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Ultradispersed electro-explosive iron powders as catalysts for synthesis of liquid hydrocarbons of CO and H₂

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Abstract

Catalytic activity of ultradispersed iron powders (UDIP) obtained by electric explosion of the conductor in media of nitrogen, carbon monoxide, and carbon dioxide in synthesis of liquid hydrocarbons by Fischer-Tropsch method was studied. It was shown that iron powder obtained in media of CO₂ has the highest specific surface area. A sample of powder was pelletized at pressure of 21 MPa during 30 seconds with use of 10 mass% polyvinyl alcohol as adhesive for experimentation in catalytic system. Catalyst fraction of 1-2 mm was selected for study. The experiments were carried out under conditions of 1 MPa, 300 mln/min of total reactants consumption, and varied values of temperature and reactants ratio. The maximal conversion level of CO was reached at 290 °C and reactants ratio of H₂:CO = 2 in the initial mixture. It was shown that UDIP has high activity at lowered concentration of hydrogen in the initial mixture. The obtained mixture of liquid hydrocarbons is applicable for further refining for upgrading and improving of operating features.

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1. Introduction

The major part of crude oil and gas wells in Russia, one of the leaders of natural gas extraction, is situated remotely from gas transmission network and gas refineries, and because of that associated petroleum gas utilization problem is to be solved. Declared as the most perspective technology of gas conversion into liquid hydrocarbons, Fischer-Tropsch synthesis (FTS) may become one of possible solutions. These hydrocarbons will be used for supply with fuel and lubricators of both refineries and other remote consumers.

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We are running out of the explored supplies of crude oil, so gas and coal refining gains the upper hand. The interest in synthesizing liquid hydrocarbon fractions is caused by ecologic problems.

Catalysts play one of the most important roles in FTS. Different fraction yield, feedstock refining completeness, and other features of process depend on choice of the catalyst. As an example, iron catalysts in comparison to cobalt ones are capable to work at low $H_2:CO$ ratio with low methane yield and high conversion level of CO, although they have less activity towards yield of the middle-distillate fraction.

Catalyst properties depend mostly on its structure. Electric explosion technology of manufacturing of ultradispersed powders¹ allows obtaining particles with high specific surface area of adjusted phase composition, multi-level structure organization, and significant amount of free energy.

So, the aim of this work is to study catalytic activity of UDIPs obtained by the method of electric explosion of conductors in different gas media in the process of synthesis into liquid hydrocarbons by Fischer-Tropsch method.

2. Literature review

Specialists from all over the world are interested in improvement of FTS. There are three units of obtaining synthetic liquid fuels in Sasolburg (SAR) of 2 m. tn/yr of productivity and 5 m. tn/yr of total capacity². The scientists from China and Great Britain improved Co/MnO_x catalyst that had light olefins selectivity of 15.7 % in the research³. Light olefins yield reached 42.2 % with the obtained catalyst that is 26.5 % more than the predecessor had.

The researchers from China and USA notice in their works^{4,5} that FTS may be used for producing aviation fuels. They used different supplies of feedstock as mineral products (natural gas) or renewable resources of syngas (wood chips, soybean, rapeseed, jatropha, sugar cane). Such lead-up allows solving two problems simultaneously: improvement of gas refining technologies in the first case and mastering of new hydrocarbons sources in the second one.

It's possible to use nickel-molybdenum-potassium catalyst doped with carbon nanotubes for producing both ethanol and higher alcohols⁶. The possibility of obtaining a product containing up to 36.1 % of ethanol (oxygenate selectivity 67.3 %) was shown in this research.

FTS also touches upon adjacent spheres of science and technology – efficient production of syngas and ecology problems. The authors of the research work⁷ carried out coal gasification and analyzed the obtained product by the laser absorption method. It allowed fast and correct note of any changes in reaction conditions for obtaining syngas of adjusted component composition. Biomass gasification is not less efficient than coal gasification. It's possible to obtain syngas with $H_2:CO$ ratio from 1.0 to 1.3⁸ as well as with heightened hydrogen content ($H_2:CO$ equals from 1.8 to 2.2)⁹ by this method. Ecology enhancement is topical for Russia: our countrymen work out different efficient methods of associated petroleum gas (APG) refining. The authors of work¹⁰ developed the way of APG conversion to mixture containing methane and hydrogen predominantly, and conversion of heavy hydrocarbons exceeds 95–99 % in 270–360 °C temperature range. An experimental unit while using it in industry has less payback time than its analogs. Also the work¹¹ is notable because there the method of single-stage conversion of APG to syngas is considered. The obtained yields of the aimed products corresponded to the predicted ones by thermodynamics, so it allows controlling the reaction efficiently, in particular, by changing initial pressure.

3. Method

UDIPs obtained in media of nitrogen, carbon monoxide, and carbon dioxide were used for the experiments. The samples of powder were produced in the Institute of high technologies physics of National research Tomsk polytechnic university with use of the technologies and hardware described in the work¹.

The electro-explosive iron powders have developed surface. The images of UDIPs surfaces made by the scanning electron microscope are shown in Figure 1, the modes of making photographs are noted on the images.

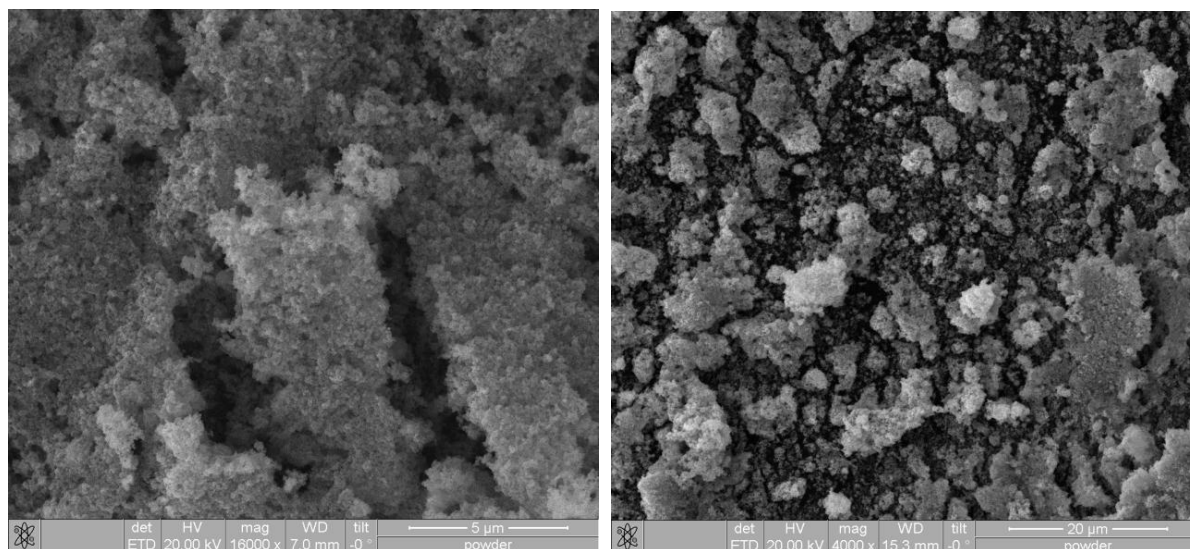


Fig. 1. UDIPs surfaces

The most perspective from the phase composition viewpoint electro-explosive iron catalyst is the $\text{Fe}(\text{CO})$ powder, as shown earlier¹².

Initially all powders were pelletized at pressure of 21 MPa with use of 10 mass% polyvinyl alcohol as adhesive. Sample holding time under pressure was 30 seconds. The catalyst fraction of 1-2 mm was selected for the study.

The obtained fractions were studied on catalytic system working at heightened pressure, which scheme is shown in Figure 2.

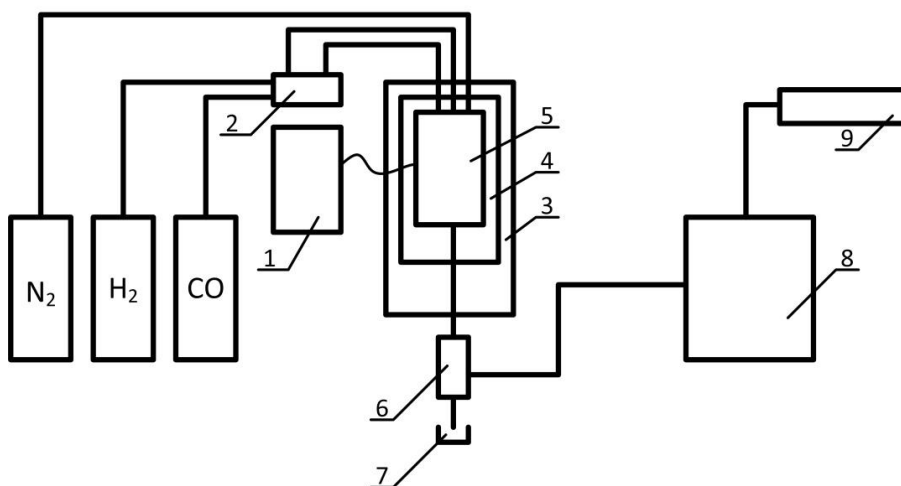


Fig. 2. Catalytic system scheme: 1 – temperature controller, 2 – gas metering unit, 3 – heat chamber, 4 – reactor jacket, 5 – reactor, 6 – separator, 7 – receiver, 8 – gas chromatograph, 9 – air vent.

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

The loaded catalyst volume was 8 cm^3 , total reactants consumption – 300 ml/min. All experiments were carried

out under pressure of 21 MPa. $H_2:CO$ ratio was equal to 2, 1.5 and 1. Any experiment duration was 1 hour since the moment of the stable mode setting. 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”.

4. Results and discussion

Measurement of total specific surface area was carried out by the multiple-point BET method with use of nitrogen as adsorbate for all samples of catalyst. The results are shown in Table 1.

Table 1. Specific surface area of UDIPs

UDIP sample	Specific surface area, m^2/g
Fe(N_2)	5.573
Fe(CO)	8.035
Fe(CO ₂)	8.323

The UDIP sample obtained in media of nitrogen has the least specific surface area, that may be explained by absence of chemical reactions between iron and gas media at the moment of powder production. The specific surface areas of powders obtained in media of CO and CO₂ differ insignificantly. Powder phase composition analysis described in the research¹³ showed that Fe(CO) powder is the most perspective UDIP catalyst, as described in the work. Fe(CO) catalyst may be used for FTS without preliminary reduction because during electric explosion in media of carbon monoxide phase composition is formed required for synthesis reaction activation of hydrocarbons of mixture of CO and H_2 .

Study of catalytic activity of Fe(CO) catalyst sample was carried out in the catalytic system. The experiments were carried out under conditions of 1 MPa, the catalyst layer temperature varied from 270 to 290 °C, 300 mln/min of total reactants consumption. Synthesis was carried out without preliminary reduction of catalyst in hydrogen or inert gas stream. The time of catalyst switching to working mode was 1 hour. The obtained results are shown in Figures 3 and 4.

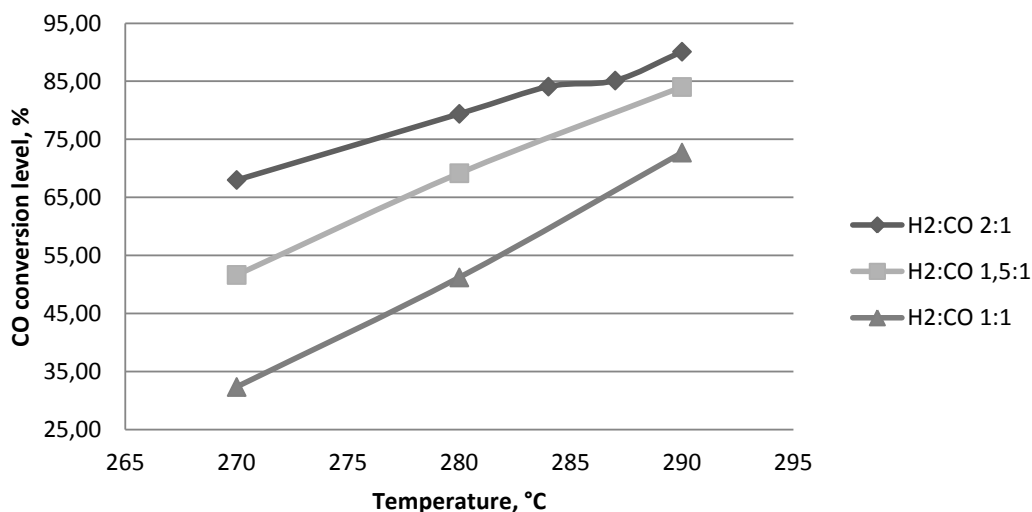


Fig. 3. Dependence of total CO conversion level on synthesis temperature.

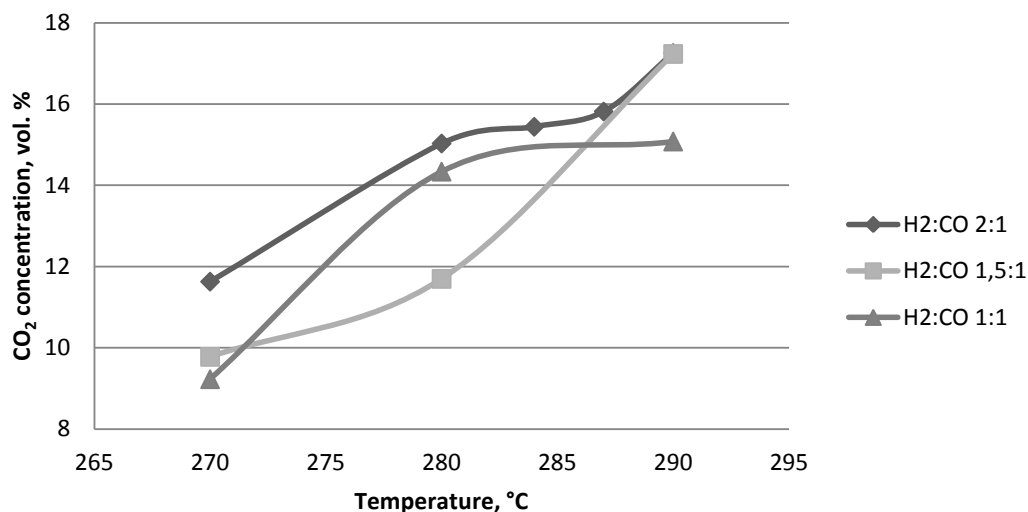


Fig. 4. Dependence of total CO₂ concentration on synthesis temperature

Analysis of dependences presented in Figures 3 and 4 showed that carbon monoxide conversion level increases proportionally with temperature growth up to value ca. 84 % at 284 °C. Further temperature increase doesn't lead to a significant rise in conversion level, but leads to growth in yield of by-product – CO₂. Carbon dioxide doesn't take part in formation of the aimed products. The absolute value of CO conversion level at the studied synthesis temperatures is high enough that is proved by comparison of the obtained experimental data with the literature data¹⁴. The total conversion level of CO decreases with fall in hydrogen concentration in the initial mixture. The maximal decrease in conversion level reaches 32 % at 270 °C, and H₂:CO = 1. Herewith by-product yield holds at same level – ca. 10 %. In this case we can make a conclusion that this catalyst is applicable for synthesizing hydrocarbons of CO and H₂ at low concentration of hydrogen in the initial mixture.

Analysis of liquid products synthesized at 290 °C and H₂:CO = 2 showed that oxygenates are completely absent that determines low octane number of liquid product (ca. 60 points according to chromatographic analysis). Also produced liquid contains many isoparaffins, low olefins, and aromatics.

Concentration of paraffins with the amount of carbon atoms from 10 to 12 practically equals 4.4–5.4 mass %, paraffins of C₁₄ and higher are completely absent. Such distribution of paraffins by composition determines low octane number of liquid mixture. The total isoparaffins content is 25.7 mass %, and the substances with the amount of carbon atoms from 5 to 11 prevail. These isoparaffins have high octane number. There is high amount of aromatic hydrocarbons in the mixture (28 % mass), and their carbon atoms amount varies from 9 to 12.

Decrease in synthesis temperature led to the change of composition of liquid hydrocarbons mixture obtained experimentally. Decrease in temperature led to rise in paraffins concentration to 36 mass %. Distribution of paraffins by carbon atom amount became more steady from 1.9 to 3.3 mass%. Content of isoparaffins and olefins remained constant that allows us to make such a conclusion: in the limits of carried out experimentations changing synthesis temperature leads to changing concentration of paraffins; synthesis temperature decrease leads to rise in paraffin of 7–15 carbon atoms amount concentration. Temperature decrease doesn't affect too much concentration of aromatic hydrocarbons and naphthenes. Oxygenate concentration under these conditions remains stable.

5. Conclusions

1. UDIP obtained by the method of electric explosion of the conductor in media of carbon monoxide has high catalytic activity in the process of synthesis of CO and H₂ into liquid hydrocarbons. The total conversion level of CO at H₂:CO = 2 reaches 90 %.

2. The ultradispersed iron catalyst has high activity in case of decreasing hydrogen concentration in the initial mixture to ratio $H_2:CO = 1$. The total conversion level at 290 °C and $H_2:CO = 1.5$ reaches 84.59 %, and at $H_2:CO = 1$ it is 72.71 %.

3. Changing technological conditions of the process will affect specific composition: thus, increase in synthesis pressure leads to heightened yield of naphthenes. The produced mixture of liquid hydrocarbons is applicable for further refining in order to upgrade it and improve its operating features.

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