

NEW CATALYSTS OF HYDROCARBON PYROLYSIS

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Lower olefins – ethylene and propylene – occupy a leading position in the feedstock base of domestic and foreign petrochemistry. Thermal pyrolysis of hydrocarbons in tube furnaces, which ensures the almost maximum yield of target products, is the basic production process. This is due to continuous improvement of the basic equipment in the process units. In pyrolysis furnace block structures, it was directed toward making the process conditions more severe to attain the maximum yield of target products.

Wide studies of the technology and equipment in pyrolysis have evolved in the following basic directions:

- creation of units, “flexible” with respect to the feedstock, since the feedstock base of the process has expanded with inclusion of liquefied gases and heavy crude oil cuts;
- modernization of pyrolysis furnaces of large and medium unit capacity, optimization of process conditions in the stages of pyrolysis and quenching of pyrolysis gas;

Table 1

Indexes	Pyrolysis catalyst				
	KVB*/MC	MgO/MC	MgSO ₄ /MC	SrCl ₂ /MC	SrO/MC
Content of active mass, wt. %	5	1.5	4.2	5.8	3.5
Contact time, sec	0.1	0.1	0.1	0.1	0.15
Yield of basic products of pyrolysis, wt. %					
gaseous	78	78.5	78.7	79.8	77.5
H ₂	1	0.87	1	0.8	1.1
CH ₄	15	16.8	17.5	16.8	15.7
C ₂ H ₄	34.9	35.5	35.5	34.9	36.4
C ₃ H ₆	14.4	13.3	12.5	14	14.3
C ₄ H ₈	3.5	3.4	3.8	4.9	3.8
C ₄ H ₆	4	4.3	3.7	4.2	3.3
liquid	22	21.5	24.7	20.2	22.5
C ₂ H ₄	49.3	48.8	48	48.9	50.7
CH ₄ : C ₂ H ₄	0.43	0.47	0.49	0.48	0.43
Note.	*Vanadium catalyst modified with boron oxide.				

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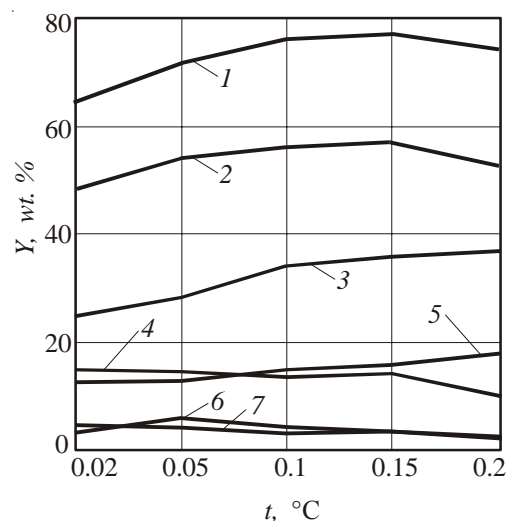


Fig. 1. Yield B of basic products of pyrolysis on SrO/MC catalyst vs. contact time t :
 1) gas; 2) sum of unsaturated hydrocarbons; 3) ethylene; 4) propylene; 5) methane;
 6) butenes; 7) butadiene.

- development of promising pyrolytic processes such as the process on heterogeneous catalysts, homogeneously initiated pyrolysis, pyrolysis in a superheated steam stream, etc.

Thermal pyrolysis, despite the great advances in its development, still has many important drawbacks: difficulties in delivering large amounts of heat through the tube walls; high consumption of alloyed steel; relatively low yield of ethylene, etc.

The use of heterogeneous catalytic systems which allow conducting pyrolysis in milder conditions with an increase in the yields of target products and selectivity is one promising direction in improving the pyrolysis process.

Research is being conducted in our country and abroad on use of different catalytic systems in pyrolysis of hydrocarbons. Metals were initially investigated as catalysts – nickel, molybdenum, tungsten, aluminum, iron, copper, etc. However, they were ineffective, since they primarily activated exhaustive decomposition of hydrocarbons with formation of hydrogen, methane, and coke [1].

The support plays an extremely large role in formation of the properties of a catalyst for any process. Catalysts on different supports are used in high-temperature processes: clays, active aluminum oxide, silica gels, zeolites, etc. [2]. Of the catalysts of pyrolysis of hydrocarbon feedstock proposed by different investigators, a vanadium catalyst on a support modified with boron oxide has been most completely developed [3]. Developing catalysts of pyrolysis suitable for industrial implementation required a large number of theoretical and process studies. As a result of studying catalytic pyrolysis of individual hydrocarbons and mixtures, fundamental concepts concerning the mechanism of the process were formulated and its features and basic characteristics were revealed [4].

We looked for new efficient, readily available, and environmentally clean catalytic systems for pyrolysis. Group II metal compounds were used as the initial components of such systems: $Mg(NO_3)_2$, $MgSO_4$, $SrCl_2$, $Sr(NO_3)_2$. The catalysts were prepared by impregnation of the support – mullite-corundum (MC) with an aqueous solution of the active mass.

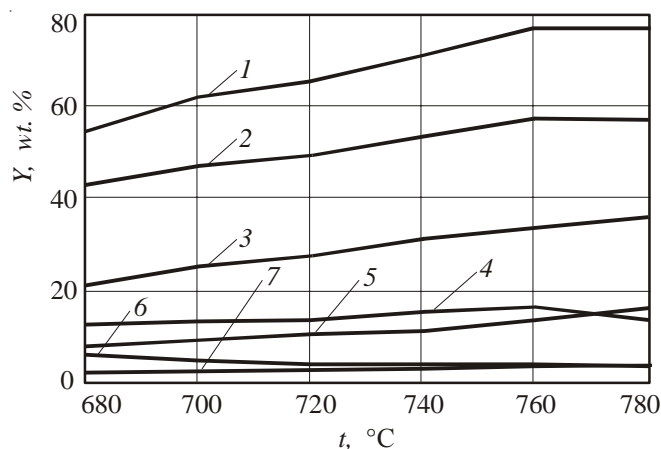


Fig. 2. Yield Y of basic products of pyrolysis on SrO/MC catalyst vs. temperature t :
 1) gas; 2) sum of unsaturated hydrocarbons; 3) ethylene; 4) propylene; 5) methane;
 6) butenes; 7) butadiene.

The results of tests of synthesized catalysts during pyrolysis of naphtha in optimum conditions (temperature: 780°C, degree of dilution of feedstock with steam: 70%) are reported in Table 1. The SrO/MC catalyst prepared from strontium nitrate which is converted into strontium oxide after drying and calcinations is the most active and selective catalyst.

The experiments showed that a temperature of 780°C and contact time of 0.15 sec are optimum for such a catalyst. In these conditions, the yields of products were, wt. %: 36.4% ethylene; 14.3% propylene; 50.7% ethylene + propylene. The selectivity for ethylene ($\text{CH}_4:\text{C}_2\text{H}_4$) was 0.43. These indexes are much higher than those obtained in testing the vanadium catalyst and several others in semi-industrial conditions.

The yield of ethylene increased, attaining 37% at $\tau = 0.2$ sec with an increase in contact time τ at the optimum temperature of 780°C and 70% degree of dilution of the feedstock with steam. However, the yield of propylene, which attained the maximum at $t = 0.15$ sec, decreased to 10% at $\tau = 0.2$ sec. As a consequence, $\tau > 0.15$ sec is not expedient. For longer contact, the yield of butenes decreased monotonically from 6.6 to 3.8%, while the yield of butadiene changed little and was 2-3.4 wt. %.

The observed characteristics are also characteristic of other catalysts of pyrolysis, but the yield of ethylene and sum of ethylene and propylene on this catalyst was much higher.

The yield of ethylene increased from 24.8 to 37 and the yield of methane increased from 13.1 to 17.5, while the yield of propylene decreased from 15 to 10 wt. % with an increase in the temperature from 680 to 780°C (Fig. 2) at a contact time of 0.15 sec and degree of feedstock dilution with steam of 70 wt. %.

Many studies have shown that the degree of dilution of the feedstock by steam significantly affects the pyrolysis indexes with catalysts based on transition metal oxides and potassium chloride. On the vanadium catalyst, pyrolysis takes place efficiently only in the presence of steam, which causes more complete reduction of the catalyst to V^{4+} [5, 6]. The important effect of steam is also observed with the indium-oxide catalyst due to oxidation of indium to In^{3+} [5, 7]. Steam can thus play the role of not only reducing agent but also oxid

In consideration of these features of catalysts of pyrolysis, we investigated the effect of the degree of dilution of the feedstock and nature of the diluent on the indexes for pyrolysis of naphtha with

Table 2

Products of pyrolysis	Yield (wt. %) at degree of dilution with							
	steam, %					nitrogen, %		
	0	25	50	70	100	38.9	77.8	108.9
Gaseous	68.15	70.61	73.54	78.51	78.16	67.34	68.16	69.85
H ₂	0.84	0.86	0.91	1.11	1.06	0.87	0.85	0.93
CH ₄	19.31	18.42	17	15.73	15.64	18.5	19.5	19.35
CO+CO ₂	0.12	0.06	0.14	0.17	0.17	0.1	0.2	0.22
C ₂ H ₂	0.32	0.59	0.87	0.41	1.16	0.7	0.5	0.55
C ₂ H ₆	3.2	3.13	2.57	2.77	2.54	2.5	2.14	2.18
C ₂ H ₄	28.65	30.05	34.59	36.42	37.61	29.1	29.59	30.63
C ₃ H ₈	0.26	0.28	0.27	0.28	0.31	0.17	0.1	0.13
C ₃ H ₆	9.5	10.74	11.03	14.28	12.39	10.9	10.7	11
C ₄ H ₁₀	1.15	0.27	0.26	0.28	0.23	0.2	0.1	0.21
ΣC ₄	2.58	2.68	2.45	3.81	2.96	2.1	2.06	2.04
C ₄ H ₆	2.22	3.53	3.45	3.25	4.09	2.2	2.42	2.61
Liquid + losses	30.85	28.04	25.66	21.79	21.24	32.66	31.98	30.15
Coke	1	0.9	0.8	0.7	0.6	–	–	–
Σ of unsaturated C ₂ – C ₄	43.27	47.59	52.39	58.17	58.21	45	45.27	46.83
CH ₄ : C ₂ H ₄	0.67	0.61	0.49	0.43	0.42	0.64	0.66	0.63

Table 3

Indexes	Pyrolysis	
	thermal	catalytic
Temperature, °C	820 – 830	780
Degree of feedstock dilution, %	50	70
Yield of basic products, wt. %		
H ₂	1.0	1.1
CH ₄	14.7	15.1
C ₂ H ₄	23.0	36.4
C ₃ H ₆	15.0	14.3
Σ C ₄	7.2	7.0
C ₂ H ₄ + C ₃ H ₆	38	50.7
CH ₄ : C ₂ H ₄	0.64	0.41

the SrO/MC catalyst. The results of the experiments at 780°C and 0.15 sec contact time are reported in Table 2. With no diluent, the process indexes are close to the results obtained on the pure support.

The yields of ethylene and propylene and the total yield of gas increased and the yield of methane decreased with an increase in the degree of dilution of the feedstock with steam. In dilution with nitrogen, the process indexes differed little from the data obtained without dilution. It is thus obvious that the steam reacts with the catalyst with formation of active sites that accelerate the reaction, and this suggests some hypotheses concerning the mechanism of its action.

According to the published data, strontium oxide can occur in three forms: Sr_2O , SrO , and SrO_2 . However, reduction to Sr_2O takes place in the 1140-1300°C temperature range and is energetically very difficult. As a consequence, SrO cannot be reduced in the conditions of catalytic pyrolysis (temperature of 780-800°C). i.e., Sr^{1+} active sites are not present. The formation of SrO_2 is totally possible, although in a very low concentration. As a hypothesis, we suggest that steam plays the role of an oxidant of SrO .

The results of comparing the process indexes of thermal and catalytic pyrolysis in optimum conditions are reported in Table 3.

The data obtained show that use of heterogeneous catalysts increases the efficiency of pyrolysis of hydrocarbons.

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