

## ELECTRO-EXPLOSIVE IRON POWDERS AS A CATALYST OF SYNTHESIS LIQUID HYDROCARBONS FROM CO AND H<sub>2</sub> IN FISCHER-TROPSCH PROCESS

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### Abstract

Disperse composition and particles morphology of electro-explosive iron powders was studied using complex of current methods such as laser measuring of particle size, determination of specific surface area and pore volume. Catalytic activity of ultrafine iron powders in hydrocarbons synthesis from CO and H<sub>2</sub> by method of Fischer-Tropsch was estimated by concentration of paramagnetic particles determined by electron paramagnetic resonance. Catalytic activity of derived catalyst samples was studied at laboratory catalytic unit working at increased pressures, qualitative and quantitative of derived liquid synthesis products was carried out.

**Keywords:** Fischer-Tropsch process; electroexplosive iron powders; catalyst, synthesis from CO and H<sub>2</sub>.

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### 1. Introduction

The relevance of use of production of liquid hydrocarbons for from syngas technology, in particular, the Fischer-Tropsch synthesis (FTS), currently in Russia primarily due to the processing and utilization of associated oil and gas of fields located at large distance from gas processing plants and gas transmission networks. The processing of hydrocarbon gas into synthetic liquid hydrocarbons is recognized as the most perspective trend of conversion gas into motor fuel, diesel fuel, paraffins, olefins, etc., both for consumption on site (fuels and oils for vehicles, particularly for diesel generators), and for transporting to other regions for consumption in the liquid (energy-compact) form [1].

Disposal of biological waste currently results in a significant problem and of growing economic importance. The use of technology of gasification of biowaste (waste of woodworking industry, livestock, municipal solid waste) and subsequent processing of the obtained gas into liquid products will not only reduce the amount of harmful emissions and environmental pollution, but also will achieve significant economic effect [2].

The catalyst for modern gas-to-liquid manufacturing plays the key role in the process design. The choice of the catalyst type depends primarily on the the market needs in the final products and the properties of the feedstock. So, for example, cobalt catalysts which have a high hydrogenating ability, have a greater yield of a middle fraction in comparison to iron ones, however, they are not able to operate at low ratios of H<sub>2</sub>:CO with a high conversion rate and low yield of methane [3].

Electro-explosive technology of ultrafine powders production allows to synthesize particles of the specified phase composition, with high specific surface area, multi-level structure organization and significant amount of free energy.

In application to the problems of catalysis, this means the emergence of the possibility of significant influence on the structure and properties of the powders during their preparation.

Previously [3-4] it was shown that the most perspective from the point of view of phase composition, electro-explosive iron powder catalyst is Fe(CO)-iron powder derived in media of carbon monoxide.

Thus, the aim of this work is to study the catalytic activity of ultrafine iron powder derived by the method of electrical explosion of wire in media of carbon monoxide in the synthesis of liquid hydrocarbons by the method of Fischer-Tropsch.

## 2. Materials and methods of research

To the study carrying out was used ultrafine iron powder derived in media of carbon monoxide. The powder sample was derived at the Institute of high technology physics of National research Tomsk polytechnic university with the use of technologies and equipment described in [6].

The study of the granulometric composition was carried out using a laser particle size measurer "HORIBA LA-950S2". This device allows work with particles in the range from 0.01 to 3000 micrometers. To determine the powder specific surface area and its porosity was used the "SORBI-M" apparatus. In this definition the high purity nitrogen was the adsorbate gas. Measurement of the specific surface area includes several cycles of adsorption-desorption and it is fully automated. X-ray phase analysis of samples was carried out on diffractometer Shimadzu XRD-7000 S with independent scanning mode  $\theta-2\theta$  (Bragg angle) of the sample and use of the counter with the attachment for the rotation of the sample, the radiation is  $\lambda=1,541 \text{ \AA}$ . The angles  $2\theta$  ranged from 5 to 100 degrees. The tube voltage was 40 kV, current was 30 mA. A scan step was 0.02 degrees. Phase identification was performed using database PDF-2.

The process of powder tableting is described in detail in [3]. The derived fraction was studied on the catalytic unit operating at increased pressures, which scheme is shown in figure 1.

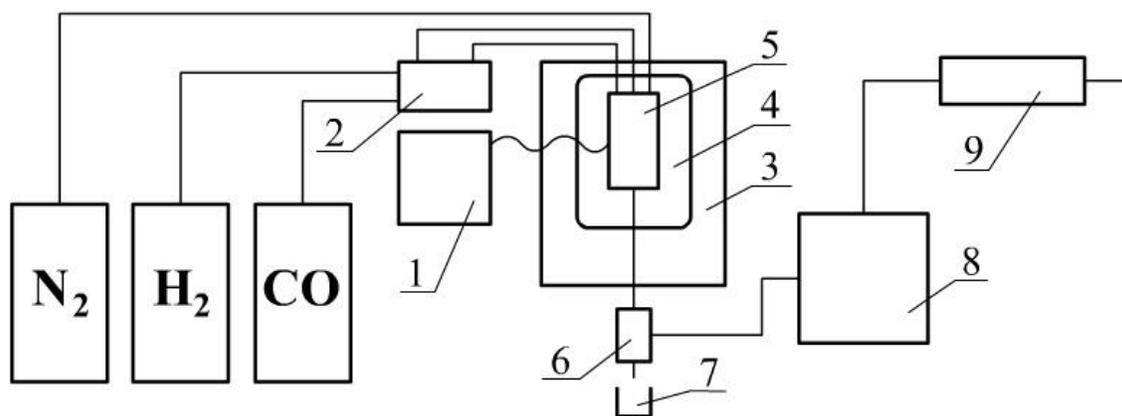


Figure 1. Catalytic unit scheme: 1 – temperature controller, 2 – gas metering unit, 3 – heat chamber, 4 – reactor jacket, 5 – reactor, 6 – separator, 7 – receiver, 8 – gas chromatograph, 9 – air vent.

Initial gas reactants going through gas metering unit 2 mix together and get to the upper part of the reactor 5 situated in the heat chamber 3. Gas-product mixture goes out of the reactor, cools down in shell-and-tube cooler and sets out to the dividing into separator 6. Gas from separator moves to the gas chromatograph 8, liquid gathers in the receiver 7 for analysis. Temperatures inside a catalyst layer, reactor jacket 4 and of air in the heat chamber sets by microcomputerized temperature controller 1.

Loaded catalyst volume was  $8 \text{ cm}^3$ , total reactants consumption— $300 \text{ mln/min}$ . All experiments were carried out under pressure of  $1,1 \text{ MPa}$ . The ratio  $\text{H}_2:\text{CO}$  was equal to 2, duration of the experience after the turning of catalyst into stationary mode was 100 hours. The gaseous products of the synthesis were analyzed directly during carrying out of experiments on the chromatographic complex "Crystal 5000". Liquid products of the synthesis were withdrawn and stored in a freezer for analysis according to GOST R 52714-2007 "Motor gasoline". Individual and group hydrocarbon composition were determined by capillary gas chromatography.

### 3. Results and discussion

The results of the study of the powder particles distribution by size using the method of laser diffraction is presented in figure 2.

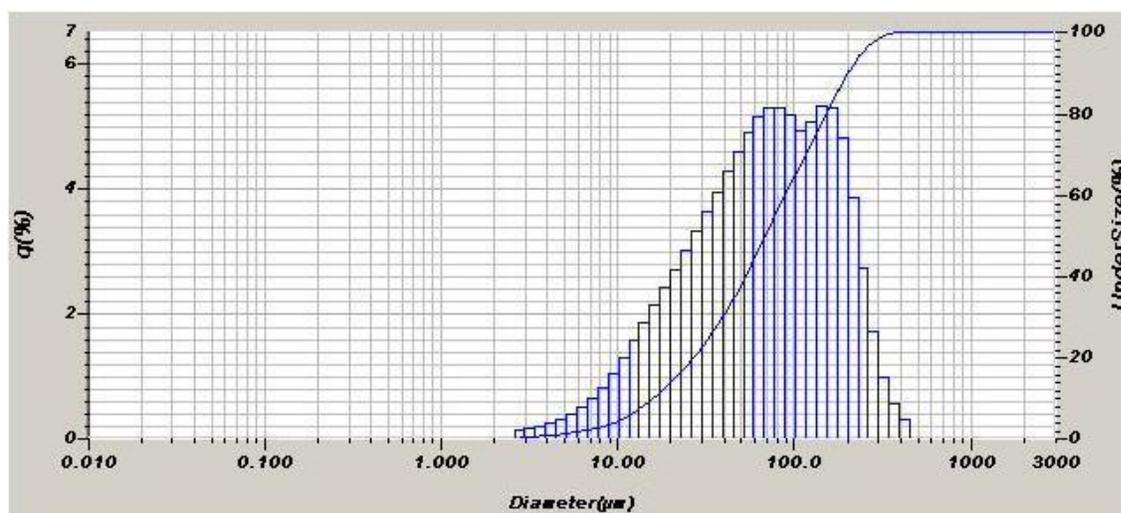


Figure 2. The catalyst particles distribution by diameter

The graph shows that 80 % of the catalyst particles have a diameter equal to 80 and 105 micrometers. The drop in the area of maximum is characterized by the current pause during the electrical explosion, during which metal loses its electrical conductivity when heated to high temperatures.

The results of specific surface area measuring is shown in table 1.

Table 1. Results of study by BET method

Metal (media)	Fe (N)	Fe (CO)	Fe (CO <sub>2</sub> )
Sarea, m <sup>2</sup> /g	5,63	8,03	8,35
Total pore volume, cm <sup>3</sup> /g	1,30	2,06	2,13
Average pore width, Å	114,48	90,18	126,40
Specific volume of the monolayer, cm <sup>3</sup> /g	1,26	1,84	1,92

The results show that this type of catalyst relates to macroporous ones (over 50 nm). The catalyst is derived in media of carbon dioxide has the greatest specific surface and the porosity. This catalyst also has more active centers on the surface than other samples (a greater volume of monolayer indicates this). General view of the BET adsorption isotherm is presented in figure 3.

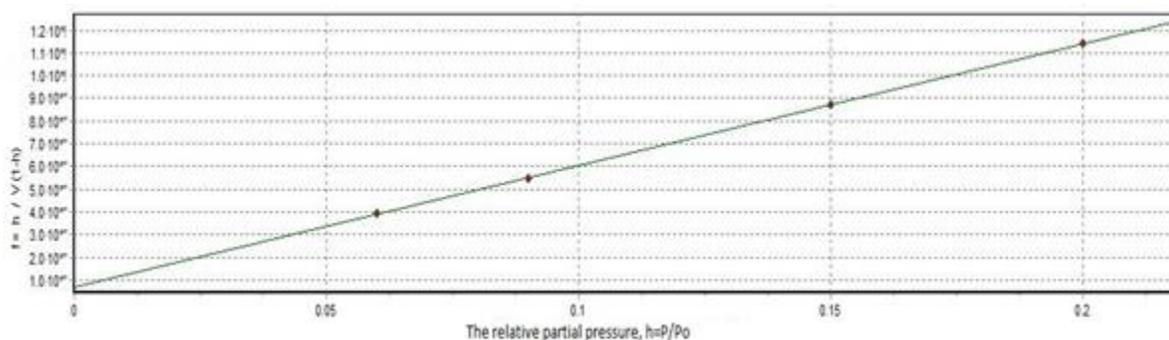


Figure 3. BET adsorption isotherm

X-ray phase analysis of iron powders shown that the most of the substance is in X-ray amorphous condition.

The presence of iron monoxide (wustite) was detected in the composition of the catalyst derived in media of carbon dioxide. Wustite is formed by decay of carbon monoxide and due to forming atomic oxygen, which can be easily inculcated into the metal pattern. Wustite is not detected in the samples derived in media of nitrogen and carbon dioxide. All the samples contain the different modifications of iron, mostly  $\alpha$ -Fe (fig. 4–6).

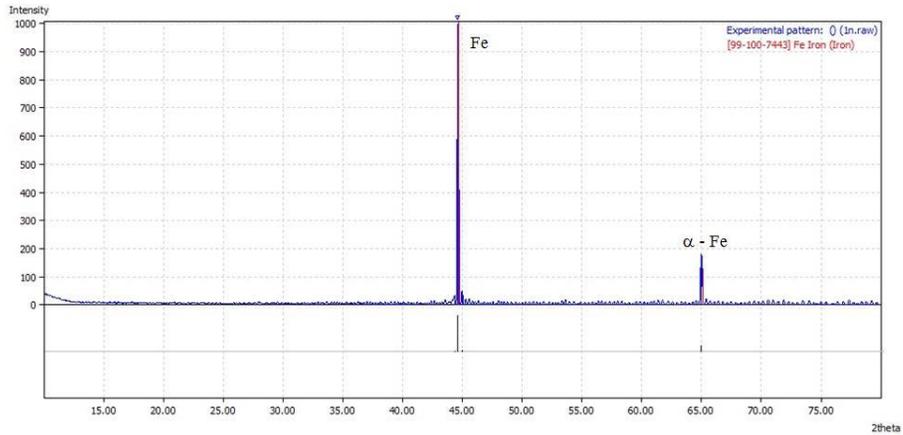


Figure 4. The catalyst derived in media of nitrogen radiograph

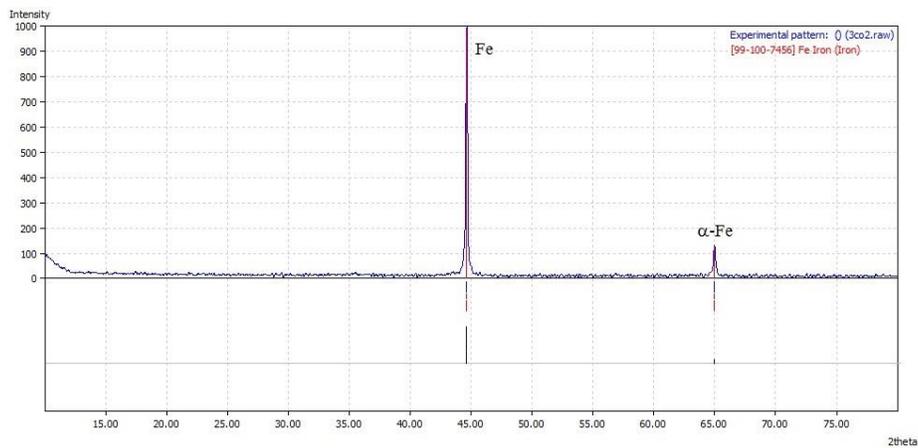


Figure 5. The catalyst derived in media of carbon dioxide radiograph

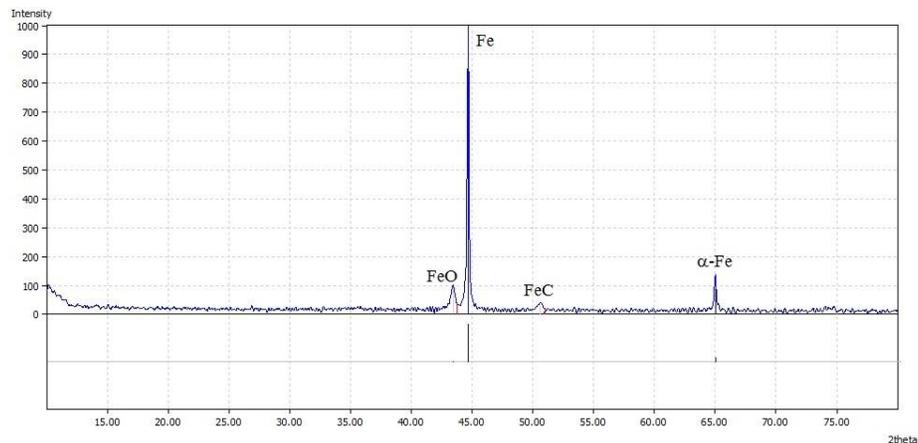


Figure 6. The catalyst derived in media of carbon monoxide radiograph

$\alpha$ -Fe iron has high thermal stability (910°C) and it is the most active modification of iron. Due to the formation of oxide and carbide at the stage of preparation of the catalyst, the need of reduction disappears what significantly reduces the cost of the catalyst.

Research electroparamagnetic resonance shown that all powders are highly paramagnetic, what indirectly confirms the high catalytic activity of the samples. Every second electron is unpaired, imbalanced by opposite spin. Spin number (unpaired electrons) proportionally to the amount of microwave energy absorbed during an electronic spin resonance (ESR). The value of the absorbed microwave energy is represented by the intensity (area) of the obtained spectrum (figure 7).

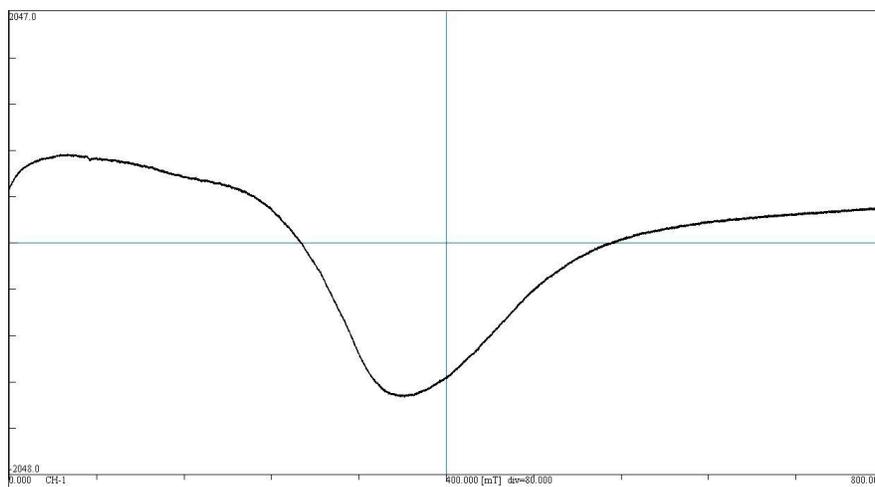


Figure 7. Iron powder electro-paramagnetic resonance spectrum

The amount of unpaired electrons of ultrafine iron catalyst derived in media of carbon monoxide is  $1,162 \cdot 10^{16}$ .

The second phase of research was carrying out study of the iron powder activity in Fischer-Tropsch synthesis in catalytic laboratory unit operating at increased pressures. To carry out the study the powder derived in media of carbon monoxide was selected, because previous studies have shown that it has the most appropriate structure and best properties. The experiment was carried out at increased temperature (285°C) for 100 hours. During the whole experiment time portions of gas products of the synthesis were periodically withdrawn for analysis by the capillary gas chromatography method. The level of carbon monoxide conversion throughout the experiment remained almost constant and did not fall below 85 %, what allows to make a conclusion about the absence of deactivation of the catalytic system under these conditions.

In conditions of high temperatures and accordingly high conversion levels of carbon monoxide a large concentration of carbon dioxide emerges (it is the main by-product of the synthesis) – 12 wt %. As shown earlier, lowering the temperature of synthesis leads to the decreasing of CO<sub>2</sub> yield that allows to make a conclusion about possibility of use of this catalytic system in the technological scheme with the organization of unreacted components recycle.

The analysis of liquid synthesis products shown that paraffin hydrocarbons with carbon atoms amount from 6 to 11 prevail in the mixture.

Hydrocarbons with carbon atoms amount above 15 were absent. In the mixture there were aromatic hydrocarbons with concentration of 10.5 wt. %. and carbon atoms amount from 6 to 12 (the concentration of benzene was 0,114 % wt.), isoparaffins with a concentration of 17.6 wt. %. and the carbon atoms amount from 4 to 13, olefins with a concentration of 13 % wt. and carbon atoms amount from 3 to 10, naphthenes with a concentration of 4 wt. % and carbon atoms amount from 5 to 11.

Fractional composition calculated on the basis of component analysis of liquid products is presented in table 2.

Table 2. Fractional composition of liquid products

Distillate, %	0,5	20	40	60	80	99,5
Temperature, °C	39,334	92,767	115,609	137,383	171,150	279,283

#### 4. Conclusions

1. It is possible to derive products with defined and desired properties and structure (phase composition, particle sizes and structure), suitable for the manufacture of catalytic systems in conditions of electrical explosion of iron conductors.
2. Ultrafine iron powder derived by electric explosion of a conductor in media of carbon monoxide, has a high catalytic activity in the synthesis of liquid hydrocarbons from CO and H<sub>2</sub>. The total conversion level of CO reaches 85 % at reagents ratio in the initial mixture H<sub>2</sub>:CO = 2.
3. Paraffin and isoparaffin hydrocarbons with carbon atoms amount from 5 to 11 prevail in the liquid synthesis products.

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