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Catalytic Pyrolysis of the Propane–Butane Hydrocarbon Raw Material

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Abstract—Principal characteristics are determined of the process of pyrolysis of the propane–butane hydrocarbon raw material in a steel reactor in the presence of catalysts (ceramic film type polyphosphate covering on the steel reactor walls) containing metals of II and III groups of Periodical Table with the overall composition $Me_xO_y{\cdot}z(P_2O_5)$, where x = 1, 2; y = 1, 3; z = 2, 3. By the investigation a sequence of catalytic activity of the samples of the metal-containing coverings by their effect on the yield of ethylene and propylene is elucidated: Zn > Cd > Sr > Ce. The similar sequence corresponds to inhibiting activity at the cocking inhibition.

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The most widespread process of industrial ethylene and propylene producing at the polymer manufacturing is thermal pyrolysis of paraffin hydrocarbons in the tube type reactors, the pyrolysis furnaces, at the temperature in the range 780–900°C. This process is disadvantageous in several aspects, of that the most important are the low yield of ethylene (35% or less) and a significant yield of soot (coke) accumulated in the pyrolysis coil pipes of the furnaces, that shortness the inter-regeneration period of the furnaces operating and the service life of the pipes. Commonly the time consumed for cleaning the reactors from the soot is practically the same as that of producing the light olefins [1].

It is obvious that an alternative to the thermal pyrolysis is catalytic pyrolysis that can provide high conversion of raw material at the lower, as compared with thermal pyrolysis, temperature of the process. Application of catalysts can reduce the energy consuming by the process and increase selectivity of the pyropysis of hydrocarbons.

In this work we determined basic characteristics of the process of thermal pyrolysis of propane-butane hydrocarbons in quartz and in steel reactors in the absence and in presence of catalysts containing the metals of II and III groups of the Periodic system.

The process of pyrolysis was carried out according to the traditional scheme with dilution with steam that decreases partial pressure of reacting components and diminishes formation of high-molecular products of polycondensation and polymerization reactions [2].

Earlier [3] has been shown that there are no inert surfaces at the pyrolysis process. Many tested materials including quartz in a certain degree catalyze the process of pyrolysis of hydrocarbons. For some materials has been defined the sequence of their catalytic activity [1]: Ni > Fe > Cu > Ti > Cr > quartz > iron sulfide. This sequence coincides with the sequence of thermal stability of the metal compounds formed at the pyrolysis from the material of the pipes, and with the sequence of the solubility of hydrogen in these metals.

For the study of the effect of the reactor material on the olefin (ethylene and propylene) yield at the pyrolysis of hydrocarbon raw material we carried out experiments using not treated quartz and steel (steel 12Kh18N19T) reactors. The results of investigation are depicted in Figs. 1 and 2.

From these data is seen that yields of propylene formed at the pyrolysis of hydrocarbons in both quartz

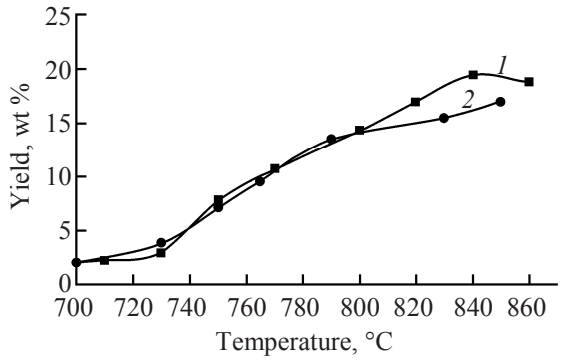

Fig. 1. Yield of propylene at the thermal pyrolysis of propane–butane hydrocarbon raw material in quartz and steel reactors: (*1*) quartz reactor, (*2*) steel reactor.

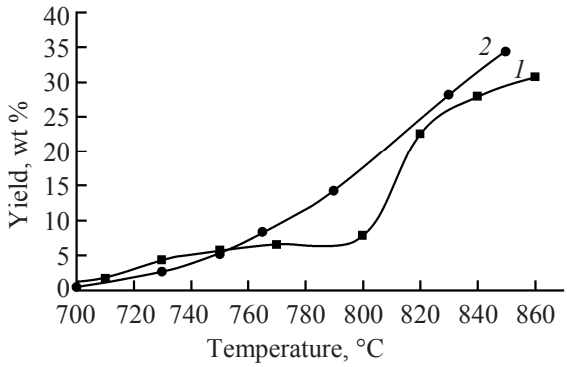

Fig. 2. Yield of ethylene at the thermal pyrolysis of propane–butane hydrocarbon raw material in quartz and steel reactors: (*1*) quartz reactor, (*2*) steel reactor.

and steel reactors are similar in a wide temperature range (Fig. 1), while the yield of ethylene is higher in steel resactor (Fig. 2). However, amount of coke sedimentation on the reactor wall is 5-fold higher in the steel reactor as compared with the quatrtz one (this will be discussed below) that is consistent with the known published data [4].

However, quartz can not be used for design of industrial reactors by several reasons.

(1) Quartz is of much lower theroconductivity than iron alloys, and owing to dynamic equilibrium in the reaction system the feeding gas mixture is not heated to required temperature.

(2) Application of quartz at industrial rates of gas flow is not safe.

Earlier [5] has been established that phosphorus-containing compounds are effectve inhibitors of coking in the process of pyrolysis of hydrocarbons. The inhibiting effect is a result of formation of strong and thermally stable compounds on the internal surface of the pyrolysis pipes. On the walls of a metallic reactor a protecting film can be formed, consisting, besides phosphorus compounds, of boron, sulfur and bismuth derivatives. Versatility of derivatives of these elements (borides, phosphides and bismuthites) at the inhibition (in the form of protecting film) against coking falls to the sequence: S > B > P > Bi [6]. From the published data [7] and from our earlier results [8] is known that presence in a catalytic system of metals and elements of II–VIII groups of Periodic system, e.g., Ni, Zn, V, Zr, Ti, Fe, Co and other promote increase in selectivity of the catalyst toward low olefin hydrocarbons.

In connection with the above said we studied effect of modifying additives of the salts of active metals of II and III groups of the Periodic system in the compositions of phosphorus-containing catalysts on the process of pyrolysis of hydrocarbons. In Table 1 are listed results of pyrolysis of propane-butane raw material in a not treated steel reactors and in the steel reactors with internal surface covered by the polyphosphate film containing zinc, cadmium or cerium. From the results is seen that the nature of the metal in the composition of the covering although do not affect general character of the plots of hydrocarbon conversion and products yield, influences significantly the yields of ethylene, propylene and methane and their ratio. The highest yield of low olefin hydrocarbons C_2–C_3 (62.2 wt %) and lowest coking (Tables 1 and 2) are achieved at the pyrolysis of hydrocarbon raw material with the Zn-containing catalyst. Besides, with the Cd- and Zn-containng catalysts increase in temperature leads to increase in propylene yield that than falls in account of further reactions of the formed compounds.

From the data presented in Table 2 is seen that the fraction of propane and butane consumption with formation of ethylene is higher in the catalytic process with the zinc-containing catalyst (0.81) than in thermal process (0.75). Therewith grows total yield of ethylene and propylene as compared with the thermal pyrolysis. In the case of the zinc-containing catalyst the formation of carbon cake is minimum and is comparable with the caking in quartz reactor (Table 2).

It is known [9] that at the thermal pyroplysis due to high catalytic activity of coil pyropipes that basically

Table 1. Results of catalytic pyrolysis of propane–butane hydrocarbon raw material at $\tau = 1.5$ s

Catalyst	*T*, °C	Conversion of hydrocarbons, %	Yield, wt %					Selectivity on C_2H_4, %
			CH_4	C_2H_6	C_2H_4	C_3H_6	$\sum C_2$–C_3 alkenes	
Zn-containing covering	740	13.4	1.8	1.6	3.8	6.2	10.0	28.4
	760	20.9	3.0	1.5	6.5	9.9	16.4	31.1
	775	27.9	4.9	1.0	10.2	11.8	22.0	36.6
	800	28.9	4.6	0.9	10.9	12.5	23.4	37.7
	820	42.9	8.7	1.2	17.4	15.6	33.0	40.6
	845	69.9	15.2	1.5	33.8	19.4	53.2	48.4
	855	79.5	14.8	2.5	46.2	16.0	62.2	58.1
Cd-containing covering	730	8.7	1.5	0	2.8	4.4	7.2	32.2
	760	17.7	3.9	0.6	6.8	6.4	13.2	38.4
	785	34.3	7.4	2.5	12.4	12.0	24.4	36.2
	800	40.3	8.7	2.4	15.1	14.1	29.2	37.5
	840	68.4	17.0	3.5	29.7	18.2	47.9	43.4
	855	81.4	21.8	4.9	36.9	17.8	54.7	45.3
Sr-containing covering	750	18.6	2.1	0.3	6.0	10.2	16.2	32.3
	770	28.2	4.6	0.4	8.9	14.3	23.2	31.6
	790	37.9	7.2	1.2	13.0	16.5	29.5	34.3
	810	48.2	10.5	2.0	18.6	17.1	35.7	38.6
	830	57.7	11.6	3.5	24.6	18.0	42.6	42.6
	850	74.3	17.6	4.8	31.8	20.1	51.9	42.8
Ce-containing covering	730	5.1	0.5	2.1	0.7	1.8	2.5	13.7
	760	11.0	1.5	2.1	2.9	4.5	7.4	26.4
	790	17.0	3.2	2.3	4.7	6.8	11.5	27.6
	810	29.9	5.3	2.5	9.7	12.4	22.1	32.4
	845	45.6	9.4	3.1	17.3	15.8	33.1	37.9
	860	68.7	15.5	3.7	29.5	20.0	49.5	42.9
Steel reactor, no covering	730	8.6	1.6	0.5	2.7	3.8	6.5	31.4
	750	21.9	4.1	1.5	7.1	9.2	16.3	32.4
	765	24.5	4.9	2.0	8.4	9.2	17.6	34.3
	790	39.7	8.0	3.9	14.3	13.5	27.8	36.0
	830	63.9	13.2	7.0	28.2	15.5	43.7	44.1
	850	76.0	17.1	7.4	34.5	17.0	51.5	45.4

Table 2. Selectivity of pyrolysis of propane–butane hydrocarbon raw material (T = 850°C)

Catalyst and contact	C_2H_4/CH_4	C_3H_6/CH_4	C_2H_4/C_3H_6	α[a]	Coke, wt %
Quartz reactor	1.70	1.04	1.63	0.71	0.23
Steel reactor non-covered	2.02	0.99	2.03	0.75	1.12
Steel reactor, covered					
Zn-containing covering	3.12	1.08	2.89	0.81	0.24
Cd-containing covering	1.69	0.82	2.07	0.76	1.20
Sr-containing covering	1.81	1.14	1.58	0.70	1.25
Ce-containing covering	1.90	1.68	1.48	0.70	1.05

[a] $\alpha = n_e(n_e + n_p)$, where n_e and n_p are numbers of moles of ethylene and propylene, respectively, in the reaction mixture at the outlet.

are made of chromium-nickel alloys occurs intensive coking with formation of so-called solid tape dendrite or needle coke with high content of metal moieties (up to 0.9–2.2 wt % of nickel, chromium and iron), resulting in significant shortening in the working period of the pyrolysis furnace and damaging the pirolysis coil pipes; removing of such coke is very difficult.

We found to confirm this that in the IR spectrum of coke precipitates formed at the internal surface of steel reactor (Table 2) occurs a strong absorption band with the maximum at 914 cm^{-1}, that relates to the phase of metal carbides [10]. In the IR spectrum of the coke formed in a quartz reactor and in the steel reactor with the zinc-containing covering such band is absent. Thus, in the quartz reactor and in the steel reactor with the zinc-containng covering dominates formation of amorphous isotropic coke which can be relatively easily removed from the walls by burning out in air flow.

The results of the experiments allows estimate qualitatively the change in basic pathways of pyrolysis (1)–(4) leading to formation of ethylene and propylene [2]. We determined the mass ratio in the yield of the components C_2H_4/CH_4 for the targeted pathways, that allow to estimate approach of the products yields to stoichiometry [theoretically C_2H_4/CH_4 = 1.75 for pathway (1), C_3H_6/CH_4 = 2.63 for pathway (3)]:

$$C_3H_8 \rightarrow CH_4 + C_2H_4, \quad (1)$$

$$C_3H_8 \rightarrow H_2 + C_3H_6, \quad (2)$$

$$C_4H_{10} \rightarrow C_3H_6 + CH_4, \quad (3)$$

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

By these investigation we derive the following sequence of catalytic activity of the samples of metal-containng coverings in respect of ethylene and propylene yield: Zn > Cd > Sr > Ce.

The same sequence of the metals corresponds to their activity of inhibiting the process of coke formation.

The highest catalytic activity of the zinc-containing covering probably is connected with the lower degree of oxidation of the metal and as a sequence with its higher hydrogenating activity that allows to diminish the formation of the products of polycondensation. The oxides of other metals in turn promote reaction of aromatization of hydrocarbon raw material and increase coking on the catalytic surface [11].

EXPERIMENTAL

The catalysts are ceramic film-type polyphosphate coverings with the density up to 50–70 g m^{-2} (Table 3), that were prepared directly on the internal surface of steel reactor by treatment with aqueous solutions or suspensions of compounds of II–V groups elements of Periodic system (zinc, cadmium, strontium, cerium and phosphorus) with the overall composition $Me_xO_y \cdot z(P_2O_5)$, where x = 1, 2; y = 1, 3; z = 2, 3.

The catalysts were examined on a laboratory flow-type installation at the contact duration (τ) 1.5 s, and the raw material–vapor ratio 2:1. As the raw material was used the propane–butane hydrocarbon fraction (technological product of petrochemical plant Sibur-Neftekhim) with the composition, wt %: C_2H_6 3.6, C_3H_8 70.5, i-C_4H_{10} 7.8, n-C_4H_{10} 18.1. The raw material was pyrolyzed in the reactors with internal diameter 40 mm and length 500 mm at the temperature 730–860°C , volume ratio on the raw material 100 ml min^{-1}.

Table 3. Some characteristics of the examined catalysts

Catalyst	Content, wt %		P_2O_5/Me_xO_y
	Me_xO_y	P_2O_5	
Zn-containing covering	2.9	7.1	2.45
Cd-containing covering	0.9	2.0	2.21
Sr-containing covering	0.6	1.8	2.99
Ce-containing covering	0.8	1.7	2.09

The final reaction mixture composition was determined by chromatigrraphy on a Tsvet-102 device with the column 2 m length filled with the silica gel KSK-2.5, and equipped with a thermal conductivity detector. For quantitative estimation of the components in gas phase (methane, ethane, ethylene, propane, propylene, isobutene and *n*-butane) was applied calibration on individual hydrocarbons, calculation was carried out by the procedure of absolute calibration. Conversion of the raw material was calculated from the ratio of reacted to fed raw material. Yield of reaction products was determined from the ratio of the amount of product formed at a given temperature to the overall amount of raw material passed into the installation. Selectivity on ethylene was calculated as the ratio of the amount of the product (ethylene) to the total amount of the products (methane, ethane, ethylene, propylene). Amount of carbon cake formed in the process of pyrolysis was calculated from the reactor weight gain.

The IR spectra were registered on Shimadzu IR Prestige-21 instrument in the range 4000–400 cm^{-1} from the KBr pellet samples.

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