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Abstract

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INHIBITION OF THE CRACKING OF HYDROCARBONS IN MOLTEN SODIUM AND POTASSIUM HYDROXIDE

Many metals in the molten or highly dispersed state react with hydrocarbons and hydrocarbon radicals with the formation of organometallic compounds, and also exert a catalytic effect on their transformations ([1–12]). In this connection, a detailed study of the reactions of hydrocarbons with various metals in the most reactive, i.e., molten, state, including high temperatures, under conditions in which free radicals are formed, is of great interest.

In the present work, the transformation of *n*-heptane and cyclohexene in the presence of sodium and potassium hydroxide at atmospheric and elevated pressure was studied; for comparison, results are also given for the cracking of *n*-heptane in the presence of molten aluminum. Experiments under pressure were carried out in an autoclave, and at atmospheric pressure in a flow apparatus. Vapors of *n*-heptane were continuously passed through a layer of molten metal or a packing with potassium hydroxide, 150 mm high, placed in a reactor. The contact time of the vapors with the packing at 700–800° was $\sim$ 0.5 sec. Potassium hydroxide was deposited on activated carbon of grade KAD. The reaction products were collected and analyzed.

Characteristics of the starting products

Sodium: density 0.971, m.p. 97.7°, b.p. 880.9°; *n*-heptane: b.p. 98°, d_4^{20} 0.6803, n_D^{20} 1.3960; cyclohexene: b.p. 83–84°, d_4^{20} 0.8072, n_D^{20} 1.4480, iodine number 276; potassium hydroxide: chemically pure reagent, nomenclature No. 946; technical aluminum containing 99.5–99.7% aluminum, m.p. 659.8°.

From the data of Table 1 it is evident that sodium and potassium hydroxide have an inhibiting effect on the cracking of *n*-heptane even at 800°: in experiments with them the conversion is 5–7%, whereas in their absence it is 34–57%.

On contact with aluminum, deep transformations of *n*-heptane are observed; in this case the conversion increases with increasing temperature and residence time in the reaction zone: the conversion reaches 65.3% at 700° and approaches 100% at 800°, which is almost twice as high as in experiments without aluminum.

The gas from the cracking of *n*-heptane in contacts with sodium and KOH differs markedly in composition from the gas of thermal cracking: the bulk of the gas (60–85%) is represented by hydrogen with a low content of unsaturated hydrocarbons.

On contact of *n*-heptane with aluminum, gaseous and liquid reaction products characteristic of deep pyrolysis are obtained. Condensation products, including carbides, are also formed.

The condensate obtained from the cracking of *n*-heptane in contacts with sodium and with KOH consists of unchanged *n*-heptane, i.e., under these conditions no liquid reaction products are formed.

Table 1

Conditions and balance of cracking of *n*-heptane

Temp., °C	Feed rate of raw material, ml/hour	Gas yield, wt. %	Condensate yield, wt. %	Conversion, wt. %	Temp., °C	Feed rate of raw material, ml/hour	Gas yield, wt. %	Condensate yield, wt. %	Conversion, wt. %
Experiments with sodium					**Experiments with activated carbon KAD**				
200	68	gas formation and cracking do not occur	gas formation and cracking do not occur		600	107	5,7	91,8	9,7
300	57	0,1	94,2	0,1	700	105	11,5	86,6	17,9
450	71	1,8	80,3	1,8	800	102	23,7	73,5	34,7
500	51	2,5	75,1	2,5	**Experiments with aluminum**				
600	60	5,6	74,2	5,6	700	100	50,7	43,7	65,3
700	83	6,8	74,0	6,8	750	100	78,0	9,7	97,1

Temp., °C	Feed rate of raw material, ml/hour	Gas yield, wt. %	Condensate yield, wt. %	Conversion, wt. %	Temp., °C	Feed rate of raw material, ml/hour	Gas yield, wt. %	Condensate yield, wt. %	Conversion, wt. %
750	85	5,5	91,1	5,5	800	100	72,5	12,3	99,5
800	108	5,4	83,8	5,4	700	112	27,5	67,5	49,0
Experiments without sodium					700	66	36,9	58,7	71,0
700	107	12,2	86,6	29,0	800	140	45,7	44,6	78,2
800	104	27,9	64,3	57,5	800	86	77,3	14,0	100,0
Experiments with potassium hydroxide deposited on activated carbon KAD					800	69	71,0	6,4	100,0
600	100	1,4	98,6	1,4					
700	99	3,9	96,1	3,9					
800	96	7,4	92,6	7,4					

Table 2

Composition of the gas from cracking of *n*-heptane

Temp., °C	C_nH_{2n}, vol. %	H_2, vol. %	C_nH_{2n+2}, vol. %	Weight of 1 l of gas, g	Temp., °C	C_nH_{2n}, vol. %	H_2, vol. %	C_nH_{2n+2}, vol. %	Weight of 1 l of gas, g
Experiments with sodium					**Experiments with potassium hydroxide deposited on activated carbon KAD**				
200		gas formation does not occur	gas formation does not occur		600	6,7	61,8	31,5	0,55
300	2,2	75,0	22,8	0,45	700	5,4	76,3	18,3	0,45
450	3,0	77,0	20,0	0,45	800	7,3	62,7	30,0	0,54
500	10,8	70,3	18,9	0,57	**Experiments with activated carbon KAD**				
600	7,3	78,5	14,2	0,30	600	22,9	47,9	29,2	0,82
700	2,5	83,5	14,0	0,34	700	22,5	43,1	34,4	0,74
750	1,0	84,6	14,4	0,25	800	30,0	39,0	31,0	0,90
800	0,5	83,6	15,9	0,27	**Experiments with aluminum**				

Temp., °C	C_nH_{2n}, vol. %	H_2, vol. %	C_nH_{2n+2}, vol. %	Weight of 1 l of gas, g	Temp., °C	C_nH_{2n}, vol. %	H_2, vol. %	C_nH_{2n+2}, vol. %	Weight of 1 l of gas, g
Experiments without sodium					700	50,2	15,3	34,5	1,17
700	40,4	12,2	47,4	1,06	750	42,3	24,2	33,5	0,97
800	44,0	22,5	34,0	0,993	800	36,2	30,5	33,3	0,85

It may be assumed that in the initial stage at 300—800° the formation of sodium-organic compounds takes place with the evolution of hydrogen, which, at the moment of formation, adds to olefins, and in this way cracking, which is a chain process promoted by olefins, is inhibited.

$$C_7H_{16} + Na \to C_7H_{15}Na + H; \quad C_nH_{2n} + 2H \to C_nH_{2n+2}$$

or

$$2C_7H_{16} + C_nH_{2n} + 2Na \to 2C_7H_{15}Na + C_nH_{2n+2}.$$

Table 3

Individual composition of the gas from cracking of *n*-heptane in molten aluminum
(in volume percent)

Component	At 700°	At 800°	Component	At 700°	At 800°
Hydrogen	16.15	31.3	*n*-Butane	0.24	0.13
Methane	26.50	30.6	Butene + butene-1	1.84	1.83
Ethane	8.95	5.8	Butene-2 cis, trans	0.58	0.14
Ethylene	31.15	21.91	Butene-2 + C_4H_6 cis, trans	0.90	0.51

Component	At 700°	At 800°	Component	At 700°	At 800°
Propane	0.48	0.26	*iso*-Pentane + 3-methylbutene-1	0.48	0.41
Propylene	11.15	6.5	*n*-Pentane	0.15	–
iso-Butane	0.34	–	Pentene-1	1.11	0.61

Table 4

Characteristics of the condensate from cracking of *n*-heptane

Temp., °C	Fractional composition, %: up to 98°	Fractional composition, %: 98°	Fractional composition, %: above 98°	d_4^{20}	n_D^{20}	Iodine number
Initial *n*-heptane	0	100	0	0.6803	1.3960	0
Experiments with sodium						
200	0	100	0	0.6808	1.3960	0
300	0	100	0	0.6870	1.3960	0
450	0	100	0	0.6814	1.3950	0
500	0	100	0	0.6825	1.3960	0
600	0	100	0	0.7000	1.4050	3.1
700	0	100	0	0.6846	1.3960	1.3
750	0	100	0	0.6820	1.3950	0.8
800	0	100	0	0.6803	1.3980	1.2
Experiments without sodium						
700	1.3	85.0	13.7	0.6863	1.3985	15.0
800	5.3	82.4	12.3	0.6882	1.3985	12.0

Temp., °C	Fractional composition, %: up to 98°	Fractional composition, %: 98°	Fractional composition, %: above 98°	d_4^{20}	n_D^{20}	Iodine number
Experiments with potassium hydroxide deposited on activated carbon KAD						
Initial *n*-heptane	0	100	0	0.6859	1.3880	0
600	0	100	0	0.6854	1.3880	1.5
700	0	100	0	0.6853	1.3880	3.4
800	0	100	0	0.6859	1.3889	4.0
Experiments with activated carbon KAD						
600	1.0	98.5	0.5	0.6878	1.3890	4.2
700	2.2	96.8	0.6	0.6886	1.3880	11.0
800	3.3	96.0	0.7	0.6849	1.3880	14.0
In molten aluminum						
700	15.4	80.0	4.6	0.7031	1.4110	31.8
800	16.0	80.0	14.0	0.8535	1.5470	55.8

Conversion of cyclohexane

The experiments were carried out in an autoclave with a capacity of 50 ml. By gradual heating, the specified temperature of 400 or 500° was reached. In this process the pressure increased to 20–70 atm; these conditions were maintained for two hours, then the···

the heating was switched off, and the autoclave gradually cooled. The autoclave with the thermocouple was placed on a shaker, by means of which stirring was carried out. For each temperature, experiments were conducted in the presence of sodium and in its absence.

At 500° in the absence of sodium, cyclohexene began to be converted into a viscous resinous product (specific gravity 0.9103), with formation of 2% gaseous products. In the presence of sodium, small changes were observed: a decrease in the iodine number and formation of about 1.4% gas.

Table 5

Characteristics of cyclohexene heated in an autoclave

Heating temperature	Iodine number	n_D^{20}	d_4^{20}	Note
Initial cyclohexene	276	1.4480	0.8072	
400° with Na	274	1.4480	0.8097	Light-colored, homogeneous
400° with Na	278	1.4480	0.8122	Dark
500° with Na	203	1.4570	0.8192	Light-colored, homogeneous
500° with Na	74	1.4640	0.9103	Dark, resinified
500° with KOH	117	1.4475	0.8097	Slightly colored

Thus, it has been shown for the first time that molten sodium and potassium hydroxide strongly inhibit the pyrolysis of *n*-heptane at 700–800° under atmospheric pressure, as well as the condensation of cyclohexene at 500° in an autoclave under pressure, whereas molten aluminum exerts an accelerating effect on the cracking of *n*-heptane at 700–800° and atmospheric pressure; i.e., cracking of *n*-heptane in a medium of molten aluminum proceeds to a greater depth, and 3–5 times more gas is formed than when the reaction is carried out in the absence of aluminum.

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Note: Figure translations are in progress. See original paper for figures.