

Conversion of Benzene-Propane Mixtures on M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ -HM Catalytic Systems

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ABSTRACT

The conversion of $\text{C}_6\text{H}_6:\text{C}_3\text{H}_8$ mixtures on a mechanical catalyst mixture (MC) consisting of HY, HM or HZSM-5 zeolite and M, $\text{Re}/\text{Al}_2\text{O}_3$ was studied. As a result of propane activation in the presence of benzene on the catalytic system, the components of the benzene-propane mixture at low temperatures (473-673 K) are converted into alkylaromatic hydrocarbons C_9 and propene. It was found that propane dehydrogenation to propylene occurs already at 523 K with benzene as a stoichiometric reaction component. Based on the obtained data on the dependence of the yield of propylene and isopropylbenzene on the experimental conditions, an assumption was made about a common intermediate compound preceding the formation of these products. Thermodynamically unfavorable reactions of benzene dehydroalkylation with propane and the process of propane dehydrogenation are explained by the occurrence of conjugate oxidation-reduction interaction due to cyclic proton transfer between the zeolite and partially reduced centers of the metal component of the MC and alternating oxidation and reduction of these centers. As a result of the studies, the effect of benzene on the low-temperature activation of propane on mixed catalysts consisting of a mixture of (50 x 50) M, $\text{Re}/\text{Al}_2\text{O}_3$ + H-zeolite, leading to the formation of isopropylbenzene, propylene and C_9 -alkylaromatic hydrocarbons, was established; the dependence of the yield of the conversion products of the $\text{C}_6\text{H}_6:\text{C}_3\text{H}_8$ mixture on the reaction conditions and the nature of the zeolite component of the mixed catalyst was established.

Keywords: Conversion of Mixtures $\text{C}_6\text{H}_6:\text{C}_3\text{H}_8$, Isopropylbenzene, Propene, C_9 , Alkylaromatic

INTRODUCTION

The light alkanes such as C_1 - C_3 are at present among the most

available and inexpensive hydrocarbons. The creation of the economically profitable ways of these alkanes refining is one of the vital tasks of today petrochemistry. Up to now, there is no efficient commercial process for functionalization of light alkanes. One of the possible ways for the realization of the above task is the involving alkanes to the combination reactions with the other compounds, in particular, with aromatic hydrocarbons. However, the studied reactions of the aromatic compounds, for instance, benzene carried out with olefins, oxygen-containing compounds, etc. [1-4].

At the same time, the investigations known on aromatization of light alkanes C_2-C_3 whereby the alkylaromatic compounds are formed [5,6]. This permits to suggest the alkylation of aromatic hydrocarbons by light alkanes over the zeolite-containing catalytic systems. Such suggestion confirmed by the investigations of benzene interaction with C_2-C_4 hydrocarbons over ZSM-5 zeolite catalysts containing also the metallic additives of platinum or zinc [4,5]. That kind of researches conducted at 723-873 K. Later the efficient benzene alkylation with light alkanes performed on the similar model catalytic systems at lower temperature 623 K [6,7]. Our researches [6,8] carried out over the mixture of catalysts Ni, Re / Al_2O_3 +HY showed the possibility for benzene alkylation with propane even at 453K. Thus, benzene alkylation with propane is possible under the temperature conditions close to the conditions of benzene alkylation with propane. Under the conditions of low-temperature alkylation of benzene with propane, propylene formed, too [9,10]. The dehydroalkylation of benzene as the dehydrogenation of propane at relatively low temperatures (473-573 K) rank among the unfavourable reactions and require the additional studies.

This work devoted to the results of the study of propane activation over the mixed catalysts (MC), comprising zeolite H-form and bimetallic aluminium oxide catalyst and discussion of the data obtained.

EXPERIMENTAL SECTION

Materials

The investigations were carried out on metal (Pt, Ni, Co),

rhenium-alumina catalyst (NiRAC) prepared by the procedure [4,6] H-forms of zeolites Y, M and ZSM-5 and over their mechanical mixtures with MRAC (MC).

Spherical $\gamma-Al_2O_3$ precalcined in air at 1023 K for 5h used for PRAC synthesis. The catalyst prepared by the absorptive impregnation of H_2PtCl_6 and NH_4ReO_4 from the aqueous solution. The sample after filtration dried at 353 and 393 K and then calcined at 823 K and 1023 K (3 h). Platinum and rhenium content in the catalyst prepared that way were 0.3 and 0.5 wt %, respectively.

The Y, M and ZSM-5 zeolite H-form of have been prepared from the initial Na-form of the commercial zeolites NaY, NaM and NaZSM-5. The fully exchanged zeolite H-forms were obtained by ionic exchange of the initial zeolites with aqueous ammonium chloride at 353K (6h) followed by drying at 353 (12 h) and calcination at 823 K (5 h). The obtained H-forms of zeolites shaped with the aluminogel binder (20 at % Al_2O_3).

The starting reagents propane and benzene were of purity > 99% (GC).

The conversion of propane, benzene and the mixtures $C_6H_6:C_3H_8$ at different mole ratio studied in a flow reactor at 453-723 K, atmospheric pressure and space velocity (GHSV) 125-1000h⁻¹. In contrast to the conversion of the individual components (C_6H_6 , C_3H_8) products yields of $C_6H_6:C_3H_8$ mixtures conversion calculated on total carbon number basis.

The catalysts treated with air at 673 K (1h) before the experiments.

RESULTS AND DISCUSSION

The researches carried out over MRAC and zeolites indicated that these catalysts up to 673K were inactive in propane conversion reactions. Only on the mixed catalysts at temperatures 573-673 K the formation of small amounts of hydrocarbons C_2H_4 , C_4H_8 and hydrogen observed. The results of the study of $C_6H_6:C_3H_8$ conversion over MC are set in table 1. Unlike the metallic MRAC and acidic HY components, MC activates the conversions of these mixtures.

Table 1. Conversions of $C_6H_6:C_3H_8$ mixture as a function of their mole ratio on NiRAC+HY, T=423 K, HSV=500 h⁻¹

Content, mole %		Yield of products % C*		
C_6H_6	C_3H_8	IPB	C_3H_6	ArH
0	100	-	-	-
10	90	3.6	0.5	-
25	75	6.2	0.7	2.2
50	50	6.4	0.4	2.6
100	0	-	-	-

*The mole yields of hydrogen are equal to the conversion of propane

One can note that introduction of 10 mole % of benzene into reaction leads to propane conversion. The products of $C_6H_6:C_3H_8$ mixtures conversion are isopropyl benzene (IPB), propylene and hydrogen. The data of table 1 show that under the above-mentioned conditions the reaction products yield depends on the ratio of $C_6H_6:C_3H_8$ mixture components with increase of $C_6H_6:C_3H_8$ ratio, benzene conversion grows and in the reaction products, the formation of C7-C8 aromatic hydrocarbons (ArH) observed.

Propane reacts with benzene forming an alkylaromatic hydrocarbon but at the same time, a part of propane consumed for propylene formation. Note that with increase of $C_6H_6:C_3H_8$ mole ratio the propylene yield passes through the maximum at $C_6H_6:C_3H_8=1:3$. The further increase of benzene concentration decreases propylene yield and practically does not effect on the alkylaromatic hydrocarbons yield.

Taking into account that IPB and propylene are the major hydrocarbon products of reaction, only the results of studies

of the mixture $C_6H_6:C_3H_8=1:9$ conversion are set forth below. The results of study of space velocity effect on a conversion of this mixture shown in table 2. When the GHSV changes from 125 to 1000h⁻¹ both conversion of the mixture components and reaction products distributions change.

As seen from the data of table 2, at space velocity below 500 h⁻¹ the increase of IPB formation observed at practically full absence of propylene.

The special interest attracts the data indicating the dependence of $C_6H_6:C_3H_8$ mixture separate components conversion on space velocity. From table 2 follows that with space velocity growth the benzene conversion and IPB yield decrease. On the other hand, propane conversion with space velocity increase passes through maximum corresponding to 500 h⁻¹ and then increases again. At this space velocity propylene formation starts and growth of its yield with space velocity increase.

Table 2. Effect of the GHSV on $C_6H_6:C_3H_8=1:9$ mixture conversion over NiRAC+HY, T=523K

GHSV, h ⁻¹	Conversion, %		Yield of products, % C		
	C_6H_6	C_3H_8	IPB	C_3H_6	ArH
125	21	2.4	5.9	-	0.4
250	18	2.0	5.4	-	trace
500	12	1.9	3.6	0.5	0
750	9.8	2.5	2.9	1.2	0
1000	7.6	4.7	2.3	3.4	0

The changes of benzene and propane conversions as well as dependence of their conversion products yield on space velocity permits to suggest that the formation of the common intermediate obeys the thermodynamic control and the

product yield to the kinetic one.

The data on temperature effect on $C_6H_6:C_3H_8$ mixture conversion over PRAC+HY catalyst are set in table 3.

Table 3. Temperature effect on C₆H₆:C₃H₈=1:9 mixture conversion over NiRAC+HY, GHSV=500 h⁻¹

Temperature, °C	Conversion, %		Yield of products, % C				
	C ₆ H ₆	C ₃ H ₈	IPB	C ₃ H ₆	ArH	C ₁ -C ₂	n-PB
453	1.0			0	0	0	0
473	5.0	0	0.3	0	0	0	-
523	12.0	1.9	3.6	0.5	0	0	0.2
573	34.2	6.3	9.0	2.2	trace	0	0.4
593	62.1	12.6	12.5	5.0	4.7	0	1.4
623	41.3	17.2	6.4	11.2	5.2	0	0.7
648	16.1	19.3	0.3	15.5	4.2	0	0.3
673	7.9	7.9	0.1	6.3	2.3	trace	trace
723	10.5	7.1	trace	2.0	3.1	2.5	-

As is seen from the data within the temperature range 453-723 K the conversion of C₆H₆:C₃H₈ mixture has complex nature. This follows from the change of catalyst activity and expansion of the composition of mixture conversion products. So, the temperature rise from 453 to 593 K leads to the growth of benzene conversion to IPB and other ArH. The similar growth of catalyst activity observed also in propane conversions. The further increase of temperature from 593 to 648K leads to the drop of benzene conversion. At the same time propane, conversion with the temperature rise within this temperature range monotonely increases but then at 673K sharply decreases.

It noted that at 723 K benzene conversion again increases. However, as a result of benzene conversion, ArH and low-molecular hydrocarbons C₁-C₂ formed. In spite of slight change in benzene conversion, propylene yield at 723 K sharply decreases and under these conditions, IPB practically not formed.

The above data (tables 1-3) indicate the dependence of the yield of C₆H₆:C₃H₈ mixture conversion products on the reaction conditions. The results of the studies of zeolite type effect on C₆H₆:C₃H₈ mixture conversion over MC are set in table 4. They show that in replacement of zeolite Y by the zeolites Mordenite or ZSM-5 the nature of C₆H₆:C₃H₈ mixture conversion over MC does not change. With temperature rise from 473 K to 593 K benzene conversion increases. Within the temperature range 623-673 K benzene conversion and aromatic hydrocarbons, formation decreases and at 723 K again increases.

In contrast to benzene, the conversion of propane monotonely increases to 648 K and decreases at 673 K. According to the data obtained, the formation of propylene begins at 423 K and with the temperature growth; it changes synchronously with the changes of propane conversion.

Table 4. Effect of MC zeolite component temperature on C₆H₆:C₃H₈=1:9 mixture conversion. GHSV=500 h⁻¹

Temperature, °K	Conversion, %		Yield of products, %, C				
	C ₆ H ₆	C ₃ H ₈	IPB	C ₃ H ₆	n-PB	ArH	C ₁ -C ₂
Catalyst NiRAC + HM							
473	4.8	0.6	1.4	0	0	0	0
523	11.4	2.2	3.4	0.6	0	0	0
573	31.7	7.6	8.7	2.9	0.8	0	0
593	59.6	14.8	13.9	7.1	3.2	0.8	0
623	37.0	22.8	6.5	15.3	3.4	1.2	0
648	18.7	23.8	1.7	21.4	1.7	2.2	0
673	8.1	5.4	trace	3.5	0.4	1.5	trace
723	11.3	3.3	0	1.5	trace	1.5	2.2
Catalyst NiRAC + HZSM-5							
473	4.3	0.5	1.3	0	0	0	0
523	10.5	2.3	3.2	0.8	0	0	0
573	26.5	7.8	5.2	3.6	2.6	0	0
593	43.7	16.0	8.6	8.4	4.5	0	0
623	35.2	24.2	5.6	15.8	4.8	0.5	0
648	20.5	30.7	1.5	22.5	2.1	2.6	trace
673	12.9	5.8	trace	3.4	0.3	3.4	1.2
723	16.5	2.1	0	0	0	6.8	2.6

The comparison of table 3 and 4 data shows that when Y zeolite component of MC replaced by the zeolite component of M or ZSM-5, among the aromatic hydrocarbon products, the yield of n-propyl benzene markedly increases and the formation of ArH occurs at higher temperatures.

EFFECT OF CATALYST PRETREATMENT

MC activity in conversion of $C_6H_6:C_3H_8$ mixture depends on the catalyst pretreatment. Figure 1 shows a typical curve of

IPB yield as a function of time on stream over the pretreated by air MC. These data demonstrate that the catalyst activation period is characteristic for $C_6H_6:C_3H_8$ mixture conversion over air pretreated MC. During 5 min. treatment, the conversion of benzene and formation of hydrocarbon products not observed and CO_2 and H_2O were the major gase-phase products. After 5-7 min reaction time, benzene conversion and IPB yield started increasing, while CO_2 and H_2O formation decreased continuously as the reaction proceed.

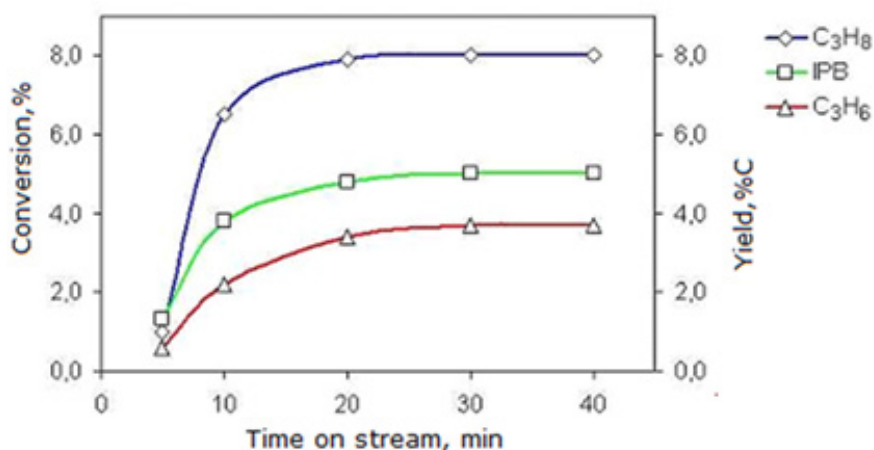


Figure 1. Benzene conversion, IPB, and C_3H_6 yield on MC NiRAC as a function of an experiment time. $T=573$ K, $GHSV=500$ h⁻¹, $C_6H_6:C_3H_8 = 1:9$, MC NiRAC + HM.

It noted that all experiments using propane and NiRAC showed CO_2 and H_2O formation within the marked time corresponding to catalyst activation period, followed by the decline in the yields of formation of these products practically to zero within 15-20 min. Moreover, MC pretreatment by propane, irrespective of the zeolite component type, leads to the complete disappearance of the activation period at subsequent $C_6H_6:C_3H_8$ mixture conversion.

Thus, the catalytically inactive substance activated by pretreating NiRAC with propane. These observations suggest that propane treatment is necessary to reduce NiRAC metallic component to the catalytically active state. Use of CO for the same purpose at the reaction temperatures does not give the positive effect. It is possible that in this case MRAC component of MC reduced more than necessary, since after the sample treatment with the air (for some minutes) the catalyst activity has been completely reproduced.

Additional information on NiRAC role in the conversion of $C_6H_6:C_3H_8$ mixture obtained by treatment of MC with hydrogen at 673 K. In this case, the catalyst full deactivation observed that associated by the change of state of NiRAC metallic

centers.

DISCUSSION

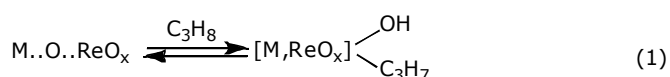
The researches on the conversions of benzene and propane up to the temperatures 723 K over MRAC and zeolites HY, HM and HZSM-5 showed that only NiRAC at the temperatures above 673 K begins to manifest activity in propane dehydrogenation. Propane conversion on the mixture of NiRAC with H-form of zeolite (MC) at 573-673 K leads to the formation of small amounts of C_2H_4 , C_4H_8 and hydrogen. These conversion products correspond to the products of propylene metathesis.

The data of table 1 reveal that introduction of small amounts (10 moles %) of benzene to the reaction even at 523 K leads to the dehydrogenation of propane to propylene and formation of alkylaromatic hydrocarbon IPB. Thus, in passing $C_6H_6:C_3H_8$ mixtures over MC there have been formed the products of two thermodynamically unfavourable reactions: dehydrogenation of propane and dehydroalkylation of benzene.

For explanation of the data obtained, it is necessary to note that benzene is able to go into the alkylation reaction under

the studied conditions of $C_6H_6:C_3H_8$ mixtures conversion. However, these conditions are unfavorable for propane activation. Hence, in the course of reaction propane activates over MC with the participation of benzene. The use of the mixed catalysts as the objects of investigation permits to establish both the role of the separate components in the catalytic act and a role of benzene in this process.

The data obtained demonstrate that only the metal-containing component can activate propane. This connected with the presence of a bridged oxygen bound with platinum and rhenium on the metallic centers [3,6,9]. Actually, the prerduced with hydrogen, MRAC is inactive in the reaction of $C_6H_6:C_3H_8$ mixtures conversion. At the same time, only a part of MRAC bound oxygen participates in propane activation. This explains the activation period prior the formation of products of $C_6H_6:C_3H_8$ mixtures conversion (Figure 1). Propane activation is a result of the possible dissociative adsorption on MRAC metallic centres by the scheme.



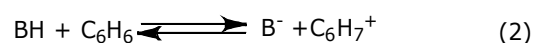
The further conversion of propane may occur at higher temperatures ($\geq 723K$). Due to the MC zeolite component participation in the process at temperatures 573-673K propane slight conversions are observed forming hydrogen and the products of propylene disproportionation.

The possibility for realization of the indicated reaction is connected with propane interaction with β -acidic centres of zeolite component and formation of intermediate $\{C_nH_{2n+3}\}^+$. The slight yields of propane conversion products are associated with the remote metallic and β -acidic centres [11-13]. However, even the slight yields of propane conversion products supposed the reach space-divided metallic centres by the Intermediates $\{C_3H_9\}^+$ and acidic-basic interaction with formation of H_2O and $\{C_3H_7\}^+$, $[M,ReO_x] \begin{array}{l} \text{OH} \\ \diagdown \\ C_3H_7 \end{array}$, responsible for the future progress of a reaction. Propane activation at low temperatures (e.g. 453-573 K) occurs due to the protons transfer on PRAC, appearance in this case of the conjugated system of redox and acidic-basic interaction. The zeolite component of MC due to the protons carrier between the space-divided centres can play a role of an acidic-basic component (donor of protons).

The dehydrogenation of propane to propylene over MC at the temperatures 523-573 K in the presence of benzene allows considering this compound as an stoichiometric component

of this reaction. The data obtained allow assuming benzene to be a carrier of the protons from MC zeolite component to MRAC. The interaction of benzene with the zeolite acidic centres, leads to the formation of benzonium $[C_3H_7]^+$ ions. These formations are more stable than $\{C_3H_9\}$.

Therefore, introduction of benzene to the reaction favours the formation of propane disproportionation products due to the interaction (2).



And the ions $[C_6H_7]^+$ themselves intensify the above mentioned conjugated interaction. On the other hand, benzene is capable to interact with the propyl carbocations and to form isopropyl benzene cation $\{C_6H_6:C_3H_7\}^+$. This carbocation depending on the reaction conditions, giving a proton to corresponding basic sites subjected to the further transformation to the products.

The change of the products yield in $C_6H_6:C_3H_8$ mixtures conversion with increase of benzene concentration suppose three possible reactions: a) alkylation of benzene; b) dehydrogenation of propane and c) formation of alkylaromatic hydrocarbons C7-C8 (ArH). The proceeding of these reactions depends on the conditions of $C_6H_6:C_3H_8$ mixtures contact with MC. For instance, in $C_6H_6:C_3H_8=1:9$ mixture conversion at GHSV 500 h⁻¹ and 523 K the formation of ArH in the conversion products is not observed. However, with decreasing space velocity from 500 h⁻¹ to 250 h⁻¹ and 125 h⁻¹ along with IPB, ArH formed in the absolute absence of propylene. With increase of space velocity the propylene yield increases and that of IPB decreases. In this case, ArH is lack in the reaction products.

The temperature exerts the strongest influence on $C_6H_6:C_3H_8$ mixtures conversion. As seen from the data of Table 3, the $C_6H_6:C_3H_8$ mixtures conversion occurs even at 453-473 K. In this case, IPB is the only product of this conversion. With temperature rise to 473 K in the reaction products propylene is fixed and at the temperatures above 573 K – the formation of ArH.

With temperature increase, to 673 K benzene conversion decreases (tables 3-4). Within the temperature range 673-723 K practically the absolute cessation of IPB and propylene occurs, and the formation of ArH, as the conversion of benzene, passes through the minimum and increases again. These changes in benzene conversion and ArH yield

accompanied by the formation of low-molecular alkanes C_1 - C_2 . Taking into consideration the chemical stability of aromatic nuclei under the conditions of experiments, one can suppose that the low-molecular weight hydrocarbons and ArH formed due to propane destruction [7,14-16]. At the same time at temperatures 573-648 K, the formation of low-molecular weight hydrocarbons not observed, and ArH yield is high. These data point to the different mechanisms of ArH formation at temperatures below and above 673 K. At the high temperature ArH formation proceeds by the mechanism proposed in [8,9,11-13].

Comparing the regularities of IPB and ArH formation (tables 1-3) at 453-673 K one can assume that ArH formation occurs by successive-parallel scheme, i.e. due to both IPB isomerization and because of the common intermediate conversions. However, as ArH increase accompanied by IPB yield decrease, one can assume that the successive mechanism makes a basic contribution to ArH formation. The contribution of the parallel

process in ArH formation takes place at temperatures above 573 K and it is possibly, not great. Thus, IPB and propylene are the major products of $C_6H_6:C_3H_8$ mixture conversions.

Comparing the data in tables 3 and 4 shows that irrespective of the nature on MC zeolite component propylene formation starts at 923 K and increases with temperature rise reaching the maximum values at 648K. At the same time, as is seen from some data the maximum conversion of benzene and yield of IPB observed at 593 K, i.e. the maximum yields of the major products, IPB and propylene takes place at different temperatures.

Summarizing the data on the influence of the reaction a stoichiometric component of propane dehydrogenation one can note: I) lack of propane activation in the absence of benzene; II) change of propylene with the change of benzene concentration in a reaction mixture (table 1); III) change of propylene yield with the growth of space velocity (table 2).

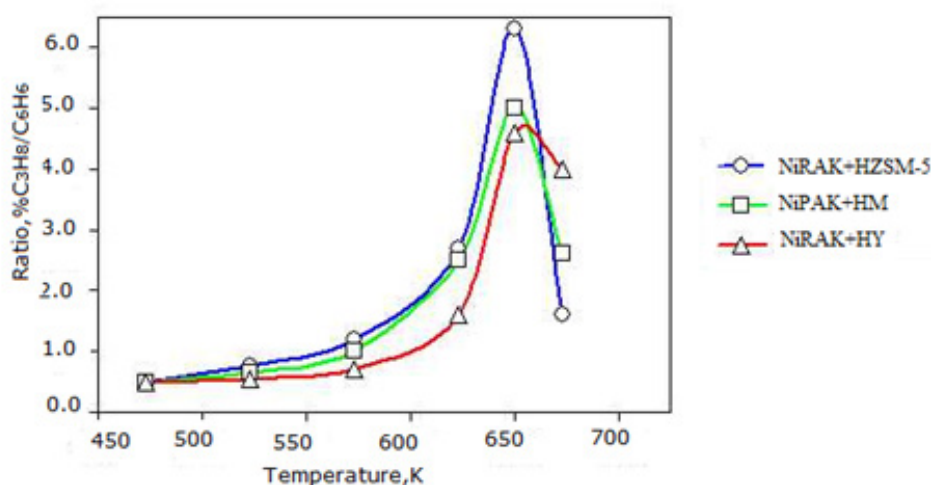


Figure 2. Ratios of the converted amounts of propane and benzene as a function of temperature.

In addition to these data, figure 2 shows the relations of the converted propane and benzene molecules over MC as a function of a temperature. As seen, irrespective of zeolite type within the temperature region of 593-673 K a sharp splash of propane conversion over MC occurs, which accompanied by a propylene formation. Thus, a zeolite type exerts a little influence on the conditions of $C_6H_6:C_3H_8$ mixture conversion. At the same time, a zeolite type exerts influence on conversion and yield (selectivity) of $C_6H_6:C_3H_8$ mixtures conversion products. So, at temperature 593 K benzene conversion

decreases depending on MC zeolite component type in the order of $Y > M > ZSM-5$.

At temperature 648 K, this series transformed to a series $ZSM-5 > M > Y$. It noted that there is slight difference between the common activities of the studied MC.

It follows from the data of tables 3 and 4, that the replacement of MC zeolite component changes the distribution of $C_6H_6:C_3H_8$ mixture conversion products. In a series of zeolite components of MC (Y, H, ZSM-5) propylene, n-propyl benzene yield increases

as well as increasing the temperature of ArH formation. Such changes usual for alkyl aromatic hydrocarbons conversions over the used zeolites and connected with their molecular sieve properties [17-21]. Therefore, one can suppose that an intermediate $\{C_6H_6 \cdot C_3H_7\}^+$ formed on NiRAC and its further conversions over MC zeolite component involves stage of interaction with a proton centers formed by scheme [2]. In the course of a reaction, a proton cyclic transfer completed by the formation of $C_6H_6:C_3H_8$ mixture conversion products. In the first part of this reaction benzene plays a role of stoichiometric component of a reaction and in the second part it acts as a substrate interacting with carbocation $\{C_3H_7\}^+$. Thus, the unfavorable formation of IPB and propylene at relatively low temperatures of experiments is associated with the stability of an intermediate $\{C_6H_6 \cdot C_3H_7\}$ formed because of conjugated redox and acidic-basic interaction due to the protons cyclic transfer.

CONCLUSION

The alkylation of benzene with propane revealed that due to the protons cyclic transfer from B-acidic sites of zeolite on the metallic centres and by an intermediate on zeolite the conjugated redox – acidic-basic interaction appears facilitating the unfavourable reactions proceeding.

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