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## Ultradispersed Hydrocarbon Synthesis Catalyst from CO and H<sub>2</sub> Based on Electroexplosion of Iron Powder

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### Abstract

The structure and properties of disperse particles of electroexplosive iron-based powder are studied with a laser diffraction method, transmission electron microscopy analysis and X-ray photography. The catalytic activity of ultradispersed iron powders in the synthesis of hydrocarbons from CO and H<sub>2</sub> by Fischer – Tropsch method is measured by concentration of the paramagnetic particles with electron paramagnetic resonance. In the laboratory of catalytic plant, hydrocarbons are synthesized at various feed mixture. Composition of liquid and gas products of synthesis are studied. Under explosion conditions, the electric wires of iron powders can be prepared with the specified properties (phase composition, particle size and structure). Powder of Fe (CO) can be used as a catalyst of the Fischer – Tropsch synthesis without reduction since during electrical explosion in an atmosphere of carbon monoxide generated phase structure needed to activate hydrocarbon synthesis reaction of a mixture of CO and H<sub>2</sub>.

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### 1. Introduction

Permanent increase in world oil prices and general willingness to search alternative sources of energy, attention of large companies specialists are increasingly focusing on ways to transform hydrocarbons into usable forms. The greatest interest leads to application of the gas to liquid technology (GTL) for transformation of gas into liquid phase. Relevance of technology GTL, particularly Fischer-Tropsch synthesis, currently in Russia is due, processing

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and utilization of associated gas of oil fields, far from the gas processing plants and transporting networks. Processing of hydrocarbon gas into synthetic liquid hydrocarbons - motor fuels, oils, waxes, etc., is recognized as the most promising direction for consumption on the production sites (supply of fuel and oil for vehicles, diesel generators, etc.), and for transportation to other regions in the liquid form<sup>1</sup>. In addition, the cost of transporting fuel gas per unit of energy compared to liquid hydrocarbons is very high, so the business of gas transportation to places of consumption is extremely complex and requires huge investment for the construction of main gas pipelines or construction of plants to produce liquefied natural gas. In other words, often to transport gas from the gas fields is unprofitable.

Slower growth of proven oil reserves also advocates the use of Fischer – Tropsch synthesis in the near future. According to experts, due to the continuous growth of the world consumption of motor fuels, proven oil reserves should last for about 40 years. Therefore, the problem of using other types of hydrocarbons, particularly natural gas, increases dramatically. Today natural gas reserves are considered to be practically inexhaustible, because reserves including those in the oceans in the form of methane hydrates may be sufficient for tens of thousands of years.

Another factor in favor of the use of Fischer – Tropsch synthesis is the "Kyoto Protocol" which in 1997 was accepted by 160 industrialized countries to reduce 2008-2012 emissions of gases that contribute to the greenhouse effect. Consequently, all requirements to reduce flaring of natural gas, associated and other hydrocarbon gases at oil and gas fields, refineries, gas processing plants, petrochemical plants become tougher.

The catalyst for present GTL production plays a key role in the design process. Choice of catalyst depends primarily on the requirements of the market to the end products and raw materials. Thus, for example, cobalt catalysts have high hydrogenating ability to have a high yield of middle fractions in comparison with iron catalysts, however, they are not capable of operating at low ratios of H<sub>2</sub>:CO for high conversion and low methane yield.

Accumulated scientific data on physical-chemical principles of hydrogenation of CO and catalysis theory allow concluding that the reliable scheme formation of the active centres of iron catalysts and formulating the basic requirements for the production of powders - catalysts based on iron. Technology for producing powders should mainly ensure the presence of the particles of  $\alpha$ -Fe and  $\gamma$ -Fe, about 10 wt.% of FeO, and not more than 5 wt.% of Fe<sub>3</sub>O<sub>4</sub>. Choice of iron depends on the fact that other conditions are equal, the iron-based catalysts are preferable from economic point of view (compared with cobalt and nickel)<sup>2</sup>.

## 2. Literature Review

A large number of publications in leading scientific journals in Europe and Russia speak for a great interest to the process of Fischer-Tropsch synthesis. The authors use all the modern research methods for the study and modeling of the process for producing liquid fuels from synthesis gas.

A large number of papers is devoted to the study of the surface of the catalysts of the Fischer-Tropsch synthesis using quantum chemistry methods. In researches<sup>3,4</sup>, the processes on the surface of various catalysts of the Fischer-Tropsch process are described in detail. For the most comprehensive study of the process, modern methods of quantum chemical calculations, namely the Density Functional Theory, are used. The authors of these studies confirm the prospect of iron catalysts in the synthesis of hydrocarbons from synthesis gas. Iron clusters have developed surface indicating their great activity during synthesis. These conclusions are confirmed by means of quantum-chemical calculations.

The authors<sup>5</sup> studied in detail the synthesis process mechanism on the surface of the catalyst in the Fischer-Tropsch process. In this paper, it is concluded that the surface of the catalyst is based on cobalt (Co 0001), most likely the formation of compounds of type CHO cells. This compound is the most energetically favorable according to the calculations the results of which are given in the article.

In the article<sup>6</sup>, the authors proved the possibility of olefins synthesis from synthesis gas on iron catalysts promoted manganese oxide. The maximum CO conversion was 15%, the yield of olefins in the liquid products was about 24%. Raising the manganese content increases power conversion of CO, but reduces the yield of olefins. Optimum manganese content was about 15-20%.

Much attention is paid to obtain synthesis on CO and H<sub>2</sub> chemical compounds such as alcohols and dimethyl ether. Dimethyl ether can be used as a substitute for diesel fuel in internal combustion engines. The authors<sup>7,8</sup> demonstrated the possibility of dimethyl ether synthesis from synthesis gas with zeolite catalysts for methanol

synthesis.

Much attention is currently paid to environmental issues. Many authors consider production of synthesis gas promising and, accordingly, the following steps the liquid hydrocarbon from biological waste. Such an approach would improve the ecological environment and reduce pollution of soils.

The papers<sup>9-11</sup> show the possibility of processing the biomass of different composition to the synthesis gas followed by obtaining liquid hydrocarbons. For the synthesis of liquid hydrocarbons, a multifunctional catalyst based on potassium, iron, cobalt, molybdenum and aluminum oxide is used. The obtained results allow considering this direction of biological waste disposal promising. There is a pilot plant processing biological waste into liquid fuels currently operating<sup>12, 13</sup>. The authors designed and manufactured setting, which is the raw material of different composition biomass processing into synthesis gas. In the second stage, the fuel gas is produced. Power developed the installation of 8 MW.

### 3. Materials and methods

Samples of powder were obtained for research in the Institute of High Technologies of Tomsk Polytechnic University, and the procedure is described in<sup>14</sup>. Weight of obtained powder in each experiment was not less than 100 g. Working environment in which explosions were produced, in different cases – N<sub>2</sub>, CO, CO<sub>2</sub> and argon. Energy input to the conductor in the explosion was determined from the current waveforms using the procedure described in<sup>14</sup>. Detailed methods and results of powders structure studies are described in<sup>2</sup>.

Ultradisperse powder catalyst was subjected to tableting for studies in the laboratory. Polyvinyl alcohol with a concentration of 8 wt. % was used as a binder. Ultradisperse 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.

Testing of catalyst in the laboratory is schematically shown in Fig. 1.

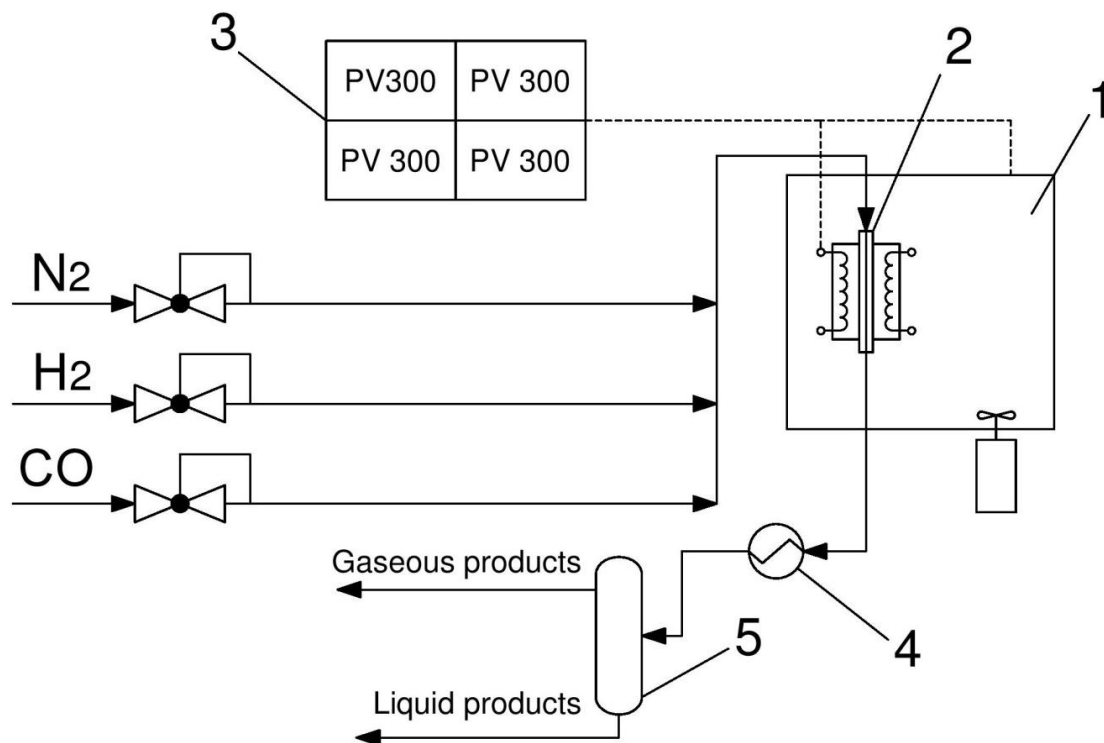


Fig 1. Scheme of laboratory catalytic position: 1 - oven; 2 - reactor; 3 – microprocessor of temperature controller; 4 - products refrigerator; 5 - products separator.

Source gases are mixed and fed into the reactor 2 type tubular of 12 cm<sup>3</sup>, arranged in the oven 1. Jacket temperature, temperature of air in the oven and temperature of catalyst layer are controlled by microprocessor controller 3. Gas-product mixture from the reactor is fed into the refrigerator 4, wherein it is partially condensed. Finally, products are condensed and separated in the separator 5. Experiments were conducted for 6-8 hours, the catalyst activation time does not exceed 3 hours. For chromatographic analysis of products, "Crystal Hromatek-5000" complex is used

#### 4. Results and discussion

At the first stage, a set of experiments was conducted with a selected catalyst by Fischer-Tropsch synthesis at atmosphere pressure and different temperature. Time to catalyst operation was 1 hour. The results are shown in Table 1. Schulz-Flory coefficient describe product distribution by the molecular weight.

Table 1. Results of Fe (CO) catalyst synthesis at 260 °C.

Key indicators	Ratio H <sub>2</sub> :CO				
	2:1	1.5:1	1:1	2:1	2:1
	Test № 1			Test № 2	After regeneration
Conversion of CO, %	83	71	45	42	58
Selectivity, % C	0.65	0.70	0.85	0.78	0.70
CH <sub>4</sub>	5.6	4.2	1.9	3.8	5.5
C <sub>2</sub> -C <sub>4</sub>	10.8	9.0	4.5	6.7	8
C <sub>5+</sub>	65.8	71.3	85	74.1	67
CO <sub>2</sub>	17.8	15.4	8.6	15.3	20
Schulz-Flory Coefficient	0.6	0.6	0.5	0.4	0.4

Consistent decline in the ratio of gas led to a drop in CO conversion probably due to carburization of the catalyst. After regeneration under hydrogen (in tech. 8 h), conversion increased, but remained at a low level compared with the first experiment.

The selectivity of the reaction liquid C<sub>5+</sub> products decreases with the lowering of the gas ratio. However, considering the substantial reduction in CO conversion in general, this fact is not determinative in the synthesis. Payback of GTL plants in the world ranges from 5 to 6 years in the conversion of 65-80 % respectively.

In the second step, experiments were conducted by the Fischer-Tropsch process at elevated pressure (1 MPa), a catalyst is obtained by the method of electric conductors in argon atmosphere. Synthesis was carried out without pre-reduction catalyst-up time did not exceed 3 hours.

CO conversion remained approximately at the same level. In this case, was obtained by a very low concentration of unsaturated compounds, which is not typical for iron catalysts having no high hydrogenating ability compared with cobalt and nickel compounds. Was also low and the concentration of oxygenates that speaks more stringent conditions of synthesis. The octane number of the liquid fraction calculated with the program «Compounding»<sup>15</sup> was the research method 61 points, and by the motor - 56.6 points. The aromatics content is about 15 wt. %.

#### Conclusions

1. Ultradisperse iron-based powders may be used as the catalyst in the Fischer-Tropsch process without complicated additional prior preparation and recovery as electric explosion in the phase conductor forming composition required to activate hydrocarbon synthesis reaction of a mixture of CO and H<sub>2</sub>.

2. Study of process of hydrocarbon synthesis for ultradisperse iron catalyst showed some flexibility of the process: change in the process conditions allows influencing the composition of the obtained products, and thus affecting their operation.

3. Liquid products of the Fischer-Tropsch process may be used as additives in gasoline and diesel fuels, as well as for obtaining thermal or electric energy.

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