THE JOINT PROCESSING OF GASEOUS ALKANES AND NATURAL GASOLINE OVER THE H-ZEOLITE/WO_4^{2-}(SO_4^{2-})ZrO_2 CATALYTIC SYSTEMS.

Safa Abasov[1], Aynura Aliyeva[1], Surayya Agayeva[1], Rizvan Zarbaliyev[1],

Malahat Mamedova[1], Nahida Jafarova[2], Hikmet Ibrahimov[1], DilqamTagiyev[3]

1. Azerbaijan National Academy of Sciences, Y.H. Mammadaliyev Institute of Petrochemical Processes, Baku, Azerbaijan, email:

2. Azerbaijan State University of Oil and Industry, Baku, Azerbaijan

3. Azerbaijan National Academy of Sciences, Institute of Catalysis and Inorganic Chemistry, Baku, Azerbaijan

Abstract

The composite catalysts (CC), which components are HMOR or HZSM-5 or Al_2O_3, and the other components which are sulfated or tungstate ZrO_2 were studied in the joint conversion of C_2-C_4 gaseous (butane fraction; BF) and liquid (gasoline; NQ) paraffins at 0.1 mPa and 150-220°. Unlike Al_2O_3 containing CC on the H-zeolite-containing CC at 150-200°, occurs intensive consumption (conversion) of C_4-C_7 paraffins and accumulation of C_5-C_6 (syncretization) or C_5-C_7 (disproportionation) of alkanes, mainly branched structure.

It was assumed that the formation of C_5-C_6 or C_5-C_{7+} products is the result of formation of bimolecular intermediates from C_4- and C_{7+} alkanes and their subsequent decomposition depending on the composition of CC and the conditions of the process. The replacement of HMOR or HZSM-5 in the CC leads to the increаб́зну́ксing of the yield of disproportionation products. Exceeding the ratio of BF:NQ>1 leads to sharp decreasing of C_4 and C_{7+} paraffins conversion.

Key words: gaseous alkanes, natural gasoline, zeolite, catalyst, conversion, isomerization.

1.Introduction.

The modern requirements for environmentally pure gasolines demands the decrease of the contents of aromatic hydrocarbons to preserve of high octane rating. The solution to this problem is the transition of processing of normal and weakly branched alkanes from high-temperature dehydrocyclization to low-temperature isomerization. The isomerisation process of individual C_4-C_6 n-alkanes has been well researched over the sulphated or tungstated zirconia (SZ, WZ, accordingly) [1-6].

Isomerization processing of natural gasoline (NG), which is a mixture of C_5-C_7 and C_{7+} paraffins has certain difficulties. For example, if the WZ promoted by platinum or other transition metals has sufficiently high efficiency in the isomerization of C_6-C_7 n-alkanes [3,8], the presence of C_{7+} n-paraffins can lead to undesirable formation of gaseous products due to hydrocracking or hydrogenolysis of branched isomers [5,6,9]. Therefore, to maintain the high isomerizing efficiency of the catalyst, it is necessary to limit the content of C_{7+} paraffins in the feed. On the other hand, taking into account the importance of high-octane isomers of C_5-C_6 alkanes for modern gasolines, it is necessary to increase their resources due to normal and weakly branched paraffins.

International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-3, Issue-6, June 2017
ISSN: 2395-3470
www.ijseas.com

However, similar conversions of C_{7+} paraffins, without the formation of gaseous products, have not been studied.

It is known two possible mechanisms for the formation of intermediates, preceded to the formation of branched alkanes, either monomolecular or bimolecular. In the first case, the skeletal isomerization of the n-alkane occurs without changing the monomolecular weight, but in the second due to the splitting of the bimolecular intermediate the process can be accompanied by the formation of saturated hydrocarbons of large and smaller molecular weight than the substrate [10]. Passing of isomerization through the step of the formation of bimolecular intermediate is preferable for n-butane [5-6], but is also allowed for C_5-C_6 n-alkanes [2]. Therefore, it can also be assumed the acceptability of the formation of bimolecular intermediate from C_{6+} molecules and a gaseous alkane in their jointly conversions. The skeletal isomerization and hydrocracking (β-splitting) of similar intermediates will lead to the formation of C_{5+} molecules, distinct substrate molecules. This approach allows to involve in the isomerization process C_{7+} the components of NG and at least the C_4 fraction of alkanes (BF) to obtain branched C_5-C_6 alkanes. We have shown earlier a similar conversion of C_4H_{10}:n-C_6H_{14} mixture over the Ni/HMOR/SO_4^{2-}·ZrO_2 catalytic system at 140-200º [11].

The aim of this work is to show the possibility of involvement of a mixture of butane fraction and natural gasoline in the process of increasing the resource of C_5-C_6 alkanes, required for obtaining high-octane gasolines over the H-zeolite -SO_4^{2-} or WO_4^{2-}·ZrO_2 composite catalytic systems.

2.Experimental part

The object of study is composite catalysts, which the components are A(γ-Al_2O_3) or zeolites M(HMOR, SiO_2/Al_2O_3=17) or Z(HZSM-5, SiO_2/Al_2O_3=23) and sulphated or tungstened, and as well as sulfated, tungstened zirconia dioxide (SZ or WZ; SWZ; A-WZ; M-SZ; M-WZ; M-SWZ;,Z-SZ).

In the synthesis of catalysts, the zirconia gel was prepared by hydrolyzing $ZrOCl_2$ with a solution of 25% ammonia at pH 8-9 [12]. For this purpose, a solution of ammonia added dropwise to the solution containing 1 g $ZrOCl_2$·$8H_2O$ in 300 ml of water heated to 80°. The formed suspension was kept during 2 hours in the solution at the temperature of 80°, then filtered and washed with distilled water and dried at 100° for 24 hours. Then gel $Zr(OH)_4$ was treated with the solution of ammonium sulfate or metatungstate according to [6,12]. The gel was placed at room temperature in 25% solution of ammonium sulfate or metatungstate, taken in given amount and mixed for 1.5 hours. Then, the aqueous portion is evaporated, the wet residue is carefully mixed with the powders of H-forms of zeolites or with Al_2O_3 until homogeneous state. The obtained mass was dried at 120° (for 3 h.) and slowly raising the temperature (5°/min) was calcined in the air at the temperature of 600° (sulphation) and 700° for 5 h.. After calcination, the samples were pounded and mixed

International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-3, Issue-6, June 2017
ISSN: 2395-3470
www.ijseas.com

with binder and then of granule to a particle size of 1,5 mm x 3-4 mm and re-dried and calcined (3 hours) by the manner described above. The prepared composite catalyst is 65% mass. Al_2O_3, 15% SZ or WZ, the rest is binder. The content of tungsten content in WZ according to ICP-500 is 11.8 wt%, and the sulfur is 9 wt%.)

A mixture of NG and butane fraction (BF) have been used as a raw material. The composition of the used mixtures is shown in the corresponding tables.

The tests of the catalytic activity of the samples were carried out in flow quartz reactor, at atmospheric pressure, at temperatures of 140-300 °C, H_2/ hydrocarbon molar ratio 3 and space velocity (WHSV) for NG is 2,5 ч$^{-1}$, and (GHSV) for BF is 250 ч$^{-1}$. Before loading to the reactor the catalyst was diluted with quartz particles of 1.5-2.5 mm to 10 cm^3. The sample loaded into the reactor was pretreated in dry air of nitrogen and then with electrolytic hydrogen (30 cm^3/min) at 200° (1 h) and 500°(2 h). By the similarly way the samples were regenerated after catalytic tests.

The analysis of the reaction products were done by gas chromatography method using «Auto System XL, Perkin Elmer» chromatography provided with the appropriate computer program.

3. Results and discussions.

Composite catalysts (CC), which are SZ or WZ and aluminum oxide, practically do not affect the initial reactant in the process of contacting with BF: NQ mixture at the temperature range of 150-220º. The composition of the off-gas was insignificantly differ from the composition of BF:NG mixture entering to the reactor. The contacting of BF:NG mixture with the CC, one of the components which is the H-zeolite at temperatures of 140-200º leads to a noticeable change in the hydrocarbon composition, enriching the formed products with C_5-C_6 alkanes.

The data showing the changes in the composition of BF:NG mixture with a small total content of BF components, as a result of contact with the M-WZ with CC is presented as an example in Table 1. It is seen that at the temperature range of 150-220^0 occurs an intensive transformation of the composition of initial reactant. It follows from these data that increase of consumption (conversion) of C_4 is observed at the temperature range from 150 to 200º. The similar increase of C_{7+} consumption is observed at the temperature range of 150-180^0. At this temperature range occurs the enrichment of conversion product of BF:NG with C_5-C_6 alkanes (desirable products), which value increases till 12-15% (Table 1).

Table 1: The temperature effect on the distribution change of conversion products of BF:NG and C_4 and C_{7+} components conversion. Catalyst M-WZ, τ=30-45min.

Temperature	The composition of the reaction products,mass.%			The change of reactant composition, mass.%		
The initial reactant, mass%	C_4	C_5-C_6	C_{7+}	C_4*	C_5-C_6**	C_{7+}**
0	5.5	70.8	23.7	0	0	0
150	2.8	82.9	14.3	-49.1	+17.1	-39.7
180	1.2	85.7	13.1	-78.2	+21.0	-44.8
200	1.0	68.5	30.5	-81.8	-3.2	+28.7
220	7.8*	73.2	18.5	+41.8	+3.4	-21.9

International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-3, Issue-6, June 2017
ISSN: 2395-3470
www.ijseas.com

*- C_1-C_3~3%; **, «-», «+» correspond to the consumption and accumulation of C_{4+} and C_{7+} alkanes.

As seen from the table 1, the process at 150-180º occurs with the participation of reactions leading to the accumulation of C_5-C_6 hydrocarbons and the consumption of C_4 and C_7. By increasing temperature from 180 up to 200º at the high conversion of C_4 (81.8%) the content of C_5-C_6 is decreased in the conversion products of BF:NG mixture, but C_{7+} is accumulated.

The increase of temperature above 200°C changes the character of conversion of BF:NG mixture. As seen from the data of table 1, not only the content of C_4 increases in comparison with the initial one, but C_1-C_3 alkanes are also fixed, and besides that in the products the content of C_5-C_6 is increased again, but C_{7+} is decreased. Taking into account the formation of C_1-C_3 alkanes and the appreciable conversion of C_{7+} at the temperature of 220°(21.9%), it can be concluded that C_{7+} hydrocarbons on the used CC begin to undergo to undesirable hydrocracking at temperatures above 200º. Therefore, the studies of conversion of BF:NG mixtures were limited by the temperatures not exceeding 200°C.

The efficiency of processing of BF:NG mixtures can be characterized by three factors: change in the concentration of C_4; accumulation in the products of C_5-C_6 alkanes; involvement to the process (conversion) C_{7+} alkanes. The parameters which characterize the activity of some CC in the conversion of BF:NG has been presented in the fig.

1. As seen from the data, that in all other equal conditions the CC in the composition of Z-SZ has higher efficiency than the samples consisting of the tungstated zirconia and H-mordenite. As seen from the fig. 1, that he simultaneous tungstated and sulphated of zirconium oxide leads to the decreasing of CC efficiency in comparison with separately sulphated or tungstened zirconium oxide.
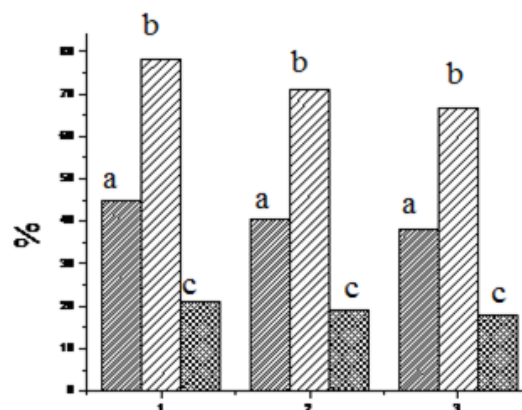

Fig.1 The conversion of C_4 (a) and C_7 (в) the components of BF:NG and accumulation of C_5-C_6 (c) on composite catalysts.

1- Z-SZ; 2- M-WZ;3- M-SWZ

$$T = 180c, \tau = 3min.$$

The data characterizing the influence of time on stream of experiment on catalytic parameters of two most active of CC noted above are presented in fig 2. As seen from these data that the more active CC Z-SZ is less stable comparison with the sample M-WZ, which activity remains stable for more than 1 h. It should also be noted that additional studies which have been carried out with the butane fraction, showed that M-WZ practically does not noticeable activating impact on the conversion of BF at 150-180º. The sample Z-SZ

International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-3, Issue-6, June 2017
ISSN: 2395-3470
www.ijseas.com

has some activity in the skeletal isomerization of n-butane (at 160º about 10%), but as it is mentioned noted above, the M-WZ sample is stable in the conversion of the BF: GB mixture. Therefore the results of the conversion of diluted BF: GB mixture over this CC were presented in the table 2.
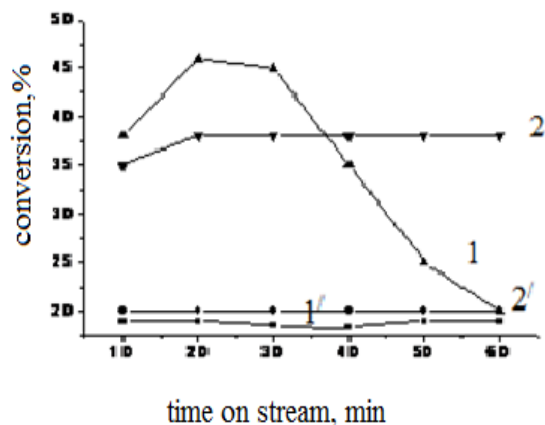

Fig 2. Time on stream of effect on the consumption of C_4 and C_{7+} the components of BF:NG

1.(C_{7+}) 1 ′(C_4)-1- M-SZ ; 2.(C_{7+}) 2 ′ (C_4)- M-WZ ; T=180C;

As follows from this data the intensive change of reactant composition is observed with the contacting of BF:NQ=1:1 with M-WZ catalyst at 160º. The butane fraction is intensively consumed with complete absorption of C_2-C_4 and up to 60% of n-C_4. However, in this case the decreasing of high-molecular components of C_{7+} (50-70%) is also observed. The conversion products of the mixture are enriched with hydrocarbons of iC_5- iC_7 isomeric composition to 30-35%, and the total content of C_5-C_6 alkanes increases from 39 till 82%. It follows from the data of table 2 that the consumption of BF and C_{7+} depends on the process temperature. The increasing of temperature from 160 to 180º exerts

insignificant influence on the content of iC_5-iC_7 in the process products. At the same time, if the consumption of BG is not practically changed, the conversion of C_{7+} is changing by increasing temperature from 40 till 70 %. And the correlations of iC_5-iC_7 components is changed to the direction of increasing the yield of iC_5.

Table 2:The influence of the temperature and time on stream effects on the conversion of the BF:NG; The catalyst M-WZ.

	The composition of hydrocarbons,%									
	C_2	C_3	iC_4	C_4	iC_5	C_5	iC_6	C_6	iC_7	C_{7+}
Initial reactant, mass%.	5	17.8	9.9	16.7	15.1	12.3	8.1	3.7	2.4	9
160ºC										
30	-	-	-	6.8	28.3	27.8	23.6	2.8	8	2.7
45	-	-	-	6.5	28.5	28.6	22.6	1.8	8.5	3.5
65	-	-	-	6.2	28.5	28.5	23.4	1.6	8.5	3.3
180ºC										
15	-	-	-	6.5	31	28.2	20.2	2.3	5.6	6.2
30	-	-	-	6.4	31.2	28.3	20.6	2.2	5.2	6.1
60	-	-	-	6.2	31.3	28.4	20.1	2.5	5.4	6.1
200ºC										
15	-	-	-	2.5	21.9	25.5	23.8	2.3	8.8	15.2
30	-	-	-	2.1	22	23.2	26.5	2.8	8.2	15.2
60	-	-	-	2.3	23.8	21.5	26.5	2.4	8.4	15.1

A further increase of temperature up to 200° C leads to the decrease of content of iC_5, increase both the concentration of iC_6 and iC_7 and C_7. It should be specially noted that if the consumption of BF at the temperature range of 160-180ºC is practically constant (83%), so by increasing temperature up to 200ºC its value reaches 90%. The consumption of C_7 at 200º is sharply differ from the consumption of BF(accordingly 60 and 32%,

table 2). In this case the inverse process takes place – the accumulated of C_{7+} hydrocarbons are~ 50% (table 2).

It was shown earlier that the conversion of mixture of n-butane:n-hexane (1:1) under the similar conditions leads to the formation of C_5 and C_7 hydrocarbons of isomeric structure [11]. A similar transformation of $n-C_4H_{10}:nC_6H_{14}$ was explained by the bimolecular character of the formation of C_{10} intermediate and by subsequent disintegration with the formation of C_5 or C_7 alkanes of skele a isomeri a cture.

The results of the conversion of BF and NG given above indicate that the products of this conversion is also formed by i erization disproportionation mechanism (c 1,2). As a result of this conversion is the accumulation c C_5-C_6 hydrocarbons, so takes place averaging of the molecular weight of the hydrocarbons (syncretization) which are in the reactant. Comparison of the data with Table 1 and Table 3 shows that the process can depend on the ratio of the butane fraction to natural gasoline. Additional studies to elucida of such depen a ce have shown th B ality of this assum B

As seen from the data given in Fig 3, the conversion c BF and the accumulation of C_5-C_6 alkanes pass through a maximum with the increase of contents of gaseous hydrocarbons in the reaction mixture: the exceeding of ratio of BF: NG 1: 1 leads to decreasing of all parameters characterizing the efficiency of the syncretization process.

The table 3 data show that BF in NG mixture of is capable to enter into reaction over other composite catalysts. The involvement of mixture of BF:NG in the process of syncretization over Z-SZ at 180° lead not only to the accumulation of isomers of C_5-C_7 alkanes and also C_{7+}. Hence the zeolite component and bond of zirconia with the corresponding anion are significantly affected to the BF:NG syncretization process.
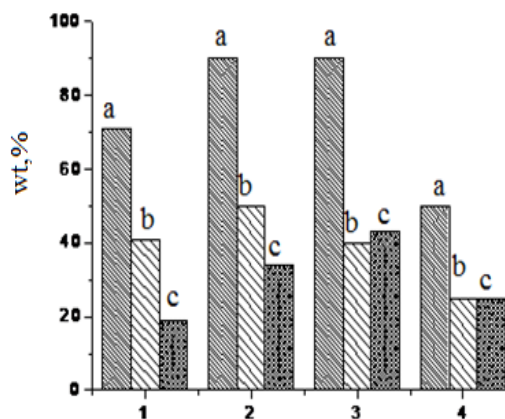

Fig.3 The effect of consentration of butane fraction on the conversion BF:NG mixture and accumulation of C_5- C_6 alkanes over M- WZ at 180^0C; $\tau = 45$min ; a- BF conversion; b-conversion C_{7+}; c-C_5-C_6 accumulation; The BF:NG concentration (wt,%) 1-5,5; 2-35; 3-50; 4-75.

Table 3: The conversion of BF:NG over the Z-SZ catalyst T=180°

International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-3, Issue-6, June 2017
ISSN: 2395-3470
www.ijseas.com

	The composition of hydrocarbons,%									
	C_2	C_3	iC_4	C_4	iC_5	C_5	iC_6	C_6	iC_7	C_{7+}
Initial reactant	5	17.8	9.9	16.7	15.1	12.3	8.1	3.7	2.4	9
min										
15	-	-	-	3.5	26.5	18,1	21,5	4,5	10,2	15,7
30	-	-	-	3,4	27,4	21,1	21,5	2,4	11,1	13,1
45	-	-	-	3,2	28,3	25,4	15,5	2,5	10,7	14,4
60	-	-	-	4,2	24,2	27,4	14,4	2,4	8,8	18,6

Thus combined processing of butane fraction (gaseous alkanes) and natural gasoline over the CC, which consists of H-zeolite and tungstated or sulphated zirconia, can be effective method to make liquied components of associated petroleum gas and formation of alternative way to obtain high octane gasolines without aromatic hydrocarbons.

4. Conclusion

Composite catalysts consist of H-zeolites (MOR or ZSM-5) and tungstated and / or sulfated zirconia, are capable to activate the conversion of a mixture of C_2-C_4 alkanes and natural gasoline at temperatures of 150-200°. The main characteristics of the efficiency of the process depended on the conditions of its realization are: the accumulation of C_5-C_6 alkanes in products and the consumption of initial C_4 and C_{7+} n-paraffins. The process with participation of gaseous and liquid alkanes proceeds through the steps of formation of common bimolecular intermediate with intramolecular skeleton isomerization and its subsequent splitting into the paraffins with either average weight (sincretization) or molecular weight higher than C_{7+}. Syncretization of gaseous alkanes with components of natural gasoline is realized at 150-180° mainly with accumulation of C_5-C_6 alkanes of isomeric structure.

The efficiency of joint conversion of mixture of gaseous alkanes and natural gasoline depends on their correlation and sharply falls when the value of this parameters exceeds unit. By increasing temperature up to 200° or substitution of zeolite component of composite catalyst HMOR for HZSM-5 leads to the change of character of mixture conversion from syncretization to disproportionation, but C_{7+} paraffins is accumulated in the conversion products with high consumption of C_4 alkanes.

5.References
[1] K.Arata, Adv. Catal.37 (1990) 3.
[2]T.Wakayama, H.Matsuhashi J. Mol.Catal.A:chem.. 299 (2005), 32
[3] E.Jglesia, D.G. Barton, S.L. Soled, S.Miseo, J.E. Baumgartner, W.E.Gates, G.A.Fuentes, G.D. Meitzner. Stud. Surf.Sci. and Catal. 101 (1996) 533
[4] A.V. Ivanov, T.V.Vasina, O.V. Masloboishikova, E.G. Khelkovskaya-Sergeeva, L.M. Kustov, Catal.Today 73 (2002) 95.
[5]Y.Ono Catal. Today 81 (2003) 3.
[6]G.Caeiro, R.H.Carvalvo, X.Wang, M.Lemos, F.Lemos, M.Guisnet, F.Ramoa Riviero,
[7]J.Mol.Catal. A:chem..255 (2006), 131
K.Shimizu,T.Sunargawa, K/Arimura, H.Hattroi, Catal. Lett 63(199)185

[8]M.A.Arribas, F.Marquez, A.Martinez, J, Catal.
190 (2000) 309

[9]K.Chao, H.Wu, L.Leu, Appl.Catal.
A:Gen.143(1996)223

[10]H.Matsuhashi, H.Shibata, K.Arata,
Appl.Catal.A:Gen. 187 (1999) 99

[11]S.Abasov, S,Agayeva, R.Starikov,
M.Mamedova, A. Iskenderova, E.Isayeva,
A.Imanova, B.Tagiyev. Catal. in Industry
168(2015) 73

[12]J.Santiestevan, J.Vartuli, S.Han, R. Bastian,
C.Chang J.catal. 168 (1997) 431