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Catalytic Pyrolysis of Propane–Butane Hydrocarbon Mixture on the Composite Ceramic Materials in an Open System

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Abstract—Catalytic pyrolysis of propane–butane hydrocarbon mixture on the composite ceramic materials with the surface modified with zinc-, cadmium- phosphorus- and silicon-containing compounds in an open system was studied in the temperature range 500–850°C, at the rate of the gas mixture flow 20–200 ml min^{-1}, contact duration 0.75–155 s, and the values of the heterogeneity factor 2.0 to 2.9×10^5 cm^{-1}. The catalytic activity of the systems under similar conditions was compared, the influence of various factors on the yield of ethylene and propylene was investigated and the sooting was estimated.

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A major challenge of oil and gas industry is the development of new methods of processing hydrocarbon raw materials to obtain ethylene and propylene, the products valuable for organic synthesis. Although many studies have been carried out in this area [1, 2], the problem of improving the efficiency of the oil refining remains urgent. Modern methods of industrial production of ethylene are based on the high temperature pyrolysis of hydrocarbons. A significant drawback of this process is a necessity to carry it out at a high temperature, which leads to deeper cracking of alkanes with the formation of coke, and consequently, the process must be stopped periodically. According to modern view, both thermal and catalytic pyrolysis of alkanes proceeds by radical-chain mechanism without branching, as proven by the method of freezing the radicals in the ESR spectrometer probe [3].

Currently, many studies are focused on finding an efficient catalyst capable of prolonged working at a high temperature to provide high yield not only of ethylene, but also of propylene; on the determining the optimal conditions of catalytic pyrolysis with a possible decrease in the reaction temperature and the catalyst coking [4], and on exploring the mechanism of action of the catalyst surface on the ratio of homogeneous and heterogeneous contributions into the pyrolysis process [3].

Previously, we have studied the process of pyrolysis of propane–butane hydrocarbon mixture in a steel reactor in the presence on the reactor surface of a catalyst as a ceramic polyphosphate coating film containing the metals of groups II–III of the Periodic system with the overall composition $Me_xO_y{\cdot}zP_2O_5$, where x = 1,2; y = 1,3; z = 2,3; Me = Zn, Cd, Sr, Ce. The following sequence of catalytic activity of the metal-containing coatings on the yield of alkenes has been revealed: Zn > Cd > Sr > Ce. The same sequence corresponds to the ability of the metals to inhibit the process of coking [5].

The aim of this work was a search for the optimal catalytic systems based on the composite ceramic materials [6] modified by processing with zinc-, phosphorus-, silicon- and cadmium-containing compounds, for the pyrolysis of propane–butane hydrocarbon mixture (PBHM). We estimated the effect of the reactor material, the method of processing the ceramic material filling the reactor, the heterogeneity factor S/V (where S is surface area of the catalyst, V is the reactor free volume), the contact duration (τ) on the yield of lower alkenes (ethylene and propylene), catalysts selectivity toward ethylene in the pyrolysis PBHM, and sooting.

Table 1. Characteristics of catalysts for the pyrolysis of propane–butane hydrocarbon mixture

Comp. no.	Reactor material	Reactor diameter, cm	Treatment of reactor	Ceramic carrier	Treatment of ceramics carrier	S/V, cm^{-1}	Cocking, wt %
I	quartz	0.4	–	–	–	10.0	0.23
II	steel	0.4	–	–	–	10.0	3.55
III	steel	0.4	polyphosphate Zn-containing coating	–	–	10.0	0.38
IV	steel	0.4	polyphosphate Zn-containing coating; ETS-40	–	–	10.0	1.04
V	steel	0.8	polyphosphate Zn-containing coating; ETS-40	–	–	5.0	1.65
VI	steel	2.0	polyphosphate Zn-containing coating	–	–	2.0	8.4
VII	steel	2.0	polyphosphate Zn-containing coating; Cd salts	–	–	2.0	3.02
VIII	quartz	0.8	–	granules	polyphosphate Zn-containing coating; ETS-40	2.9×10^5	0.13
IX	steel	0.8	polyphosphate Zn-containing coating	granules	polyphosphate Zn-containing coating	2.9×10^5	3.52
X	steel	0.8	polyphosphate Zn-containing coating; ETS-40	granules	polyphosphate Zn-containing coating; ETS-40	2.9×10^5	1.21
XI	steel	2.0	polyphosphate Zn-containing coating	grids	polyphosphate Zn-containing coating	2.3×10^5	0.39
XII	steel	2.0	polyphosphate Zn-containing coating	grids	polyphosphate Zn-containing coating; ETS-40	2.3×10^5	6.0
XIII	steel	2.0	–	grids	phosphoceramics composition	2.3×10^5	6.0
XIV	steel	2.0	polyphosphate Zn-containing coating	grids	polysilicon acid	2.3×10^5	–
XV	steel	2.0	polyphosphate Zn-containing coating	grids	Polysilicon and polyphosphoric acids composition	2.3×10^5	5.12

The composition of the studied catalysts (CT) and the main results of the propane–butane pyrolysis are given in Tables 1 and 2.

The study of the influence of reactor material (quartz, steel) showed that by the main parameters (yield of ethylene and propylene, total yield of alkenes and sooting) the quartz reactor (CT **I**) exceeded the untreated steel reactor (CT **II**) at the same diameter of the reactor, S/V ratio, and contact time. However, applying polyphosphate Zn-containing film coating (CT **III**) on the inner walls of the steel reactor made it close to the quartz reactor by the main parameters, and slightly inferior in sooting. Simultaneous applying to the steel reactor wall of coating from polyphosphate Zn- and Si-containing films (CT **IV**) did not improve the main parameters of pyrolysis, the reactor was inferior to that made of quartz (CT **I**).

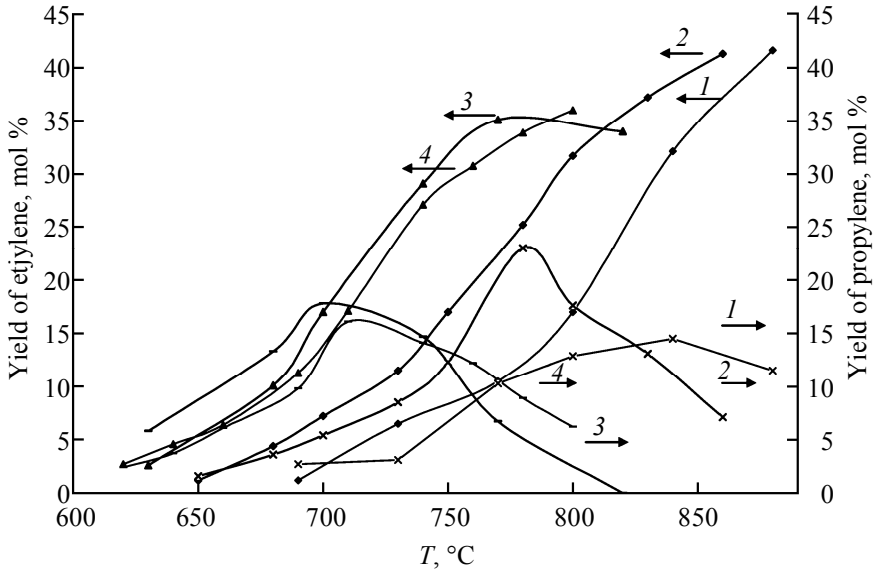
Pyrolysis of propane–butane mixture in a reactor of larger diameter (d 2.0 cm) with polyphosphate Zn-containing film coating (CT **VI**) at longer contact time (τ 37.7 s) as compared with CT **III** at low contact time (τ 1.5 s) allows a reduction of the primary pyrolysis

Table 2. Results of pyrolysis of propane–butane hydrocarbon mixture (PBHM) on composite catalysts

Comp. no.	τ, s	*T*, °C	PBHM conversion, %	Yield on raw material, mol %					Selectivity on C_2H_4, %
				CH_4	C_2H_6	C_2H_4	C_3H_6	ΣC_2–C_3 alkenes	
VIII	5.3	750	50.7	18.0	3.4	17.0	12.3	29.3	33.6
		860	95.3	42.2	4.7	41.3	7.1	48.4	43.4
IX	4.7	760	42.7	18.6	8.5	10.9	8.4	19.3	25.5
		860	92.7	38.3	11.2	34.9	8.3	43.2	37.7
X	4.0	760	60.6	20.9	4.8	19.1	15.8	34.9	31.5
		820	92.5	39.9	4.6	38.6	9.4	48.0	41.7
XI	31.0	760	81.5	36.2	6.1	30.0	12.2	39.2	31.1
		800	94.4	44.2	8.0	36.0	6.2	42.2	38.2
	15.5	800	92.3	40.0	7.0	34.2	11.1	45.3	37.1
XII	31.0	750	82.3	29.1	4.5	24.8	23.9	48.7	30.1
		820	96.4	45.5	5.3	37.9	7.7	45.6	39.3
XIII	155.0	750	97.4	50.7	7.6	32.4	6.7	39.1	33.3
	31.0	750	97.5	56.3	7.2	30.7	3.3	34.0	31.5
XIV	30.0	700	45.6	19.0	3.8	10.3	12.5	22.8	22.6
		770	88.7	41.0	7.7	25.7	14.3	40.0	29.0
XV	60	670	77.9	31.0	11.4	24.7	12.9	37.6	31.7
		700	96.9	46.4	12.4	35.1	3.3	38.4	36.2
	30	700	46.3	15.8	6.1	13.6	12.9	26.5	29.3
		750	81.2	33.0	5.2	28.7	15.0	43.7	35.3

temperature from 700 to 630°C. Therewith the pyrolysis at the temperature above 800°C led to the appearance in the reaction products of dark-red condensed substances, which according to the mass-spectrometric analysis contained naphthalene, methylnaphthalene, acenaphthene, cyclopentanaphthalene, methylfluorene, phenanthrene, and α-pyrene. Further processing of the steel reactor with cadmium salts (CT **VII**) did not improve the yield of alkenes, but led to 2.7-fold reduction in the sooting.

When the pyrolysis of hydrocarbons was carried out under the conditions of free-radical process in the reactors filled with ceramic granules or nets subjected to different treatment, the following results were obtained. The influence of heterogeneity factors (*S*/*V*) is complex, as was shown on four pairs of catalysts: **I, VIII; II, IX; V, X** and **VI, XI**, which passed the same surface treatment, but differed by the heterogeneity factors. In the case of quartz reactor, increase in *S*/*V* 10^5 times by filling it with ceramic granules treated with Zn- and Si-containing compounds (CT **I, VIII**), resulted in an increase in the yield of ethylene and propylene (see the figure). In the reactors filled with ceramics, the low alkenes appeared at lower temperatures (650–670°C) than in the unfilled reactors. On the curve of dependence of the propylene yield on the temperature a pronounced maximum is observed associated with the fact that at high temperatures propylene enters into secondary reactions associated with the formation of high-condensed products. Similar effects were observed at the increase in the *S*/*V* of the catalysts **V** and **X** after the similar treatment. However, at applying polyphosphate Zn-containing film to ceramics, the 10^5 times increase in *S*/*V* did not result in the increased yield of ethylene and propylene but led to its decrease (CT **III, IX, VI–XI**) by 5–10 mol %. This may be due to the fact that Zn-



Effect of the heterogeneity factor on the temperature dependence of the ethylene and propylene yields in quartz [(*1*) CT **I**, S/V 10 cm^{-1}; (*2*) CT **VIII**, S/V 2.9×10^5 cm^{-1}] and steel [(*3*) CT **VI**, S/V 2.0 cm^{-1}; (*4*) CT **XI**, S/V 2.3×10^5 cm^{-1}] reactors.

containing active centers on the surface of ceramics suppresses the reaction of alkenes formation. According to the modern view [3], the activity of catalysts depends on the ability of active centers on its surface to form surface compounds with hydrocarbon radicals with a certain bonding energy. Depending on the reactivity of the active center of the catalyst, four types of the surface effect on the process of pyrolysis are possible: inhibiting, neutral, accelerating heterogeneous contribution and accelerating homogeneous contribution. In this case, we probably observe inhibitory type of the surface effect.

At the temperatures above 780°C, the effect of S/V on the yield of alkenes decreases, indicating a substantial contribution of homogeneous phases into the process of pyrolysis.

On the basis of experimental data on the influence of temperature on the conversion of initial components (propane and butane), and the yield of major products of the propane–butane pyrolysis (ethylene and propylene) we calculated kinetic and activation parameters of the overall processes of decomposition of initial alkane and of reaction products formation (Table 3). The calculation was performed for two groups of catalysts **III, IX; V, X**, distinguished by the value of S/V and surface treatment. The effective activation energy (E_a) of the propane and butane decomposition (110–310 kJ mol^{-1}) is less than the

Table 3. Kineric and activation parameters of the overall processes of conversion of propane–butane hydrocarbon mixture and of reaction main products formation (ethylene, propylene)

Comp. no.	C_3H_8			C_4H_{10}			C_2H_4			C_3H_6		
	E_a,[a] kJ mol^{-1}	k_0, s^{-1}	k, s^{-1} 750°C	E_a, kJ mol^{-1}	k_0, s^{-1}	k, s^{-1} 750°C	E_a, kJ mol^{-1}	k_0, s^{-1}	k, s^{-1} 750°C	E_a, kJ mol^{-1}	k_0, s^{-1}	k, s^{-1} 750°C
III	110.0	9.2×10^4	0.22	310.0	9.4×10^{14}	0.14	113.8	8.3×10^5	1.27	191.2	7.6×10^9	1.30
IX	128.0	1.9×10^5	0.06	250.0	7.3×10^{11}	0.12	63.5	8.2×10^2	0.47	138.4	5.1×10^6	0.40
V	143.0	1.0×10^9	0.10	196.0	2.5×10^6	0.12	58.9	4.4×10^2	0.43	57.0	3.2×10^2	0.39
X	196.5	2.1×10^9	0.19	190.4	1.45×10^9	0.27	62.8	1.1×10^3	0.68	44.3	1.27×10^2	0.69

[a] Error in activation energy was not exceeding 5%.

energy of the weakest C–C bond in these molecules (326 kJ mol^{-1}). Calculated first-order rate constants (k) at 750°C for the initial components and the products confirm previous conclusions about the nature of the joint influence of surface treatment and heterogeneity factor. The data in Table 3 show that for the catalysts **III** and **IX** with the Zn-containing film coating the rate constant of decomposition of initial materials and formation of products decreases with the increasing S/V. In the case of composite Zn- and Si-containing films (CT **V** and **X**) the trend is opposite: The growth of S/V leads to permanent increase in the reaction rate.

Study of the effects of contact time on the temperature dependence of the reaction products yield showed (by the example of CT **VIII**) that in the reactors filled with ceramics, as in the case of unfilled reactors, the increase in the contact time resulted in a marked increase in the yield of ethylene and in the total yield of alkenes. The maximum propylene yield remained unchanged, but the maximum shifted toward lower temperatures (from 710 to 665°C). The effect of the influence of contact time on the yield of the major products of pyrolysis is the most pronounced at temperatures up to 760°C. At increasing the temperature above 800°C the yield of alkenes hardly depended on the contact duration.

We studied the influence of the method of processing ceramics carrier on the main parameters of pyrolysis. In the case of filling the reactor with the ceramics granules with dispersion 0.5–2.0 mm at the values of S/V 2.90×10^5 cm^{-1} at the contact duration 4–5 s (CT **VIII, IX, X**) the best results in the yield of ethylene showed the catalysts which were simultaneously processed with Zn- and Si-containing film compositions, as compared with only Zn-containing film coating. The material of reactor (quartz, steel) practically did not influence the yield of the major products of pyrolysis. On the curves of dependence on the temperature the yield of propylene in the case of the quartz reactor filled with ceramic catalyst, as in the case of empty reactors, there was a pronounced maximum at 790°C (with the yield of propylene 23 mol %); in the case of steel reactor the maximum was observed at a lower temperature, 760°C (with the propylene yield 15 mol %). The smallest soot formation was observed in the quartz reactor (CT **VIII**) filled with ceramic granules treated with composite Zn- and Si-containing film coating, and the largest, in the steel reactor filled with the granules with Zn-containing film coating (CT **IX**).

We compared the activity of catalysts, which are the porous ceramic grids passed through a variety of processing (CT **XI–XV**), with values of S/V 2.3×10^5 cm^{-1} and the contact duration 31 s. The temperature dependence of the yield of ethylene with these catalysts is shown in the figure. By the yield of the major products in the range of 720–760°C and by sooting, the studied catalysts form the following series: By the yield of C_2H_4: **XIII** > **XI** > **XV** > **XIV** > **XII**; by the yield of C_3H_6: **XI** ≥ **XII** > **XV** > **XIV** > **XIII**; by the total yield of alkenes: **XII** > **XV** > **XI** > **XIII** = **XIV**; by sooting: **XIV** < **XI** < **XV** = **XII** = **XIII**.

The experimental results show that by ethylene yield and sooting the polyphosphate Zn-containing films on the ceramic grids at long contact (31 s) is better than in the case of the film compositions containing simultaneously Zn and Si, but the latter showed better results by the total yield of alkenes. The grids treated by Si-containing composition (CT **XIII**), giving better results on the yield of ethylene, are inferior to other catalysts by the propylene yield and sooting. With the ceramics grids treated with polysilicon acid (CT **XIV**) no soot formation was registered. These catalysts maintain stable catalytic activity for several days.

Thus, in the case of ceramic catalysts with applied Zn- and Zn,Si-film compositions, there is ambiguity in the effect of the coating composition on the yield of alkenes and formation of soot in dependence of contact duration.

When the process of pyrolysis was carried out in the quartz reactor, the formation predominantly occurred of amorphous isotropic coke easily removable from the reactor by burning in the air stream. Analysis of the infrared spectra of solid products of pyrolysis formed on the surface of steel and the quartz reactors showed the presence of carbon of disordered structure (1000–1500 cm^{-1}). In the steel reactor there were also the particles of iron and hematite, formed by the mechanism of the carbide cycle. The IR spectrum of a sample of the solid products from the quartz reactor contained absorption bands corresponding to amorphous hydrogenated silicon carbide and quartz. The data of IR spectroscopy were confirmed by electron microscope studies. In the solid products of PBHM pyrolysis fullerenes were not found, although there are some data [7] on their formation in the metal of the coil pipes working at high temperature in the

ovens for the pyrolysis of hydrocarbon raw material with the diffusion of carbon coke directed inside the surface. We investigated by the method of IR spectroscopy the chemical composition of the surface of ceramic catalyst **XIV** before and after PBHM pyrolysis. The IR spectra confirmed the presence of phosphate and silicate groups (1000–1300 cm^{-1}), but intensity of the respective bands decreased after the reaction, indicating a change in the content of the oxide phases and the occurrence of the processes of condensation. The lack of the vibration band of the carbon backbone –C–C– and –C=C– in the spectrum allows to conclude that at the pyrolysis on the ceramic catalyst the coking does not occur.

Thus, the carried out study on kinetic regularities of catalytic pyrolysis of PBHM in the open system showed that increased the reaction temperature, contact duration and heterogeneity factor enhances PBHM conversion and yield of ethylene, and the formation of propylene passes through a maximum. It was shown that the best material of the reactor to reduce coking is quartz. Using ceramics material treated with Zn- and Si-containing compositions as a catalyst reduces the temperature of pyrolysis and amount of the formed coke in comparison with the pyrolysis without catalyst.

EXPERIMENTAL

In this study we used the propane–butane hydrocarbon mixture, the crude product of the Sibur-Neftekhim Neftekhimzavod with the following composition (mol %): methane 0–3.2; ethane 0–6.2; propane 39.3–72.7, *n*-butane 6.6 –36.5; *i*-butane 6.9–24.8.

As a carrier for catalysts was used synthetic ceramic material "Khipek" composed of mineral and organic substances [6] which is characterized by high thermal stability up to 1000°C, 70–80% porosity and high compression strength, up to 300 N cm^{-2}. The ceramics carrier was used either in the fragmented state, faction 0.3–0.5 mm, or in the form of ceramics grid with the size 1.5 × 1.5 × 1.5 cm, which were obtained by applying crude ceramics mass on polyurethane foam grids followed by drying at 200°C for 3 h and then at 500°C for 3h. This polyurethane foam grids completely burn out, and the ceramic material got the shape of the initial grid. Specific surface of the material was 80 m^2 g^{-1}. Ceramic material was processed by the following compositions: polyphosphate Zn-containing composition of an inorganic zinc salt dissolved in orthophosphoric acid, followed by heating to form a Zn-containing film; ethylsilicate-40 (ETS-40), an industrial product (technical certificate according to TU 2435-427-05783441-2004), containing 40% of tetraethoxyisilane solution in ethanol. Heating of this material gives a modifying cover with the average composition corresponding to the oligomer $(RO)_3Si[OSi(OR)_2]_4OSi(OR)_3$; for ceramic composition, consisting ETS-40, ethanol, additives (1–3 wt %) of concentrated nitric and acetic acids, and water.

Investigation of pyrolysis of propane–butane mixture was carried out in the flow-type reactors of 0.4, 0.8 and 2.0 cm diameter in the temperature range 500–880°C, the PBHM flow rate 20–200 ml min^{-1}, duration of the contact of reacting mixture with the catalyst 0.75–155 s. The contact duration was calculated by the formula $\tau = V/F$, where V is free volume of the reactor, equal to the difference of its full volume and the volume of ceramic granules, F is the PBHM flow rate. In this investigation we used steel (12X18H10T) and quartz reactors. The heterogeneity factor S/V, where S is the reactor surface area, V is its volume, varied from 2.0×10^5 to 2.9×10^5 cm^{-1}. The pyrolysis of the propane–butane mixture was carried out in a flow-type laboratory installation based on a Tsvet-100 chromatograph. The raw material was fed from a metallic cylinder to the reactor placed in the pyrolysis furnace with a rate controlled by a rheometer. The furnace temperature was monitored with a tungsten-rhenium thermocouple. Before entering the reactor, the hydrocarbon mixture passed a steam generator, in which it was diluted with steam in a ratio of 2:1. From the propane–butane flow samples were taken of fixed amount, at the different temperatures in the reactor. The analysis of pyrolysis products was carried out by gas chromatographic method (3 m column filled with silica gel KSK-2.5; oven temperature 50°C, detector katharometer, carrier gas helium, F 30 ml min^{-1}).

The main gaseous products of pyrolysis of propane–butane mixture were methane, ethane, ethylene, and propylene. The quantitative composition of the gas was determined by the method of absolute calibration. Analysis of soot was carried out on a Shimadzu Fourier-transform infrared spectrometer IR-Prestige-21 and a scanning probe microscope SPM Solver PRO. Analysis of liquid products of pyrolysis was carried out on a Polaris Q/Trace GC Ultra chromato-mass spectrometer.

REFERENCES

1. Aleksandrov, Yu.A., Tipailov, A.M., Shekunova, V.M., Didenkulova, I.I., Tsyganova, E.I., and Pishchurova, I.A., *Neftekhimiya i Neftepererabotka*, 2004, no. 8, p. 30.
2. Kazanskii, V.B., *Kinetika i Kataliz*, 1977, vol. 18, no. 1, p. 43.
3. Vasil'eva, N.A. and Buyanov, R.A., *Khimiya v Interesakh Ustoichivogo Razvitiya*, 2004, no. 12, p. 661.
4. Aleksandrov, Yu.A., Shekunova, V.M., Didenkulova, I.I., and Pishchurova, I.A., *Zh. Obshch. Khim*., 2008, vol. 78, no. 10, p. 1662.
5. Aleksandrov, Yu.A., Shekunova, V.M., Pishchurova, I.A., Didenkulova, I.I., and Tsyganova, E.I., *Zh. Obshch. Khim*., 2009, vol. 79, no. 6, p. 945.
6. Aleksandrov, Yu.A., Tsyganova, E.I., Shekunova, V.M., and Didenkulova, I.I., RF Patent no. 2345973, 2006, *Byull. Izobret*., 2009, no. 4.
7. Zakirnichnaya, M.M., *Doctorate Sci. (Tech). Dissertation*, Ufa, 2001.