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Catalytic Pyrolysis of Propane and Butane over Silica Surface

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Abstract—Pyrolysis of raw propane–butane mixture at 500–800°C in helium atmosphere in a quartz flow reactor was studied in the presence and in the absence of disperse silica packing. Under the conditions excluding radical chain propagation, the process was found to occur as catalytic decomposition of the initial hydrocarbons over silica surface.

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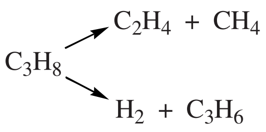
One of the main methods for large-scale preparation of ethylene [1] is based on pyrolysis of raw propane–butane mixture. This process is performed in a steel flow reactor, and its significant disadvantage is profound pyrolysis of a considerable amount of the initial hydrocarbon mixture to give coke. As a result, periodical process shutdown is necessary to remove coke. Various protective coatings are applied to reactor walls to reduce amount of coke. Among these, the best results were obtained with the use of SiO_2 and, probably, $SiO_{2-x}(OH)_x$ [2, 3].

The goal of the present work was to estimate the effect of silica surface on the pyrolysis of raw propane–butane mixture in helium medium, i.e., under the conditions which suppress radical chain process and coking.

Detailed study on the pyrolysis of propane in a quartz reactor [4] showed that the process in the gas phase follows radical chain mechanism, formalistically along two pathways:



No participation of the reactor surface in the process.

We used a raw propane–butane mixture strongly diluted with helium which is incapable of participating in chain propagation; therefore, the pyrolysis process in an inert gas may be considered to not involve radical chain reaction. Typical experimental results are collected in Table 1. It is seen that the yield and ratio of the pyrolysis products depend on both contact time and contact surface. On the basis of the temperature dependence of the yields of pyrolysis products we calculated the energies of activation of the overall decomposition process and formation of particular products (Table 2).

It should be noted that the effective activation energies for decomposition of propane and isomeric butanes in an empty quartz reactor (179–303 kJ mol^{-1}) are smaller than the energy of the weakest C–C bond in their molecules (up to 326 kJ mol^{-1} [5]); the difference is comparable with the heat of physical adsorption of hydrocarbons by silica [6]. Presumably, adsorption of propane and butane on silica surface precedes their homolytic decomposition, and the subsequent pyrolysis process occurs mainly on the silica surface. This assumption is consistent with published data [7].

EXPERIMENTAL

The kinetics of pyrolysis of raw propane–butane mixture in helium medium were studied using a setup consisting of a flow quartz tube reactor (0.46–0.5 cm i.d.) equipped with a pulse batcher (the hydrocarbon mixture was supplied in 7.5×10^{-5}-mol portions) and a sampler. Propane–butane–helium mixture was supplied to the pulse batcher from a special rough-vacuum tank. The amount of the supplied hydrocarbons was

Table 1. Pyrolysis of raw propane–butane mixture[a]

Contact	Temperature, °C	Conversion, %	Yield, mol % (calculated on the reacted hydrocarbons)			
			methane	ethane	ethylene	propylene
Empty reactor (τ 6.6 s)	700	43.0	13.7	–	20.0	9.3
	725	69.6	22.9	–	37.5	9.2
	750	81.2	28.0	–	45.5	7.7
	780	87.7	34.9	–	50.9	1.9
	800	87.2	37.5	1.1	47.6	1.0
Empty reactor (τ 9.0 s)	700	43.5	23.4	2.6	17.5	–
	725	64.6	31.5	4.1	29.0	–
	750	82.3	37.4	5.2	39.7	–
	780	94.7	41.1	5.3	46.3	2.0
	800	95.7	41.9	5.5	46.5	1.8
Silica[b] (τ 0.75 s)	700	31.2	6.9	1.0	12.7	10.6
	725	50.0	11.2	3.0	22.1	13.7
	750	78.5	37.9	3.0	27.9	9.7
	780	89.5	43.0	4.0	34.4	8.1
	800	98.8	38.3	5.0	48.0	7.5

[a] No coking was observed. [b] The reactor was filled with silica (grain size 0.3–0.5 mm).

Table 2. Energies of activation for the overall decomposition process of propane and butane and formation of methane and ethylene in the pyrolysis of raw propane–butane mixture in helium medium

Contact	Contact time τ, s	E_a, kJ mol^{-1}			
		CH_4	C_2H_4	C_3H_8	$\sum C_4H_{10}$
Empty reactor	6.6	62.6±3.9	85.1±16.5	211.9±9.2	302.9±19.2
Empty reactor	9.0	37.8±3.2	77.0±8.6	179.0±14.9	287.6±16.3
Silica	0.75	35.9±2.7	109.4±14.8	211.6±20.7	196.6±23.0

determined from the pressure reduction and composition of the mixture.

In serial experiments the hydrocarbon mixture was supplied to the reactor from the batcher with a stream of helium (carrier gas flow rate 30 ml/min). The calculated time of contact τ was 6.6–9.0 s in empty reactor and about 0.75 s in the reactor filled with silica. The initial propane–butane mixture was produced by the *Sibur-Neftekhim* joint-stock company, and it contained 7.3 mol % of methane, 4.2 mol % of ethane, 75.2 mol % of propane, 7.7 mol % of isobutane, and 5.6 mol % of butane. The selectivity of pyrolysis of the hydrocarbon mixture in a stream of helium was studied in the temperature range from 500 to 800°C. The gas mixture was analyzed for methane, ethane, ethylene, propane, propylene, isobutane, and *n*-butane using a Tsvet 100M chromatograph equipped with a thermal conductivity detector and a 2-m column packed with 10% of KOH on Al_2O_3. The product concentrations were determined by the absolute calibration technique using standard hydrocarbon samples.

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