ASSESSMENT OF THE THERMODYNAMIC PROBABILITY OF NAPHTHENES FORMATION BY HYDROGEN TRANSFER REACTIONS FROM CYCLOOLEFINS, DURING THEIR PROCESSING ON ZEOLITE

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Nowadays, one of the most actively developing areas in the field of catalysis is the use of zeolite catalysts [1]. In recent years, increasing attention has been focused on zeolites as catalysts for oil and gas processing, as well as the synthesis of certain organic substances.

One of the processes in which zeolites are used as catalysts is zeoforming. The zeoforming process provides an increase in the antiknock rating of gasoline, and, unlike catalytic reforming, in this process, the expensive platinum catalyst and circulation of hydrogen-burning gas are not used.

The use of mathematical models of productions on a physical and chemical basis is becoming more and more relevant in the refining industry. To build a mathematical model of zeoforming process requires knowledge of the process chemistry, the main reactions, as well as knowledge of thermodynamic and kinetic parameters of these reactions.

The formalized scheme of the transformation of stable gas condensate on the zeolite catalyst in-

Table 1. Thermodynamic parameters of reactions

№	Reaction	Δ*H*, kJ/mol	Δ*S*, kJ/mol•K	Δ*G*, kJ/mol
1	**2**	**3**	**4**	**5**
	648 K			
1	3(6-methylcyclohexene-1)=2(methylcyclohexane)+toluene	–177.28	1.93	–178.53
2	3(6-ethylcyclohexene-1)=2(ethylcyclohexane)+ethylbenzene	–177.94	–15.62	–167.81
3	3(3,6-dimethylcyclohexene-1)=2(1,4-dimethylcyclohexane)+p-xylene	–182.74	17.66	–194.18
4	3(3-ethyl-6-methylcyclohexene-1)=2(1-ethyl-4-methylcyclohexane)+1-ethyl-4-methylbenzene	–188.40	–26.14	–171.46
5	3(5,6-dimethylcyclohexene-1)=2(1,2-dimethylcyclohexane)+o-xylene	–176.68	–31.84	–156.04
6	3(5-methyl-6-ethylcyclohexene-1)=2(1-methyl-2-ethylcyclohexane)+1-methyl-2-ethylbenzene	–171.81	–7.75	–166.79
7	3(3,5,6- trimethylcyclohexene-1)=2(1,3,4- trimethylcyclohexane)+1,3,4-trimethylbenzene	–192.98	25.52	–209.51
	673 K			
1	3(6-methylcyclohexene-1)=2(methylcyclohexane)+toluene	–177,33	1,85	–178,58
2	3(6-ethylcyclohexene-1)=2(ethylcyclohexane)+ethylbenzene	–178,03	–15,81	–167,39
3	3(3,6-dimethylcyclohexene-1)=2(1,4-dimethylcyclohexane)+p-xylene	–182,80	17,57	–194,62
4	3(3-ethyl-6-methylcyclohexene-1)=2(1-ethyl-4-methylcyclohexane)+1-ethyl-4-methylbenzene	–188,68	–26,57	–170,80
5	3(5,6-dimethylcyclohexene-1)=2(1,2-dimethylcyclohexane)+o-xylene	–176,76	–31,96	–155,25
6	3(5-methyl-6-ethylcyclohexene-1)=2(1-methyl-2-ethylcyclohexane)+1-methyl-2-ethylbenzene	–171,88	–7,85	–166,60
7	3(3,5,6- trimethylcyclohexene-1)=2(1,3,4- trimethylcyclohexane)+1,3,4-trimethylbenzene	–193,03	25,43	–210,15

End of table 1.

1	2	3	4	5
	698 K			
1	3 (6-methylcyclohexene-1) = 2 (methylcyclohexane) + toluene	–177.38	1.78	–178.62
2	3 (6-ethylcyclohexene-1) = 2 (ethylcyclohexane) + ethylbenzene	–178.09	–15.93	–166.98
3	3 (3,6-dimethylcyclohexene-1) = 2 (1,4-dimethylcyclohexane) + p-xylene	–182.85	17.48	–195.06
4	3 (3-ethyl-6-methylcyclohexene-1) = 2 (1-ethyl-4-methylcyclohexane) + 1-ethyl-4-methylbenzene	–188.96	–26.98	–170.13
5	3 (5,6-dimethylcyclohexene-1) = 2 (1,2-dimethylcyclohexane) + o-xylene	–176.82	–32.06	–154.44
6	3 (5-methyl-6-ethylcyclohexene-1) = 2 (1-methyl-2-ethylcyclohexane) + 1-methyl-2-ethylbenzene	–171.95	–7.94	–166.41
7	3 (3,5,6- trimethylcyclohexene-1) = 2 (1,3,4- trimethylcyclohexane) + 1,3,4-trimethylbenzene	–182.48	10.91	–190.09

cludes the reactions of naphthenes formation by hydrogen transfer in the cycloolefins. The aim of this work is to calculate the thermodynamic parameters of these reactions.

The following tasks have been addressed to achieve this goal:

1) Analysis of the stable gas condensate zeoforming products, using the chromatographic methods, has been carried out;

2) A list of theoretical possible reactions has been drawn up;

3) Thermodynamic parameters in the Gaussian software (GaussianView 5.0) the package was calculated for the formed list of reactions [2].

The calculation was carried out under the conditions of the zeoforming process temperature: 648, 673, and 698 K (375, 400, and 425 °C, respectively), pressure 2.5 atm.

The table shows the results of the calculation of thermodynamic parameters of hydrogen transfer reactions in cycloolefins at three different temperatures.

The presented results allow us to conclude that the course of all the reactions considered in the context of the process of zeoforming of light hydrocarbon feedstock is thermodynamically possible ($\Delta G < 0$). In addition, the results show that Gibbs energy highest for reaction No. 7, the product of which is 1,3,4-trimethylcyclogexane.

References

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