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CONVERSION OF C₄ FRACTION OF HYDROCARBON PYROLYSIS PRODUCTS OVER ZVM+2 % Zn HIGH-SILICA ZEOLITE CATALYST

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Abstract. Conversion of C₄ fraction of hydrocarbon pyrolysis products over high-silica zeolite catalyst ZVM modified by 2 mas % of Zn within the temperature range of 623–823 K and volumetric flow rates of 1000–10000 h⁻¹ has been investigated. The yield and chemical composition of gaseous and liquid products have been determined under various conditions. It has been shown that the initial fraction is converted almost completely (98–100 %); the yield of C₆–C₈ lower arenes is 44.2–65.4 % within all investigated ranges of temperature and volumetric flow rates.

Keywords: high-silica zeolite, ethylene, propylene, lower arenes, C₄ fraction, catalysate, volumetric flow rate.

1. Introduction

The production of lower olefins *via* hydrocarbons pyrolysis is constantly growing. The general productivity of pyrolysis plants in the world exceeds 100 million tons of ethylene per year. As mentioned in [1], in the nearest future the general world production of ethylene will achieve 150 million tons. At many lower olefins plants propylene is produced together with ethylene production. The yield of propylene is 40–50 % of ethylene yield. In Ukraine there are two lower olefins plants: “Lukor” concern, Kalush, and refinery in Lysychansk. At the majority of lower olefins plants gasoline and gas oil fractions are used as raw materials. At the pyrolysis of the mentioned raw materials the total yield of ethylene and propylene does not exceed 50 mas %; C₄, C₅, C₆–C₈ and C₉ fraction, heavy products (resins), and dry gas (methane and hydrogen) are obtained as well.

The C₆–C₈ fraction contains mainly lower aromatic hydrocarbons (benzene, toluene, xylenes, and ethylbenzene). Benzene is produced from the mentioned fraction using hydrodealkylation. The benzene yield achieves ~10 mas % and essentially rises the production profitability [2, 3].

To achieve high techno-economic indexes of the hydrocarbons high-temperature pyrolysis, usage of other

fractions, namely C₄ fraction, is of great importance. The yield and composition of C₄ fraction depends upon fractional and chemical compositions of the initial raw material and pyrolysis conditions. At the pyrolysis of gasoline and gas oil fractions at the temperatures of 1103–1123 K C₄ fraction contains mainly butenes (1-butene, 2-*cis*-butene, 2-*trans*-butene, *iso*-butene) and 1,3-butadiene. The total content of butenes (mas %) is 50–52 and the content of 1,3-butadiene is 44–48. The C₃, C₅, *iso*- and *n*-butanes, methylacetylene, and vinylacetylene are present in negligible quantities in C₄ fraction. The fraction yield is 8–10 mas % of the raw material.

In a number of countries at large petrochemical plants C₄ fraction is divided into separate components and it is a main source of 1,3-butadiene, *iso*-butene and *n*-butenes production with further using of the obtained products for the production of caoutchouc, methyltertbutyl ether and other products of organic synthesis. The block of C₄ fraction processing using extraction methods of its division is a part of large-tonnage pyrolysis plants [2, 3]. However, the implementation of such variant is highly capital and energy consuming and may be economic only using complex processing of hydrocarbon raw materials and complex application of obtained products.

At some lower olefins plants, particularly in Ukraine, C₄ fraction is hydrated to butanes, which are further directed to the pyrolysis furnace. At such a way of C₄ fraction processing, taking into account additional outlay on hydration, its cost is practically equal to the cost of pyrolysis raw material and is considerably lower than that of the pyrolysis main products: ethylene, propylene, and benzene. Due to the above reasons the search of a more economic method of C₄ fraction processing is of great practical interest. The processes which allow to obtain valuable products at minimum possible capital and energy outlay with maximum possible usage of existing technologies and pyrolysis equipment attract a special interest. One of the ways of C₄ fraction processing at industrial pyrolysis plants could be production of lower arenes and C₂–C₃ gaseous alkenes in the result of the

conversion of butenes and butadienes presented in C₄ fraction over high-silica zeolites.

A great amount of experimental and theoretical works is dedicated to the problem of catalytic conversion of gaseous hydrocarbons including C₂-C₄ alkenes over high-silica zeolite catalysts [4-8]. The regularities of alkenes conversion within the temperature range of 573–873 K and volumetric flow rates (ratio between volumetric gas consumption and catalyst volume) of 300–3000 h⁻¹ were investigated over non-modified and modified by various metals (Zn, Ga, Cd, Ni, Co) high-silica zeolites of the ZSM type. Under corresponding conditions the alkene conversion is almost complete; the liquid catalyzate yield containing mainly lower arenes is 60–80 % [9, 10]. During the process the catalyst is carburized and in 5–6 h its activity essentially reduces. After carbon burning with air the catalyst activity recovers [11]. The industrial processes of lower arenes production *via* conversion of gaseous alkanes [12] and gases containing a considerable amount of alkenes [13] are well-known. Reactors with fluidized catalyst bed are widely used in the mentioned processes.

The work [14] deals with the results concerning alkenes conversion over modified high-silica catalyst ZVM + 2 mas % of Zn within a wide range of volumetric flow rates (VFRs). It has been established that at 773 K and VFRs of 10000–20000 h⁻¹ the high conversion of propylene and butylene (~ 90 %), as well as high yield of the liquid catalyzate (~ 55 %) are achieved. Under the mentioned conditions it is possible to implement the process of arenes production from gaseous alkenes of hydrocarbons cracking processing in the reactor with multi-stage location of the fixed catalyst bed. Depending upon productivity and serving cycle of the catalyst the number of stages may be from 10 to 20. In such reaction block with two reactors raw material will be supplied to separate stages by turns and regeneration of the catalysts of these stages will be done simultaneously. The implementation of the mentioned process allows to cut down capital and energy outlay as well as to reduce losses of the expensive catalyst compared with the fluidized bed reactor.

It has been shown in [15] that at C₄ fraction conversion (with the joint content of butenes and 1,3-butadiene of 95 mas %) at the temperatures of 750–800 K and VFRs of 1000–2000 h⁻¹ almost complete conversion of the initial hydrocarbons is reached and the liquid catalyzate yield is 70 mas %. The liquid catalyzate contains lower arenes mainly. In order to specify the industrial process conditions the investigations of the mentioned fraction conversion were carried out at different temperatures within the wide range of VFRs over high-silica zeolite catalyst ZVM + 2 mas % of Zn. The yield and composition of the liquid catalyzate and gaseous products were determined.

2. Experimental

C₄ fraction (BBF) obtained from the pyrolysis of liquid hydrocarbon raw material was provided by Kalush concern "Lukor" (Ukraine). The fraction composition is as follows (mas %): 1,3-butadiene – 44; total butenes – 51; other compounds – 5. The catalyst was obtained on the basis of ZVM zeolite (ammonium form) which was prepared at Angarsk catalyst plant (Russia). The characteristics of the used zeolite are described in [14, 16]. We obtained the hydrogen form of zeolite by calcination in the hot air and then modified it by aqueous solution of zinc acetate using infiltration method. Zinc concentration was varied from 0.5 to 2.5 mas %. The catalyst activity and selectivity were determined using fractional conversion of the raw material and the yield of liquid catalyzate. The catalyst modified with 2 mas % of Zn had the best results with regard to activity and selectivity of desired products. In order to increase the catalyst mechanical strength we used γ -Al₂O₃ as a binding agent. The experiments were carried out at a laboratory plant of continuous type. The reactor was a quartz tube with internal diameter of 6 mm situated in the electric furnace. There was a layer of fine-grained catalyst inside it. The catalyst volume was 2 cm³. The scheme of the laboratory plant, experimental procedure and analysis methods are described in [14, 17].

3. Results and Discussion

The experiments were carried out within the temperature range of 623–823 K at 1000 h⁻¹ and within the VFR range of 1000–10000 h⁻¹ at 773 K. The results are represented in the Table.

One can see from the results that under the mentioned conditions almost complete conversion (98–100 %) of unsaturated compounds of C₄ fraction is achieved with the formation of liquid catalyzate and gaseous products. The yield of the liquid catalyzate is from 73.2 to 76.4 mas %. The temperature decrease from 823 to 623 K insignificantly decreases the initial hydrocarbons fractional conversion and the liquid catalyzate yield. The VFR increase from 1000 to 10000 h⁻¹ at 773 K has the same effect.

Similarly as at C₂-C₄ alkenes conversion over high-silica zeolite modified by metals, the obtained liquid catalyzate mainly contains lower arenes (benzene, toluene, xylenes). At the temperatures of 773–823 K the lower arenes content is ~85 % mas in the liquid catalyzate. One can see the changes in its composition depending upon reaction temperature and VFR. The increase of temperature decreases the content of aliphatic hydrocarbons and C₉₊ fraction, significantly increases the toluene content and to a lesser degree - the content of xylenes and benzene. The VFR increase from 1000 to 10000 h⁻¹ and corresponding reduction of reaction time decrease the toluene content and increase the content of xylenes and benzene.

Table

Catalytic conversion of the C₄ fraction over ZVM + 2 % mas of Zn

Temperature, K	Volumetric flow rate, h ⁻¹	Composition of gaseous products, % mas										Composition of liquid catalyzate, % mas					C ₄ fractional conversion, %	Yield of liquid catalyzate, % mas	Mass ratio : benzene : toluene : xylenes
		H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	ΣC ₄ H ₁₀	BBF	Aliphatic hydrocarbons	Benzene	Toluene	Xylenes	C ₉₊					
623	1000	3.66	2.49	4.4	12.57	48.58	15.04	12.51	0.75	22.5	17.2	24.2	19.1	17.0	99.6	73.2	1.41:1:1.1		
673	1000	4.56	4.9	4.7	11.4	47.63	14.4	12.2	0.21	18.2	19.1	25.8	20.4	16.5	99.9	75.9	1.35:1:1.1		
723	1000	4.82	5.41	6.12	11.2	45.24	13.12	14.09	-	10.2	20.1	32.4	22.2	15.1	100.0	76.0	1.35:1:1.1		
773	1000	5.03	6.49	6.47	11.84	43.86	11.02	15.2	-	4.3	21.6	35.9	26.1	12.1	100.0	76.4	1.7:1:1.1		
823	1000	5.12	7.21	5.98	11.51	43.65	10.71	15.82	-	3.3	20.9	39.3	26.3	10.2	100.0	75.4	1.8:1:1.25		
773	2000	5.00	6.02	6.28	11.66	43.02	14.35	18.83	-	4.1	21.4	33.4	29.1	12.0	99.6	76.1	1.6:1:1.34		
773	5000	4.6	4.70	5.8	12.56	47.46	8.01	16.77	-	4.3	22.0	31.3	30.3	12.4	99.2	75.8	1.4:1:1.37		
773	10000	4.4	4.4	5.3	12.5	46.88	7.53	17.10	2.24	4.2	22.4	31.7	32.5	9.2	98.9	75.5	1.4:1:1.5		

The investigated catalyst has acid activity [18] and at the mentioned temperatures the disproportionation reaction may proceed: $2C_6H_5CH_3 = C_6H_6 + C_6H_4(CH_3)_2$. At the achievement of thermodynamic equilibrium at 700–900 K molar ratio of toluene : benzene : xylenes (total *ortho*-, *para*-, *meta*-xylene) is 0.47:0.265:0.265 (1.77:1:1) [19]. The corresponding mass ratio of the mentioned components in the equilibrium mixture is 2.09:1:1.36. The toluene amount is the greatest (47 mas %). The results from the Table show that the mass ratio differs from the equilibrium one. The toluene amount is lower compared to the equilibrium amount.

The possible reason is that at the conversion of 1,3-butadiene and butenes over high-silica zeolite modified by zinc the amount of each formed lower arene and their corresponding amount in the liquid catalyzate are determined by the kinetics of formed compounds and intermediate products of their conversion. At the same time the results show the possibility of proceeding of the above mentioned disproportionation reaction. The increase of temperature increases the reaction rate and toluene content in the liquid catalyzate. At 823 K and VFR of 1000 h^{-1} the real mass ratio between the mentioned compounds is equal to the equilibrium ratio. Obviously, the change in products composition with the change of VFRs is also connected with the disproportionation reaction proceeding. At the decrease of VFR and corresponding increase of disproportionation reaction time toluene : benzene : xylenes the mass ratio verges toward equilibrium resulting in the increase of toluene content in the liquid catalyzate.

Gaseous products of C_4 conversion contain hydrogen, alkanes and alkenes. The increase of temperature increases the content of hydrogen, methane, and ethane and decreases the content of propylene, propane, and butanes in the products. The increase of VFR from 1000 to 10000 h^{-1} leads to the minor decrease of hydrogen and methane content in the gaseous products. The propane content increases slightly. The content of other reaction products (ethylene, propylene, butanes) changes insignificantly with the change of VFR. It should be noted that at C_4 fraction conversion over high-silica catalyst ZVM + 2 mas % of Zn the methane content in gaseous products is small (~4.5 mas %). The fractional conversion of initial hydrocarbons into methane is about 1 mas %. Gaseous products mainly contain C_2 - C_4 hydrocarbons out of which the total content of ethylene and propylene is ~20 mas % and the content of C_2 - C_4 alkanes is ~70 mas %.

Taking into account experimental results the industrial catalytic process of C_4 fraction conversion should be implemented under atmospheric pressure at the temperature of 773 K and VFR of 10000 h^{-1} . The high fractional conversion of the raw material (98 %) and high yield (65.4 mas %) of lower arenes (C_6 - C_8) are achieved under such conditions. The process may be implemented in

the reactor with multi-stage location of the catalyst fixed bed. If the plant productivity is 100000 tons of C_4 fraction per year (~12 tons per hour, 5000 m^3 of gaseous mix per hour), ~0.5 m^3 of the catalyst should be placed in the reaction zone of one stage. For 10–20 stages the total catalyst volume should be 5–10 m^3 .

At C_4 fraction conversion over ZVM + 2 mas % of Zn under the conditions mentioned in the Table the obtained chemical compounds are similar to those produced during the high-temperature industrial pyrolysis. Therefore, the developed process allows to direct the reaction products to the general flow of hydrocarbon pyrolysis products after tube furnace. It is necessary to quench pyrolysis products before and then they may be fractionated and processed. Correspondingly, benzene will be produced from lower arenes; ethylene and propylene are desirable products of pyrolysis plant; ethane, propane and butanes will be directed to the pyrolysis furnace.

At such C_4 fraction conversion at the industrial pyrolysis plants the yield of benzene is ~53 mas %, ethylene and propylene – 5 mas %, total yield of C_2 - C_4 alkanes, which are used as pyrolysis raw material – 15 mas %.

Industrial implementation of the mentioned process requires relatively low capital outlays on the creation of the above described reaction block. Existing equipment is used to divide the reaction products and obtain benzene from C_6 - C_8 arenes.

4. Conclusions

Almost complete conversion (98 %) of C_4 fraction of hydrocarbon pyrolysis products is achieved at 773 K and volumetric flow rate of 10000 h^{-1} over high-silica zeolite catalyst ZVM modified by 2 mas % of Zn. The yield of lower arenes C_6 - C_8 is sufficiently high (~65 mas %). It is advisable to introduce the described process of lower arenes obtaining *via* conversion of C_4 fraction over ZVM + 2 mas % of Zn into industrial production of lower olefins.

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**ПЕРЕТВОРЕННЯ ФРАКЦІЇ C₄ ПРОДУКТІВ
ПІРОЛІЗУ ВУГЛЕВОДНЕВОЇ СИРОВИНИ
НА МОДИФІКОВАНОМУ
ВИСОКОКРЕМНЕЗЕМИСТОМУ ЦЕОЛІТОВОМУ
КАТАЛІЗАТОРІ ЦВМ+2% МАС. Zn**

Анотація. Проведені дослідження реакції перетворення фракції C₄ продуктів піролізу рідкої вуглеводневої сировини на модифікованому цинком висококремнеземистому цеолітовому каталізаторі ЦВМ + 2 % мас. Zn за температур 623–823 K і об'ємних швидкостях 1000–10000 год⁻¹. За різних умов перебігу реакції визначено вихід і хімічний склад газоподібних і рідких продуктів реакції. Показано, що за вказаних умов досягається практично повне перетворення вихідної фракції (98–100 %); вихід нижчих аренів C₆-C₈ становить 44,2–65,4 % мас.

Ключові слова: висококремнеземисті цеоліти, етилен, пропілен, нижчі ариени, фракція C₄, каталізатор, об'ємна швидкість.