Kinetic Model for Fischer-Tropsch Synthesis over Nanoparticles Iron Catalysts with Polymer Matrix in a Slurry Reactor*

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Influence of additives of synthetic polymers of various natures on reactionary ability of the nanostructured iron catalysts in the three-component Fe–paraffin–polymer system in Fischer-Tropsch (FTS) in the slurry reactor was studied. The polymers used: polyacrylonitrile (PAN), polyvinyl alcohol (PVA), polystyrene, cross-linked with divinylbenzene (PS-DVB), polyamide-6 (PA). The catalysts obtained by droplet thermolysis is influenced by, the nature of the stabilizing polymer. Besides the conversion of the synthesis gas depends on the contact time and is between 10 to 80%. The highest rate of FTS is observed in the Fe–paraffin– PAN. The conditions of synthesis in Fe–paraffin–polymer systems produced a wide range of saturated and unsaturated compounds. It is found that the nature of the stabilizing polymer also affects the olefin / paraffin ratio. Based on experimental data the analysis of kinetic models for the flow of CO is carried out, a kinetic and thermodynamic characteristics of the process was obtained. The relationship between the values of the activation energies and the nature of the stabilizer was established.

Keywords: *Fischer-Tropsch synthesis, nanocomposite iron catalysts, polymers, reaction kinetics.*

Introduction

In several years the mankind will celebrate the 100th anniversary of an outstanding achievement in the field of catalysis and chemical technology: Fischer-Tropsh synthesis (FTS). This process is of huge practical value due to the really immeasurable quantity of products: paraffins, olefins, alcohols etc. Technologically and commercially available synthesis gas (CO + H_2) forms a wide range of hydrocarbons from C_1 to C_{100}. Thus, FTS is the main method for obtaining synthetic liquid fuel [1]. This process can be presented as two simultaneous reactions [2]:

Fischer-Tropsh synthesis (FTS):

$$CO + (1+ m/2n)H_2 = 1/nC_nH_m + H_2O \qquad (1)$$

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and water gas conversion of (WGC):

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad (2)$$

where n is the average number of carbon atoms in the chain, m is the average number of hydrogen atoms in the hydrocarbonic product.

Cobalt and iron were the first catalysts that Fischer and Tropsh used for the synthesis gas conversion. These substances were used also in the industrial hydrocarbon synthesis. FTS is carried out at elevated pressure. The main products obtained in the presence of the iron catalyst are hydrocarbons of the gasoline fraction and lower compounds [3]. Almost all water formed in FTS is consumed in reaction (2). At the same time water almost does not affect FTS rate, obviously, due to weaker adsorption on the catalyst surface as compared to CO [4].

The use of new methods for the preparation of metal polymer composites was an important factor in heterogeneous catalysis development. Nanosized particles considerably change the physical and chemical properties of polymers and ceramics, the technological features of obtaining and using catalysts [5, 6]. For example, catalysts can be formed by the thermolysis of an iron precursor upon roasting polymer-paraffin melt. An advantage of this method is that particles are at once included in a matrix, and due to this they are not agglomerated [7, 8]. The effect of polymers used as stabilizers on the preparation of Co and Fe nanoparticles is described [9]. The products of the primary FTS reaction are olefins. Paraffins are formed mostly due to the subsequent hydrogenation. The olefin/paraffin ratio is affected by the catalyst nature and the process conditions [10, 11].

Previously we showed [7] that when carrying out FTS in the presence of a ternary Fe-paraffin-polymer system in a slurry-reactor, a wide range of saturated and unsaturated compounds is formed.

The emphasis of this work is upon studying the effect of the polymeric stabilizer nature on the catalytic activity of nanosized iron particles in Fischer-Tropsh synthesis. The addition of polymers to nanosized metal-containing suspensions allows preventing sedimentation and results, in general, in the formation of an entirely new active catalytic system with unique properties.

Experimental

The catalysts were synthesized by thermal decomposition of a solution of metal precursor salts in paraffin-polymer disperse medium in an inert gas atmosphere. The following polymers were used as additive stabilizing nanosized particles: polyacrylonitrile (PAN) with a molecular weight of 220000; polyvinyl alcohol (PVA) with a molecular weight of 5000–20000; polystyrene cross-linked with divinyl benzene (PS-DVB); and polyamide (PA) with a molecular weight of 20000–50000.

A melt containing 10 g of a polymer in 100 ml of paraffin was preliminarily prepared at 100°C. Then it was heated to 280°C under stirring in a flow of argon. Iron-containing suspensions were obtained by introducing dropwise iron nitrate solution into the hot suspension (6 g of iron per 100 ml of the suspension). Nanosized iron particles were obtained by reducing the catalytic system with carbon monoxide for 24 h at 300°C.

The size of the catalytic suspension nanoparticles was determined by dynamic light scattering (DLS). DLS spectra of reaction systems showed bimodal distribution [7]. The obtained results are presented in Table 1.

Table 1. Average particle sizes for catalytic systems depending on the introduced polymer nature

Introduced polymer	Average particle size, nm		Fe particles distribution, %	
	Region I	Region II	Region I	Region II
PVA	680	136	14	86
PA	932	236	55	45
PS-DVB	669	180	17	83
PAN	872	274	26	74

The obtained results indicate a fundamental difference of the effect of the nature of the polymers stabilizing the iron nanoparticles. In case of PVA, PAN and PS-DVB the content of iron in particles with an average size of 136–274 nanometers prevails (74–86%) over larger aggregates (14–26%). Another picture is observed in case of PA, where the iron fraction in large aggregates (55%) significantly increases because of the low stabilizing ability, which negatively affects catalytic activity.

FTS was carried out in a flow catalytic block with the catalyst suspension in a liquid (slurry) at a pressure of 2 MPa within a temperature range of 220–320°C. Synthesis gas (H_2, CO и N_2) flow rate was 1–2 l/kg·h. An inert gas (N_2) was added to increase pressure in the system. The equimolar $CO:H_2$ ratio in all the experiments was maintained constant. Programmable growth of temperature was 20°C within 12 h. When the final temperature was achieved, samples of the gas and liquid were taken for analysis. The gas composition at the autoclave inlet and outlet was determined by gas chromatography with the use of a Kristalluks-4000 chromatograph equipped with a heat conductivity sensor. Helium was used as a carrier gas. A column (3 m × 3 mm) with CaA molecular sieves was applied in the isothermal mode at 80 °C for the analysis of CO and N_2. In order to analyze CO_2 and C_1–C_4 hydrocarbons a HayeSep packed column (3 m × 3 mm) was used in a programmable temperature mode (80–200°C) at a pitch of 8°C/min.

Results and Discussion

It was found that when keeping the system within five days at a temperature of 220–320°C, a pressure of 2 MPa and a synthesis gas ($CO:H_2 = 1:1$) flow rate of 1–2 l/[(g of cat)·h], the size of iron particles increases up to 100 nm – 1.6 μm.

Synthesis gas conversion

The temperature dependence of CO conversion (C_{CO}) at a ratio of components 1:1 is presented in Figure 1. Synthesis gas conversion has the maximum value in case of a sample with PAN (80%), and minimum, in case of a sample with PA (10%). The other samples show intermediate values under the same conditions.

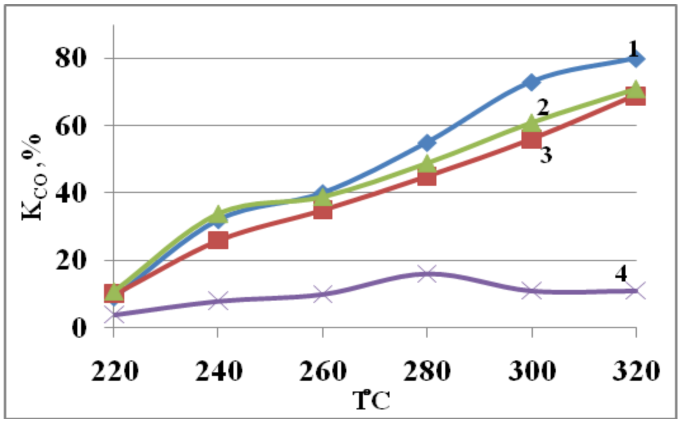

Figure 1. The dependence of CO conversion on synthesis temperature obtained in the presence of catalytic system Fe–paraffin–polymer:

1 – PAN, 2 – PS-DVB, 3 – PVA, 4 – PA

[K_{CO} means C_{CO}]

Influence of polymer nature on the structure of FTS products

The use of stabilizing polymers of various nature significantly affects the alkene/alkane ratio in the FTS products (Figure 2). The PAN-based catalyst shows higher selectivity with respect to alkanes. The highest C2–C6 alkene/alkane ratio is also observed when using this system. The polymer nature practically does not affect the C8–C11 alkene/alkane ratio. It is interesting that in case of C7 and C12–C17 hydrocarbons the alkene/alkane ratio is much higher when using the system with PS-DVB (~5), while their content is lower (2–2.5) when using other polymers. The obtained result is probably due to the nature of polymeric molecules decomposition [7, 8, 12]: they undergo partial destruction even in the studied temperatures range. PVA [13] and PS [12] decomposition is accompanied by the formation of unsaturated compounds. They can also participate in FTS. In case of polystyrene they consist mainly of the styrene monomer, dimer and trimer.

When heating PAN to 250°C, the polymer color changes from light to dark-brown, which is due to the formation of conjugated bonds as a result of nitrile groups polymerization according to the radical mechanism [12]. Simultaneously, ammonia (from the terminal imino groups NH of the conjugated structures) and hydrogen cyanide evolve.

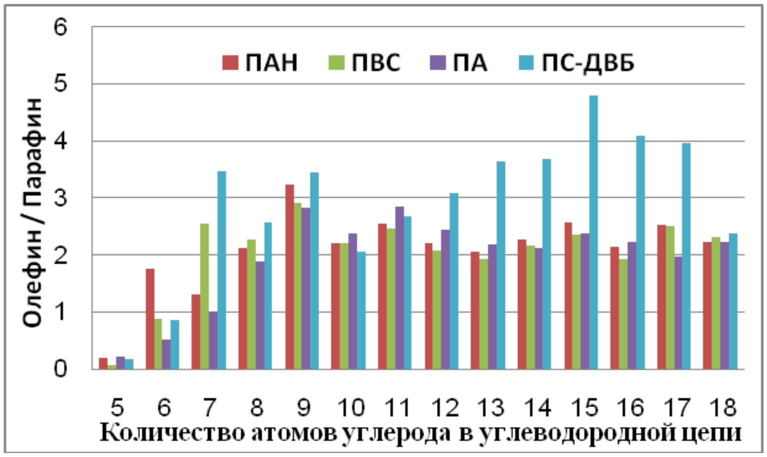

Figure 2. Alkene/alkane ratio for various hydrocarbons in catalytic system Fe–paraffin–polymer when using various polymers.

[ПАН means PAN; ПВС means PVA; ПА means PA; ПС-ДВБ means PS-DVB; Олефин/Парафин means Olefin/paraffin; Количество атомов углерода в углеродной цепи means The number of carbon atoms in the carbon chain

The composition of liquid fractions of C_nH_m hydrocarbons in FTS also depends on the type of the polymer (Figure 3).

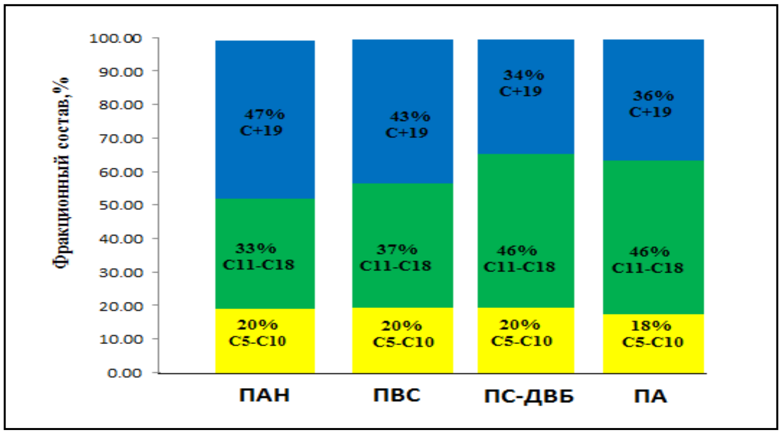

Figure 3. Fractional composition of FTS products of obtained in Fe–paraffin–polymer system at 320°C.

[Фракционный состав means Fraction composition; ПАН means PAN; ПВС means PVA;

ПА means PA; ПС-ДВБ means PS-DVB]

A small difference in the composition of fractions when using various polymers is observed only in case of C19+ fractions.

Determination of reaction rates in Fischer-Tropsh synthesis

Fischer-Tropsh reaction rate (r_{FTS}) was determined by the difference of the rates of CO consumption (r_{CO}) and CO_2 formation ($r_{\mathrm{CO_2}}$) according to the following equation:

$$r_{\mathrm{FTS}} = r_{\mathrm{CO}} - r_{\mathrm{CO_2}}$$

Table 2 and in Figure 4 show temperature dependences of r_{FTS} in case of using various catalytic systems. These results are in agreement with the data obtained by other researchers [14, 15].

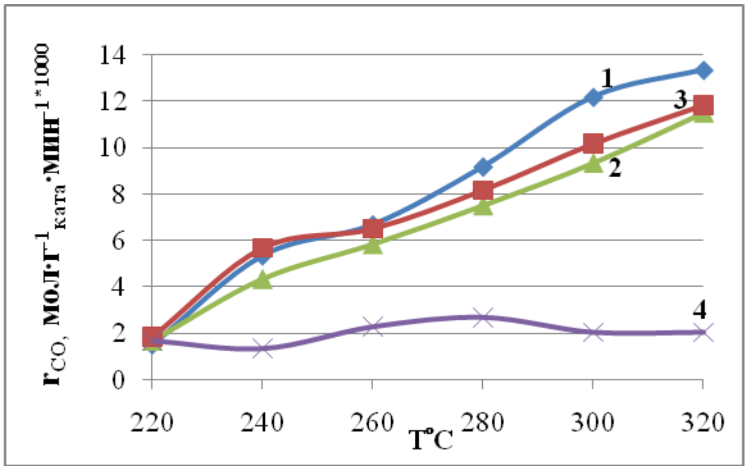

Figure 4. Temperature dependence of CO consumption rate in the presence of Fe–paraffin–polymer catalytic system: 1 – PAN, 2 – PS-DVB, 3 – PVA, 4 – PA.

[$\text{мол}\cdot\text{г}^{-1}_{\text{ката}}\cdot\text{мин}^{-1\cdot 1000}$ means $\text{mol}\cdot\text{g}^{-1}_{\text{cat}}\cdot\text{min}^{-1\cdot 1000}$]

Description of kinetic model of Fischer-Tropsh reaction

In order to describe the mechanism of Fischer-Tropsh reaction a number of schemes differing in the adsorptive capacity of reagents and products [2, 4, 7, 14–16] were suggested. The equations considering water adsorption on the surface of iron nanoparticles are use seldom, because almost all water is consumed at the limiting stage of CO_2 formation in WGC reaction. Two mechanisms and the related equations for CO consumption rate are used most often. They take into account either the primary adsorption of only CO or the consecutive adsorption of both CO and H_2 on the surface of iron [14].

Table 2. Experimental data for various catalytic systems Fe–paraffin–polymer

Catalyst	Temperature, ^oC	p_{CO}, atm	p_{H2}, atm	K_{CO}, %	r_{CO}, $mol \cdot g^{-1}_{cat} \cdot min^{-1}$
Fe–paraffin+PAN	220	9.2	9.6	9	0.0015
	240	8.15	9.3	32	0.005333
	260	7.6	9.0	40	0.006667
	280	6.6	8.33	55	0.009167
	300	4.6	7.25	73	0.012167
	320	3.74	6.81	80	0.013333
Fe–paraffin+PVA	220	8.86	9.92	10	0.001667
	240	7.95	9.65	26	0.004333
	260	7.5	9.08	35	0.005833
	280	6.9	9.02	45	0.0075
	300	6.0	8.45	56	0.009333
	320	4.6	7.98	69	0.0115
Fe–paraffin+PS-DVB	220	8.55	10.22	11	0.001833
	240	7.48	9.5	34	0.005667
	260	7.18	9.29	39	0.0065
	280	6.7	8.78	49	0.008167
	300	5.57	8.19	61	0.010167
	320	4.58	7.5	71	0.011833
Fe– paraffin+PA	220	8.88	10.1	4	0.000667
	240	8.86	10.09	8	0.001333
	260	8.7	10.1	10	0.002067
	280	8.6	9.97	16	0.002667
	300	8.6	10.12	11	0.001933
	320	8.6	10.08	11	0.001933

Mechanism I

$$CO + S = COs \quad (I.1)$$

$$COs + H_2 = H_2COs \quad (I.2)$$

$$H_2COs + H_2 \rightarrow CH_2s + H_2O \quad (I.3),$$

where S is the reaction center on the catalyst surface.

Reaction rate equation: $r_{CO} = k_{obs.}P_{CO}P_{H2} /(1 + aP_{CO})$

Mechanism II

$$CO + S = COs \qquad (II.1)$$

$$H_2 + S = H_2s \qquad (II.2)$$

$$COs + H_2s \rightarrow H_2COs \qquad (II.3)$$

$$H_2COs + H_2s = CH_2s + H_2O \qquad (II.4)$$

Reaction rate equation: $r_{CO} = k_{obs.} P_{CO} P_{H2} /(1 + aP_{CO})^2$

The reaction rate equations were obtained assuming that stage 3 for both mechanisms is limiting, and it is possible to neglect the member of sum in the denominator considering H_2 adsorption, because the heats of CO and H_2 adsorption on the surface of iron considerably differ.

We made an attempt of comparing two equations and mechanisms for the catalytic systems based on iron nanoparticles with polymeric stabilizers taking into account the temperature dependences of the rate constant:

$$K_{obs.} = A \cdot \exp^{(-Ea/RT)}$$

For the mechanism of the reaction with preceding equilibrium stages and limiting stage 3 the observed E_a contains the limiting stage energy $E_{a,lim}$ and the change in the enthalpy of the preceding equilibrium stage of CO adsorption:

$$E_a = E_{a,lim.} + \Delta H_{ads.}$$

In this case the Arrhenius equation takes the following form:

$$K_{obs.} = A \cdot e^{[-(Ea,lim. + \Delta Hads.)/RT]}$$

For adsorption coefficients it is possible to write:

$$a = a_0 \cdot e^{(-\Delta Hads.)/RT}$$

The reaction rate equation in case of mechanism I is transformed as follows:

$$r_{CO} = k_{obs.} P_{CO} P_{H2} /(1 + aP_{CO})$$

$$P_{CO} P_{H2} / r_{CO} = 1/k_{obs.} + aP_{CO} /k_{obs.}$$

$$P_{CO}P_{H2} / r_{CO} = 1/[A\cdot e^{(-Ea,lim. - \Delta Hads.)/RT}] + *a_0\, P_{CO}\cdot e^{(-\Delta Hads.)/RT} / [A\cdot e^{(-Ea,lim. - \Delta Hads.)/RT}]$$

$$P_{CO}P_{H2} / r_{CO} = 1/[A\cdot e^{(-Ea,lim.)}\cdot e^{(-\Delta Hads.)/RT}] + *a_0\, P_{CO}\cdot e^{(-\Delta Hads.)/RT} /[A\cdot e^{(-Ea,lim.)}\cdot e^{(-\Delta Hads.)/RT}]$$

After simplification we obtain:

$$[e^{(\Delta Hads)/RT} + a_0\, P_{CO}] / (P_{CO}P_{H2} / r_{CO}) = [A\cdot e^{(-Ea,lim./RT)}]$$

Let us introduce the following notation:

$$Y = [e^{(\Delta Hads.)/RT} + a_0\, P_{CO}] / (P_{CO}P_{H2} / r_{CO})$$

$$Y = A\cdot e^{(-Ea,lim./RT)}$$

After logarithming we obtain the following straight-line equation:

$$\ln Y = \ln A - (E_{a,lim.}/R)\cdot 1/T)$$

Let us transform similarly the equation for mechanism II:

$$(P_{CO}P_{H2} / r_{CO})^{1/2} = 1/k^{1/2}{}_{obs.} + a/k^{1/2}{}_{obs.}\cdot P_{CO}$$

After simplification we obtain:

$$\{[1/e^{(-1/2\cdot\Delta Hads.,co)/RT}] + P_{CO}a_0\cdot([e^{(-1/2\cdot\Delta Hads.,co)/RT}])\}/(P_{CO}P_{H2}/r_{CO})^{1/2} = [A^{1/2}\cdot e^{(-1/2\cdot Ea,lim.)/RT}]$$

Let us introduce the following notation:

$$Y' = \{e^{(1/2\cdot\Delta Hads.,co)/RT}) + P_{CO}\cdot a_0\cdot e^{(-1/2\cdot\Delta Hads.,co/RT)}\}/(P_{CO}P_{H2} / r_{CO})^{1/2}\}$$

Finally:

$$Y' = A^{1/2}\cdot e^{(-Ea,lim)/2RT}$$

or in the logarithmic form:

$$\ln Y' = 1/2\cdot\ln A - (1/2\cdot E_{a,lim.}/R)\cdot(1/T)$$

$\Delta H_{ads.,CO}$ is the heat of CO adsorption on the surface of iron. It is known from a number of works [14] that it is constant and equal to –47 kJ/mol, and a_0 is equal to $8.3\cdot 10^{-8}$ mmol/g·atm. Therefore, in order to compare the mechanisms we used the heat of CO adsorption on the surface of iron: $\Delta H_{ads.,CO} = -47$ kJ/mol. The value of a_0 was varied in a wide range. The minimum deviations from the experimental data were observed for $a_0 = 8.3 \cdot 10^{-8}$ mmol/g·atm.

The obtained dependences of ln*Y* on 1/*T* for both mechanisms are shown in Figure 5.

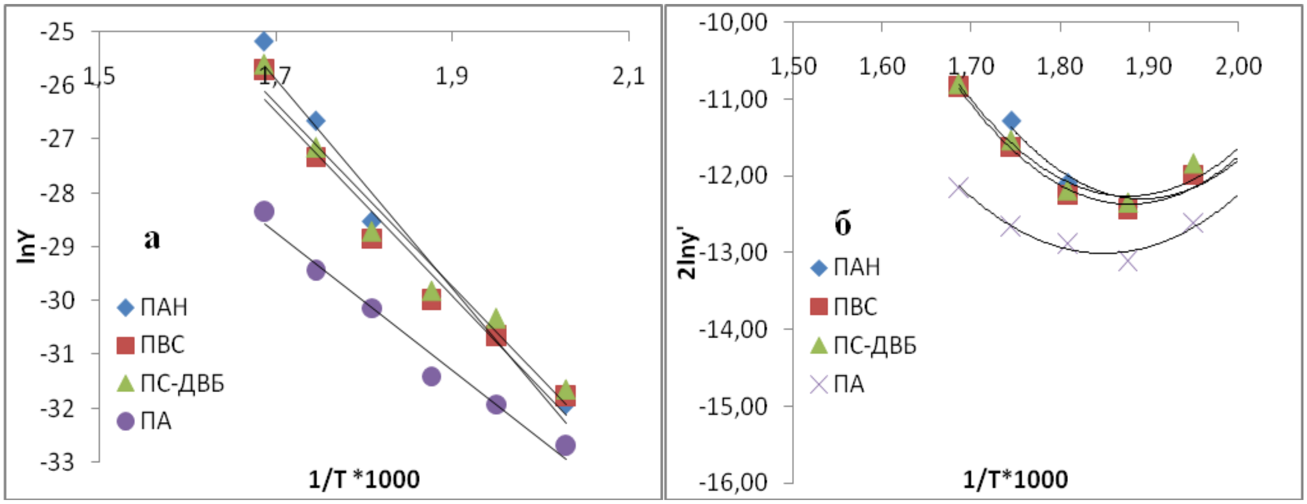

Figure 5. Dependences of ln*Y* on 1/*T*: a) mechanism I; b) mechanism II.
[a means a; б means b; ПАН means PAN; ПВС means PVA;
ПА means PA; ПС-ДВБ means PS-DVB]

Processing the presented results shows that mechanism I well describes the experimental data, in contrast to mechanism II.

The data of statistical processing of the straight lines obtained for various polymers according to mechanism I allowed estimating the kinetic characteristics of FTS reaction in Fe–paraffin–polymer system (Table 3).

Table 3. Kinetic characteristics of Fischer-Tropsch reaction in Fe–paraffin–polymer system

Polymer	$\Delta H_{\text{ads.}}$, kJ/mol	a_0, mmol/L·min·atm	$E_{\text{a, lim.}}$, kJ/mol	$E_{\text{a, gen.}}$, kJ/mol
PAN	–47000*	$8.30 \cdot 10^{-8}$*	105.98	58.98
PVA			140.69	93.69
PS-DVB			142.78	95.78
PA			161.01	114.01

* According to [14].

The generalized values of activation energy that well correlate with the literature data [14, 16] were added to Table 3:

$$E_{\mathrm{a,\ gen.}} = E_{\mathrm{a,\ lim.}} + \Delta H_{\mathrm{ads.,CO}}$$

Analysis of the experimental data allows determining the most adequate kinetic model of the reaction mechanism with preferential adsorption of only CO and interaction with H_2 from the gas reaction mixture.

It can be seen from Table 3 that the obtained $E_{\mathrm{a,\ lim.}}$ values depend on the polymeric stabilizer structure, which is in agreement with the obtained data and is confirmed by the high rates of Fischer-Tropsh reaction with PAN and the smallest reactivity of PA. Comparing the systems for various polymers shows that the energy of the limiting stage 3 (see the reaction mechanism) changes 1.6-fold upon transition from PAN to PA, which is agreement with the kinetic data and with the change in the sizes of the nanosized iron particles in the presence of the polymeric stabilizers (see Table 1).

The conducted study enables concluding that the reactivity of a catalyst considerably depends on the stabilizing polymer nature, and the Fe nanocatalyst stabilized by polymers shows activity in the synthesis of liquid hydrocarbons from CO and H_2. The difference in the reactivity of systems with polymeric stabilizers it largely due to the nature of the polymers decomposition at temperatures above 250°C.

On the basis of processing the kinetic data on CO consumption in FTS in the ternary Fe–paraffin–polymer system the optimal model of the mechanism of hydrocarbons formation with preferential adsorption of CO molecules on the surface of the nanosized iron particles was chosen. The effect of the polymeric stabilizer nature is in agreement with the values of activation energy of the limiting stage.

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