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OBTAINING OF HIGH-OCTANE COMPONENTS BY CONVERSION OF HYDROCARBON RAW MATERIAL ON HIGH-SILICA ZEOLITES

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Abstract. Catalytic conversion of gaseous alkanes, alkenes and gasoline fractions over high-silica zeolites of ZSM-5 type has been studied. The optimal condition for the production of high-octane components of motor fuels over ZVM+2% mass of Zn modified catalyst and non-modified catalyst ZVN have been established.

Keywords: zeolite-containing catalyst, arenes, isoalkanes, petrol fractions, catalyzate.

1. Introduction

Development of combustion engines and increase of ecological requirements to petrol entailed the necessity in high-octane components of motor fuels. Today high-octane components are produced using reforming, alkylation and isomerization, which are power-consuming and capital-intensive processes. Therefore, the development of new processes of high-octane components production including processes with alternative raw material is of great importance.

The number of foreign firms carries out researches of hydrocarbon gases conversion over high-silica zeolites. Industrial processes of aromatic hydrocarbons production are implemented [1, 2]. In Ukraine the processes of high-octane components production by catalytic conversion of hydrocarbon raw material over high-silica zeolites are absent.

2. Experimental

At the Department of Chemical Technology of Oil and Gas Refining of Lviv Polytechnic National University catalytic conversion of gaseous alkanes, alkenes as well as petrol fractions of primary and secondary origin over high-silica zeolites of ZSM-5 type has been investigated. Zeolite catalysts based on zeolites of ZVM and ZVN types are produced at Angarsk catalyst plant. Physico-chemical characteristics of above mentioned zeolites are presented in Table 1.

Table 1

Characteristics of ZVM and ZVN zeolites

Index	Zeolite brand	
	ZVM	ZVN
Silicate module (SiO_2:Al_2O_3)	23	26
Specific surface, m^2/g	400-450	420-500
Static adsorption capacity, cm^3/g:		
– by water vapors	0.08	0.06
– by heptane vapors	0.16-0.18	0.17-0.20
Na_2O content, mass %	<0.01	<0.05

ZVM and ZVN zeolites are differed by their method of preparation and usage of organic additions. ZVM is a high-silica zeolite obtained by crystallization of alumo-silica gels under hydrothermal conditions without organic components. ZVN is a catalyst of the pentasyl class with a very low content of inorganic cation. The essential principle of its synthesis is a considerable cross-linking effect of cation of a strong organic bases, which is able to operate as a compensating cation. Amine alcohols or amines (1,6-diaminehexane, 1,3-diaminepropane, etc.) are organic bases of the catalysts.

ZVM zeolite modified with 2 mass % of zinc and non-modified ZVN zeolite were used as catalysts. 30 % of the linking agent (g-Al_2O_3) was added to ZVM zeolite for the increase of the catalyst mechanical strength. The industrial ZVN catalyst is used in the processes of petroleum refining and petrochemistry and has the sufficient strength.

3. Results and Discussion

The results of researches of catalytic conversion of gaseous alkanes, alkenes and petrol fractions over mentioned catalysts are represented in [3, 4, 5, 6]. Aromatic hydrocarbons are main products obtained over ZVM+2 mass % Zn. Isoalkanes and aromatics are obtained over ZVN.

This work deals with the generalized experimental results of catalytic conversion of gaseous alkenes and petrol fractions over above-mentioned catalysts with the purpose of obtaining motor fuel high-octane components.

Results of the propylene catalytic conversion over ZVM+2 mass % Zn and ZVN are presented in Table 2. Almost complete propylene conversion and high selectivity to liquid catalyzate formation are achieved under experimental conditions. The liquid catalyzate consists of alkanes and arenes. It should be noted that the high selectivity to high-octane components formation is achieved at lower temperatures over ZVN catalyst in comparison with ZVM+2 mass % Zn. Since over ZVN catalyst with the temperature increase the part of cracking reactions increases as well.

Liquid products obtained at propylene conversion over ZVM+2 mass % Zn contain mainly aromatic hydrocarbons. Therefore, at propylene conversion over ZVN catalyst aliphatic liquid hydrocarbons of isometric structure are the main products. The composition of the catalyzate obtained at propylene catalytic conversion over ZVN under optimum conditions, is presented in Fig. 1.

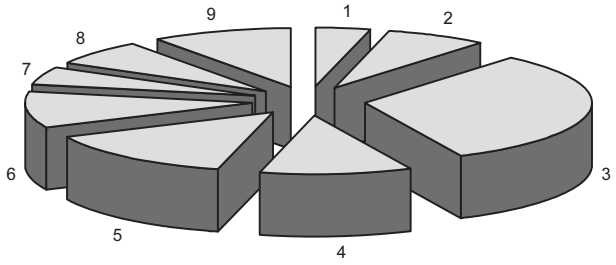

Fig. 1. Composition of catalyzate obtained at propylene conversion (ZVN catalyst, T = 623 K, W = 1000 hour^{-1}) 1 – n-pentane (4%); 2 – i-pentane (7%); 3 – 2,3-dimethylbutane (32%); 4 – 2,2,3-trimethylbutane (11%); 5 – 2,2,-dimethylbutane (14%); 6 – benzene (10%); 7 – toluene (5%); 8 – xylenes (7%); 9 – C_{9+} (10%)

We can see from Fig. 1 that the iquid catalyzate mainly contains alkanes and C_5-C_7 isoalkanes, in particular: isopentane with the octane number O.N.= 90; dimethylbutane – O.N.= 95; 2,2,3-dimethylbutane –O.N.= =101; 2,2-dimethylbutane – O.N.= 96.

Gaseous products mainly consist of hydrogen, C_1-C_4 alkanes andC_2-C_4 alkenes. Their total concentration varies from 6 to 8 %.

The similar composition of the products is obtained at ethylene and butylene conversion over ZVN catalyst.

Under assigned conditions the modified and non-modified ZVN catalysts have the low selectivity in the reactions of gaseous alkanes conversion. The liquid catalyzate yield does not exceed 20 % since cracking reactions mainly proceed.

The results of the catalytic conversion of the straight-run petrol fraction and the petrol fraction of the low-level thermal cracking over ZVM+2 mass % Zn and ZVN catalysts under optimum conditions are represented in Tables 3 and 4, the maximum yield of the high-octane catalyzate is achieved.

As we can see from the tables, the catalyzate obtained at the conversion of the petrol fraction of low-level thermal cracking over ZVM+2 mass % Zn, mainly consists of aromatic hydrocarbons (benzene-toluene-xylenes). Under similar conditions aromatics content exceeds the content of arenes in the catalyzate obtained at conversion of straight-run petrol by 30 %. Conversion degrees of alkanes and cycloalkanes obtained at low-level thermal cracking are higher in comparison with degrees of similar hydrocarbons of straight-run petrol. It is explained by the fact, that alkenes are active in the aromatization reaction and increase the conversion rate of initial alkanes and cycloalkanes. In other words, the presence of alkenes favors the deeper aromatization of raw material.

Table 2

Propylene catalytic conversion

Temperature, K	Space velocity, hour^{-1}	Conversion degree, %	Catalyzate yield, mass %	Composition of liquid catalyzate , mass %					Composition of gaseous products, vol. %								
				aliphatic hydrocarbons	benzene	toluene	C_8	C_9-C_{12}	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	iso-C_4H_{10}	n-C_4H_{10}	ΣC_4H_8
ZVM+2 mass % Zn catalyst																	
773	1000	96.7	66.2	3.2	21.7	45.9	26.1	3.1	47.7	10.1	5.7	3.1	27.1	2.9	2.0	1.4	-
ZVN catalyst																	
673	1000	97.8	66.0	65.2	11.4	5.9	9.1	8.4	28.5	1.2	6.3	5.9	39.2	9.2	4.7	5.0	-

Table 3

Conversion of straight-run petrol fraction (hydrocarbon type content, mass %: arenes - 10.1; n-alkanes - 31.2; isoalkanes - 37.4; cycloalkanes - 21.3; alkenes - 0.1)

Temperature, K	Space velocity, $hour^{-1}$	Catalyzate yield, mass %	Hydrocarbon type content of catalyzate, mass %					Composition of gaseous products, vol. %								Carbon part (%) of initial hydrocarbons converted into:		
			arenes	n-alkanes	isoalkanes	cycloalkanes	alkenes	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	ΣC_4H_{10}	ΣC_4H_8	arenes	gaseous alkanes	gaseous alkenes
ZVM+2 mass % Zn catalyst																		
773	6	68.2	28.0	12.0	35.1	22.7	2.2	24.7	3.6	3.2	9.2	31.3	12.4	14.9	0.7	23.1	3.4	72.9
ZVN catalyst																		
673	6	72.8	21.8	11.6	42.3	21.7	2.6	13.6	2.8	2.6	5.6	36.2	10.2	22.6	4.4	17.9	5.2	76.1

Table 4

Conversion of petrol fraction with unsaturated hydrocarbons (hydrocarbon type content, mass %: arenes - 13.2; n-alkanes - 32.8; isoalkanes - 27.0; cycloalkanes - 18.8; alkenes - 8.2)

Temperature, K	Space velocity, $hour^{-1}$	Catalyzate yield, mass %	Hydrocarbon type content of catalyzate, mass %					Composition of gaseous products, vol. %							Carbon part (%) of initial hydrocarbons converted into:		
			arenes	n-alkanes	isoalkanes	cycloalkanes	alkenes	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	ΣC_4H_{10}	arenes	gaseous alkanes	gaseous alkenes
ZVM+2 mass % Zn catalyst																	
823	3	58.0	87.0	2.3	6.3	4.4	-	65.0	8.7	5.4	5.0	11.4	3.2	1.4	50.8	34.6	11.4
ZVN catalyst																	
673	6	70.7	42.3	9.2	24.0	20.9	3.6	14.3	0.9	2.3	5.1	36.7	5.5	35.2	37.2	53.4	5.4

Higher selectivity to arenes formation as well as selectivity to gaseous alkenes formation is achieved at lower temperatures over ZVN catalyst in comparison with those achieved over ZVM+2 mass % Zn.

At the petrol conversion over ZVN catalyst the aromatic hydrocarbons yield is less, in comparison with their conversion over ZVM+2 mass % Zn. The catalyzate obtained at straight-run petrol conversion over ZVN catalyst contains 21.8 % of arenas and at the conversion of petrol of low-level thermal cracking – 42.3 %. Benzene content does not exceed 4 mass %.

4. Conclusions

The material balance analysis of of certain classes of hydrocarbons conversion reactions shows that alkanes and alkenes are mainly converted over ZVN catalyst with the formation of aromatic hydrocarbons and gaseous products. Conversion degrees of isoalkanes and cycloalkanes are insignificant. Therefore, the catalyzate mainly contains arenas, isoalkanes and cycloalkanes. The content of sulphur-containing compounds decreases in liquid products.

Thus, the catalyzate with the high content of arenes may be obtained over ZVM+2 mass % Zn by catalytic conversion of refinery gases containing alkenes and petrol fractions of the secondary origin. The conversion of the same raw material over ZVN catalyst results in obtaining of the catalyzate containing the considerable amount of isoalkanes and cycloalkanes, as well as arenes. Investigated processes may be alternative ones to reforming and isomerization.

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ОДЕРЖАННЯ ВИСОКООКТАНОВИХ КОМПОНЕНТІВ ПЕРЕТВОРЕННЯМ ВУГЛЕВОДНЕВОЇ СИРОВИНИ НА ВИСОКОКРЕМНЕЗЕМИСТИХ ЦЕОЛІТАХ

Анотація. *Вивчено каталітичне перетворення газоподібних алкенів і алканів та бензинових фракцій на висококремнеземистих цеолітах типу ZSM-5. Встановлені оптимальні умови одержання високооктанових компонентів моторних палив на модифікованих та немодифікованих каталізаторах марок ЦВМ+2% мас.Zn і ЦВН.*

Ключові слова: *цеолітвмісні каталізатори., арени, ізоалкани, бензинові фракції, каталізат.*