Ultrafine Metal Powders Used as Gas to Liquids Catalysts

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Abstract. The paper deals with the effect of synthesis parameters on the reactivity of Fischer-Tropsch iron-based catalyst resulting from electrical wire explosion in a carbon monoxide medium. The technology provides the synthesis of ultrafine particles with a large specific surface area and a given phase composition. A mixture resulting from the synthesis of liquid hydrocarbons contains hydrocarbons of a paraffinic and aromatic structure, and its further use requires additional refinement.

1. Introduction

Today, the Fischer-Tropsch process (FTP) is particularly relevant for the Russian industry due to the utilization of associated petroleum gas from the fields located at a distance from gas processing plants. Besides significant CO₂ emissions, gas flaring entails loss of valuable hydrocarbons [1, 2].

It is true that metallic nanodispersed powders produced by exploding wire method (EWM) have proved to be effective catalysts in the production of hydrocarbons from synthesis gas [3-7]. The paper [4] presented the results of a study towards the properties of nanopowders obtained by EWM in the air composition of N₂, Ar, CO, and CO₂. It was found that the higher the electric strength of the gas, the finer the nanodispersed particles. EWM in gaseous media that have a high dissociation energy (CO and N₂) ensures metal powders consisting of crystalline γ-Fe and α-Fe. The EWM products obtained in a CO₂ atmosphere consist of divalent iron oxide and α-Fe. The aforementioned papers described the conditions for obtaining and exploring the catalytic properties of nanopowders produced in optimized EWM modes.

This paper will provide some data on the preparation of finely dispersed powders from metal waste (“crusts”) that are formed on the walls of an explosive chamber. Thus, during the EWM process large droplets of molten metal scatter in different directions (all around the explosive chamber) and, having reached the walls, condense on the surface. Moreover, the thickness of these formations can vary from some fractions of a millimeter to several millimeters. Elongated irregular particles sized 5-10 mm were derived from these metal wastes. Pulverisette 6 classic line (Fritsch) planetary ball mill was used for grinding tasks.

Metal feedstock was poured into a shell made of solid alloy steel (with a volume of 300 cm³). The shell was filled with 38 metal balls (with a diameter of 13 mm) made of solid alloy steel (the shelland balls were first washed and dried), and the shell was covered with a lid of the same material. The shell was fixed on a rotating platform in the mill, the rotor speed was set at 300 rpm, the mill cover was closed and the facility was activated for 5 minutes. The duration of operations was monitored automatically by a built-in timer. After that, the balls were taken out of the shell. The entire dispersed feedstock was poured from the shell into a sieve (a mesh size of 0.4-0.5 mm) and sieved. The powder that passed
through the sieve was collected in a sealed container with a lid, and large residues left on the sieve were returned back to the shelf for re-grinding, until more than 85% mass of the weight of the feedstock was crushed. Using a Sorbtometer-M analyzer, the specific surface area (by the BET method) of the metal powder obtained on the planetary mill was measured. It amounted to 0.5 m$^2$/g. Finally, the obtained powder was tested as a GTL catalyst.

2. Methods
A study was conducted on a catalytic pressure installation, the scheme of which is shown in figure 1.

![Figure 1. Schematic presentation of a catalytic installation: 1 – temperature controller, 2 – gas flowmeter, 3 – furnace, 4 – jacket, 5 – reactor, 6 – separator, 7 – receiver, 8 – chromatograph, 9 – exhaust hood.](image)

Once through the gas flowmeter 2, the feed gases are mixed, and then enter an upper part of the reactor 5 located in the furnace 3. After leaving the reactor, the gas-product mixture is cooled in a tube condenser and transferred for separation into the separator 6. The gas from the separator is fed for analysis into the gas chromatograph 8, while its liquid part is taken for analysis to the receiver 7. The temperatures inside the catalyst, the jacket 4 and the air in the furnace are regulated by the controller 1. The outputs were further analyzed through the capillary gas chromatography.

Ultrafine powder catalyst was subjected to tableting for studies in the laboratory. Polyvinyl alcohol with a concentration of 8 wt. % was used as a binder. Ultrafine powder is treated with a solution of the binder, then pressed under a pressure of 25 MPa, with a holding time of 30 seconds. The obtained pellets were dried at room temperature for 1 day. To test the installation, the catalyst fraction of 1-2 mm. is used.

The gas products of synthesis were immediately analyzed during the experimentation on the chromatographic complex “Crystal 5000”. The liquid products of synthesis were withdrawn and kept in the freezing chamber for analysis according to GOST R 52714-2007 “Motor gasoline. Determination of special and fractional hydrocarbon composition by the method of capillary gas chromatography”.

3. Results and discussion
At the first stage, catalytic activity was studied at a “classical” H2:CO ratio. The experiment was carried out at a temperature of 270 °C, followed by its increase to 290 °C. The CO conversion rate and the amount of carbon dioxide – a by-product of synthesis are presented in figure 2.

Graphical dependencies shown in figure 2 indicated that higher temperatures lead to higher CO conversion rates to a value of 84% at a temperature of 284 °C. A further increase in temperature does not entail a significant increase in the conversion rate, although, the amount of a by-product, CO2, increases. Carbon dioxide does not participate in the formation of target products. The absolute value of CO conversion rate at the current synthesis temperatures is quite high, which is confirmed by the experimental data [5, 6].
At the third stage, synthesis gas was used as the feedstock to study catalytic activity. It had a low H₂:CO ratio so 1.5:1; 1:1. The results are shown in figure 3 and figure 4.

**Figure 2.** Total CO conversion rate and amounts of CO₂ vs synthesis temperature.

**Figure 3.** Total CO conversion rates vs synthesis temperature.

**Figure 4.** Amounts of CO₂ vs synthesis temperature.
The results presented in figure 3 and figure 4 show that a lower hydrogen content in the feedstocks leads to lower CO conversion rates. The reduction in the conversion rate is maximum at a temperature of 270 °C and a H2:CO ratio of 1:1 – up to 32%. Moreover, a by-product amount remains at the same level – about 10%. In this case, the catalyst can be applied for the synthesis of hydrocarbons from CO and H2 at a low concentration of hydrogen in the feedstock.

Liquid end-products were studied via capillary gas chromatography. The resulting liquid mixture consisted almost entirely of normal paraffin hydrocarbons and aromatic compounds with carbon atoms from 10 to 13. There was a limited content of naphthenes and olefins. The octane number of the resulting feedstock, calculated chromatographically, averaged 61 points. Hence, the end-product requires further refinement.

4. Conclusion
In the course of research were comprehensively studied the characteristics of iron powder obtained by an electric explosion. It was found that iron powder has catalytic activity in the Fischer-Tropsch synthesis, and the catalyst is active without preliminary reduction. The influence of technological parameters on the activity of the catalyst was studied, the main dependencies were obtained. The liquid product turned out to be very diverse in composition, and a change in the parameters studied has an ambiguous effect on the composition, which indicates the complexity of the mechanism.

At temperatures exceeding 240 °C, there is a significant increase in the rate of reaction of water gas, expressed in the concentration of CO2 in the exhaust gas. The use of long-term reduction with increasing temperature leads to a change in the selectivity of the catalyst: after recovery, the selectivity to paraffins is replaced by selectivity to olefins with the level of isoparaffins remaining almost unchanged. There is also a tendency to decrease the concentration of aromatic hydrocarbons.

Iron-based powders produced by exploding wire method in a carbon monoxide medium have a high catalytic activity during the synthesis of liquid hydrocarbons from CO and H2. The total CO conversion rate at a H2:CO ratio of 2:1 reaches 90%.

The obtained iron catalyst has a high activity at a lower amount of hydrogen in the feedstock up to a H2:CO ratio of 1:1. The total conversion rate at a temperature of 290 °C and a H2:CO ratio of 1:5:1 is 84.59%, and at a H2:CO ratio of 1:1 it is 72.71%.

A mixture resulting from the synthesis of liquid hydrocarbons contains hydrocarbons of a paraffinic and aromatic structure, and its further use requires additional refinement.

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