SRYAHWA PUBLICATIONS

Research Journal of Nanoscience and Engineering
ISSN: 2637-5591 | Volume 7, Issue 1, 2025
https://doi.org/10.22259/2637-5591.0701001

RESEARCH ARTICLE

Dehydroalkylation of Benzene with Propane on Oxide and Zeolite Catalysts

Babayeva F.A., Abasov S.I.

Academiciany Y.H.Mammadaliyev Institute of Petrochemical Processes, Azerbaijan.

Received: 27 January 2025 Accepted: 12 February 2025 Published: 19 February 2025.

Corresponding Author: Babayeva F.A, Academiciany Y.H.Mammadaliyev Institute of Petrochemical Processes, Azerbaijan.

Abstract

The ability of mixture of catalysts (MC) of M,Re/$Al_2O_3$where (M = Ni, Co, Pt) and H-zeolite (Y, MOR, ZSM-5) to activate low-temperature transformations of C_3H_8 in the presence of C_6H_6 was studied. It was shown that as a result of the activation of the C_3H_8 component of C_6H_6:C_3H_8 mixtures, isopropylbenzene and other C_9-alkylaromatic hydrocarbons, as well as C_6H_6 and H_2, were formed. The influence of the experimental conditions and M-components of the MC on the activity and distribution of the transformation products of C_6H_6:C_3H_8 mixtures was discussed.

Keywords: Conversion of Mixtures C_6H_6:C_3H_8, Isopropylbenzene, Propene, C_9alkylaromatic.

1. 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 profitableswayes 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. [1-9].

At the same time, the investigations known on aromatization of light alkanes C_2-C_3 where by 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 .That kind of researches conducted at 450-600°C. Later the efficient benzene alkylation with light alkanes performed on the similar model catalytic systems at lower temperature 350°C.

Our researches [6] carried out over the mixture of catalysts M, Re /Al_2O_3+ H-forms of zeolites Y, MOR, ZSM-5 showed the possibility for benzene alkylalation with propane even at 180 °C. 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 [7, 9]. The dehydroalkylation of benzene as the dehydrogenation of propane at relatively low temperatures (200-300°C) 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.

2. Experimental

The investigations were carried out on metall (Ni, Co, Pt), rhenium-alumina catalyst prepared by the procedure [1,7] H-forms of zeolites Y, MOR and ZSM-5 and over their mechanical mixtures with MC.

Citation: Babayeva F.A, Abasov S.I. Dehydroalkylation of Benzene with Propane on Oxide and Zeolite Catalysts. Research Journal of Nanoscience and Engineering 2025; 7(1): 1-5.

Spherical γ-Al_2O_3 precalcined in air at 750°C for 5h used for AMR 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 80 and 120°C and then calcined at 550 and750°C (3 h). Metall 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 80°C (6h) followed by drying at 80°C (12 h) and calcination at 550°C (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 200-450°C, atmospheric pressure and space velocity (GHSV) 125-1000h^{-1}. The catalysts treated with air at 400°C (1h) before the experiments.

3. Results and Discussion

Formation of products conversion of benzene-propane mixtures MC is accompanied by the occurrence of three reactions: a) the alkylation of benzene; b) the propane dehydrogenation; c) the formation of alkylaromatic hydrocarbons (ArH). The course of these reactions depends on the contact conditions of the studied mixtures with MC.

Conversion C_6H_6 : C_3H_8 mixtures at atmospheric pressure and low temperatures (< 200 °C) results in the formation. IPB (isopropyl benzene). With increasing temperature, the product composition changes, so at 250 °C propylene is fixed, and above 300 °C formed an ArH (aromatic hydrocarbons). However, a further increase temperature to 400 °C leads to a decrease of benzene conversion. In the temperature range 400-450 °C IBT and propylene yield is reduced to zero, and the formation of ArH, as a result of the conversion of benzene, passed through a minimum increase again. These changes in the conversion of benzene and the yield of aromatic hydrocarbons are accompanied by the formation of low molecular weight alkanes C_1-C_2. These data indicate different mechanisms of ArH formation at temperatures below and above 400 °C. Comparing the laws of formation of isopropyl benzene, aromatic hydrocarbons at temperatures of 175-400°C it can be assumed that the ArH formed by series-parallel diagram, namely through as isomerization, and by converting the total intermediate. An increase in the yield of the ArH with a simultaneous decrease in the yield of IPB shows that the main contribution to the formation of the ArH is connected to the serial conversion of IBT. An increase in the yield of ArH with a simultaneous decrease in the output of IPB shows that the main contribution to the formation of ArH is associated with the successive conversion of IPB. It is shown that isopropyl benzene and propylene are the main products of the conversion of benzene-propane mixtures.

Table 1. *Effect of temperature on the conversion of a mixture of* C_6H_6 : C_3H_8 *(1 : 9 mol). On MC; V = 500* h^{-1}

T, °C	Conversion,%		Productyield,%				
	C_6H_6	C_3H_8	IPB	C_3H_6	NPB	ArH	C_1-C_2
200	4.8	0.6	1.4	0	0	0	0
250	11.4	2.0	3.1	0.6	traces	0	0
300	31.7	7.6	8.7	2.9	0.8	0	0
320	59.6	4.8	13.9	7.1	3.2	0.8	0
350	37.0	22.8	6.5	15.3	3.4	1.2	0
375	18.7	23.8	1.7	21.4	1.7	2.2	0
400	8.1	5.4	traces	3.5	0.4	1.5	traces
450	11.3	3.3	0	1.5	traces	1.5	2.2

The results show that regardless of the nature of the zeolite component of the MC, carrier Bronsted acid centers, propylene begins to form at a temperature of 250 °C and its yield increases with temperature reaching a maximum value at 375 °C, i.e. the maximum values of benzene conversion, and yield IPB (320 °C), and propylene are different (Table 1).

Note that the type of zeolite affects the conversion and the yield (selectivity) product is converted mixture. Thus, at a temperature of 320 °C the conversion of benzene is reduced depending on the component type zeolite CS as follows: Y > MOR > ZSM-5. At a temperature of 375 °C, this range is converted: ZSM-5 > MOR > Y. It should also be noted a slight difference between the total MCactivity studied. Replacement of the zeolite component changes the distribution of MC C_6H_6/C_3H_8 mixture transformation products. Among the MC zeolite components (Y, MOR, ZSM-5) yield of propylene and n-propyl benzene (NPB), increases, and also increases the temperature of formation ArH.

This a change corresponds to the usual conversion of aromatic hydrocarbons on used zeolites and is associated with their molecular sieve properties. Wherein, the ratios of the yield of IPB and propylene are limited by thermal control, and the formation of other (secondary) products given their dependence on the microporous structure of the zeolite, – kinetic. The latter is also connected with the IPB reactivity depending on the reaction conditions, so IPB yield decreases with increasing temperature due to dealkylation at acidic centers. Consequently, low-temperature de-hydrogenation of propane is a result of the decay of the intermediate IPB (NPB), and benzene, plays the role of an astechiometric component.

Results of studying the conversion of $C_6H_6 : C_3H_8$ mixtures MC showed that only in the presence of benzene MChas activity in a low temperature (≥ 180 °C) conversion of propane. The introduction of small amounts of benzene into propane (for example, 10 mol %) leads to its transformations and the formation of hydrogen, the molar value of which corresponds to the total molar conversion of propane. Eduction of hydrogen in the conversion of benzene-propane mixtures is a total reflection of the noted reactions. Conversion $C_6H_6 : C_3H_8$ mixtures depends on the pretreatment of the catalyst. Eduction hydrogen subjected to standard processing air MC characterized by a period of activation. This activation period MC is associated exclusively with the interaction of propane with AMR catalyst and, by analogy with methane,may be a consequence of the partial reduction of the metal component of MC (table 2).

Table 2. *The effect of the ratio of benzene conversion of propane and a mixture of* C_6H_6*:* C_3H_8*.* $T = 250\ ^oC$, $V = 500\ h^{-1}$

Content, mol. %		Conversion, %		The product yield, % C		
C_6H_6	C_3H_8	C_6H_6	C_3H_8	IPB	C_3H_6	ArH
125	100	-	0	-	-	-
250	90	12	1.9	3.6	0.5	-
500	75	14	7.2	6.2	0.7	2.2
750	50	23	7.7	6.4	0.4	2.6
1000	0	0	-	-	-	-

It is seen from Table 2, that the yield of conversion products C_6H_6: C_3H_8 mixtures depends on their ratio. Changing the molar ratio of C_6H_6: C_3H_8 from 1 : 9 to 1 : 1 leads to an increase in conversion of benzene and C_9 growth ArH composition.

Table 3. *The effect of volume speed rate of reactants on the conversion of benzene-propane mixture at MC;T = 250 °C*

V, h^{-1}	Conversion,%			ProductYield,%		
	C_6H_6	C_3H_8	IPB	C_3H_6	NPB	ArH
125	18.2	2.7	4.3	0.1	0.3	0.4
250	15.8	2.2	4.0	0.4	0.2	0.1
500	11.4	2.0	3.1	0.6	traces	0
750	10.2	2.9	2.8	1.4	0	0
1000	8.5	5.7	2.3	3.9	0	0

Varying the volume speed of from 125 to 1000 h^{-1} changes as the conversion of components of $C_6H_6 : C_3H_8$ mixture and distribution of the reaction products (table 3) – below than 500 h^{-1} is increased yield IPB and formations NPB and ArH with slight amounts of propylene. Increasing the volume speed leads to a monotonic decrease of benzene conversion, while the conversion of propane in the range of V = 125-500 h^{-1} is reduced, and then increases again with growth the volume speed of from 500 to 1000 h^{-1}.

Varying the ratio of metal and acid MC components leads to a change in the transformation products $C_6H_6 : C_3H_8$ mixtures.

The data show that the type of zeolite influences the conversion of individual components of the reaction mixture and the yield (selectivity) of the reaction products.

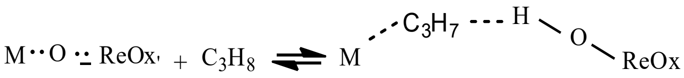
The results obtained show that at sufficiently low temperatures contacting benzol-propane mixture on the mechanical mixture of catalysts leads to the formation of products of two thermodynamically difficult reactions: dehydrogenation of propane and dehydroalkylization of benzol propane.

Taking into account the above mentioned facts: a) absence of activity in the reconstructed MC samples;

b) activation of propane only by the non-reconstructed metal-containing MCcomponent; c) presence of a catalyst activation period associated with partial recovery of the MC metal component may suggest the following scheme of MCactivation.

$$M,\ ReOx/\ Al_2O_3 \xrightarrow[-CO_2,\ -H_2O]{C_3H_8} M^{\cdot\cdot}O \underline{\cdot\cdot}\ ReOx^1$$

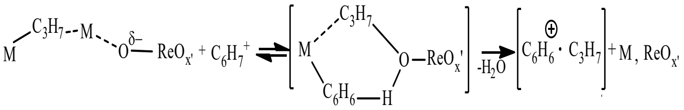
contributing to the formation of some active bridge form of bound oxygen involved in the activation of C_3H_8.



The interaction of benzene with the H-zeolite component of MC promotes the formation of a stable benzolonium ion.

$$H\text{ - zeolite} + C_6H_6 \rightleftharpoons \left[\text{zeolite}\right]^{\ominus} + C_6H_7^{\oplus}$$

able to migrate to the metal-containing component of MC and interact with activated propane.



The formed carbocation$\left[C_6H_6^{\oplus}\cdot C_3H_7\right]$ undergoes stabilization (with isomerization, depending on reaction conditions) on the zeolite component of MC

$$\left[\text{zeolite}\right]^{\ominus} + C_6H_6^{\oplus}\cdot\ C_6H_7 \rightleftharpoons H\text{- zeolite} + \text{products}$$

It was found for the first time that on mechanical mixtures of catalysts consisting of bimetal-aluminum oxide catalysts M, Re/Al_2O_3, low-temperature (≥ 180 ºC)) alkylation of benzene with propane to form isopropylbenzene and the product of its dealkylation and isomerization. With the change in the ratio of C_6H_6: C_3H_8 from 1: 9 to 1 : 1 at P = 0,1 MPa, T = 250 °C and V = 500 h^{-1} a conversion of reactants changes from 12 to 23% and from 1.9 to 7,7%, respectively, and the selectivity for IPB from 100 to 71% .

It was shown that the alkylation of benzene of propane on spatially separated centers of mechanical mixtures (bimetal alumina and H-zeolite) catalysts proceeds by cyclic transport of protons from acid centers on the metal reduction-oxidation and and back ions C_6H_{7+} and C_6H_6 C_3H_{7+}.

It was found that, depending on the reaction conditions: the conversion of C_6H_6:C_3H_8 = 1:9 to MC at 320 °C is accompanied by a benzene conversion of 62.1% and a selectivity for isopropylbenzene of 67.5%, and at 375 ºC, propane conversion is 19.35%, with propylene selectivity 80.3%.

4. Conclusion

A catalytic system consisting of a mechanical mixture of M, Re/Al_2O_3 and H-zeoliteis capable of activating low-temperature propane conversions in the presence of benzene.

As a result of propane activation on this catalytic system, the components of benzene-propane mixtures are converted into C_9-alkylaromatic hydrocarbons and propene. The ratio of the formed C_3H_6:C_9-alkylaromatic hydrocarbons is subject to thermodynamic control, and the distribution of alkylaromatic hydrocarbons is kinetic.

5. References

1. 1. Abasov SI., Babayeva FA., Zarbaliyev RR., Rustamov MI. Low-temperature catalytic alkylation of benzene by propane // Applied Catalysis A: General September 2003; 251(2):267-274 . doi:10.1016/S0926-860X(03)00342-9.

2. 2. Abasov SI., Babayeva FA., Tagiyev DB., Rustamov, M.I. Inıtıatıon of unfavourable reactıons by proton cyclıc transfer over zeolıte-containing catalysts . Proceedings of the 14th International Zeolite Conference, Cape Town , South Africa. Studies in Surface Science and Catalysis. 2004;154: 2339-2346. doi:10.1016/S0167-2991(04)80495-6.

3. 3. Abasov SI., BabayevaFA.,Rashidova AA., Tagiyev DB. Influence of the zeolite nature on low-temperature conversions of C_6H_6 :C_3H_8 mixes on catalytic systems Pt, Re/Al_2O_3+H-zeolite. Processes of Petrochemistry and oil refining. 2004; 3(18):87-93. ISSN:1726-4685.

4. 4. Huang X., Sun X, Zhu S. Benzene Alkylation with Propane over Mo Modified HZSM-5. Catalysis Letters. 2007; 119 (3-4): 332-338. doi: 10.1007/s10562-007-9240-4.

5. 5.Abasov SI., Babayeva FA., İsayevaES., et.al. Dehydroalkylation of Benzene with Propane and Dehydrogenation of Propane over Me-ReOx/Al_2O_3 Contacts. VIII International Conference “Mechanisms of catalytic reactions”, dedicaded to the 70th anniversary of the birth of prof. K.I. Zamaraev, Novosibirsk Russia: June 29- July 2, 2009; 108-109.

6. 6. Gerzeliev IM., MyachinSI.,Tasueva ID., Khadzhiev SN. Synthesis of ethylbenzene on zeolite catalysts. Neftekhimiya. 2009; 49(1): 62–68. doi:10.1134/S0965544109020157.

7. 7.Babayeva FA.,Abasov SI.,Rustamov MI. Conversions of Mixtures of Propane and Benzene on Pt,Re/Al_2O_3

+ H-Zeolite Systems. Petroleum Chemistry, Moscow. 2010; 50(1): 42-46. ISSN: 0028-2421.

8. 8. Ebrahimi AN, Zolfaghari A., Seyyed S., Mousavi A., et.al. Modification and optimization of benzene alkylation process for production of ethylbenzene .Chemical Engineering and Processing. January 2011; 50(1):31-36. .doi: 10.1016/j.cep.2010.10.011.
9. 9. Abasov SI., Isaeva YS, Ismailov EH., Tagiyev DB.Alkylation of benzene by propane over Ni-ReO$_x$/Al$_2$O$_3$+HZSM-5 catalyst.Eleventh International Symposium on Heterogeneous Catalysis. Bulgaria. 2015; 25-26.