processing, the Fischer-Tropsch process (FT) is distinguished [1–3]. It allows diversifying the raw material base of petrochemical industry by processing

coal, gas, shale and other carbon-containing raw materials into synthesis gas and then converting it into higher hydrocarbons. The FT process is a complex set of sequential and parallel transformations occurring on the surface of a heterogeneous catalyst [4–7]. The main reactions are the hydro- polymerization of CO with the formation of paraffins and olefins. In general, the Fischer-Tropsch synthesis, depending on the composition of the synthesis gas, can be written down by the following equations:



It is possible to form hydrocarbons from CO and H₂ of any molecular mass, type and structure except for acetylene and its derivatives, but the principal

importance of this process is, primarily, in its role in the production of liquid and solid C_{5+} hydrocarbons. The obtained products serve as components of motor fuels (gasoline and diesel fuel), and are also designed for further processing of hydrocarbons in petrochemical processes, in particular, in linear alcohols and α -olefins. The nature of the catalyst used, the temperature, the ratio of CO and H_2 significantly affect the distribution of products.

The catalysts of the FT process are metals of group VIII. The greatest catalytic activity is exhibited by Ru, Fe, Co, and Ni. Ruthenium is already active at 100 °C, high-molecular weight paraffins are formed in its presence at elevated pressure, but this metal is too expensive and is not used as an industrial catalyst.

Nickel catalysts at atmospheric pressure provide mainly direct hydrogenation of CO to methane. At elevated pressure, a volatile nickel carbonyl $Ni(CO)_4$ is easily formed and the catalyst is leached from the reactor [3, 8]. Cobalt catalysts were the first catalysts used in industry. A pressure of 1–50 atm and a temperature of 180–250 °C are typical for their work. Under these conditions, linear paraffins are mainly formed. However, Co also has significant hydrogenating activity, so part of CO inevitably turns into methane [9]. Iron-based catalysts are much cheaper in comparison with cobalt, they operate in a wider temperature range (200–360 °C), and allow a wider range of products to be obtained, but due to low hydrogenating activity, the surface of iron contacts rapidly decarbonates, and their service life is several weeks [10].

A common shortcoming of modern catalysts for the FT process is the complexity and energy intensity of the preparation process. Most often the method of their preparation includes impregnation with soluble metal salts of a carrier based on ceramic materials (γ -aluminum oxide, aluminosilicates, magnesium silicate, silicon dioxide, zinc oxide, clays, zeolites and combinations thereof), followed by decomposition of salts to oxides and their reduction to metals in a stream of hydrogen at an elevated temperature.

The development of original catalysts for the FT synthesis, the search for ways to efficiently control the selectivity of the process and the development of new methods for the preparation of catalysts are urgent tasks for the further development of efficient methods for the synthesis of hydrocarbon raw materials of high practical value.

In the present study, new polymetallic catalysts with a nanostructured cobalt-based surface with promoter additives that do not contain precious metals and exhibit high activity in the FT process are investigated.

Experimental

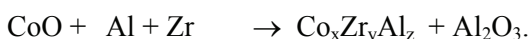
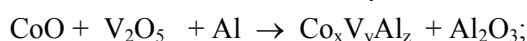
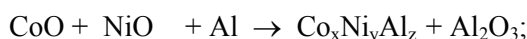
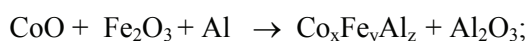
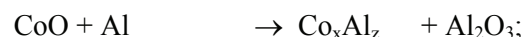
The general research procedure includes the following main stages:

- synthesis of cast intermetallic Co-based alloys (precursors) by the method of SHS metallurgy. Investigation of the influence of synthesis conditions (the ratio of the initial components, the effect of overload, the introduction of functional additives, etc.) on the combustion (synthesis) regimes, the formation of the phase composition and structure of intermetallic compounds;
- preparation of catalysts by crushing the obtained intermetallic alloy and subsequent alkaline etching in order to remove aluminum and obtain a highly porous metal phase.
- investigation of the catalytic activity of the resulting catalysts in the FT process in a laboratory setup.

Synthesis of cast intermetallic alloys

For the synthesis of polymetallic materials, the SHS-metallurgy method was used [11, 12]. It combines two material-forming processes – the SHS [13, 14] and the metallothermy [15]. The essence of the process lies in the occurrence of highly exothermic reactions in the combustion wave between the powder components of the metal oxides and the reducing metal. The high temperature of the process (above the melting point of the reaction products, up to 3000 °C) leads to the formation of a melt of synthesis products consisting of two phases – a multicomponent intermetallide and aluminum oxide. Due to their mutual insolubility and difference in densities, the phase separation and crystallization occur. The resulting ingot is a two-layered product in which the lower layer forms a metallic phase, and the upper one forms an oxide phase (Al_2O_3).

Below are the investigated SHS systems of the term type:



In the experiments, the content of oxides and Al was varied. Combustion of the original formulations was carried out under conditions of the centrifugal force (overload). The general view and the scheme of the centrifugal SHS setup used is described in [16, 17]. Optimal conditions for complete phase separation and

formation of a metal ingot were determined in experiments conducted at different (from 50 to 500 g) values of the overload (centrifugal acceleration).

Preparation of catalysts

The intermetallic ingot was subjected to grinding and classification on standard equipment. The isolated fractions of granules with a size of 0.5 to 1.5 mm were leached with an aqueous solution of alkali metal hydroxide in the active mode by boiling for 1 hour, followed by exposure for 24 hours, washing the catalyst to neutral wash water and stabilizing with a 10 % solution hydrogen peroxide [17].

Investigation of catalytic activity

The catalytic activity of the obtained catalysts in the FT process was studied in a steel tubular reactor at a pressure of 2.0 MPa, with a fixed catalyst bed. The reactor was charged with 2 cc (3.7–3.8 g) of catalyst diluted with 8 cc of quartz crumb to prevent local overheating. The catalyst was previously activated in a hydrogen stream at 400 °C. Test conditions: CO : H₂ = 1 : 2 + 5–7 % Ar as internal standard, volumetric flow rate of synthesis gas was 3750 h⁻¹, the temperature was increased from 160 to 190–220 °C with 10° increments every 5 hours of operation.

CO conversion, product yield and conversion selectivity were determined by chromatographic analysis of the off-gas. Liquid hydrocarbons of synthesis (C₅₊) were collected and analyzed by gas-liquid chromatography.

Results and discussion

The conducted studies of the combustion process in the initial systems with different ratios of the powder components showed that the compositions are

capable of burning in the self-propagation mode over a wide range of aluminum concentrations in the initial compositions. With an increase in the fraction of Al in the initial composition, the combustion rate of the compositions decreases and for $\alpha > 0.5$ the combustion becomes impossible. However, an overload effect of over 200 g allows the combustion interval to be expanded to $\alpha > 0.6$ and ingots with a high Al content can be obtained.

In this study, the compositions with a high aluminum content were of the greatest interest, since intensive leaching and the formation of a branched surface are possible for the compositions with an Al content of more than 50 % wt.

With increasing content of aluminum in the initial charge and in the resulting alloy, the specific weight of the metallic phase decreases. In addition, the temperature of the exothermic reaction decreases. This leads to the slowing down of the phase separation process, which does not have time to complete.

It is known that the effect of overload created in centrifugal SHS-setups leads to an increase in the completeness of phase separation [18, 19] and equalization (homogenization) in the volume composition of the multicomponent metal alloy [20]. For all investigated compositions with overload values over 200 g, the synthesis products consisted of an ingot, which consists of two layers: the lower one was an intermetallic alloy based on Al, Co, Ni, Fe, V and Zr aluminides and the upper one was a cast oxide Al₂O₃ based material (corundum). With the complete phase separation, the lower metal layer was easily separated from the upper one after a slight mechanical action.

The X-ray phase analysis and microstructural studies of the synthesized intermetallic precursors revealed five main phases: CoAl₃, NiAl₃, Ni₂Al₃, Co₄Al₁₃, Fe₄Al₁₃. The phase distribution over the

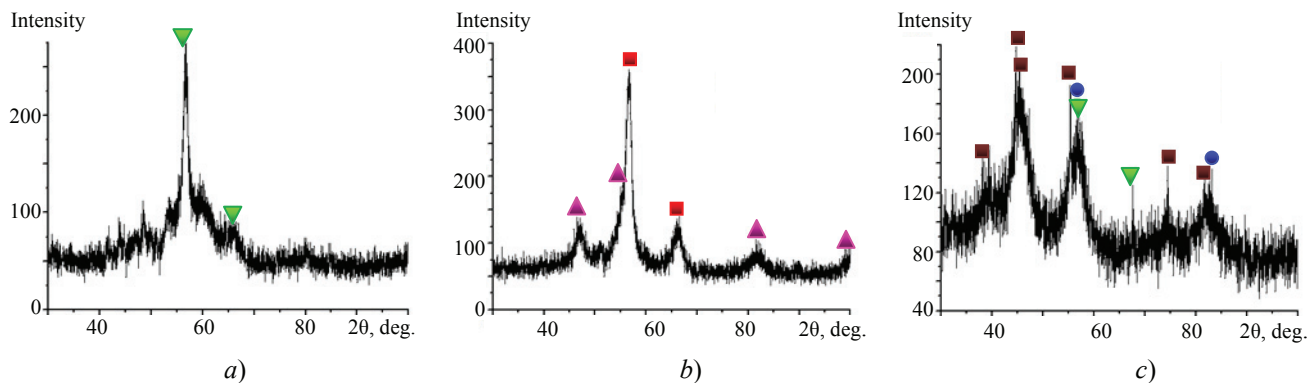


Fig. 1. Phase composition of the polymetallic catalysts after leaching:

a – cobalt catalyst; *b* – cobalt-nickel catalyst (Co:Ni ≈ 1:1); *c* – cobalt-iron catalyst (Co:Fe ≈ 1:1);

▼ – Co; ■ – Co, Ni; ▲ – CoO, NiO; ● – Fe; ■ – FeO, CoO;

volume of the ingot was fairly uniform and did not have local inhomogeneities.

During the leaching of the intermetallic alloy, aluminum was removed from the composition of higher intermetallic compounds with a decrease in its content from 47 to 10–12 % wt. in the target catalyst. The lower intermetallides were preserved and formed a sufficiently strong frame that supported the active phase.

Leaching of the initial intermetallic compounds led to a significant change in the phase composition. The diffuse peaks on X-ray diffraction patterns (Fig. 1) with a high noise level indicate a significant content of amorphous phases in the structure of samples consisting mainly of Co, Ni, Fe and their oxides.

The resulting catalyst granules had a surface area of 11.2–25.5 m²/g.

Fig. 2 shows the data of scanning electron microscopy of the microstructure of the surface of cobalt catalyst granules (composition of Co 89.2 % wt. and Al is the rest) at different magnification, which

indicate a strongly eroded character of the relief of the particles (Fig. 2a, b).

In the photographs with a larger magnification, it is seen that nanostructures are formed on the surface of the resulting catalysts, which are complex two-level structures. The main element of the structure (the first level) is correctly formed hexagons with a smooth surface (Fig. 2c, d), described with a diameter of about 1 μm and a thickness of 70–100 nm. The lateral surfaces of the hexagons have a structure of the second level (Fig. 2e, f), consisting of ordered (arrayed) hexagons of 10–15 nm in size. Similar structures were first discovered on the surface of polymetallic catalysts. Apparently, they determine the high activity and selectivity of the catalysts obtained in the Fischer-Tropsch process.

The catalysts indicated in Table 1 were used to prepare hydrocarbons from synthesis gas.

New polymetallic catalysts with nanostructured cobalt-based surface with promoter additives that do not contain precious metals and exhibit high activity in

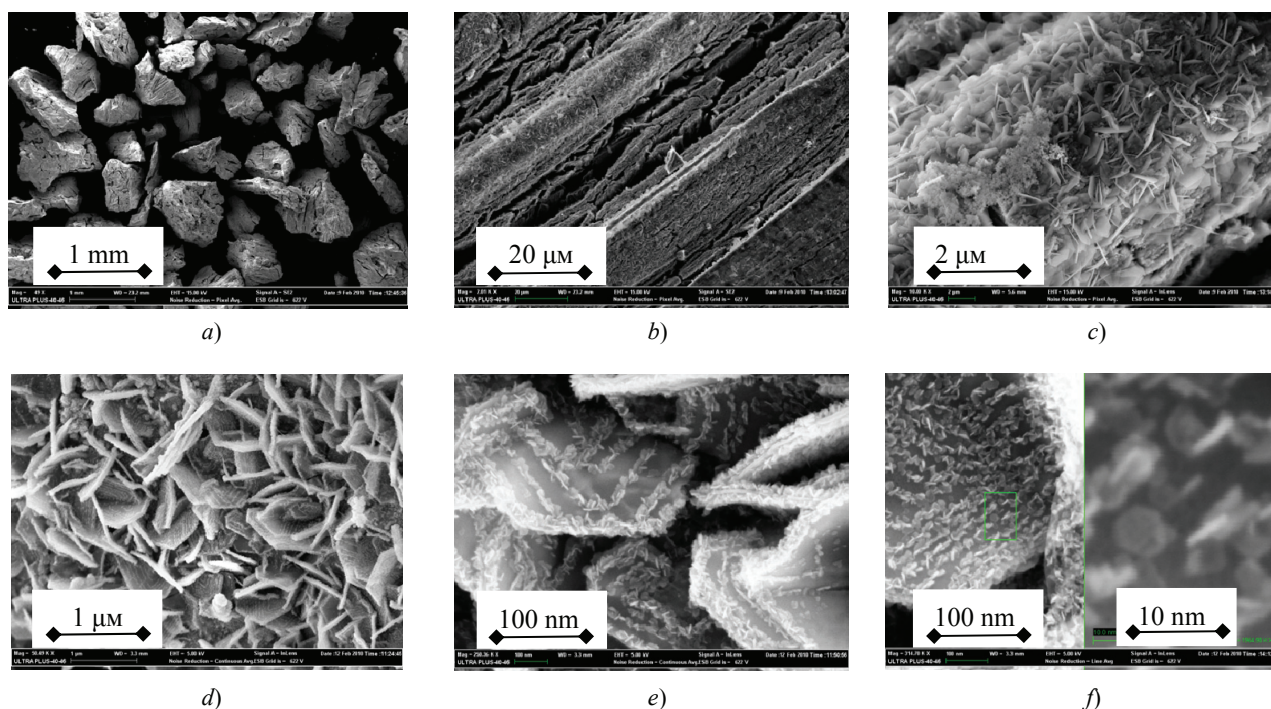


Fig. 2 . Morphology of cobalt catalyst surface

Table 1

Composition and specific surface area of polymetallic materials before and after leaching

Composition of intermetallic precursor, % wt.	Composition of catalyst granules after leaching, % wt.	Specific surface of granules after leaching, m ² /g
Co – 42.1; Al – Balance	Co – 89.2; Al – Balance	23.2
Co – 21.1; Ni – 19.8; Al – Balance	Co – 45.1; Ni – 44.3; Al – Balance	11.2
Co – 21.1; Fe – 20.1; Al – Balance	Co – 45.3; Fe – 44.2; Al – Balance	25.5
Co – 39.6; V – 5.0; Al – Balance	Co – 84.2; V – 4.7; Al – Balance	20.2
Co – 39.0; Zr – 5.0; Al – Balance	Co – 84.4; Zr – 4.8; Al – Balance	11.4

CO conversion, %

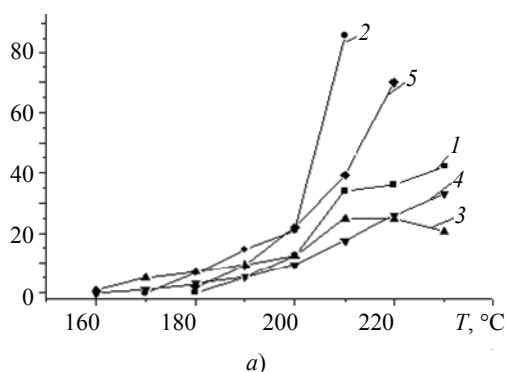
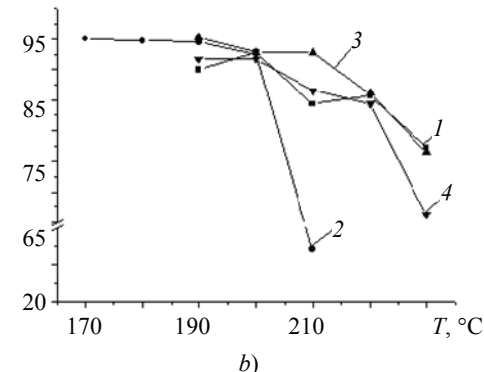
Sc₅, %

Fig. 3. Dependence of the degree of CO conversion (a) and selectivity to target hydrocarbons C₅₊ (b) on temperature: 1 – Co–Al; 2 – Co–Ni–Al; 3 – Co–V–Al; 4 – Co–Zr–Al; 5 – Co–Fe–Al

the Fischer-Tropsch process have been obtained by the method of centrifugal SHS technologies. The phase composition, microstructure and morphology of the surface of synthesized polymetallic alloys before and after the leaching of aluminum have been studied.

Investigations of the microstructure of the catalyst granules have shown that nanoprecipitates are formed on their surface. These nanoprecipitates are complex two-level structures, which, apparently, determine the high activity and selectivity of the catalysts obtained in the FT process.

Tests of catalysts in the FT process have shown a high degree of CO conversion at low temperatures, high selectivity for the output of heavy C₅₊ hydrocarbons, and the probability of chain growth to $\alpha = 0.92$.

These properties of new catalysts make them promising materials for obtaining fuel and oil fractions of hydrocarbons from synthesis gas in high yield.

The investigated method of obtaining a catalytic material does not require high energy costs, has high productivity, is environmentally friendly, and the obtained catalyst has a high level of catalytic activity in obtaining higher hydrocarbons.

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