Research Article

Khashayar Sharifi, Rouein Halladj*, and Seyed Javid Royaee

An overview on the effects of metal promoters and acidity of ZSM-5 in performance of the aromatization of liquid hydrocarbons

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Abstract: The use of liquid hydrocarbons, such as FCC naphtha, having olefin components makes an adverse impact on our environment. To deal with the problem, one could convert those lethal components, including olefin and paraffin structures, into aromatic compounds under aromatization processes. To this aim, generally zeolite catalysts, especially the ZSM-5 sample, are utilized to facilitate the aromatization processes. According to the general knowledge in this field, such parameters as the metal promoter and the amount of acidity of catalyst affect the performance of zeolite catalysts. In this paper, with the aim of getting acquainted with the conditions to form the desirable products under the best performance of the zeolites, numerous published papers were reviewed.

Keywords: aromatization, zeolite, ZSM-5, octane number, olefin, paraffin

1 Introduction

This is an absolute fact nowadays, all over the places feel that they are really in need of clean fuels. One ingredient of fuels which affects impressively the properties of gasoline is olefin. Depending upon the World Wide Fuel Character on Categories II, III, IV and V, the contents of olefin in gasolines should be reduced to 18 vol.% or less, yet the world needs more information in various aspects to acquire enough potential to overcome the current fluid catalytic cracking (FCC) gasoline with the olefin contents of 45–55 vol.%. [1].

Due to the great technological advances of the 21^{st} century, without a change in the octane number, the amount of olefins in gasolines can be diminished dramatically. The catalytic conversion of gasoline fractions by taking the advantage of zeolites having a large amount of silica within some secondary processes such as isomerization and catalytic reforming can culminate in worthwhile results. High commercial gasolines, for example, are the benefit of this type of customary reforming which is developed by the catalytic aromatization operation. There exist loads of parallel and sequential acid-base reactions within zeolite catalysts, each of which is based on an acid-base transformation, that concomitantly extract the final high octane gasoline fractions from the ordinary gasolines [2].

Furthermore, the fuels octane number can be extended by using the process of isomerization of paraffin. Hydroisomerization of n-paraffins is of key importance in the field of petroleum and chemical engineering. In order for gasoline fractions with high octane numbers to be formed engineers exploit the hydroisomerization of C_4-C_7 [3, 4]. Light straight-run naphtha contains n-paraffins in this range and the process of hydroisomerization changes them to high octane number components [5]. Generally, the hydroisomerization reaction is followed by a hydrocracking reaction which truncates the isomerized molecules. It is worth considering that the cracking reaction happens as a secondary reaction after isomerization of n-paraffins and leads to formation of the multi branched alkanes [6]. Aiming to reach a maximum recovery, engineers prepare conditions whereby they would have hydrogenation/dehydrogenation via bifunctional catalysts with metallic sites and also skeletal isomerization via carbenium ions in acid sites during isomerization reactions [7]. Olefin cracking, isomerization, oligomerization, cyclization and hydrogen transfer reaction are four sequential steps defined in an olefin aromatization. Whereas the first three steps are done on the Bronsted acid sites, the hydrogen transfer mechanism, as the lowest reaction rate (the

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***Corresponding Author: Rouein Halladj:** Faculty of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), P.O. Box 15875-4413, Hafez Ave., Fax: +98 216 640 5847, Tehran, Iran; Email: halladj@aut.ac.ir
Khashayar Sharifi, Seyed Javid Royaee: Petroleum Refining Division, Research Institute of Petroleum Industry, P.O. Box 1485733111, Tehran, Iran

Reactions on Bronsted Acid Site

- Isomerization
- Cracking
- Oligomerization
- Cyclization

Reactions On Lewis Acid Site

- Hydrogenation
- Dehydrogenation

Figure 1: Types of reactions on acid sites of zeolite

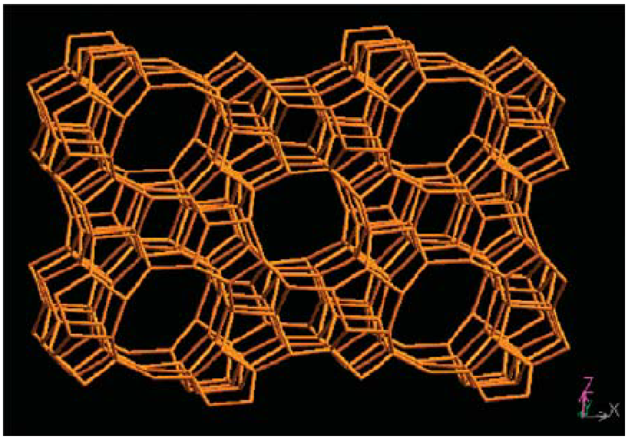


Figure 2: Zeolite structure of ZSM-5

rate-controlling step), is handled on the Lewis acid sites. Owning to that, the synergistic between the two kinds of acid sites makes an impact positively on the aromatization reaction rate [8].

There are several parameters that can enhance the hydrocarbons aromatization. One of the promising ways is utilizing zeolites such as ZSM-5. As it was alluded in many papers, the good operation of zeolites is under different factors, some of which are metals as promoter and acidity of the zeolites. The aromatization of some alkanes were studied meticulously by the authors of this manuscript [9–11]. The first aim of this work is scrutinizing the influence of the factors mentioned above over aromatization processes in order to comprehend how various catalysts conditions can make a change in the production of aromatic components.

2 ZSM-5 Zeolite effect in Octane Enhancement

As mentioned in preceding section, of zeolite solid acid catalysts, ZSM-5 is so popular that has a wide range of applications in fuel enhancing and new material producing in petrochemical industries. Thanks to the strong acid sites available on ZSM-5, it could find a high reputation in aromatization processes. This also is contributed with its intersecting 10-member ring micro pores (5.5 Å × 5.1 Å; 5.3 Å × 5.6 Å), which explain its suitable selectivity and coke resistance power [12]. This kind of zeolites is made up of crystalline networks of SiO_4 and AlO_4 components through a tetrahedral geometry in 3-dimensional frameworks. In detail, there exist straight and elliptical pores in each cross section of zeolite frameworks in which both of the pores intersect each other at the right angle in a zigzag pattern [13, 14]. The ZSM-5 activities are followed by charge imbalance between ions in the frameworks including the silicon and aluminum ions [15]. The structure to be considered is shown in Figure 2.

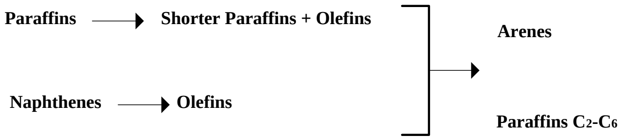
Physicochemical properties of ZSM-5 zeolites are massively affected by such parameters as alkalinity, chemical composition of the synthesis gel, template, the silica alumina ration, time of crystallization, temperature, zeolite synthesis procedure (static or rotating conditions) and other operating conditions prevalent in hydrothermal synthesis [16, 17]. These factors might have remarkable influences on its stability, activity and selectivity [10].

Zeolites wide applications as adsorbents, molecular sieves, and catalysts are related to their specific features including adsorption, ion exchange, and molecular sieve properties because of the ordered crystalline structure, chemical and thermal stability, and the presence of pores compatible with the molecules sizes in the reaction medium [18].

Clearly, olefins are the potential component for improving octane number of a gasoline and decrement of olefins surely brings sacrifice to gasoline's octane rating. However, one of the most influential ways is using ZSM-5 as an additive to FCC catalyst to better FCC naphtha octane. It is widely believed that at low amounts, the presence of ZSM-5 rises the octane number initially by favoring the catalytic cracking and turns the low octane compound to a number of lighter and more branched products [19, 20].

Indeed, as many great researchers [19, 21] suggested, rising of the number of aromatics seen in the cracked naphtha including ZSM-5 is solely related to concentration effect, a consequence of the selective cracking of many hydrocarbons and the absolute numbers of aromatics left essentially unchanged. However, other researchers [22] believed that aromatics could be strengthened in the attendance of ZSM-5 from the lower olefin and lower paraffin created from the large hydrocarbon molecules.

Generally, the conversion of hydrocarbons involves the basic steps given below [2]:



The cleavage of a C–C bond of hydrocarbons is the first step that happens and the formation of intermediate olefin fragments which have a high endothermic thermal influence occurs at this moment. Thereafter, olefins convert into paraffins and aromatic hydrocarbons because of the migration process and rearrangement of hydrogen that follows. This step is concomitant with a high exothermic effect. While basic processes take place, some side reactions occur, namely the alkylation of iso-paraffins and aromatics by intermediate olefins and the isomerization of paraffins and naphthenes (Figure 3). Although some steps are heat releasing, the whole process of the zeolite-assisted transformation of straight-run gasoline fractions is endothermic.

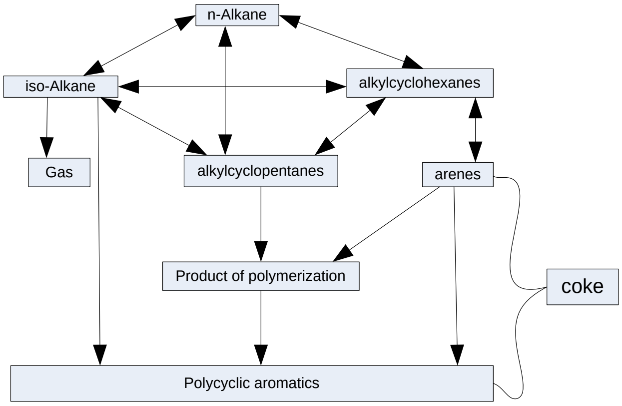


Figure 3: Conversion of hydrocarbons on zeolite catalysts [2]

Zeolite catalysts do not need preliminary removal of sulfur or hydrofining and gaseous hydrogen. The reduced content of benzene in the resulting mixtures, compared with gasolines after reforming, is the fascinating feature of a pentasile type catalyst. The thermodynamic conditions suitable for benzene formation are not accessible. Furthermore, on condition that there exists benzene in the feedstock, some parts of it would transform into C_7-C_9 aromatic hydrocarbons owning to alkylation by intermediate olefins. There is a high level of conversion of olefins when zeolite-based catalysts are used in the aromatization processes, so the unsaturated hydrocarbons of such gasoline is low. Indeed, zeolite catalysts, having a large induction period, don't need neither antioxidants nor stabilizers compared with gasolines produced with catalytic cracking. Nonetheless, it should be noted that the carbon deposition over the ZSM-5 surface attenuates the stability and activity of catalysts. That is the biggest problem of ZSM-5 zeolites for industrial applications. A proper modification can upgrade the catalysts performances. Moreover, the combination of the acid zeolite and a hydrogenation/dehydrogenation component, especially a noble metal, together can make the catalyst bifunctional. A reasonable modification technique is required for zeolites with basic properties to be formed. In contrast to acid zeolites, basic zeolites with their basic properties would not attract much attention in industrial catalysis. Furthermore, the world needs practical catalysts being able to improve the octane number and decrease the amount of sulfuric species of liquid hydrocarbons in processes.

As a result, the need of proper zeolites for aromatization processes is essential, and they could change the characteristics of products depending to customers desires. In the proceedings, we are going to study the effect of metals on zeolite performance and investigate some metals used more in the aromatization of hydrocarbons.

3 Metals

The presence of Bronsted acid sites on zeolites surfaces makes them better microporous solids for heterogeneous catalysis [23]. The appearance of 2- charge on the four coordinating oxygen atoms beside the 4+ charge on framework silicon atoms in aluminosilicate zeolites makes a neutral tetrahedral framework $SiO_{4/2}$. Nonetheless, by replacing the silicon cation with a 3+ charge, such as an aluminum cation, in the framework, the formal charge on that tetrahedral framework transforms to 1-. The produced negative charge can be balanced by either a hydroxyl proton or a metal cation to produce a strong Bronsted or a weak Lewis acid site [24, 25]. As a proton donor, a hydroxyl proton prepares a Bronsted acid site. A hydroxyl proton is situated on an oxygen bridge which joins tetrahedrally coordinated silicon with an aluminum cation on a framework position. Because of that, the mentioned OH group is generally taken as either a bridging or a structural OH group (SiOHAl). To clearly introduce Bronsted acid sites in zeolites, one should regard them as weak proton-type hydroxyl groups which connect two tetrahedrally coordinated atoms, *e.g.* Al and Si. On the other side, Bronsted acid sites in amorphous material consist of silanol groups which as electron pair acceptors and similar to Al atoms contribute to a weak interaction with adjacent atoms which perform as Lewis acid sites [26]. On condition that local structures of bridging OH groups replaced with different metal atoms such as Pt, Mo, Ga etc. are equal in zeolites, the chemical properties of the loaded atoms determine the acid strength of the hydroxyl protons. Therefore, due to this dependency, the substituted materials are influential in the catalytic activity of the zeolite catalysts [27, 28].

That the acid sites over zeolite-based catalysts are important for a wide range of petrochemical processes is obvious fact [29]. Bronsted acid sites in ZSM-5 catalysts, for instance, are applied for paraffin isomerization, production of gasoline from methanol and even olefins and ethylbenzene. In hydroxylation of aromatics to their related phenols, Lewis acid sites of hydrothermally pretreated ZSM-5 catalysts organize the catalytic activity [30].

High-silica ZSM-5 zeolites can be counted as a highly influential catalysts for the production of high-octane gasoline from various raw hydrocarbons as feedstocks [31]. The introduction of metallic elements over zeolite frameworks promotes them to work as bifunctional catalysts which combine the hydrogenation-dehydrogenation and carbocation rearrangement functions. Generally speaking, metal elements catalyze the first step while the second step is done with the help of Bronsted acid sites, *i.e.* zeolite hydroxyl groups [32]. The high surface area of metals used to modify zeolites needs to expand the contribution of surface states and to make easy the density of defects and energy. Given this, the catalysts should display a specific activity.

It is believed that the Bronsted acid sites situated on the external surface are responsible for the formation of a large quantity of carbonaceous deposits [33]. These acid sites catalyze the conversion of polycyclic aromatic components [34], which are deposited on the external surface and finally impede the paths toward the microprores [35]. Thus, the contributing of metallic elements to the zeolite frameworks culminates in neutralization of some parts of Bronsted sites by creating of new Lewis acid sites [36]. This advancement expands the application of surface groups in the aromatization reactions. Given this, the catalysts activity and selectivity depend on the distribution of metal elements as well as acid sites over the catalysts in the hydrocarbon conversion in aromatization processes. On condition that industry is in need of an especial production with specified properties, engineers should gather information about distribution of the metals over the zeolite surfaces and also about the nature and electronic state of the metals to prepare suitable catalysts for the desired products. It should be taken into account that a proper metal on catalysts can reduce cracking selectivity. One of the useful coproducts on metal-modified catalysts is dihydrogen. In the proceedings, the contribution of some more important metallic elements to ZSM-5 catalysts and their effects on ZSM-5 performances are explained.

3.1 Gallium

The aromatics selectivity can be promoted dramatically by taking the advantage of metal bifunctional zeolite catalysts. As widely alluded in literature, of the catalysts with a variety of different metals, the Ga containing zeolites can be introduced as the most influential catalysts in terms of the stability and selectivity for the aromatization processes. As a general rule, zeolites Bronsted acid sites (BAS) participate in cracking, oligomerization and cyclization reaction steps and that Ga sites play an important role in dehydrogenation of the feed alkanes and some intermediate components produced from the aromatization reaction steps.

Thanks to the good dehydrogenation and selectivity potential of Ga-containing HZSM-5 zeolites to aromatics, due to their unique pore structure as well as their reasonable acid distribution, the use of Ga-containing HZSM-5 zeolites are common [37, 38]. Over these Ga-doped catalysts, the laying down of Ga has been mostly done by post synthesis methods, such as aqueous impregnation and ion exchange. In the Ga-loaded HZSM-5 zeolites which are made by the ion exchange process with $Ga(NO_3)_3$ solution, the dispersion and concentration for Ga species and Ga^{3+}, respectively, are low [39].

According to a general rule, in comparison to other metal cations, Ga^{3+} ions cannot easily incorporate into ZSM-5 zeolites through such methods as physical admixture or impregnation techniques. The reasons behind this hardship are the high positive electrostatic charge and the size of gallium aqua complexes coupled with the hydrophobicity and weak anion field of ZSM-5 frameworks [28, 40]. Because of this, the gallium aqua complexes could not effectively penetrate into zeolite micro pores and would not have proper interaction with Bronsted sites. Given this, predominantly Ga^{3+} cations would inhabit on the external surface of zeolites as an extra crystalline Ga_2O_3. Nonetheless, several researchers indicated that Ga ions are able to disperse desirably over zeolite micro pores, as extra framework species [41, 42]. Such techniques as reducing-oxidizing pretreatment cycles, ion-exchange and chemical vapor deposition culminated in proper laying down of Ga^{3+} exactly into the micro pores Bronsted sites. The combination of Ga and ZSM-5 zeolites by the means of hydrothermal synthesis has already enhanced the aromatization reactions dramatically [43]. This

Table 1: Catalyst Synthesis [45]

	HZSM-5	Ga (ix)	Ga (imp)	Ga (mix)
Gallium Addition	-	Ion-exchange	impregnation	Ball-milling
Gallium precursor	-	$Ga(No_3)_3{\cdot}9H_2O$	$Ga(No_3)_3{\cdot}9H_2O$	$B\text{-}Ga_2O_3$
Gallium loading (wt.%)	0	18	5	5

Table 2: Aromatic selectivities at 550oC for 1-hexene aromatization [45]

	HZSM-5	Ga (mix)	Ga (ix)	Ga (imp)
Benzene, (wt.%)	2	8	25	24
Toluene, (wt.%)	5	17	33	30
p,m-Xylene, (wt.%)	4	8	9	9
o-Xylene, (wt.%)	1	2	3	2
Et-Benzene, (wt.%)	0	1	1	1
$\sum$ BTEX, (wt.%)	12	36	71	66

has been done while the presence of Ga species (its distribution) over the zeolite channels was uniform.

Gallium species also play a significant role in coordination state. In the hydrothermally synthesized galloaluminosilicates, the majority of elements gallium present on the framework positions. In comparison with the hydrothermally synthesized galloaluminosilicates, the impregnation method for preparing Ga/HZSM-5, leads most of the gallium species on the external surface of catalysts like isolated gallium oxides. As for the gallium species introduced by the ion-exchange method, their states still remain controversial. As mentioned above, one of Ga^{3+} difficulties to be exchanged as metallic ions with ZSM-5 ions is the ZSM-5 intermediate pore sizes which restrict the access of big Ga^{3+} to the intracrystalline volumes. Given this, the gallium species can only present on the external surfaces in the calcined (Ga, H)-ZSM-5 catalysts made by the ion-exchange method [40]. There exist some researchers that had another viewpoint. Mia *et al.* [44] believed that there exist no gallium species subjected by the ion-exchange method in neither the zeolite channels nor the cation-exchange positions. Instead of that, they appear as oxide species between isolated Ga_2O_3 and Ga species. Apart from that, the chemical states and the gallium species locations would be under control of the oxidative, reductive and hydrothermal treatments. The component of Ga_2O_3 can be reduced to Ga_2O, Ga^+ or Ga/H^{2+} by H_2 in the zeolite channels.

In another study Gallium/HZSM-5 zeolite catalysts were used for long chain alkenes, namely 1-hexene and 1-octene to be transformed in an aromatization process [45]. The aim of this work was investigating three different techniques for creating Gallium loaded H-ZSM-5 zeolites. The researchers tested physical mixing, ion-exchange and impregnation methods in order to add the gallium species to the zeolites. It should be added that the influence of hydrogen pretreatment on efficiency of the catalysts performances was investigated too. All reactions were conducted at the temperature range of 350-500°C. Most of details they took into consideration are tabulated in Table 1.

They analyzed the aromatic selectivity of 1-hexene aromatization under 500°C and summarized their information in Table 2. Despite the differences in preparation and the actual amounts of gallium, similar BTEX selectivities were recorded. The amount of Gallium for Ga (ix) was 18 wt.% and for the other catalysts was 5 wt.% Such researchers as Kitagawa *et al.* [46] asserted that as the gallium loading increases the selectivities to aromatics increases, but once the gallium content reaches its top value of ion exchange (100% ion exchange), the performance of the aromatization process stops advancing.

Another chance to enhance the aromatization performance with Ga loaded zeolites is to use intracrystalline mesoporosity in zeolite crystals, for this would truncate the contact time of reaction intermediates. Most of the time, the intercrystalline diffusion limitation on the reaction rate, followed by a decrease in the catalytic performance of zeolites, comes from the zeolites micro porous character [47]. That by shrinking the zeolite crystals in size, the diffusion limitations have been obviated was stated by Hartmann [48]. There are a wide range of techniques for introducing intracrystalline mesoporosity in zeolite crystals, some of which are post-synthesis modifications such as dealumination (*i.e.* acid leaching, steaming) and desilication (alkaline treatment)], direct carbon templating method, taking the advantage of composite microporous/mesoporous materials, zeolite delamination, and synthesis of wide-pore zeolite [49, 50].

Faro *et al.* [51] showed that Ga/HZSM-5 catalysts made by the impregnation of HZSM-5 with gallium nitrate solutions and then subjected to the reductive and oxidative pretreatments are able to lower the ratio of the β-Ga_2O_3 phase and develop well-dispersed gallium species. Su *et*

Table 3: Chemical composition of nanosized ZSM-5 zeolite and samples isomorphously substituted by Ga [8]

Sample	In the gel			In the products			
	Si/(Al+Ga)	Si/Al	Ga/Al	Si/(Al+Ga)	Si/Al	Si/Ga	Ga/Al
NZ5	20.0	20.0	-	16.17	16.17	-	-
Ga_2Al_8NZ5	20.0	25.0	0.25	12.97	16.45	61.23	0.27
Ga_4Al_6NZ5	20.0	33.33	0.67	11.77	20.93	26.90	0.78
Ga_5Al_5NZ5	20.0	40.0	1.0	11.93	26.53	21.68	1.22
GaNZ5	20.0	∞	∞	10.77	120.37	11.82	∞

Table 4: Textural data of nano sized HZSM-5 and samples isomorphously substituted by Ga [8]

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	$S_{external}$ (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
NZ5	407	325	82	0.254	0.133	0.121
Ga_2Al_8NZ5	443	359	84	0.266	0.148	0.118
Ga_4Al_6NZ5	434	362	72	0.257	0.150	0.107
Ga_5Al_5NZ5	426	328	98	0.301	0.138	0.163
GaNZ5	429	325	104	0.298	0.131	0.167

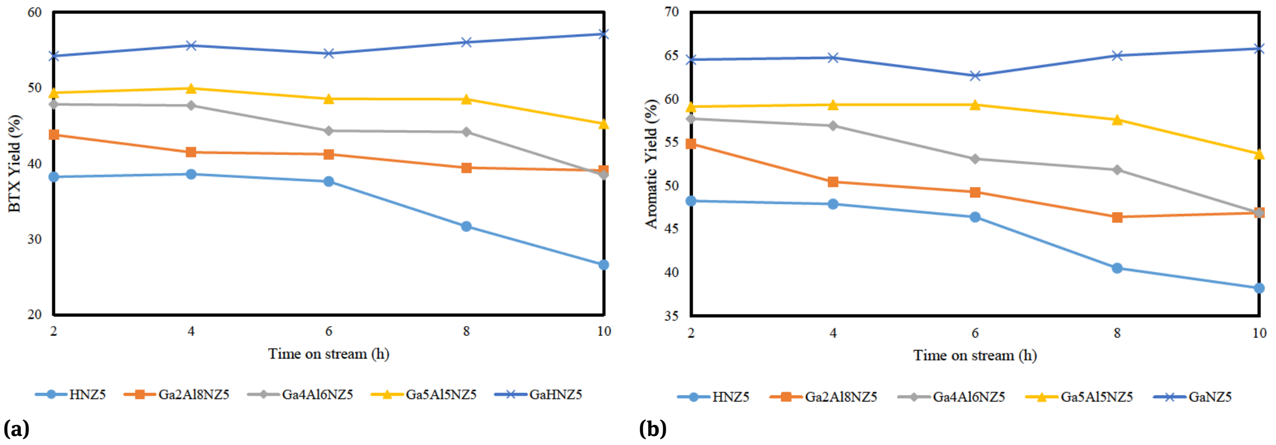


Figure 4: BTX yield (a) and aromatics yield (b) of 1-hexene aromatization over the nanosized HZSM-5 and samples isomorphously substituted by Ga [8]

al. [8], in an interesting work invented a method that the seed-induced in-situ hydrothermal synthesis of nano sized HZSM-5 zeolites that are partially or completely isomorphously substituted by gallium, denoted as GaAlHNZ5 and Ga/HNZ5, in the same order. In comparison to the traditional impregnation method, this technique develops conditions so that it could decrease a lot of organic templates in the synthesis process and properly inhibit the loss of gallium species. This technique is completely prosperous, and it should be regarded as efficient way for the synthesis of heteroatom HZSM-5 materials. In this study, nano sized HNZ5 catalysts, Ga_xAl_yHNZ5 (x = 5, 4, 2, and y = 5, 6, 8, respectively) and Ga/HNZ5, have been acquired via partial and complete isomorphous substitution by gallium, respectively, in order for the effects of different gallium species over the catalysts as well as the acidity of the catalysts with different densities of Al and Ga on their catalytic performances in the aromatization processes to be understood profoundly. The chemical compositions and the textural properties of samples are all represented in Table 3 and Table 4, respectively.

In Figure 4 the performances of these catalysts on 1-hexene aromatization are distinctly sketched. The conversion of the 1-hexene feed is 100%. As seen from the figure, the amounts of such desirable products as benzene, toluene, and xylene obtained by the catalysts isomorphously substituted by gallium are absolutely higher than the products from the HZSN5 catalyst; moreover; this could be extended provided that the gallium species in the bulk of samples were increased. As the cracking reaction weakened, the Ga/HNZ5 catalyst displayed the highest level of total aromatic yield, 64%, that was due to the milder Bronsted acid sites produced by the framework Ga and the increscent of dehydrogenation activity on the more number of Lewis acid sites, with stronger strength formed by the extra framework Ga species, such as GaO^+ and GaO(OH), as well as the optimum B/L ratio of 4.4.

As Ga content in the mixed gel increased, the concentration of both Lewis acid sites with promoted strength and Bronsted acid sites with weakened strength increased. This is true due to the addition of Ga to the HZSM-5 zeolite and the formation of the more framework Ga species. Not only was the total aromatics yield of 64.6%, as the highest production in the 1-hexene aromatization, achieved with the Ga/HNZ5 zeolite, but also catalyst deactivation lessened tremendously thanks to the weakness of acid strength, the proper B/L proportion and the formation of intergranular mesopores during the accumulation of nanocrystal particles with a smaller size which prevented producing the coke precursors.

According to the results it can be comprehended that the catalysts made with Ga isomorphous substitution can make the formation of Bronsted and Lewis acid sites easier. Apart from that, as the Ga/Al ratio increased after Ga partial or complete substitution for Al in the sample framework, the aromatics yield increased. Due to the higher amount of the weakened Bronsted acid sites and the enhanced Lewis acid sites, and the most appropriate B/L ratio of 4.4, Ga/HNZ5 displayed the highest aromatic yield of ca. 64.6%.

In another work, nanosized Ga-containing ZSM-5 zeolites were synthesized through isomorphous substitution and impregnation followed by characterized using various techniques. The catalytic capabilities of the zeolites for the 1-hexene aromatization process were investigated. A fixed-bed microreactor with a continuous-flow system was used so as for the aromatization reaction was conducted. The relative crystallinities and chemical composition of gallium-containing ZSM-5 zeolites prepared via different preparation methods are shown in Table 5.

Depending upon Table 2, it could perceive that the relative crystallinities of Ga-substituted ZSM-5 do not tangibly change, and the crystallinities of the impregnated samples reduce slightly, which is most likely due to covering by the Ga_2O_3 species. According to the chemical compositions in Table 1, the bulk Si/Al ratio of the Gax-NZ5 samples increases slightly as the Ga content increases. It implies that the introduction of aluminum into the bulk phase is more difficult due to Ga incorporation via the isomorphous substitution method. The Si/Me (Si/metal) ratio of the Gax-NZ5 samples in the bulk is lower than that in the HNZ5 sample, and the ratio decreases as the Ga content increases, which may be due to an increase in the total metal content in the zeolites.

Moreover, from the data of this table it could be understood that both the micropore and mesopore volumes grows in the Ga-substituted ZSM-5 samples because of the longer Ga–O bond in the framework and defects as well as the intergranular mesopores formed via accumulation of smaller nanocrystals, in the same order. Nonetheless, for the Gax-NZ5 samples, the micropore volume and surface area reduces with reducing the Ga content. This result arises from an increase in the extra-crystalline oxide species that are generated by incomplete incorporation of Ga species or demetalization, resulting from ion-exchange and calcination that reduce accessibility to the internal structure of the catalysts. For the impregnated samples, the porosity decreases since the poorly dispersed, extra-crystalline gallium species (Ga2O3 phase) partially block the pores in the media.

As it can be seen in Figure 5, BTEX (Benzene, Toluene, Ethylbenzene and Xylene) are the main products in each of the samples, and the C9+ aromatic fraction is less than 10 wt.%, which is beneficial for decreasing the final boiling point of the fuel. Furthermore, the aromatic yield over the Ga-containing ZSM-5 zeolites grows with increasing the Ga content. However, the extent of this increase differs for the different series.

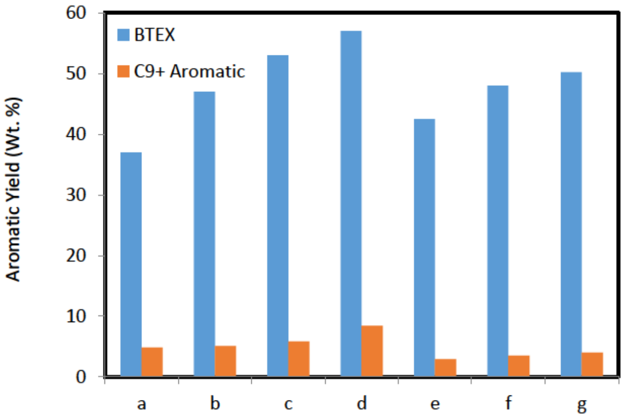


Figure 5: Aromatic Yield: a. HNZ5, b. Ga1.5-NZ5, c. Ga2.1-NZ5, d. Ga4.2-NZ5, e. Ga1.5/NZ5, f. Ga2.1/NZ5, g. Ga4.2/NZ5 [98]

Table 5: Relative crystallinities, chemical composition and Textural properties of gallium-containing ZSM-5 zeolites prepared via different preparation methods [98]

Samples	Gel Composition			Bulk Composition			Si/Me$_{FW^a}$	Ga (wt.%)	Surface Area (m^2/g)			Pore Volume (cm^3/g)		
	Si/Al	Si/Ga	Si/Me	Si/Al	Si/Ga	Si/Me			S$_{BET}$	S$_{ext}$	S$_{Micro}$	V$_{Total}$	V$_{Micro}$	V$_{Meso}$
HNZ5	50	-	50	35	-	35	35	0	386	74	312	0.284	0.137	0.147
Ga1.5-NZ5^b	50	80	35	37	75	25	25	1.5	434	73	361	0.368	0.153	0.215
Ga2.1-NZ5	50	50	25	38	52	22	16	1.9	427	73	354	0.363	0.144	0.219
Ga4.2-NZ5	50	20	14	41	24	15	12	3.5	401	80	321	0.361	0.131	0.230
Ga1.5/NZ5^c	50	-	50	34	73	23	-	2.5	358	70	288	0.274	0.125	0.149
Ga2.1/NZ5	50	-	50	35	52	21	-	3.3	352	69	283	0.257	0.123	0.134
Ga4.2/NZ5	50	-	50	35	25	15	-	5.1	336	55	281	0.247	0.121	0.126

[a] Si/Me $_{FW}$ corresponds to the framework Si/(Al + Ga) ratio calculated via Si MAS NMR.

[b] Ga*x*-NZ5 were synthesized via an in-situ seed-induced method.

[c] Ga*x*/NZ5 were prepared via an incipient wetness impregnation method

3.2 Zinc

There exist some methods for preparing Zn-containing ZSM-5 catalysts, including ion exchange in aqueous solution, incipient wetness impregnation, chemical vapor deposition, and isomorphous substitution techniques. Researchers such as Mole *et al.* [52] held the idea that in the chemical reactions, the zinc cation in Zn/ZSM-5 catalysts acts as a hydride acceptor in order to prepare a transient species, including $[Zn\text{-}H]^+$, in the dehydrogenation. In another study, Ono *et al.* [53] asserted that although gallium and zinc cations do not have a direct effect over paraffin activation, they are of key importance in transforming of olefins into aromatics. Kanai and Kawata [54] indicated that the process of n-hexane aromatization using ZnO/HZSM-5 catalysts divides into two sub-categories: 1) dehydrogenation of n-hexane into hexene 2) dehydrogenation of oligomerized products into aromatic hydrocarbons. Furthermore, they, unlike Ono *et al.* [55], believed that ZnO and H-ZSM-5 directly participate in the activation of n-hexane.

The addition of a hydrogenating metal to the zeolite catalysts leads to better paraffins conversion. Generally speaking, the metal ion prepares another path for the conversion of olefins as well as aromatics, and also it somehow prevents lower paraffins formation from cracking and hydrogen transfer reactions. The electronic characteristics of metals, added over zeolites, determine metals hydrogenation-dehydrogenation activity which controls the aromatization activity of metals [56, 57]. Kanai [54] clarified the potential of element zinc in the formation of hexane from n-hexane using the catalyst of ZnO/H-ZSM-5. Shibata *et al.* [58] confirmed the preceding opinions about the paraffin activation by zinc and acid sites. It was postulated that both of the HZSM-5 and ZnO participate in the n-hexane activation. That Zn can develop another path for aromatization was asserted in another research [59]. In addition, it was pointed out that Zn holds back the continuous oligomerization process and C_{9+} aromatics formation.

Viswanadham *et al.* [56] tried to prepare ZSM-5 (HZ) by hydrothermal synthesis, and the samples of zinc and gallium loaded ZSM-5 catalysts by applying incipient wet impregnation (ZnHZ, GaHZ) and co-synthesis methods (Zn-Al-Si and Ga-Al-Si). The n-heptane aromatization activity of the samples can be sorted by the following order: Zn-Al-Si > Ga-Al-Si > ZnHZ ∼ GaHZ > HZ. The sample of Zn-Al-Si catalyst while having the lowest acidity, exhibited the highest aromatization activity with enough stability during 360 min performance. The catalyst had higher than 80% conversions with 50-65 wt.% selectivity to aromatics for industrial raw materials including gas condensate, raffinate and light naphtha. In this process, the most available byproduct belongs to 21-23 wt.% LPG which shows this catalyst as a prosperous sample for the real world application. The conversion and selectivity to be considered are shown in Table 6.

Table 6: Performance of metal modified ZSM-5 catalysts in n-heptane aromatization [56]

Catalyst	HZ	ZnHZ	GaHZ	Zn-Al-Si	Ga-Al-Si
Conversion (%)	90	85	78	68	74.5
Selectivity (wt.%)					
Methane	14.6	4.5	4.2	6.0	6.8
Ethane	23.0	2.0	1.8	5.0	4.1
Propane	38.4	43.4	32.0	10.5	12.0
Butane	8.1	15.1	21.5	15.0	13.8
C_5^+	2.0	1.0	2.5	5.5	4.8
Aromatics	13.9	34.0	38.0	58.0	56.5

In the proceedings, the effect of various hydrocarbon components was evaluated by them. From Table 7, it can be perceived that the nature of hydrocarbon types is not too effective matter to change the selectivity of aromatics and distribution of BTX over the HZSM-5 catalyst. The products extracted from paraffins and naphthenes are comparable. It should be noted that the selectivity to toluene is not changed when consuming feeds are C_7 (such as n-heptane and methyl cyclohexane). Also, one should consider the fact that Zn-Al-Si was able to increase the benzenes selectivities with n-C_6 and toluenes ones with n-C_7 input. Therefore, the occurrence of direct dyhydrocyclzation of these n-paraffins by using Zn-Al-Si, but by not using of the HZSM-5 catalyst, can be implied. For the naphthene feeds, the one-step hydrocarbon aromatization seems more important, especially whenever the dominance of benzene selectivity from cyclohexane and toluene selectivity from methyl cyclohexane can be found in the product. From all information taken from the study, the active sites over Zn-Al-Si facilitate the one-step aromatization of naphthaenes and paraffins.

The aromatization process was conducted by means of the Zn-Al-Si catalyst over feeds of natural gas condensate, light naphtha-I/-II and raffinate. Properties of raw materials as well as the final products of the aromatization process are summarized in Table 8.

The importance of La and P contribution over aromatization reaction and physicochemical properties of Zn/ZSM-5 were tested by Long *et al.* [60]. Table 9 demon-

Table 7: Effect of Hydrocarbon types on the aromatic distribution [56]

Catalyst Feed	HZSM-5				Zn-Al-Si			
	n-hexane	n-heptane	Cyclohexane	Methyl cyclohexane	n-hexane	n-heptane	Cyclohexane	Methyl cyclohexane
Selectivity to individual aromatics (wt.%)								
Benzene	8	7	6	6	8	7	15	5
Toluene	42	45	43	45	40	45	40	60
xylene	50	48	51	49	50	48	45	35

Table 8: Feed characteristics and product selectivities over Zn-Al-Si catalyst [56]

Feed	Natural gas condensate	Light Naphtha		Raffinate
		I	II	
Feed characters				
IBP	35.1	70.0	87.0	46.1
FBP	145.1	90.0	137.0	131.9
Density	0.67	0.72	0.79	0.68
Conversion	85.0	88.0	94.0	91.0
Selectivity (wt.%)				
$C_1 + C_2$	12.0	7.5	8.0	9.5
$C_3 + C_4$	21.0	26.5	22.0	32.5
BTX	52.0	54.0	63.0	49.0
C_{5^+}	12.9	9.2	2.7	6.8
C_{9^+}	2.1	2.8	3.3	2.2

strates the main results of physicochemical property of zeolites. According to the table, after adding element Zn to the ZSM-5 the value of BET surface area of the sample decreased from 345 m^2/g to 328 m^2/g, while its micro pore volume did not have a tangible change at all. In a similar manner, with the addition of La to Zn/ZSM-5, the total surface area as well as the micro pore area decreased to 287 m^2/g and 171 m^2/g, respectively. Indeed, there was a loss of the micro pore volume (about 0.01 mL/g) after La was added to the Zn/ZSM-5 sample. This event may come from pore blockage and it even had sharper consequences when La and P were both introduced to Zn/ZA over the ZnLaP/ZSM-5 sample. The surface area as well as pore volume of the ZnLaP/ZSM-5 catalyst was extremely shrunk. The BET surface area of ZnLaP/ZSM-5 was only 235 m^2/g and its external surface area was only 56 m^2/g. As seen from Table 9 the micro pore volume of ZnLaP/ZSM-5 remained constant in size and the total pore volume was diminished by 0.06 mL/g in size when introducing P into the ZnLa/ZSM-5 sample. According to this, more P elements were accumulated on the exterior surface or in the mesopores of catalysts.

Table 10 illustrates the evaluation results of the catalysts in the FCC gasoline upgrading process.

Thus, the yields of aromatics in alkene aromatization on bifunctional catalysts can be increased on condition that the presence of the dehydrogenation reactions in the formation of dienes increases and the corresponding aromatics from cyclic intermediates catalyzed by Zn species acting as Lewis acid sites. By adding La, the element zinc support interaction as well as the amount of $[Zn(OH)]^+$ species develop; consequently, it promotes the catalyst activities in aromatization processes. By adding P, the presence of the element zinc located in the paths of nanoscale HZSM-5 increases. Provided that the distance between the Zn species and the zeolite crystals Bronsted acid sites shortens, the synergy effect between them is accentuated and then the stability of the catalyst is improved. The synergistic effect of La and P decreases the loss of zinc species and increases the amount of $[Zn(OH)]^+$ species and then improves the activity and stability of the catalysts in the FCC gasoline aromatization. The optimized ZnLaP/HZSM-5 catalyst can be named as a proper catalyst with a high catalytic performance in the FCC gasoline aromatization reaction in industry [60].

Tshabalala *et al.* [61] investigated n-Hexane aromatization under 500°C over parent and metal (*i.e.* Ga, Mo and Zn) modified HZSM-5 catalysts. The n-hexane conversion over the HZSM-5 catalyst was ca. 85% (Figure 6a). A decrease in conversion and slight catalyst deactivation with increase in time on stream (TOS) was followed by the addition of metal species to the HZSM catalysts. The activity reduction comes from the reduction of the number of strong acid sites. Mo/HZSM-5 presented better stability over Zn/HZSM-5 and Ga/HZSM-5. The n-hexane conversion over Mo/HZSM-5, Zn/HZSM-5 and Ga/HZSM-5 catalysts was ca. 75%, 75% and 60%, respectively (Figure 6b).

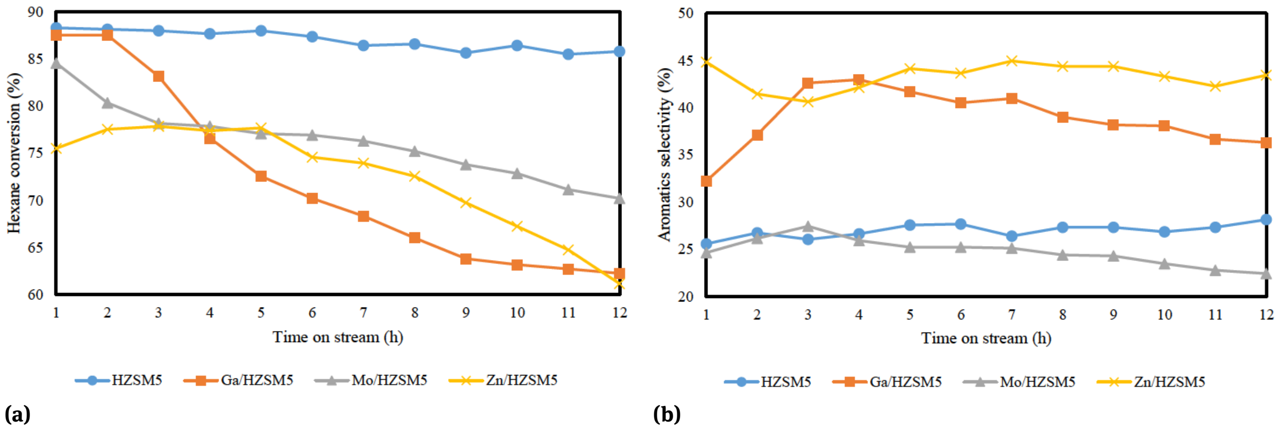


Figure 6: The catalytic conversion of n-hexane over metal promoted HZSM-5 catalysts of 2 wt.% loading as the function of time-on-stream at 500°C [61]

Table 9: The results of physical adsorption with N2 of the catalysts [60]

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	$S_{external}$ (m^2/g)	V_{total} (ml/g)	V_{micro} (ml/g)
ZSM-5	345	208	137	0.36	0.09
Zn/ZSM-5	328	199	129	0.37	0.09
ZnLa/ZSM-5	287	171	116	0.32	0.08
ZnLaP/ZSM-5	235	179	56	0.26	0.08

Table 10: Composition of FCC gasoline feed and product [60]

	Feed	Zn/ZSM-5	ZnLa/ZSM-5	ZnLaP/ZSM-5
Olefin (Vol.%)	40.1	24.7	25.0	25.9
Aromatic (Vol.%)	15.2	17.7	19.8	22.1
i-paraffins (Vol.%)	34.2	40.8	39.8	37.4
n-paraffins (Vol.%)	4.6	9.9	8.8	7.2
Naphthenes (Vol.%)	5.9	6.9	6.6	7.4
Sulfur (ppm)	174	103	121	136
RON	91.7	89.8	90.4	91.2

Table 11 displays the product distribution of the n-hexane components in aromatization processes using metal modified HZSM-5 catalysts at 77% n-hexane conversion under 500°C and space velocity of 1200 $cm^3\ g^{-1}\ h^{-1}$.

Thus, thanks to the dehydrogenation activity, a high aromatization activity associated with zinc and element gallium is obtained. Using an alternative way for the aromatization of n-hexane, zinc and gallium make up a high conversion and high selectivity to aromatic components. Besides, incorporation of molybdenum to HZSM-5 leads to different results. The aromatic products came from Zn/HZSM-5 and Ga/HZSM-5 are higher than those came from cracking. According to this, the dehydrogenation activity is involved in the aromatization process, and therefore, these catalysts have more selectivity to the formation of aromatics. From the Table, Molybdenum containing catalysts had more selectivities towards cracked products. Developing 99% conversions within 1 hour on-stream and aromatic selectivities of 55 and 57% at 550°C, gallium and zinc catalysts presented suitable activities and selectivities. As TOS increased the gallium catalyst showed better activities and stabilities. Due to the zinc volatilization, zinc catalysts showed a poor stability. It is worth surveying more to perceive the gallium based catalyst performances under different circumstances [61].

In a work done by Hodala *et al.* [63], the aromatization of C5-rich light naphtha as feedstock was studied when using a non-noble metal oxide based catalyst (ZnGa/ZSM-5)

Table 11: Product distribution [61]

Catalysts	HZSM-5	Ga/HZSM-5	Zn/HZSM-5	Mo/HZSM-5
Conversion (%)	85.3	76.4	77.3	77.5
Products	Percentage yield			
Methane	2.3	2.1	2.4	1.8
Ethylene	4.0	4.3	0.93	3.9
Ethane	6.3	2.6	3.8	6.5
Propylene	21.9	12.1	9.8	20.5
Propane	5.7	3.5	1.9	4.3
$C_{4s}^{=}$	8.9	5.0	4.3	9.5
C_{4s}	2.0	1.6	1.4	2.7
C_{5s}	2.4	1.3	1.1	3.0
C_{6s}	0.3	0.4	1.04	1.4
Benzene	4.0	6.4	10.2	3.0
Toluene	8.7	12.1	10.0	7.2
m,p-Xylene	5.8	8.9	7.9	4.1
Et-Benzene	2.1	3.3	2.3	2.5
O=Xylene	2.9	2.1	2.1	1.0
C_{9s}	1.5	3.9	9.7	1.0
$\sum$ Aromatics	23.5	32.9	32.4	19.9
Coke	6.5	6.8	8.4	5.0

for the n-hexane reaction. Gallium and zinc were loaded on H-ZSM-5 (with Si/Al = 23) by co-impregnation method with varying quantities, and then the aromatization reaction was carried out. The results are presented in Table 12.

1% Zn + 2% Ga on ZSM-5 produces high aromatic yields (61.7%) as compared to other loadings. During co-impregnation of zinc and gallium (as oxides), zinc with more possibility for ion-exchange, may decrease the acid sites by partial ion-exchange. Dehydrogenation functions of both the metal ions may play significant roles in aromatization process.

Application of co-impregnated catalyst is similar to that of 2% Ga/ZSM-5, but the effect of zinc could be observed when the amounts of benzene and methane decrease (from 4.9 to 12.4% for benzene and from 13.6 to 10.9% for methane), and the value of xylenes fraction increases (from 4.9 to 12.4%) compared with the latter.

As a result, the zinc loading is found to have a good effect when co-impregnated along with gallium on ZSM-5. The proper combination of acid sites and dehydrogenating sites could be obtained by mixing the metals. In fact, it results in an increase in aromatic yields. Among different gaseous products formed during aromatization with 1% Zn + 2% Ga on ZSM-5 catalyst, C3 +C4 fraction (LPG fuel) is predominant with 17.7% yield. The zinc and gallium in ZSM-5 may act as hydrogen adsorption/spill over sites which could be adjacent to each other and also ion-exchange with framework acid sites facilitating the formation of higher aromatics yields.

3.3 Quick review of references

In the following, we have collected the aromatization of different feedstock with zeolites and its metal in Table 13. By this table, we can find the detail of many studies in a quick view.

4 Acidity of catalyst

One of important factors affecting ZSM-5 zeolites catalytic activity and lifetime is their SiO_2/Al_2O_3 ratio. Provided that the number of Al_2O_3 component is higher than that of SiO_2 in a ZSM-5 zeolite, the zeolite has more acid sites and then has a higher activity. Unfortunately, high aluminum content has an adverse effect on the zeolite performance with time since it results in high coke production and consequently quick catalyst deactivation [62–64]. Therefore, the suitable and optimum ratio for SiO_2/Al_2O_3 should always be considered. The meticulous value helps ZSM-5 zeolites to have high activity beside a long lifetime [65, 66].

The ZSM-5 zeolite activity comes from charge imbalance among the available Si and Al ions in the frame-

Table 12: The effect of metals on catalyst performance of ZSM-5 in aromatization of n-hexane

Catalyst	HZSM-5, Si/Al = 23	2% Zn_HZSM-5	2% Ga_HZSM-5	1% Zn + 2%Ga_HZSM-5
		Product Distribution (wt.%)		
Methane	7.3	4.6	18.23	10.98
Ethylene	1.2	0.7	1.32	0.96
Ethane	14.1	12.2	9.70	8.48
Propylene+Propane	56.9	21.9	11.41	16.85
C4-hydrocarons	8.7	6.2	0.76	0.87
Hexane	0.1	0.5	0.05	0.09
Benzene	2.9	9.8	12.47	14.39
Toluene	4.6	23.6	26.09	27.63
Ethylbenzene	0.2	0.9	0.21	0.40
p-Xylene	0.4	3.2	2.82	2.93
m-Xylene	0.9	7.2	6.20	6.44
o-Xylene	0.4	3.3	2.86	3.03
Ethyltoluenes	0.1	0.8	0.19	0.3
Trimethylbenzene	0.1	0.9	0.15	0.57
C10 and others	2.2	4.2	7.56	6.07
		Performance (wt.%)		
n-Hexane conversion	99.9	99.5	99.9	99.9
C3 + C4 yield	65.6	28.1	12.2	17.7
Total aromatics yield	11.9	53.9	58.5	61.7

Conditions: Catalyst=2 g, WHSV=1 h^{-1}, H_2/ feed=2, Temperature=500°C, TOS=5 h

work. There exist several techniques including FTIR, TPD, NMR and micro calorimetry that help to know more about different acid sites over ZSM-5 zeolites [67]. Of the mentioned techniques, micro calorimetric studies of ammonia adsorption assist scientists to know the distribution of acid site strengths in zeolites [68, 69]. Both of the number and strength of acid sites in the zeolite catalysts are of key importance that play significant roles in the activity and selectivity property in various hydrocarbon transformation reactions. As mentioned, the strong acid sites, similar to a double-edged sword, have negative and positive effects on the processes. On one hand they accelerate the reaction rates of aromatic formation; on the other hand, they expand the coke formation too. Produced coke either may deposit on the strong acid sites or may block the channels of catalysts; consequently, it leads to acid sites inaccessibility for reactants and others. This also has effects on activity and product selectivity of the catalysts. As expected, the formed coke in the aromatization processes to be considered have been studied a lot in the area of effect of acidity on activity as well as deactivation [70, 71]. As stated previously, the distribution of Al ions in ZSM-5 catalysts, which determines the number and strength of acid sites, controls the catalysts activity in various reactions [72]. Indeed, the catalytic activity and selectivity can be changed either by manipulating the ratio of silica-alumina in the zeolite synthesis or by hydrothermal treatment for the dealumination of the zeolites.

However, similar to cracking reaction, undesired reactions may be evolved from a high level of zeolite acidity in some processes. Given this, controlling zeolite acidity is a key to success in most of processes. From various methods mentioned in literature, modifying the Si/Al ratio through either dealumination or ion-exchange has been attracted a lot of attention for several years. In a wide range of hydrocarbon reactions, these methods can be applied in order for the formation and rearrangement of carbonium ions to be controlled [30]. It should be considered that some kinds of components such as metals have effects on the zeolite acidity as well as zeolite efficiency in aromatization operations. Sachtler *et al.* [73] for example, combined several elements including Zn/Ga/Fe-ZSM-5 loaded with acidic cations (Zn, Ga, and Fe) and scrutinized the metal cation effects on ZSM-5 Bronsted acid sites. In an-

Table 13: Researches review in a quick view

Feed	Zeolite	Metals	T, °C	P, bar	LHSV/GHSV	TOS, hr	Reactor	Reference
n-hexane	HZSM-5	Pt, Pt/Ir	250 – 500				Pulsed Microcatalytic	[7]
1-hexene, FCC gasoline	HSM5	Ga				2 – 10		[8]
Isobutane, Propane	HZSM-5		450 – 550	1	3000 mL·gcat^{-1}·h^{-1}	0 – 30	Fixed Bed	[9]
Isobutene, Propane	HZSM-5	Zn	550	1	3000 mL·gcat^{-1}·h^{-1}	0 – 28	Fixed Bed	[10]
Propane	HZSM-5	Zn	550	1	3000 mL·gcat^{-1}·h^{-1}	0 – 28	Fixed Bed	[11]
1-hexene	(H)ZSM-5		350	5	2 h^{-1}	2 – 14	Continuous flow fixed bed	[12]
Methanol	(H)ZSM-5		400	1	28 h^{-1}	1 – 10	Fixed Bed Tubular	[13]
Propane	HZSM-5	Ga	510 – 540	1	2 – 8 g_{cat} h/mol			[37]
propane, butane and propane/butane mixture	HZSM-5	Ga	540		600 h^{-1}			[39]
Propane	HZSM-5	Ga	550			0.033	flow tubular stainless steel micro-reactor	[40]
Propane	HZSM-5	Ga	477 – 577	1			tabular reactor	[41]
Hexane, Propane	ZSM11	Ga, Pt	540	1	3.6 – 32.4	5	fixed bed tabular	[43]
1-hexene, 1-octene	HZSM-5	Ga	350 – 550	1		0.25	borosilicate glass plug flow reactor	[45]
Propane	HZSM-5	Ga	450 – 650	1	0 – 30 g h mol^{-1}		Continuous Flow	[46]
Propane	(H)ZSM-5	Zn	450 – 550	1	360 – 3600 h^{-1}		Micro Reactor	[52]
n-hexane	ZSM-5	Zn	550	1	2 – 32 h^{-1}		Tabular Micro flow	[54]
n-heptane	ZSM-5	Zn, Ga	550	1	4 h^{-1}	1 – 6	fixed-bed down flow	[56]
Propene	ZSM-5	Ga, Zn	550	1	10.8 g h mol^{-1}		Continuous Flow	[58]
n-heptane	HZSM-5	Zn	500	10			high pressure micro reactor	[59]
n-octene	ZSM-5	La/Zn, P/Zn	380	10	2 h^{-1}		Pulsed Micro Reactor	[60]
n-hexane	HZSM-5	Ga, Mo, Zn	500 – 600		1200 cm^{3}g^{-1}h^{-1}	1, 5, 10	fixed-bed microreactor	[61]
n-octene	HZSM-5	-	350 – 40	15	0–150 g h mol^{-1}		continuous flowing fixed-bed	[76]
methane	ZSM-5	Mo	700	1	1500 cm^{3}g^{-1}h^{-1}	0 – 20	fixed-bed quartz tubular	[79]
1-hexene	ZSM-5	Zn	480	5	4 h^{-1}	2 – 25	continuous flow fixed-bed	[80]

Table 14: The acidic sites of the Mo/ZSM-5 with different Mo loading from NH3-TPD and Py-IR [79]

Sample	Acid Sites from NH_3-TPD ($\times 10^{20}$ g^{-1})	Acid Sites from Py-IR ($\times 10^{20}$ g^{-1})	
	Total	Bronsted acid	Lewis acid
HZSM-5	6.7	8.0	0.2
2Mo/ZSM-5	4.7	4.7	0.4
5Mo/ZSM-5	4.3	4.2	0.5
8Mo/ZSM-5	3.7	3.2	0.5

Table 15: Acid properties of catalysts [80]

Catalyst	Acid site density	Lewis/Bronsted
ZSM-5	0.53	0.06
ZSM-5-AT	0.64	0.05
Zn-ZSM-5	0.44	0.64
Zn-ZSM-5-AT	0.53	1.31
2Zn-ZSM-5	0.49	1.59
2Zn-ZSM-5-AT	0.5	2.0
5Zn-ZSM-5	0.46	4.06
5Zn-ZSM-5-AT	0.5	4.63

other study, Coelhoet *et al.* [74] put a big effort to know the effect of basic Na ions on both of the number and the strength of acid sites. Song *et al.* [75] indicated that the kind of aromatization process and the aromatics distribution in LPG processes using HZSM-5 zeolite are directly supported by the amount of strong acid sites. Furthermore, they showed the strong acid sites make an important impact on dealkylation of poly alkyl aromatics; consequently, as the amount of strong acid sites decrease the rate of dealkylation as well as the selectivity of benzene, toluene and C_8 aromatics decrease. The influence of HZSM-5 acidity over n-octenes aromatization is the main subject of Long *et al.* [76] in their research. To carry it out, they added the element potassium into the HZSM-5 zeolite using incipient wet Impregnation. They asserted that the element potassium leads to a decrease in the amount of the strong acid sites. Their results emphasized this fact that whereas the benzene formation rate is lower during the aromatization process, toluene and C_8 aromatics are the obvious aromatic products in their tests. As the amount of the strong acid sites reduces the numbers of C_6 and C_7 carbenium ions increase while those of C_8 and C_9 carbenium ions increase. To put it another way, the concentration of benzene and toluene in the products reduces and that of C_8 and C_9 aromatics increases on condition that the amount of the strong acid sites reduces.

Of zeolites with high quality, the Ga-impregnated HZSM-5 zeolite which has a great potential to increase the activity and selectivity of catalysts in the aromatization of alkanes could be used in a wide practical operations. Its power at alkane aromatization activity is followed by bifunctional sites of none-framework gallium oxide species with redox or dehydrogenation function as well as zeolite protons with acid function, which are placed near to each other in the zeolite paths [77, 78]. In an experimental study, Li *et al.* [79] used three kinds of Mo/ZSM-5 catalyst with different numbers of Mo and then determined the acidity of catalysts. The results to be considered are shown in Table 14.

The total number of acid sites in the catalysts measured by NH_3-TPD reduced with increasing the number of Mo species. The outputs of Py-IR verified the fact that while the majority of the Bronsted acid sites in molybdenum oxides modified ZSM-5 reduced with the Mo increasing, which of Lewis acid sites significantly increased instead. In 8Mo/ZSM-5 catalyst, Bronsted acid occupied only 40% of that of the parent HZSM-5, however; its Lewis acid sites were 250% of that of the parent HZSM-5. As a result, as the concentration of Mo species loaded increased, more Mo species went into the ZSM-5 channels. Then, the Mo species with their effective interactions with the Bronsted acid sites replaced a main portion of H^+ sites. The increase of Lewis acid sites may stem from the acidic characteristics of molybdenum oxides. It is alluded that the molybdenum oxides may act on Lewis acid sites behalf.

The influence of Zn loading and alkali treated over the acidity of ZSM-5 zeolite catalyst in the 1-hexene aromatization reaction is tabulated in Table 15 [80]. Following the alkali treatment, the strength of acid of the zeolite was somewhat diminished, and the concentration of acid sites was raised from 0.53 to 0.64 mmol/g because of the preferential desilicatoin and intensifying Al concentration. The compactness of acid sites was diminished by the loading Zn in zeolites. For instance, for the Zn/ZSM-5 and Zn/ZSM-5-AT samples the values were 0.44 and 0.53 mmol/g, at the same order. The four impregnated samples, showing comparable acid site concentrations (approximately 0.5 mmol/g), suggested that the contribution of Zn leads to high decrease in original acid sites over the alkali-treated zeolites with respect to those over the untreated ones.

5 Problems of catalyst

Behrsing *et al.* [33] in 1989 stated that the Bronsted acid sites on the surface of catalysts which are implemented for aromatization reactions contribute to the creation of a large number of carbonaceous deposits. These Bronsted acid sites accelerate the production of polycyclic aromatic hydrocarbons, which fill the entrance to the micro pores by depositing on the external surface of catalysts. According to scientist's research, the major reason behind the catalyst deactivation in hydrocarbons dehydroaromatization is the production and the spread of polycyclic materials over the zeolite crystals by the passage of the time. It was stated by Tempelman *et al.* [81] the coke production during dehydroaromatization is hindered by the deactivation of active area on the BAS's surface.

In general, the secondary reaction among intermediate and cracking products that is under control of pore structure as well as acid sites on the catalysts surface culminates in coke deposition on aromatization catalysts. The opening of the ZSM-5 channels is the main position, which leads to coke deactivation. Furthermore, as reactions that transform FCC gasolines olefins (especially C_5-C_7) into aromatics and i-paraffins occur in the inner surface of active sites, acquiring sufficient information and being confidence about the converting potential of active sites in the inner surface are of key importance for researchers [82, 83] and need more research.

Taking aforementioned information into account, most of the studies concentration was on acquiring a suitable method to inhibit coke formation. Different methods have been introduced by researchers, some of which are using different zeolite frameworks [84, 85], or catalyst modification [30, 62], or addition of co-reactant [63, 64] or increasing the reaction pressure [65], modification of the reaction conditions [66], and addition of promoters. A wide range of promoters have been examined in various works. Tan *et al.* [86] added some noble metals including Pt, Pd, Ru, Ir to test the performance of new catalysts. It was indicated that Pt could enhance the power of selectivity of aromatics. The same results as Tan and coworkers tests were reported by Kojima *et al.* [87] by adding Rh. The use of W as a promoter was mentioned as well [88]. The catalysts activity was grown when scientists took the advantage of promoters such as Fe, Co, Zn [89, 90].

Thus, these strong acid sites on ZSM-5 zeolites are the highly active places for the aromatization process and coking formation [75]. It was pointed out provided that the total number of the strong acid sites on catalysts reduces, the reactions for the coke production leading to the catalysts deactivation decrease. It can be a solution, but on the other hand this reduction in the acid sites would result in lower aromatization activity at the same time. Today, most of engineers root out the framework aluminum in zeolite with different ways including thermal treatment, hydrothermal treatment at high temperatures (sometimes combined with acid leaching), acid leaching and ammonium hexafluorosilicate (AHFS) treatment in order that they can diminish the number of acid sites [91–96]. There exists another way for enhancing the stability of the zeolite catalysts as well. By synthesizing zeolites with small particles, some researchers shortened the path of diffusion of reactants/products and controlled the coke formation rates and then protected the channels and pore ways from blocking [12, 97].

6 Conclusion

The results of studying hydrocarbon aromatization over zeolite catalysts have been reviewed. Brief information on the preparation and characterization of zeolite catalysts and the mechanism of the aromatization processes with zeolites was delineated. The desirable reactions using zeolite catalysts are achievable by manipulating several factors, some of which are applying suitable metals as promoter and considering proper acidity. In the several sections, all mentioned parameters were reviewed in detail. The introduction of metals over zeolite frameworks promotes them to work as bifunctional catalysts which combine the hydrogenation-dehydrogenation and carbocation rearrangement functions. Effects of a wide range of metal elements, including gallium, zinc and platinum, over performance of ZSM-5 zeolites were alluded through loads of paragraphs. Finally, it was mentioned that there exist some solutions for coke blockage in zeolites frameworks.

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