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Effect of the VIII Group Metals on the Catalytic Pyrolysis of Lower Alkanes

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Abstract—Catalytic pyrolysis of lower hydrocarbons C_1–C_4 was studied in a continuous flow tubular reactor in the presence of complex catalysts containing the VIII group metals: Fe, Co, Ni, Pd, applied as salts on the reactor walls or on a ceramic support. The catalytic activity of the metal-containing compositions is compared, the effect of the metal nature on the yield of ethylene and propylene is studied and soot formation is estimated. The kinetic and activation parameters for decomposition of the hydrocarbon mixture and accumulation of the products are calculated. In the empty reactor, the best results were observed for the catalyst on the basis of Co-phosphate coating, while for reactors packed with coated ceramic support it was the Fe-containing catalyst.

Keywords: pyrolysis, hydrocarbons, catalysts, metal-containing coatings, ethylene, coke formation

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The most important problem of oil and gas processing industry is the improvement of the existing methods of catalytic pyrolysis of hydrocarbon raw material to lower olefins C_2–C_4, which are used in the processes of polymerization, alkylation and esterification [1].

The modern production of ethylene is based on high-temperature (above 850°C) pyrolysis of hydrocarbon raw materials, which results in deep cracking of alkanes with the formation of coke and requires an intermittent cleaning of the reactors. Therefore, a search for new effective methods of processing oil hydrocarbons, which would allow to decrease the temperature and increase the selectivity of the process toward ethylene and propylene and to reduce coke formation, is still an actual task [2, 3].

Earlier, we performed systematic studies of three types of catalytic systems for pyrolysis of light hydrocarbons C_1–C_4 in flow system: protective film polyphosphate coatings applied on the inner surface of the steel reactor containing metals of the II–III groups of the Periodic Table of the total composition $Me_xO_y \cdot zP_2O_5$, where $x = 1, 2$; $y = 1, 3$; $z = 2, 3$; Me = Zn, Cd, Sr, Ce [4,5]; composite highly disperse materials modified with organozinc, organo-phosphorus, organosilicon compounds packing the flow reactor [6, 7]; ultradisperse metal particles of 100–500 nm size, formed by electric explosion dispergation of monometallic (Ag, Al, Cu, Fe, Ni, Ti, Pt, W, Mo) and bimetallic (Mo, Cu; Fe, Al; W, Ni; W, Pt) conductors [8]. A higher catalytic activity of the ultradisperse metal particles obtained by electric explosion dispergation of metal conductors as compared to the catalysts prepared by conventional methods was observed [9].

In the present work we report on the results of investigation of the catalytic pyrolysis of light hydrocarbons C_1–C_4 in continuous flow tubular reactor in the presence of complex catalysts containing the VIII group metals (Fe, Co, Ni, Pd) applied as salts on the reactor walls or on a ceramic support with subsequent thermal treatment. The catalytic activity of the metal-containing compositions under similar conditions is compared, the effect of the metal nature

Table 1. Pyrolysis of PBHM in reactors with variously treated walls[a]

Treatment of reactor	*T*, °C	Conversion of PBHM,%	Yield to the passed raw material, wt %				Selectivity for C_2H_4, %	Coke, wt %
			CH_4	C_2H_6	C_2H_4	C_3H_6		
Without treatment	710	7.1	0.5	–	3.5	3.1	49.5	1.12
	740	13.1	2.1	–	5.0	6.1	37.8	
	800	46.2	12.0	1.8	18.3	14.1	39.6	
$Fe(NO_3)_3$	830	67.3	19.1	5.4	28.5	14.2	42.4	
	710	7.1	2.0	–	2.4	2.7	34.0	0.99
	740	16.6	4.4	–	5.4	6.9	32.3	
	800	50.8	14.1	2.5	18.3	15.9	36.1	
$Fe(NO_3)_3 + H_3PO_4$	830	64.3	19.5	3.6	25.7	15.4	40.0	
	710	7.5	1.8	–	4.3	1.4	57.4	0.14
	740	14.1	3.0	–	6.2	4.9	43.9	
	800	42.2	9.3	2.0	16.5	14.4	39.2	
$Co(NO_3)_2$	830	54.6	14.1	2.6	21.2	16.8	38.7	
	710	6.5	1.5	–	2.0	3.0	30.6	3.23
	740	13.1	3.3	0.3	3.7	5.8	28.2	
	800	44.8	11.9	3.2	13.7	15.9	30.6	
$Co(NO_3)_2 + H_3PO_4$	830	55.5	16.0	3.8	19.2	16.4	34.6	
	710	5.3	1.0	–	3.4	0.9	64.0	0.01
	740	11.2	3.2	–	5.3	2.7	47.5	
	800	45.9	11.9	2.0	18.9	13.0	41.2	
$Ni(NO_3)_2$	830	64.0	17.6	2.6	28.2	15.7	44.0	
	710	8.2	3.4	1.2	2.4	1.3	28.5	4.54
	740	15.2	6.1	2.5	4.1	2.6	27.1	
	800	50.3	15.5	4.7	15.3	14.8	30.5	
$PdCl_2 + H_3PO_4$	830	61.1	20.1	5.1	21.5	14.3	35.2	
	710	9.1	2.1	1.9	1.6	3.5	17.4	1.74
	740	20.0	4.0	5.0	4.4	6.6	21.8	
	800	55.6	16.1	12.6	15.2	11.8	27.3	
	830	64.3	19.2	6.4	23.5	15.3	36.5	

[a] $V_{PBHM} = 50$ mL/min; $\tau = 8.5$ s; $d = 0.6$ cm; $S/V = 6.7$ cm^{-1}.

on the yield of ethylene and propylene is studied, and soot formation is estimated. The kinetic and activation parameters for decomposition of the starting mixture and accumulation of the products are calculated.

Catalytic systems on the basis of film coatings containing the VIII group metals. The results of investigation of the propane–butane hydrocarbon mixture (PBHM) in the presence of catalytic systems based on the film coatings containing compounds of the VIII group metals are given in Tables 1, 2 and in Fig. 1. The main gaseous products of pyrolysis of the hydrocarbon mixture in a empty reactor with walls treated with the products of high-temperature

Table 2. Kinetic and activation parameters of propane decomposition and accumulation of PBHM pyrolysis products in reactors with variously treated walls[a]

Treatment of reactor	Compound	T, °C	$k \times 10^2$, s^{-1}	E_a, kJ/mol	$\ln k_0$
Without treatment	CH_4	710	0.16	258.6±31.6	25.5±3.6
		800	3.35		
	C_2H_4	710	0.66	144.8±11.3	12.6±1.3
		800	2.88		
	C_3H_8	710	3.47	132.7±10.6	13.0±1.2
		800	13.77		
$PdCl_2$	CH_4	710	0.65	162.6±16.5	14.9±1.9
		800	4.35		
	C_2H_4	710	0.28	181.5±11.8	16.5±1.6
		800	2.15		
	C_3H_8	710	2.27	168.4±29.4	17.1±3.4
		800	18.75		
$Co(NO_3)_2$	CH_4	710	0.24	193.5±10.3	17.7±1.2
		800	1.71		
	C_2H_4	710	0.18	172.0±2.2	14.7±0.3
		800	1.07		
	C_3H_8	710	1.08	175.5±8.7	17.0±1.0
		800	6.78		
$Fe(NO_3)_3$	CH_4	710	0.33	171.8±9.9	15.3±1.2
		800	1.96		
	C_2H_4	710	0.23	173.7±10.0	15.2±1.2
		800	1.39		
	C_3H_8	710	1.05	173.6±24.0	16.8±2.8
		800	8.47		
$Ni(NO_3)_2$	CH_4	710	0.55	119.1±6.0	9.4±0.7
		800	1.91		
	C_2H_4	710	0.21	149.9±1.8	12.2±0.2
		800	0.99		
	C_3H_8	710	2.63	109.9±6.1	9.9±0.7
		800	8.90		
$Co(NO_3)_2 + H_3PO_4$	CH_4	710	0.60	160.0±14.5	14.5±1.7
		800	3.35		
	C_2H_4	710	0.62	148.6±8.1	13.1±0.94
		800	2.94		
	C_3H_8	710	5.20	96.4±10.7	8.7±2.5
		800	12.5		

[a] $V_{PBHM} = 50$ mL/min; $\tau = 8.5$ s; $d = 0.6$ cm; $S/V = 6.7$ cm^{-1}.

decomposition of iron, cobalt, nickel nitrates, palladium chloride, and their compositions with orthophosphoric acid were methane, ethane, ethylene and propylene, whose amount increased with the temperature (Table 1).

Investigation of the mechanism of catalytic pyrolysis of lower alkanes showed that the process proceeds via homogeneous-heterogeneous radical chain mechanism including both heterogeneous and homogeneous stages [10].

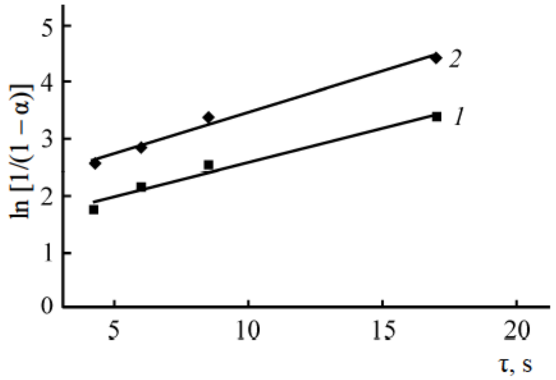

Fig. 1. ln [1/(1 – α)] vs contact time for pyrolysis of propane in reactor with walls treated with $Fe(NO_3)_3$. (*1*) 710°C and (*2*) 800°C.

Our studies have shown that at lower temperatures 700–740°C (in the heterogeneous range of pyrolysis) the yield of ethylene and propylene depends on the nature of the metal coating on the reactor walls, while at higher temperatures, above 800–830°C (homogeneous range of pyrolysis) this dependence decreases. The best results on the yield and selectivity of ethylene formation were observed with Co-containing polyphosphate coating. However, at the increase in the temperature from 710 to 800°C, a decrease in selectivity for ethylene was observed from 64.0 to 41.2 wt %. The best yield of propylene at 800°C was obtained with the Fe- and Co-containing catalysts (15.9 wt %). At the same temperature, for the Pd-phosphate coating the highest yield of methane (16.1 wt %) with the largest conversion (55.6%) was observed.

The minimum amount of carbon-containing deposits on the walls of the steel reactor was found with polyphosphate Co- and Fe-containing film coatings (0.01 and 0.14 wt % respectively), which is 8–100 times less than in the non-treated reactor. The highest amount was found for the Ni-containing catalyst (4.54 wt %), which is 4 times larger than the soot formation in the non-treated reactor. It is known that at the thermal pyrolysis, due to high catalytic activity of pyrocoils made mainly of chrome-nickel alloys, an intense coke deposition occurs on the inner surface with the formation of metal carbides, as proved by the data of IR spectroscopy, in particular, as showed the presence of a wide absorption band with the maximum at 914 cm^{-1}. Such coke is hardly removable. We have shown that in the IR spectra of the coke deposits formed by pyrolysis in the presence of Fe-, Co-, Ni-, Pd-phosphate coatings this band is lacking and a band at 1350–1500 cm^{-1} appears corresponding to carbon with a disordered structure [8]. The formed amorphous coke is relatively easily removed from the surface of the reactor by burning out in the air flow for 3 h at 500–600°C. The analysis by the method of electronic spectroscopy proved the data of IR spectroscopy of the formed soot.

Therefore, the best results on yield of ethylene, total yield of alkenes, selectivity for ethylene and soot formation were obtained with the Co-containing polyphosphate film coating, which with respect to the yield of alkenes were highly competitive with Zn-phosphate coating we had studied earlier [5], and on the soot formation were much more effective. It should be mentioned that no formation of liquid dark-red products containing condensed cycles was observed on the catalytic systems containing the VIII group metals, which were found with the earlier studied catalytic systems [5–7].

Table 2 summarizes the kinetic and activation parameters of propane decomposition and formation of the pyrolysis products (methane and ethylene) in the empty reactor with the inner surface coated by the VIII group metal compounds. The rate constants were calculated by the first order equation [11], which was proved by a linear plot in the coordinates ln [1/(1 – α)] (where α was the conversion) vs the contact time (τ), (see Fig. 1).

By the value of the rate constant of CH_4 formation in the temperature range 710–800°C the studied catalysts rank in the order: Pd > Co + H_3PO_4 > Ni > Fe > Co > non-treated, that is, CH_4 is formed with the largest rate on the Pd-containing catalyst, and with the lowest rate, in the non-treated reactor. The lowest activation energy of the methane formation was observed for the Ni-containing catalyst, and the largest one, for the non-treated reactor. By the value of the rate constant of C_2H_4 formation at 800°C the studied catalysts rank in the order: Co + H_3PO_4 > non-treated > Pd > Fe > Co > Ni, in agreement with the experimental data on the yield of ethylene. The lowest activation energies of the ethylene formation were observed for the processes in the non-treated reactor and with the Co-phosphate coating, and the largest one, with the Pd-containing catalyst. By the value of propane decomposition rate constant at 800°C the studied catalysts rank in the order: Pd > non-treated > Co+H_3PO_4 > Ni > Fe > Co, which is consistent with the experimental data for PBHM conversion, maximum on the Pd-containing catalyst. By the value

Table 3. Pyrolysis of PBHM in reactor with ceramic support[a]

Treatment of ceramic support	Content of metal in coating, %	T, °C	Conversion of PBHM, %	Yield to the passed raw material, wt %				Selectivity for C_2H_4, %	Coke, wt %
				CH_4	C_2H_6	C_2H_4	C_3H_6		
Without treatment	–	710	8.4	1.5	–	4.3	2.6	51.2	0.14
		750	25.8	4.8	–	9.8	11.2	38.0	
		800	40.2	9.4	–	19.9	10.9	49.5	
		850	74.2	19.6	1.9	39.1	13.6	52.7	
$Fe(acac)_3$	3×10^{-4}	700	28.1	4.6	0.6	8.3	14.6	29.5	5.46
		730	31.8	5.4	0.8	10.0	15.6	31.6	
		800	70.8	21.0	3.1	26.0	20.7	36.7	
		810	83.8	32.0	3.0	32.8	16.0	39.1	
$Fe(acac)_3$	3.0	700	13.5	2.6	–	4.5	6.4	33.3	3.4
		760	48.8	9.8	2.2	17.4	19.4	35.7	
		800	72.2	21.1	9.7	27.2	14.2	37.7	
		840	88.1	34.0	–	45.9	8.2	52.1	
$Fe(CH_3COO)_2$	2.3	710	15.9	5.2	2.3	6.4	2.1	40.0	0.8
		740	31.4	6.6	2.7	7.5	14.6	23.9	
		770	46.3	10.5	4.3	13.8	17.7	29.8	
		800	71.2	18.6	6.0	25.4	21.2	35.6	
$Fe(COO)_2$	2.5	710	8.8	1.8	0.7	1.7	4.6	19.1	0.8
		740	16.5	4.4	2.0	4.5	5.6	27.2	
		770	34.3	7.5	2.6	8.1	16.1	23.5	
		800	56.2	13.2	4.4	16.8	21.8	30.0	
$FeCl_3$	1.7	710	13.3	2.8	1.4	2.6	6.6	19.3	0.11
		740	28.2	6.4	2.6	5.9	13.4	20.9	
		770	40.1	9.6	4.2	10.1	16.1	25.3	
		800	57.8	15.0	4.7	17.0	20.1	29.9	
$Fe(NO_3)_3$	1.2	710	11.4	2.6	0.7	2.6	5.5	23.0	0.1
		740	24.4	4.9	1.8	5.3	12.3	21.6	
		770	37.7	8.2	3.7	9.3	16.4	24.8	
		780	57.7	14.6	4.6	16.5	22.1	28.5	
$Fe(NO_3)_3$	5.0	710	10.6	1.9	0.4	4.6	3.8	42.9	0.13
		740	16.9	2.8	–	6.9	7.2	41.0	
		800	47.7	10.6	1.5	19.2	16.4	40.3	
		830	62.8	14.9	2.5	26.5	18.9	42.2	
$Co(NO_3)_2$	5.0	710	5.1	1.2	–	2.6	1.3	51.0	0.13
		740	11.7	2.1	–	6.2	3.4	52.8	
		800	33.0	7.4	0.5	13.0	12.1	39.5	
		830	52.7	12.9	2.4	20.9	16.5	39.6	
$Ni(NO_3)_2$	5.0	710	9.8	2.2	–	2.4	5.3	24.4	6.7
		740	24.5	4.2	1.0	5.4	14.0	22.0	
		800	50.4	12.2	1.9	13.5	22.8	26.8	
		830	59.5	16.3	3.4	18.9	20.9	31.8	
$PdCl_2$	3.0	680	1.7	0.8	0.4	0.5	–	29.4	0.11
		710	7.8	1.9	0.9	1.7	3.3	21.8	
		740	18.6	5.1	2.7	5.7	5.1	30.6	
		800	52.8	12.9	5.9	16.6	17.4	31.4	

[a] $V_{PBHM} = 50$ mL/min; $\tau = 1.34$ s; $d = 0.6$ cm; $S/V = 5.6 \times 10^5$ cm^{-1}.

Table 4. Kinetic and activation parameters of propane decomposition and accumulation of products of PBHM pyrolysis in reactor with ceramic support[a]

Treatment of reactor	Compound	T, °C	$k \times 10^2$, s^{-1}	E_a, kJ/mol	ln k_0
Without treatment	CH_4	710	3.7	150.2±3.6	15.1±0.4
		800	17.9		
	C_2H_4	710	5.1	124.4±7.1	12.2±0.8
		800	18.3		
	C_3H_8	710	6.1	234.1±8.5	25.8±1.0
$Fe(NO_3)_3$		800	64.7		
	CH_4	710	7.2	102.5±5.4	9.9±0.6
		800	21.4		
	C_2H_4	710	5.1	121.5±5.7	11.9±0.7
		800	18.9		
	C_3H_8	710	15.4	165.6±10.4	18.4±1.2
$Co(NO_3)_2$		800	90.1		
	CH_4	710	5.0	118.2±6.6	11.4±0.8
		800	15.9		
	C_2H_4	710	2.9	145.3±3.7	14.3±0.4
		800	13.5		
	C_3H_8	710	7.9	199.0±4.9	21.8±0.6
$Ni(NO_3)_2$		800	64.2		
	CH_4	710	6.5	114.8±2.3	11.3±0.3
		800	20.7		
	C_2H_4	710	2.7	136.8±14.5	13.3±1.7
		800	12.7		
	C_3H_8	710	28.7	120.4±6.9	13.5±0.8
$PdCl_2$		800	104.2		
	CH_4	710	4.8	174.4±17.3	18.3±2.1
		800	24.7		
	C_2H_4	710	2.3	221.2±25.0	23.3±3.0
		800	17.3		
	C_3H_8	710	18.8	134.7±11.5	14.7±1.4
		800	60.5		

[a] V_{PBHM} = 50 mL/min; τ = 1.34 s; d = 0.6 cm; $S/V = 5.6 \times 10^5$ cm^{-1}.

of the ratio of the rate constants of methane and ethylene formation [$k(CH_4)/k(C_2H_4)$] at 800°C the studied catalysts rank in the order: Pd (2.0) > Ni (1.9) > Co (1.6) > Fe (1.4) > non-treated (1.2) > Co + H_3PO_4 (1.1). This is indicative of the fact that on the Pd- and Ni-containing catalysts, which showed the worst results on the yield of ethylene and soot formation, the rate of formation of methane is twice as that of ethylene, while on the Co-phosphate coating and in the non-treated reactor these rates are practically equal.

The comparison of the yields of the main products of pyrolysis, the rate constants and activation parameters for the studied catalysts confirms the earlier conclusions on the mechanism of pyrolysis of PBHM [9]. Propane is decomposed via two main routes, one of which is demethanation [Eq. (1)], and another one dehydrogenation [Eq. (2)]:

$$C_3H_8 \rightarrow CH_4 + C_2H_4, \tag{1}$$

$$C_3H_8 \rightarrow H_2 + C_3H_6. \tag{2}$$

At high temperatures (750–800°C) no stoichiometric formation of methane and ethylene is observed, which allows suggesting that route [Eq. (3)] is realized, which explains the enhanced yield of ethylene:

$$2C_3H_8 \rightarrow 2H_2 + 3C_2H_4. \tag{3}$$

Butane is decomposed along the Eq. (4):

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6. \qquad (4)$$

Catalytic systems on the basis of highly disperse materials modified by the VIII group metal compounds. The results of pyrolysis of PBHM in reactors packed with ceramic granules treated with the VIII group metal (Fe, Co, Ni, Pd) compounds are presented in Tables 3, 4.

Iron compounds are known to catalyze the process of pyrolysis of hydrocarbons [11]. Thus, catalysts containing up to 10–29% of FeO are used for complex processing of high-molecular oil raw materials. In the present work, we have studied the effect of various iron compounds (nitrates, chlorides, acetates, oxalates, and acetylacetonates) applied on the ceramic support with subsequent thermal treatment (up to 800°C) on the kinetic parameters of PBHM pyrolysis.

By the yield of ethylene in the range 700–740°C the iron-containing catalytic systems rank in the order: $Fe(acac)_3 > Fe(CH_3COO)_2 > FeCl_3 > Fe(NO_3)_3 > Fe(COO)_2$. Therewith the yield of ethylene on the support treated with the products of high-temperature decomposition of $Fe(acac)_3$ was almost five times higher than with $Fe(COO)_2$.

By the yield of propylene in the same temperature range these catalytic systems are placed in the order: $Fe(acac)_3 > FeCl_3 > Fe(NO_3)_3 > Fe(COO)_2 > Fe(CH_3COO)_2$, and the yield on the support treated with the products of high-temperature decomposition of $Fe(acac)_3$ was seven times higher than that for $Fe(CH_3COO)_2$. For the total yield of alkenes, the sequence of the catalytic systems is the same as for the yield of ethylene.

At higher temperatures (800–830°C), the yield of ethylene, propylene and their sum was slightly dependent on the nature of the iron salt applied on the support, which suggests a substantial contribution of homogeneous stages in the process of pyrolysis at high temperatures.

By the value of PBHM conversion at 700–740°C the studied systems rank in the order: $Fe(acac)_3 > Fe(CH_3COO)_2 > FeCl_3 > Fe(NO_3)_3 > Fe(COO)_2$; by the yield of methane: $Fe(CH_3COO)_2 > Fe(acac)_3 > FeCl_3 > Fe(NO_3)_3 > Fe(COO)_2$; by the soot formation: $Fe(acac)_3 > Fe(CH_3COO)_2 > Fe(COO)_2 > FeCl_3 > Fe(NO_3)_3$.

Therefore, by the value of conversion and the yield of ethylene and propylene the best results showed the catalytic system on the basis of iron acetylacetonate. However, for this system an intense soot formation was observed which was more than 50 times larger than for the $Fe(NO_3)_3$-based system with the content of iron in the coating of 1.2%. The $Fe(NO_3)_3$-based composition, while showing moderate results on the yield of lower alkanes, was 1.4 times better in the soot formation than non-treated ceramic support and more than 10 times than the empty reactor.

Different catalytic effect of the iron salts is apparently due to the composition of the solid phase formed on the ceramics upon thermal degradation. Thus, degradation of $Fe(acac)_3$ in the range 400–500°C leads to carbon-containing oxide coatings, whose high-temperature annealing results in Fe_3O_4; the structure of the formed films is close to amorphous [12]. The decomposition of $Fe(COO)_2$ leads to the formation of pyrophoric iron; $Fe(CH_3COO)_2$ is transformed into the mixture of FeO with pyrophoric iron, $Fe(NO_3)_3$ in Fe_2O_3, $FeCl_3{\cdot}6H_2O$ in Fe_2O_3 in the mixture with FeOCl, $Fe(OH)Cl_2$, FeO(OH).

By the example of iron nitrate and acetylacetonate we have studied the effect of the amount of metal applied on the ceramic support on the parameters of pyrolysis of PBHM. For $Fe(NO_3)_3$, the increase in the iron content in the coating from 1.2 to 5% (four times) leads to the increase of the yield of ethylene at 710°C 1.8 times, decreases the yield of methane and propylene 1.5 times, does not affect the total yield of alkenes and conversion of PBHM and slightly (1.3 times) increases soot formation. With $Fe(acac)_3$ the increase in the iron content 10^4 times (from 3×10^{-4} to 3.0%) leads to a decrease in the conversion of PBHM, decreases twice the yield of methane, ethylene and propylene, and decreases the amount of the formed soot from 5.5 to 3.4 wt %. Note that the treatment of the ceramic support with $Fe(acac)_3$ gives the maximum amount of the formed soot. The effect of the iron content in the catalyst on the principal parameters of pyrolysis of PBHM is non-additive, in contrast to that observed in [11] for the catalysts containing various amounts of FeO.

We have also studied the effect of the nature of the VIII group metals applied on the ceramic support on the principal parameters of PBHM pyrolysis (Table 3). Iron, cobalt, nickel nitrates and palladium chloride taken in the amount corresponding to 3–5% of the metal in the coating were used for the catalysts preparation. Parameters of pyrolysis were compared at

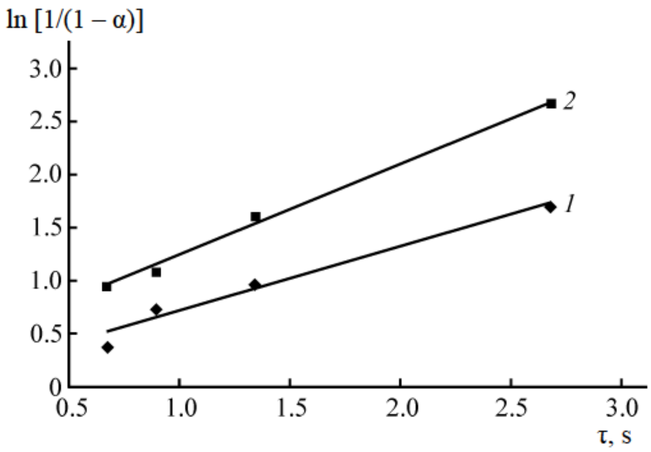

Fig. 2. ln [1/(1 – α)] vs contact time for pyrolysis of propane in reactor packed with ceramic support treated with $PdCl_2$. (*1*) 710 and (*2*) 800°C.

710°C, because the increase in the temperature to 800°C led to negligible difference in the yields of the products. By the value of PBHM conversion the catalytic systems rank in the order: Fe > Ni > ceramic support > Pd > Co. The yield of methane on these catalysts was low (1.2–2.2 wt %) and slightly depended on their nature. By the yield of ethylene the order of catalytic activity of the metal-containing coatings was as follows: Fe > ceramic support > Co > Ni > Pd. The increase of the temperature to 800°C caused the increase in activity of the Pd-containing catalyst, whose activity became close to that of the Fe-containing catalyst. By the yield of propylene, the following sequence was obtained: Ni > Fe > Pd > ceramic support > Co; by the total yield of alkenes: Fe > Ni > ceramic support > Pd > Co, by the soot formation: Ni > ceramic support > Fe ≈ Co > Pd. It was noted that the yield of soot on the Ni-containing catalyst is 50 times higher than on the Fe-, Co-, Pd-containing catalysts. Therefore, the best results in the yield of ethylene, total yield of alkenes and low soot formation were shown by the Fe-containing catalyst.

The composition of the Fe- and Co- containing catalysts was investigated by IR spectroscopy before and after pyrolysis of PBHM. The IR spectra confirmed the presence of phosphate groups absorbing at 400–500 and 1500–1350 cm^{-1}, whose intensity was unchanged after pyrolysis, which is indicative of the absence of quantitative changes of the oxide phases content and the processes of condensation.

In Table 4 the kinetic and activation parameters are presented for decomposition of propane and the formation of the pyrolysis products (methane and ethylene) in the reactor packed with ceramic support treated with Fe, Co, Ni, Pd salts. As for the empty reactor, the first order of the reaction was proved by linear plot in the coordinates ln [1/(1 – α)] vs the contact time (τ) (Fig. 2).

By the value of the rate constant of methane formation the investigated catalysts rank in the orders: Fe > Ni > Co > Pd > ceramic support (at 710°C); Pd > Fe > Ni > ceramic support > Co (at 800°C), which are in compliance with the data on the yield of CH_4.

By the value of the rate constant of formation of ethylene the orders of activity of the catalysts are as follows: Fe ≈ ceramic support > Co > Ni > Pd (at 710°C); Fe > ceramic support > Pd > Co > Ni (at 800°C). Therefore, the catalytic activity of the Pd-containing catalyst is increased with temperature, which is proved by the yields of the products.

By the value of the rate of propane consumption the activity orders are as follows: Ni > Pd > Fe > Co > ceramic support (710°C); Ni > Fe > ceramic support > Co > Pd (800°C).

By the value of the rate constants ratio of methane and ethylene formation [$k(CH_4)/k(C_2H_4)$] the catalysts form the sequence: Ni (2.4) > Pd (2.0) > Co (1.7) > Fe (1.4) > ceramic suppor t(0.7) (710°C); Ni (1.6) > Pd (1.4) > Co (1.2) > Fe (1.1) > ceramic support (1.0) (800°C). These data suggest that on the Ni- and Pd-containing catalysts the rate of CH_4 formation is twice higher than that of C_2H_4formation, whereas on the Fe-containing catalyst and on ceramic support these rates are practically equal. Similar data were obtained for the empty reactor.

From the data of Tables 2 and 4 it can be concluded that the rate constants of propane consumption on the ceramic support (heterogeneous region of decomposition) is 15–20 times higher than the corresponding constants in the empty reactor (heterogeneous region).

Therefore, by the main parameters of pyrolysis of PBHM (yield of lower alkenes and soot formation) the best results in the empty reactor were obtained with the Co-phosphate coating, and for coated ceramic support, with the $Fe(NO_3)_3$-based catalytic system with iron content in the coating of 1.2–5%.

EXPERIMENTAL

Propane–butane hydrocarbon mixture of the following composition was used, wt %: methane 0–13.1; ethane 0–17.2; propane 56.3–79.3; butane 3.3–42.9; *i*-butane 0–16.2.

Pyrolysis of PBHM was carried out in a continuous flow tubular apparatus [4] at a pressure close to atmospheric, in steel reactors (steel 12X18H10T), diameter 0.6 cm, in the temperature range 500–880°C, PBHM flow rate 25–100 mL/min, contact time (τ) with the catalyst 0.67–17.0 s. The contact time was calculated from the equation $\tau = V/F$, where V is free volume of the reactor equal to the difference of its volume and the volume of the catalyst, F is spatial flow rate of PBHM. The value of factor of heterogeneity S/V, where S is the catalyst surface, V is free volume, varied from 6.7 to 5.6×10^5 cm^{-1}. The main gaseous products of pyrolysis of PBHM were methane, ethylene, propylene, whose quantitative composition was determined by the method of absolute calibration. The amount of carbon deposits formed during pyrolysis was calculated from the additional weight of the reactor, their analysis was performed on a spectrophotometer IR-Prestige-21 Shimadzu and scanning probe microscope C3M Solver PRO.

The catalysts of the first type were formed directly on the inner surface of the reactor by treatment with aqueous solutions of iron, cobalt, nickel nitrates or solution of palladium chloride in ethyl acetate. For preparation of phosphate coatings the calculated amount of orthophosphoric acid was added to the solution of the salt. The treated reactors were heated for 2 h at 200°C, then 2–2.5 h at 700–800°C. The thermal treatment led to the formation of oxide of the composition Me_xO_y or $Me_xO_y{\cdot}zP_2O_5$, where $x = 1, 2$; $y = 1, 3$; $z = 2, 3$ [12]. For preparation of the catalysts of the second type synthetic ceramic material “Khipek” was used as a support, which is a composite of mineral and organic compounds [6] and is characterized by high thermal stability up to 1000°C, porosity of 70–80%, and high resistance to compression up to 300 N/cm^2. The ceramic material was used in a crushed state (fraction 0.3–0.5 mm), treated with solutions of the corresponding salts followed by drying for 2 h at 200°C, then 2–2.5 h at 700–800°C.

The conversion was calculated as the ratio of the amount of the reacted raw material to the total amount introduced into the reactor. The yield of the products was determined as the ratio of the amount of the formed product at a specific temperature to the total amount of hydrocarbon raw material introduced into the reactor. The selectivity with respect to ethylene was calculated as the ratio of its amount to the total amount of the products. Rate constants were calculated from the first order kinetic equation, activation parameters were calculated by the least-squares method from rate constants obtained at five temperatures.

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