

Physical-Chemical and Texture Characteristics of Coate-Fe-Ni-ZrO₂ / YuKS + Fe₃O₄ + d- FeOON

Ortiqov Nurbek Rustamovich¹, Kuybokarov Oybek Ergashovich², Khidirova Yulduz Khujanazarovna³, Khamidov Davron Ruzimurodovich⁴, Fayzullaev Normurod Ibodullaevich⁵

Abstract

The article examines the physicochemical and texture characteristics of the catalyst containing Co-Fe-Ni-ZrO₂/IOKII+ Fe₃O₄ + δ- FeOOH, used in the synthesis of high-molecular hydrocarbons from synthesis gas. As can be seen from the IR spectra, during the preparation of the catalyst, iron nitrate is decomposed in paraffin and polymer media to form iron oxide, which is confirmed by the presence of an accelerated broad line in the 605-620 cm⁻¹ region specific to Fe = O, in which case 1100 there is no anion nitrate line within cm⁻¹. Paraffin oxidation may occur during catalyst formation, as evidenced by the formation of new lines in the range of 1717 cm⁻¹ (Vc = o) and 900-1060 cm⁻¹ (Vc-o), but the intensity of these lines is not high.

¹Senior Lecturer of the Department of General Chemistry Karshi, Engineering and Economics Institute

²Karshi Institute of Engineering Economics, Assistant of the Department of "Chemical Technology",

³Senior Lecturer of the Department of General Chemistry Karshi, Engineering and Economics Institute

⁴Senior Lecturer of the Department of General Chemistry Karshi, Engineering and Economics Institute

⁵Samarkand State University, doctor of technical sciences, professor

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Introduction

Almost all reactions based on CO and H₂ are catalyzed by bifunctional active centers, which include metal (active component) and oxide, exhibiting the properties of Lewis acid. The oxidized forms of the carrier, the oxide promoter, and the active component are directly involved in the formation of such a center. Thus, the composition, structure, and size of the formed active centers of the catalytic system generally have a direct effect on the composition, structure, and properties of the contact itself. Almost all reactions based on CO and H₂ have a brightly expressed exothermic effect. Sudden heating in the reaction zone can lead to

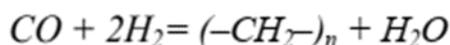
enlargement of the active phase particles of the contact and consequently to the activity and selectivity of the catalytic system. Transferring the reaction to a gas-liquid-solid body three-phase system, i.e., a system in which the catalyst is shaken in a liquid, not only balances the thermal effects of the reaction, but also regulates the formation of active phase particle size. In this case, in the liquid phase, micrometric granules of the finished, activated catalyst are distributed in the reaction zone in the reaction gas stream [1-6]. Given the complex hydrodynamic characteristics and the tendency to stratify, it is more difficult to maintain the stability of such a system. However, it is known that the durability of a suspension is determined by the size of the solid particles it contains: a reduction in their size significantly reduces the tendency of the system to separate into layers. However, the properties of ultradispersed particles of complex composition with carbon monoxide-based catalysts can be significantly different from granulated macrometric contacts. The use of nanometric catalysts in a number of reactions has led to a fundamental change in their efficiency and selectivity, due to the significant difference in the activation energy of reactions catalyzed by nanoparticles compared to conventional catalysts and the dependence of reaction selectivity on catalyst particle size [7-14].

In addition, the formation of heterogeneous nanometric catalysts in a direct three-phase system, as well as their in-situ activation properties, remain virtually unexplored at present.

It is known [15-23] that the optimal composition of the metal component in classical three-phase systems used in Fisher-Tropsh synthesis does not exceed 20%. Ultradispersion suspensions with such a concentration of solid particles are agglomerated. The problem of adhesion of metal-containing active particles distributed in dispersed media can be solved by the addition of surfactants, ionic liquids, and so on. However, these methods are not suitable for the preparation of suspensions of Fisher-Tropsh synthesis catalysts, as many stabilizers contain components that are considered catalytic poisons. A possible solution to this problem is the use of polymer systems as a stabilizing component [8-17].

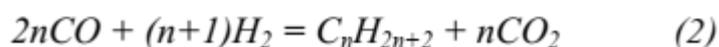
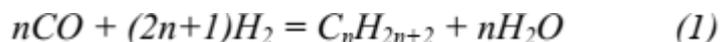
In this study, the effect of polymer additives in a hydrocarbon dispersion on the ultradispersive Fe-catalyst activity during Fisher-Tropsh synthesis under three-phase system conditions and the kinetic regularities of Fisher-Tropsh synthesis in the presence of polymer-containing nanoscale catalytic dispersions were studied.

Fisher-Tropsh synthesis follows the mechanism of the heterogeneous-catalytic radical reaction of polymerization, where the main reaction of the synthesis [6] is the CO hydropolymerization reaction:

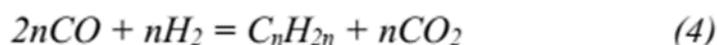
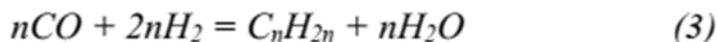


The step-by-step mechanism can be visualized in the following diagram [7]:

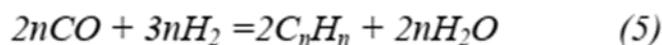
for paraffins:



for olefins:



for aromatic hydrocarbons:



Experimental Part

Catalysts were prepared by droplet thermolysis of iron or cobalt salt solution in a dispersion medium containing P-2 petroleum paraffin and polymer solution [19-39].

The choice of precursor was based on the fact that it is easily soluble in water and should be dissolved in a boiling dispersion medium (P-2 paraffin and polymer) at a temperature not exceeding 3000C . As a result, iron nitrate hexahydrate was chosen as the main promoter.

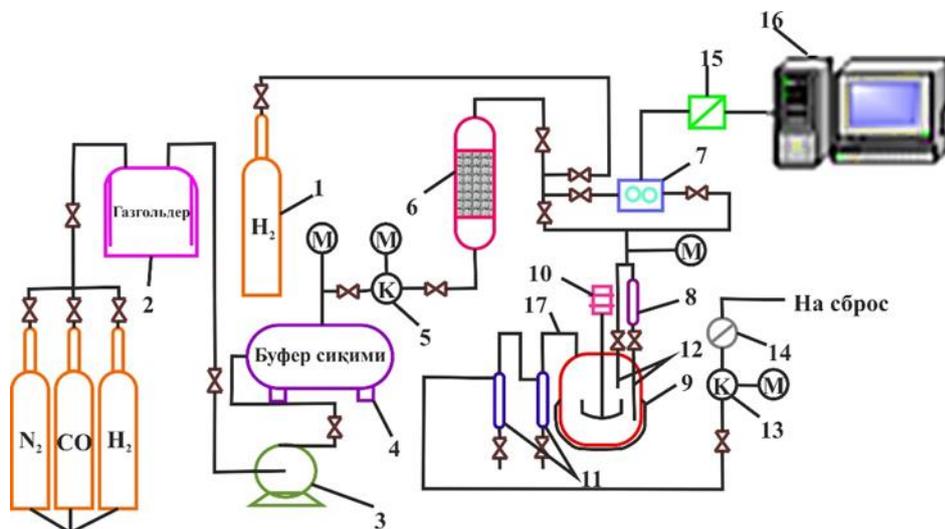
Synthesis of the metal-containing suspension was carried out by first melting 100 ml of Co-Fe-Ni-ZrO₂/IOKI₄+ Fe₃O₄ + δ- FeOOH catalyst at 100 ° C at 10 gr and then heating the system to 260-2900C by stirring in an inert gas stream (Ar). . An iron nitrate solution was then added dropwise to 20 ml of distilled water. The amount of Fe(NO₃)₃*9H₂O was obtained at the rate of 6 gr of iron per 100 ml of suspension. After the entire volume of the precursor solution was introduced, the systems were kept in inert gas current for 2 hours.

For each sample, samples were selected to measure the particle size by the 0-hour, 1-hour, and 2-hour dynamic irradiation methods of argon treatment.

The study of the basic laws of the process of interaction of carbon and hydrogen monoxide in the presence of a metal-containing catalyst was carried out in an autoclave-type flow catalytic device.

The device diagram (Figure 14) is shown. The device operates in gas flow mode. Effective dispersion of gas bubbles is achieved by synthesis-gas bubbling through the liquid

phase layer and by forced mixing of the suspension using a mechanically rotating mixer. Thus, a three-phase system in one plane is created in the reactor volume: gas-liquid-solid.



1- compressed gas cylinders; 2 - gas holder; 3-compressor; 4- buffer capacity; 5 "after" pressure regulator; 6- purification of gas synthesis from oxygen; 7- regulator of gas flow to the reactor; 8- dispenser; 9- reactor; 10-piston type mixer; 11- receiver-capacitors; Distribution devices for gas supply to reactor 12; 13 "own" pressure regulator; 14 gas hours; 15 gas flow regulator control unit; 16 computers; 17 heated communication; M-manometers.

Figure 1. Scheme of the device for the synthesis of hydrocarbons from CO and H₂ in a three-phase reactor.

Carbon monoxide exhaust gases, hydrogen and nitrogen in the cylinder (1) were mixed in the required ratio in the gas holder (2) and introduced into the buffer tank (4) using a compressor (3). The synthesis gas passed through the oxygen and water purification system (6) through the pressure regulator (5), and then through the flow regulator (7) the gas and gas inlet distribution devices (12) entered the autoclave-type reactor (9) (reactor capacity) 500ml³), equipped with a built-in mixing device (10). The gas leaving the reactor passes through three receivers-condensers (11) in series, the first of which is heated to 100oC using a thermostat, the second has water cooling, and the third is cooled by air. In the receivers, the exhaust gas is condensed and the liquid products of the reaction are separated. The unreacted gas and the gaseous products of the reaction are discharged to the discharge line after being sorted for chromatographic analysis by means of a "special" pressure regulator (13) and gas clocks (14). The pressure in the system was controlled using several manometers.

The loading of the catalyst suspension was carried out on the rector as follows: the required amount of dissolved phase (usually the volume was 100 ml) was placed in the reactor preheated to 70oC. The reactor was then heated to the desired temperature and the precursor was sprayed into the reactor through the dispenser (8). The system was then filled with hydrogen or carbon monoxide to the working pressure. 24 hours after catalyst recovery, the reactor temperature was lowered to the desired mark and transferred to the synthesis-gas system of the required composition.

Oxygen purification of the synthesis gas was carried out in a tubular reactor (6) heated to 1350C with a molten iron catalyst.

During the experiments, the following technological parameters were directly measured: gas flow to the reactor (l s), temperature in the reactor using chromel-aluminum thermocouple (oC, +1 accuracy), pressure in the reactor using a manometer (atm).

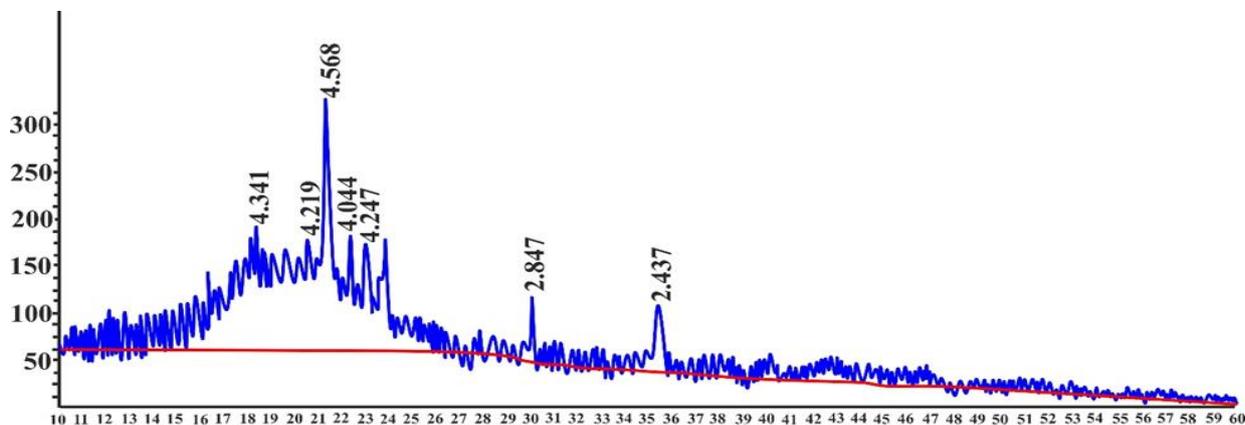


Figure 2a. Co-Fe-Ni-ZrO₂/IOKI + Fe₃O₄ + δ - FeOOH

The radiographs of the remaining synthesized catalytic dispersions are as follows:

(CH₂)_x

n-parafin

Ref: Heyding. Ret al. Powder Diffraction, 5.93(1990)

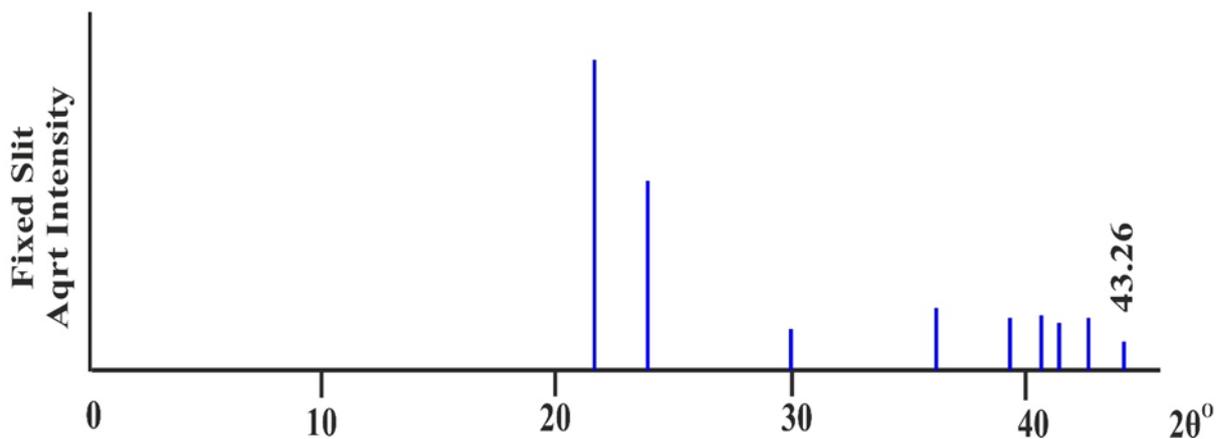
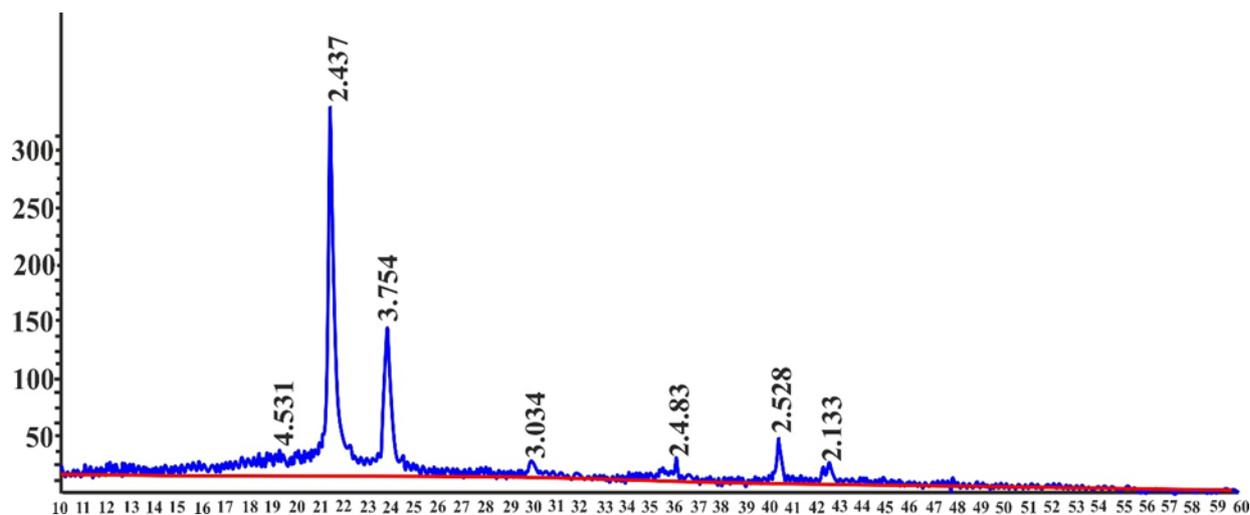


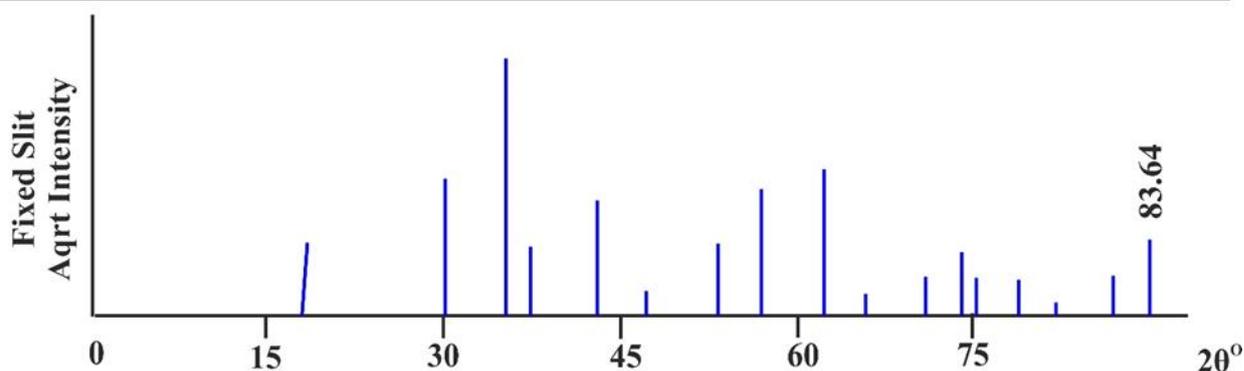
Figure 2b. Co-Fe-Ni-ZrO₂/IOKI+ Fe₃O₄ + δ - FeOOH.

Figure 2B. Co-Fe-Ni-ZrO₂/IOKI + Fe₃O₄ + δ- FeOOHFe₃O₄

n-paraffin

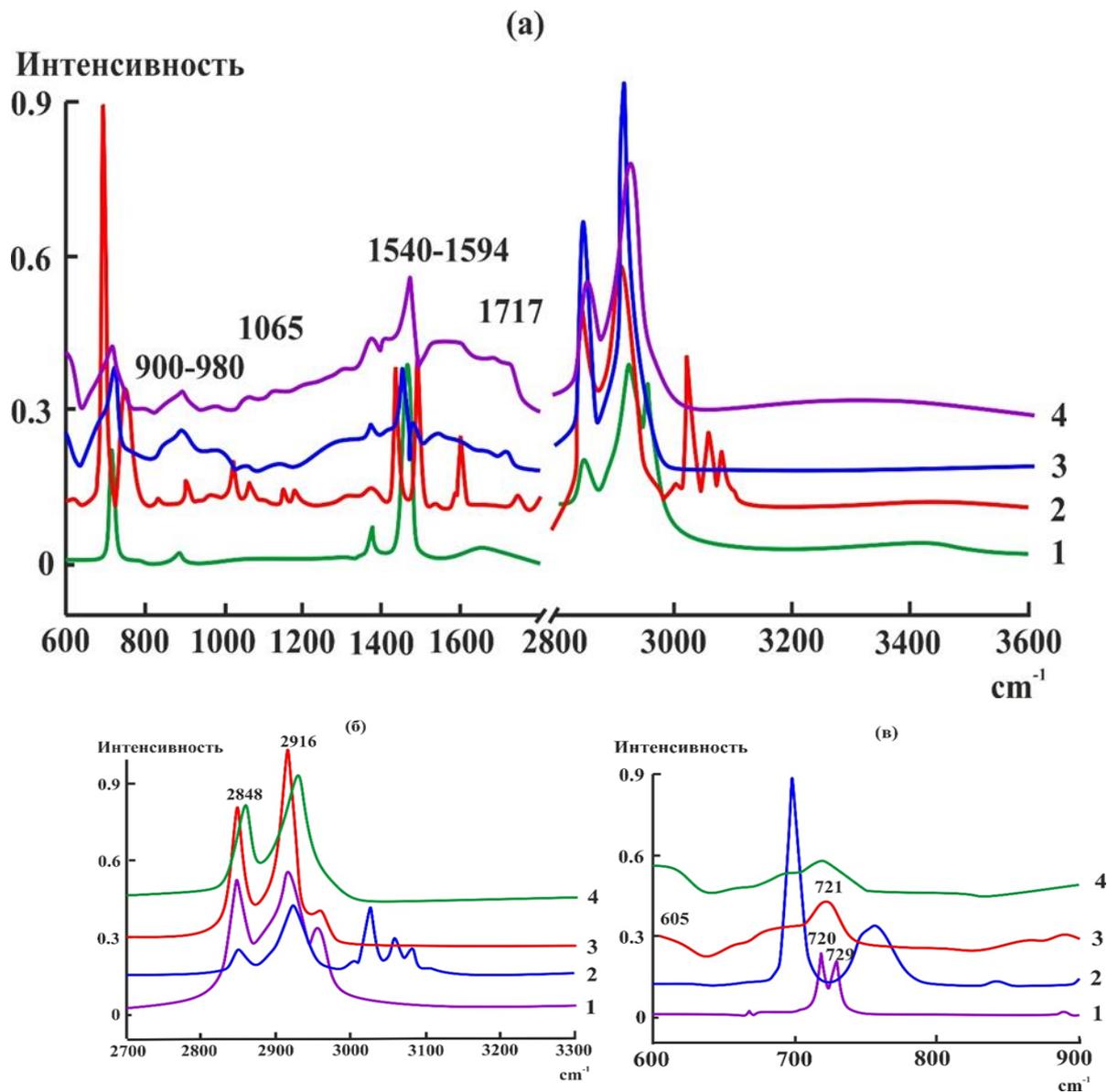
Ref: Calculated from ICSD using POWD-12++

Ref: Derbyshire, W.D., Yearian, H.J., Phys. Rev., 112, 1603 (1958)

Figure 2g. Co-Fe-Ni-ZrO₂/IOKI + Fe₃O₄ + δ- FeOOH

IK spectroscopic study of an iron-containing ultradispersal catalyst.

As can be seen from the IK spectra (Fig. 3a), during the preparation of the catalyst, iron nitrate is decomposed in paraffin and polymer medium to form iron oxide, which is confirmed by the presence of an intense broad line in the 605–620 cm⁻¹ region characteristic of Fe = O. in this case there is no anion nitrate line in the spectrum within 1100 cm⁻¹. Paraffin oxidation can occur during the formation of the catalyst, as evidenced by the formation of new lines in the range of 1717 cm⁻¹ (Vc = O) and 900-1060 cm⁻¹ (Vc-O), but the intensity of these lines is not high, i.e. synthesized. the degree of paraffin oxidation in the catalyst is not high. It should be noted that the IR spectrum of the Co-Fe-Ni-ZrO₂/IOKI+ Fe₃O₄ + δ- FeOOH catalyst is close to the IR spectrum of paraffin, while the IK spectrum of the Co-Fe-Ni-ZrO₂/IOKI+ Fe₃O₄ + δ- FeOOH catalyst is similar to that of polystyrene. there are no specific lines, which may be due to the fact that the paraffin layer on the surface of the particles does not allow to fix the spectrum of the thin layer of the polymer directly associated with the metal.



(a) comment spectrum,

(b) - Detail in the field of valence changes of C-H bonds,

(c) In the field of deformation changes of C-H bonds. 1-paraffin; 2-PC;

3- Fe-PE-Paraffin; 4- Fe-Pc-paraffin.

Figure 3. IR spectra of paraffin, polystyrene and Fe-PE-Paraffin, Fe-Ps-paraffin

Analysis of the spectral field of n-valence (Fig. 3b) and especially deformation (Fig. 3v) changes of saturated chains (CH₂) allows us to conclude that the paraffin on the surface of the catalytic particle undergoes structural changes during catalyst formation. Within 700-730 cm⁻¹, two lines from the CH₂ groups appear in the paraffin spectrum: the 720 cm⁻¹ line is specific to any methylene group, the 730 cm⁻¹ line occurs only in the spectra of sufficiently long-regulated chain hydrocarbons, and the crystallinity of the sample increases. grows in intensity. In the spectrum of catalysts with the addition of polyethylene and polystyrene, a

single broad line with a maximum of 721 cm⁻¹ appears in this area, with no line at 729 cm⁻¹ (Fig. 3c). Such changes in the field of lines from CH₂, as well as the shift of the lines in the field of valence changes Co-Fe-Ni-ZrO₂/ЮКЦ + Fe₃O₄ + δ- FeOOH no polymer in the catalyst spectrum, allows us to conclude that non-saturated molecules have a completely different conformational set.

Conclusion

Thus, all the signs of paraffin oxidation are observed in the spectrum of the prepared Co-Fe-Ni-ZrO₂/ЮКЦ + Fe₃O₄ + δ- FeOOH catalyst, where the relative intensity of the lines from C = O (1720 cm⁻¹) double bonds is much higher than in the spectra of polyethylene and polystyrene added catalysts. The absence of a 607 cm⁻¹ dynamic line from Fe = O and a 1100cm⁻¹ line from the nitrate-anion indicates that the introduction of the polymer into the disperse medium does not affect the decomposition reaction of precursor-iron nitrate (III) to iron oxide.

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