

FORMALIZED SCHEME FOR THE FORMATION OF XYLENES AND ETHYLBENZENE BY HYDROGEN TRANSFER REACTIONS IN OLEFINS DURING PROCESSING ON ZEOLITES

K.E. Mardanov, A.A. Altynov

Scientific supervisor – engineer of Division for Chemical Engineering A.A. Altynov

Linguistic advisor – engineer of Division for Chemical Engineering A.A. Altynov

Tomsk Polytechnic University

634050, Russia, Tomsk, Lenina Avenue, 30, kem2@tpu.ru

In recent years zeolites have been widely used as catalysts in the field of refining and petrochemistry. Promising zeolite-containing catalysts make it possible to obtain high-octane components of motor gasoline from light hydrocarbon feedstock without the introduction of any additives and additional compounding.

Previous studies on the composition of stable gas condensates (SGC) processed products on the zeolite derived from various fields of Western Siberia [1], using gas chromatography, have allowed to determine the content of xylenes and ethylbenzene in the obtained products. The presence of these components can be explained by the fact that the KN-30 brand zeolite catalyst, ZSM-5 structural type, provided by the Novosibirsk Chemical Concentrate Plant for this study, has an increased selectivity in relation to aromatic compounds.

Thus due to increased activity in the aromatization reactions and increased selectivity of the zeolite structural type in the zeoforming process it is possible to form xylenes and ethylbenzene through intermediate olefins.

Based on the above it was decided to include in the SGC transformation formalized scheme on the zeolite catalyst the hydrogen redistribution reaction in olefins with the formation of xylenes and ethylbenzene.

The purpose of this work is to formalize the formation scheme of xylenes and ethylbenzene by redistribution of hydrogen in olefins on the zeolite catalyst in the zeoforming process.

Based on the analysis of the feedstock and process products composition, as well as theoretical knowledge about the mechanism of the ongoing transformations, a list of possible reactions was compiled. The full list consists of 240 reactions. Tables 1, 2 provide the results of calculation of the thermodynamic parameters of xylenes (by the example of p-xylene) and ethylbenzene formation, characterized by the lowest values of Gibbs energy (ΔG).

Reaction thermodynamic characteristics were calculated using quantum chemistry techniques in the Gaussian Software Environment (Gaussian View 5.0) [2]. The calculated values of Gibbs energy showed that all reactions under the conditions of zeoforming process implementation (process temperatures of 375 °C (648 K); 400 °C (673 K); 425 °C (698 K) and pressure of 2.5 atm.) are thermodynamically possible.

It is clear from the presented results that the value of Gibbs energy reactions decreases with the temperature increase. Based on the list of reactions received the hydrocarbon transformations formalized scheme will look like this (Figure).

Table 1. Thermodynamic characteristics of hydrogen redistribution reactions in olefins with xylenes formation

No.	Reaction	ΔG at P=2.5 atm.		
		648 K	673 K	698 K
1	2(Hexene-2)+3(Heptene-2)=3(Xylenes)+9(Methane)	-837.96	-858.55	-885.64
2	7(Hexene-2)+2(Heptene-2)=4(Xylenes)+12(Ethane)	-1015.44	-1035.73	-1078.19
3	7(Propene)+5(Hexene-2)=3(Xylenes)+9(Propane)	-729.27	-725.59	-738.40
4	8(Propene)+6(Hexene-2)=3(Xylenes)+9(Butane)	-678.06	-666.44	-674.55
5	9(Propene)+7(Hexene-2)=3(Xylenes)+9(Pentane)	-614.14	-594.23	-597.33
6	10(Propene)+8(Hexene-2)=3(Xylenes)+9(Hexane)	-567.31	-539.61	-508.93
7	11(Propene)+9(Hexene-2)=3(Xylenes)+9(Heptane)	-493.47	-457.08	-450.33
8	12(Propene)+10(Hexene-2)=3(Xylenes)+9(Octane)	-466.31	-411.44	-400.51

Table 2. Thermodynamic characteristics of hydrogen redistribution reactions in olefins with ethylbenzene formation

No.	Reaction	ΔG at P=2.5 atm.		
		648 K	673 K	698 K
1	2 (Hexene-2)+3 (Heptene-2)=3 (Ethylbenzene)+9 (Methane)	-766.87	-785.35	-810.44
2	7 (Hexene-2)+2 (Heptene-2)=4 (Ethylbenzene)+12 (Ethane)	-920.65	-938.14	-977.93
3	7 (Propene)+5 (Hexene-2)=3 (Ethylbenzene)+9 (Propane)	-658.18	-652.40	-663.20
4	8 (Propene)+6 (Hexene-2)=3 (Ethylbenzene)+9 (Butane)	-606.97	-593.25	-599.35
5	9 (Propene)+7 (Hexene-2)=3 (Ethylbenzene)+9 (Pentane)	-543.05	-521.03	-522.13
6	10 (Propene)+8 (Hexene-2)=3 (Ethylbenzene)+9 (Hexane)	-496.22	-466.41	-433.73
7	11 (Propene)+9 (Hexene-2)=3 (Ethylbenzene)+9 (Heptane)	-422.38	-383.88	-375.41
8	12 (Propene)+10 (Hexene-2)=3 (Ethylbenzene)+9 (Octane)	-395.22	-338.24	-325.31



Fig. 1. Formalized scheme of xylenes and ethylbenzene formation

References

1. Altynov A.A., Bogdanov I.A., Temirbolat A.M., Belinskaya N.S., Kirgina M.V. // *Oil Processing and Petrochemistry*, 2019. – Vol. 11. – P. 9–14. (in Russ).

2. Ochterski J.W. *Thermochemistry in Gaussian. Gaussian, Inc., 2000. – 19 p.*

DIRECTIONS OF CONVERSION OF DIESEL FRACTION HYDROCARBONS, DURING THEIR HYDROGEN-FREE PROCESSING ON ZEOLITE

E.I. Martyanova, I.A. Bogdanov

Scientific supervisor – researcher of Division for Chemical Engineering I.A. Bogdanov
Linguistic advisor – researcher of Division for Chemical Engineering I.A. Bogdanov

*Tomsk Polytechnic University
634050, Russia, Tomsk, Lenin Ave. 30, martyanova.1999@yandex.ru*

The active development of the Arctic territories and the Northern Sea Route led to the need to increase the production of low-freezing diesel fuels. The development of a process for processing straight-run diesel fractions (DF) into low-freezing fuels without the use of hydrogen-bearing gas and expensive catalysts is an urgent task. The aim of this work is to study the directions of the conversion of DF hydrocarbons during their processing on a zeolite catalyst. For this, a process of hydrogen-free processing of three straight-run DFs with various compositions (Feedstock 1–3) on a zeolite catalyst

was implemented at a laboratory catalytic unit. The process technological parameters are temperature 375 °C, pressure 0.35 MPa, feedstock space velocity 0.5 ml/s.

Table 1 shown the fractional composition of straight-run DF, determined according to [1].

Table 1. Fractional composition of straight-run DF

Distillation volume, ml	Temperature, °C		
	Feedstock 1	Feedstock 2	Feedstock 3
10	170	190	183
50	242	261	263
90	348	329	369