ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 3, pp. 422–427. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.M. Shekunova, I.I. Didenkulova, E.I. Tsyganova, Yu.A. Aleksandrov, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 3, pp. 429–434.

Effect of Silicon Compounds on the Pyrolysis of Propane–Butane Hydrocarbon Mixture

V. M. Shekunova[a], I. I. Didenkulova[a], E. I. Tsyganova[a], and Yu. A. Aleksandrov[b]

[a] *Research Institute of Chemistry, Lobachevskii Nizhny Novgorod National Research University*
[b] *Lobachevskii Nizhny Novgorod National Research University, pr. Gagarina 23, Nizhny Novgorod, 603950 Russia*
e-mail: shecunova@mail.ru

Received December 20, 2010

Abstract—The effect of silicon-containing catalysts on the pyrolysis of propane–butane hydrocarbon mixture in a flow system was studied in the temperature range 500–850°C, the rate of the gas mixture flow 50–100 ml min^{-1}, contact time 0.1–12.0 s, and the value of the heterogeneity factor 0.1–2.1×10^{7} cm^{-1}. The catalytic activity of different systems under similar conditions was compared, and the influence of various factors on the yield of ethylene and propylene was studied. The most active silicon-containing catalyst for the pyrolysis of propane–butane hydrocarbon mixture was found.

DOI: 10.1134/S1070363212030103

For improving the process of production of low molecular weight alkenes, the pyrolysis of alkanes should be carried out the in the presence of substances decreasing the process temperature, increasing the rate of transformation of radicals, enhancing the process selectivity, and reducing the formation of unwanted products. To this end a search is performed for compounds (initiators, catalysts, activators, promoters) of homogeneous and heterogeneous nature allowing the increased yield of the target products and the substances (inhibitors, deactivators, passivator) reducing the formation of condensed compounds. Many types of chemicals were tested, but their wide application in industry is often limited because they are either ineffective, or difficultly available, or expensive. However, as shown in [1], the future success of petrochemical industry depend on the increase in the selectivity of the catalysts and in the degree of the raw material conversion. Studies on the mechanism of catalytic pyrolysis have shown that it proceeds by the heterogeneous–homogeneous radical-chain mechanism, which includes both heterogeneous and homogeneous phases [2]. Depending on the used catalysts, the pyrolysis mechanisms may differ from each other. The catalyst can to some extent govern the direction of the interaction of radicals with variously situated hydrogen atoms of the hydrocarbon source in the course of the chain propagation, rather than only accelerate the hydrocarbon decomposition. The order of activity of catalysts may vary when a mixture is used instead of individual hydrocarbon. Therefore, an individual hydrocarbon, or a mixture of two individual hydrocarbons cannot serve as a model system for determine-ing the activity of a catalyst at the decomposition of various hydrocarbons [3].

Previously, studying the pyrolysis of propane–butane hydrocarbon mixture in the presence of ceramic catalysts with deposited Zn and Zn–Si film compositions we have shown that the influence of the coating on the yield of alkenes and carbon black formation depends ambiguously on the contact duration [4]. In a quartz reactor, the ceramic net treated with Si-containing composition while showed the best yield of ethylene, was inferior to the other catalysts with respect to the propylene yield and the soot formation. The most effective catalyst for the pyrolysis of propane–butane hydrocarbon mixture into ethylene and propylene has not been obtained so far.

This paper presents the results of kinetic studies of the effect of the silicon-containing catalysts on the activity of pyrolysis of light hydrocarbons C_1–C_4. We assessed the influence of the nature of substrate, processing, heterogeneous factor, and contact duration on the yield of lower alkenes (ethylene and propylene) and the selectivity of the catalysts towards ethylene

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

Catalyst no.	Reactor diameter, cm	Treatment of reactor	Catalyst		S/V, cm^{-1}	Coke formation, wt %
			substrate	substrate treatment		
I	2.0	Polyphosphate Zn-containing coating	Metal plates	Polyphosphate Zn-containing coating, ETS-40	0.1	2.72
II	0.8	–	Carbide cords	″	0.2	0.14
III	0.4	–	HIPEC ceramics	″	1.8×10^5	0.56
IV	0.6	–	″	Polysilicon acid, 5.6 wt %	5.5×10^5	–
V	0.4	–	″	–	5.6×10^5	0.02
VI	0.8	–	″	Forceramic composition (annealed at 600°C)	1.1×10^6	0.36
VII	0.8	–	″	Tetraethoxysilane	1.8×10^6	0.27
VIII	0.8	Polyphosphate coating	″	Forceramic composition	2.7×10^6	–
IX	0.8	–	″	″	3.2×10^6	–
X	0.4	–	Silica gel KSK-2.0	Nitric acid solution	3.5×10^6	1.30
XI	0.4	Polyphosphate Zn-containing coating	Quartz granules	–	3.7×10^6	0.02
XII	0.8	–	Ceramic granules (China)	Tetraethoxysilane	4.1×10^6	–
XIII	0.6	–	Silica gel KSK-2.0	Forceramic composition	7.4×10^6	0.82
XIV	0.4	–	Polysilicon acid	–	2.1×10^7	–

formation. We found the most effective silicon-containing catalyst for the pyrolysis. As one of the advanced industrial methods of ethylene production is based on the pyrolysis of propane–butane hydrocarbons, we have investigated the activity of the silicon-containing catalysts on a crude propane–butane hydrocarbon mixture from Sibur-Neftekhim.

Earlier [5] we have shown that no one material can be considered as inert in the pyrolysis process. Many of the tested materials, including quartz, to a certain degree catalyze the pyrolysis of hydrocarbons.

Tables 1 and 2 show characteristics of the studied catalysts depending on the mode of the treatment of substrate, and the main results of kinetic measurements of the pyrolysis of propane–butane hydrocarbon mixture in the presence of silicon-containing catalysts in the range 730–810°C.

The investigation of the influence of different carriers showed that their composition, processing, porosity, and grain size influence their catalytic activity in the decomposition of the investigated hydrocarbon mixture. The maximal carbon deposition was observed on the catalysts **I**, **III**, **VI**, **X**, and **XIII**, while with the catalysts **IV**, **VIII**, **IX**, **XII**, and **XIV** the coke deposits were practically unnoticed (Table 1). The catalyst substrates characterized by the absence of the coke formation are as follows: HIPEK ceramics, polysilicon acid, and Chinese silicon-containing ceramic granules with the magnitude of the heterogeneity factor in the range 5.5×10^5–2.1×10^7. The catalysts **I** and **II** with a low heterogeneous factor (0.1 and 0.2 cm^{-1}, respectively) are featured by the coke formation, the first one in particular.

The formation of coke deposits has not been found in the case of polysilicon acid (catalyst **XIV**) and the HIPEK ceramic with deposited polysilicon acid in an amount of 5.6 wt % (catalyst **IV**), in contrast to untreated HIPEK ceramics (catalyst **V**). Besides, there was an increase in the sooting from 0.27 to 0.56 wt % on this ceramic treated with tetraethoxysilane (catalyst **VII**), or with forceramic composition followed by

Table 2. The results of the pyrolysis of propane–butane hydrocarbon mixture on the silicon-containing catalysts

Catalyst no.	Contact time τ, s	*T*, °C	Conversion, %	Yield with respect to to the passed hydrocarbon mixture, mol %					Selectivity to C_2H_4 formation, %
				CH_4	C_2H_6	C_2H_4	C_3H_6	$\Sigma C_2–C_3$	
II	12.0	750	43.8	14.5	0	19.8	9.5	29.3	45.2
		800	70.4	29.9	0	30.4	10.1	40.5	43.2
III	3.4	770	65.8	23.6	2.5	27.5	12.2	39.7	41.8
		800	79.5	30.1	3.8	33.5	12.1	45.6	42.1
IV	5.8	730	39.8	13.8	2.0	11.8	12.2	24.0	29.6
		770	66.8	24.8	4.4	22.8	14.8	37.6	34.1
		800	86.1	36.8	3.9	30.0	15.4	45.4	34.8
V	1.7	750	35.6	11.6	0	13.6	10.4	24.0	38.2
		800	53.4	20.1	0	24.4	8.9	33.3	45.7
	0.8	740	18.8	6.1	0	7.4	5.3	12.7	39.4
		800	49.3	16.9	1.3	19.6	11.5	31.1	39.8
VI	7.9	765	77.9	26.2	6.4	29.0	16.3	45.3	37.2
		800	89.5	34.1	7.2	36.2	12.0	48.2	40.4
VII	6.1	760	77.3	27.5	4.1	29.6	16.1	45.7	38.0
		800	90.6	35.6	6.9	35.5	12.6	48.1	39.2
VIII	4.6	755	65.3	21.4	7.0	24.2	12.7	36.9	37.1
		800	85.2	33.2	7.5	34.6	9.9	44.5	40.6
IX	4.1	750	55.1	17.6	2.9	20.4	14.2	34.6	37.0
		805	86.6	32.5	5.6	34.9	13.6	48.5	40.3
X	2.0	750	44.9	18.1	4.8	13.1	8.9	22.0	29.2
		800	75.7	31.5	5.2	23.1	15.9	39.0	30.5
XI	0.8	735	16.0	4.3	0	7.5	4.2	11.7	46.9
		760	28.9	8.4	0.5	12.0	8.0	20.0	41.5
	0.4	760	61.7	24.4	0	26.7	10.6	37.3	43.3
XII	2.4	760	41.2	14.5	0	18.0	8.7	26.7	43.7
		805	73.9	31.0	0	32.9	10.0	42.9	44.5
XIII	2.6	770	56.9	21.4	1.4	20.8	13.3	34.1	36.6
		810	75.8	37.3	1.7	26.0	10.8	36.8	34.8
XIV	0.1	750	52.0	16.4	2.7	18.0	14.9	32.9	34.6
		790	72.3	23.5	4.1	28.1	16.6	44.7	38.9

annealing at 600°C in air (catalyst **VI**), and with Zn- and Si-containing film compositions (catalyst **III**).

It is noteworthy that the processing of the inner surface of the steel reactor with a polyphosphate coating does not affect the coke formation in the case of HIPEK ceramic coated with a forceramic composition (catalyst **VIII, IX**). This fact confirms that the catalytic pyrolysis of propane–butane hydrocarbon mixture occurs mainly on the surface of the ceramic catalyst, otherwise the reactor material would affect the coke formation [4]. Hence, at the use of the HIPEK ceramics coated with forceramic composition for the pyrolysis the necessity of treating the internal surface of steel reactor can be neglected.

It follows from the results of the study of kinetic regularities of the pyrolysis process on these catalysts

(Table 2) that the maximum yield of alkene with the maximum propane–butane conversion is reached with the HIPEK ceramics treated with a forceramic composition (catalysts **VIII** and **IX**), although the selectivity of C_2H_4 formation is somewhat higher with catalysts **XI** and **XII**. Catalyst **VI** and **VII** exhibit sufficiently high conversion of hydrocarbons and selectivity to C_2H_4, but during the pyrolysis a significant amount of coke is formed (0.36 and 0.27 wt %, respectively). The increase in the amount of polysilicon acid (catalyst **IV** and **XIV**) has little effect on both ethylene and propylene yield, although the contact time therewith decreased significantly, from 5.8 to 0.1 s. The polysilicon acid affects mainly the conversion of propane–butane hydrocarbon mixture.

Coating silica gel KSK-2.0 with a forceramic composition (catalyst **XIII**) leads to an increase in selectivity to ethylene by 4–7% compared with catalyst **X** not processed with a silicon-containing composition. However, in both cases, the pyrolysis proceeded with significant coke formation (Table 1) and low yield of alkenes (Table 2).

Pyrolysis in the presence of Chinese ceramic granules treated with tetraethoxysilane (catalyst **XII**), in contrast to the similarly treated HIPEK ceramics (catalyst **VII**), is characterized by the absence of soot formation at the almost identical values of the heterogeneity factor (Table 1). However, catalyst **XII** showed lower yield of alkenes compared with the HIPEK ceramics treated with a forceramic composition (catalyst **VIII** and **IX**).

With the untreated HIPEK ceramics (catalyst **V**) the twofold increase in contact time and raising the temperature increased the selectivity to ethylene. Thus, to increase the yield of ethylene it is necessary to increase the contact time and temperature, but raising the latter above 800°C is impractical due to the sharp increase in the yield of condensed products of pyrolysis and coke formation. It was shown previously [4] that when the temperature rose above 800°C the yield of light alkenes little depended on the contact time because of increased contribution of homogeneous steps to the pyrolysis process. At the same time, in the case of a reactor filled with quartz granules (catalyst **XI**) the twofold increase in the contact duration showed little effect on the selectivity to ethylene, but almost twice reduced the conversion of the hydrocarbons. Slight formation of pyrolytic carbon in the presence of quartz confirms the role of the latter catalyst for the transformation of ethylene into condensed products [6].

We have carried out XRD phase analysis of the HIPEK ceramics both coated with the forceramic composition and without coating (catalyst **IX** and **V**, respectively). Diffraction patterns before pyrolysis include a set of peaks indicating a high degree of crystallinity [7]. The main reflections correspond to a trigonal-rhombohedral lattice of SiO_2 (α-quartz) and tetragonal lattice of α-cristobalite SiO_2, and to the lattice of mullite and hematite. Diffractograms of catalysts **IX** and **V** after pyrolysis remained identical with those before pyrolysis indicating their thermal stability and stability in the pyrolysis process.

We studied the chemical composition of the surface of catalyst **IX** before and after pyrolysis of hydrocarbons using infrared spectroscopy. The IR spectra contain absorption bands in the region of 1000–1300 cm^{-1} confirming the presence of phosphate and silicate groups. The intensity of the bands decreases after pyrolysis, indicating quantitative changes in the content of the oxide phases and the occurrence of the condensation processes. The absence of vibrations of the carbon skeleton C–C and C=C bonds helped to confirm the absence of coke formation on this catalyst.

The IR spectra of solid pyrolysis products formed in the presence of catalysts **III** and **VI** showed the presence of carbon with disordered structure, which was confirmed by the studies with electron microscopy. In the carbon-containing products fullerenes were not detected, in contrast to results reported in [8].

The pyrolysis products on catalysts **VI** and **XI** at a temperature above 800°C contained dark red condensed products (less than 0.5 wt %), which by the data of mass spectrometric analysis include naphthalene, methylnaphthalene, anthracene, cyclopentanaphthalene, methylfluorene, phenanthrene, α-pyrene, and biphenyl.

We found that at high temperatures (730–805°C) in the presence of the HIPEK ceramics treated with a silicon-containing compound (catalyst **III**, **V–IX**) the yield of ethylene was higher than that of methane, in contrast to the low temperatures (605–630°C) for which the yields of methane and ethylene were similar and which appeared almost simultaneously. At low temperatures, the conversion of hydrocarbons is due to the pyrolysis of propane, while butane and isobutane remain undecomposed, which is consistent with the data of [9] on the pyrolysis of propane. Propane can be decomposed in two main directions: demethanation [Eq. (1)], and dehydration [Eq. (2)]:

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

$$C_3H_8 \rightleftarrows H_2 + C_3H_6. \quad (2)$$

At high temperatures (750–800°C) the formation of methane and ethylene [Eq. (1)] is not stoichiometric, and the pyrolysis includes probably the direction [Eq. (3)], which explains the increased yield of ethylene.

$$2\,C_3H_8 \rightarrow 2H_2 + 3\,C_2H_4. \quad (3)$$

Based on the kinetic data, the butane decomposition probably proceeds according to [Eq. (4)]:

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

These results indicate the significant contribution of the chain propagation reaction involving the catalyst surface. The reaction proceeds in a heterogeneous region, and the catalyst promotes the formation of additional radicals or other species of the heterogeneous surfaces shifting the optimal product yields to the region of lower temperatures compared to thermal pyrolysis.

Kinetic studies confirm the undoubted effect of the silicon compounds on the catalytic pyrolysis of hydrocarbons on the HIPEK ceramics surface. Thus, the ethylene yield at 800°C on the untreated HIPEK (catalyst **V**) is 24.4 mol %, while on catalysts **III**, **IV**, **VI–IX** modified with various silicon-containing compounds it attains the range from 30.0 to 36.2 mol % (Table 2).

It can be assumed that the surface of the HIPEK ceramics modified by the decomposition products of silicon-containing compounds has active Si-centers capable of chemisorbtion of dissociatively weak acids, including propane [10]. The sorption occurs on two atoms (ions) of the catalyst: silicon and oxygen of the catalyst lattice, with the formation of strongly bound atomic-adsorption structures that are comparable by the bond strength with the C–C and C–H bond in hydrocarbon molecules. The surface centers abstract homolytically hydrogen atom and hydrocarbon fragment from the propane molecule, and then the reaction proceeds as the splitting of C–H and C–C bonds with the formation of ethylene molecule. With increasing temperature, the adsorbed hydrogen atom and methyl fragment of the propane molecule recombine with the elimination of a methane molecule.

The catalytic pyrolysis at high temperatures is characterized by the dissociation of adsorbed CH_3 radicals followed by binding the split off hydrogen atoms and the formation of carbene particles, thereby decreasing the thermodynamic restrictions [3], therefore the necessary reaction temperature decreases. Further the desorption of the carbene particles leads to the formation of ethylene.

The secondary reactions of alkene conversion can proceed as homogeneous and heterogeneous processes with the formation of the condensation products.

Thus, the study of kinetic regularities of catalytic pyrolysis of propane–butane hydrocarbon mixture in an open system in the presence of various silicon-containing compounds showed their different activity affecting the yield of alkenes (ethylene, propylene) and the selectivity to ethylene and coke formation. The modification of various substrates by the products of thermal decomposition of silicon-containing compounds leads to an improvement of pyrolysis characteristics, changing activity and selectivity of the catalysts in the formation of alkenes. The effect of silicon as a catalyst component is reduced to the suppression of a nonselective transformation of the hydrocarbon mixture at the pyrolysis. We found that the most effective catalyst for the pyrolysis of propane–butane hydrocarbon mixture is the HIPEK ceramics modified by forceramic composition: It is characterized by a highest yield of alkenes without the coke formation.

EXPERIMENTAL

As the substrates for catalysts various materials were used (Table 1), including those with a highly developed surface like silica gel KSK-2.0, polysilicon acid, quartz, and Chinese ceramic granules, synthetic ceramic material HIPEK which is composed of mineral and organic substances [4] and characterized by high thermal stability up to 1000°C, 70–80% porosity, and high compressive strength, up to 300 N cm^{-2}. The ceramic granules (production of China) contain about 93 wt % of Al_2O_3 and 5 wt % of SiO_2. Silica gel KSK-2.0 is a porous polar adsorbent produced by polycondensation of orthosilicic acid and contains up to 99.7 wt % of SiO_2. The ceramic substrates were crushed (the fraction 0.3–2.0 mm was used) and treated with the following compositions: (a) polyphosphate Zn-containing composition consisting of an inorganic zinc salt dissolved in phosphoric acid; its heating led to the Zn-containing film coating; (b) tetraethoxysilane hydrolyzed with a weak solution of nitric acid; (c) ethyl silicate 40 (ETS-40), a commercial product (TU 2435-427-05783441-2004) containing 40% solution of tetraethoxysilane in ethanol; its heating gives the modified coating of the average composition corresponding to the oligomer $(RO)_3Si\cdot[OSi(OR)_2]_4OSi(OR)_3$; (d) forceramic composition consisting of ETS-40, ethanol and additives (1–3 wt %) of concentrated nitric and acetic acids, and water.

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

The investigation of pyrolysis of the hydrocarbon mixtures was performed using steel reactors (steel grade 12X18H10T), diameter 0.4, 0.6, 0.8, and 2.0 cm, in the temperature range 500–850°C, the flow rate of hydrocarbon mixture 50–100 ml min^{-1}, the contact time (τ) of the reacting mixture with the catalyst 0.1–12.0 s. The contact time was calculated with the formula: $\tau = \Delta V/F$, where ΔV is the reactor free volume equal to the difference of the reactor total volume and the catalyst volume, F is the flow rate of the hydrocarbon mixture. Heterogeneous factor $S/\Delta V$, where S is the catalyst surface area and ΔV is free volume, ranged from 0.1 to 2.1×10^7 cm^{-1}. The kinetics of the pyrolysis process was studied in a laboratory flow-type setup, which included a chromatograph Tsvet-101 [4]. The main gaseous products of pyrolysis are methane, ethane, ethylene, and propylene, the quantitative composition was determined by the method of absolute calibration. The amount of carbon deposits formed in the reactor at the pyrolysis was found as the weight gain. The deposits were analyzed using a Shimadzu Fourier transform infrared spectrometer IR-Prestige-21 and a scanning probe microscope SPM Solver PRO. The analysis of high molecular liquid products of pyrolysis was performed on a gas chromatograph–mass spectrometer Polaris Q/Trace GC Ultra. For X-ray studies a DRON-3M instrument was used.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Industry and Innovation of Nizhny Novgorod region.

REFERENCES

1. Chernykh, S.P., Adel’son, S.V., and Mukhina, T.N., *Neftekhimiya*, 1991, vol. 31, p. 688.
2. Vasil’eva, N.A. and Buyanov, R.A., *Kinet. Katal.*, 1993, vol. 34, no. 5, p. 38.
3. Galikeev, A.R., *Neftekhimiya*, 2007, vol. 47, no. 5, p. 387.
4. Aleksandrov, Yu.A., Tsyganova, E.I., Shekunova, V.M., Didenkulova, I.I., Pishchurova, I.A., and Belov, D.E., *Zh. Obshch. Khim.*, 2010, vol. 80, no. 4, p. 581.
5. Aleksandrov, Yu.A., Shekunova, V.M., Didenkulova, I.I., and Pishchurova, I.A., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 10, p. 1662.
6. Gashimov, F.A., *Zh. Prikl. Khim.*, 2009, vol. 82, no. 5, p. 9.
7. Kovba, L.M. and Trunov, V.K., *Rengenofazovyi analiz* (X-Ray Phase Analysis), Moscow: Mosk. Gos. Univ., 1976, p. 146.
8. Zakirnichnaya, M.M., *Doctorate (Tech.) Dissertation*, Ufa, 2001.
9. Volcan, A.J. and April, G.C., *Ind. Eng. Chem. Proc. Des. Dev*, 1977, vol. 16, p. 429.
10. Garrone, E. and Stone, F.S., *Proc. 8th Int. Congress on Catalysis*, 1984, vol. 3, p. 441.