



Aromatization of n-hexane over H-ZSM-5: Influence of promoters and added gases

D. Bhattacharya, S. Sivasanker *

National Chemical Laboratory, Pune-411008, India

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Abstract

The influence of promoters such as ZnO, Ga₂O₃, Fe₂O₃ and Cr₂O₃ on the aromatization of n-hexane over H-ZSM-5 is reported. While ZnO and Ga₂O₃ increase aromatization, Fe₂O₃ and Cr₂O₃ decrease the aromatization. The addition of N₂ to the feed increases aromatization over H-ZSM-5, while H₂ decreases aromatization. Increasing the total pressure to 15 bars does not significantly decrease the yield of aromatics. Investigations on the influence of the promoters, added gas and total pressure on the rate of deactivation of the catalyst are also reported.

Keywords: Aromatics; Aromatization; Deactivation; H-ZSM-5; n-Hexane; Promoters

1. Introduction

The transformation of lower hydrocarbons (C₂–C₆) into aromatics over zeolites is an industrially important reaction. A number of processes such as the Cyclar (BP-UOP) [1], M-2 forming (Mobil) [2] and Aroforming (IFP/SALU-TEC) [3] for the transformation of C₂–C₆ hydrocarbons are available. These processes are believed to be based on promoted H-ZSM-5. The oligomerization of light hydrocarbons (especially the saturates) into aromatics is also interesting from an academic point of view. As a result, many studies on the aromatization of light hydrocarbons over H-ZSM-5 based catalysts are now available in the literature [4–14]. It has also been observed that the addition of promoters such as Ga₂O₃ or ZnO to the zeolite (H-ZSM-5) improves its aromatization activity [7,8].

* Corresponding author. Tel./fax. (+91-212) 334761, e-mail siva@ncl.ernet.in

Table 1
Physico-chemical properties of the catalysts used in the aromatization of n-hexane

Catalysts	SiO ₂ /Al ₂ O ₃ ^a	BET surface area (m ² /g) ^b	Total acidity (mmol/g) ^c	Metal loading (as oxide)	Adsorption of n-hexane (g/100 g)
H-ZSM-5	40	423	1.1	—	12.0
Ga ₂ O ₃ /H-ZSM-5	40	401	1.2	3.1	11.8
ZnO/H-ZSM-5	40	389	0.8	3.2	11.8
Cr ₂ O ₃ /H-ZSM-5	40	375	1.0	2.8	9.7
Fe ₂ O ₃ /H-ZSM-5	40	340	0.9	3.0	9.5

^a From XRF analysis.

^b N₂ adsorption.

^c Estimated from desorbed NH₃ (see text).

In this reaction, the yield of aromatics becomes significant only at temperatures beyond 753 K and the reaction is often conducted around 800 K. At these elevated temperatures, catalyst deactivation tends to be rapid necessitating frequent regenerations. In fact, the Cyclar process operates in a continuous catalyst regeneration mode [1]. We now report our studies on the influence of different promoter oxides on product yields and deactivation characteristics of H-ZSM-5 in the aromatization of n-hexane. The studies have been carried out at different pressures and in the presence of gases such as H₂ and N₂.

2. Experimental

H-ZSM-5 was obtained from United Catalysts India Ltd. It had a crystallite size of < 1 μm. Samples of H-ZSM-5 were loaded with metal oxides by impregnation using nitrate salts and calcination at 773 K in dry air. The physicochemical properties of the catalysts used are presented in Table 1. Adsorption of n-hexane was carried out at a p/p_0 of 0.5 at 298 K (Cahn Electrobalance; model C-2000) over samples degassed in vacuum (10⁻⁵ mm) at 723 K. The sorption was rapid over the samples and equilibrium sorption occurred within an hour (Table 1). Acidity measurement of the samples were carried out as follows. The sample (~ 1 g) was held vertically inside a silica tube (10 mm diameter) and activated in a flow of dry N₂ at 773 K for 6 h. It was then cooled in flowing N₂ (flow rate: 100 ml/min). NH₃ gas (25 ml/min) was introduced into the nitrogen stream for 1 h, after the sample had cooled to 300 K. Subsequently, the sample was flushed with N₂ (25 ml/min) for 15 h at 300 K to desorb the physically adsorbed NH₃. The sample was then heated at the rate of 10°C/min in N₂ flow (25 ml/min) and held for 1/2 h at 773 K. The NH₃ desorbed while raising the temperature was absorbed in 1 M HCl and estimated. The NH₃ desorbed represents the total acidity (weak and strong) present in the samples (Table 1).

The catalytic experiments were carried out in a commercial high pressure reactor (Autoclave Engineers, Erie, PA, USA). The reactor (SS 316) had an I.D of 8 mm. 2.5 ml of catalyst granules (20–30 mesh, obtained by compacting the catalyst powder in a hydraulic press (10 tons/sq inch, approx. 140 kg/cm²), and crushing and 2.5 ml of quartz chips (20–30 mesh) were mixed and loaded in the reactor. The l/d ratio of the catalyst bed was ~ 10 . The catalyst was activated before runs by drying at 793 K with N₂ (6 h). Coke contents of the catalysts were estimated by careful burning of the hydrocarbons with O₂ at 773 K. The gases were passed through a bed of Pt (0.3%)–Al₂O₃ at 773 K prior to absorption in alkali and estimation by titrimetric methods.

Mass balances for the runs were carried out by analysis of both the liquid and gaseous products collected periodically. The mass balances were accurate to $\pm 5\%$. The results are reported after normalization to 100% in all cases. The liquid products were analyzed using a capillary column (50 m \times 0.5 mm; HPI, methylsilicone gum) while the gaseous (C₁–C₅) fraction was analyzed in a refinery gas analyser (HP 5880 A/RGA) using multiple packed columns.

3. Results and discussion

The characteristics of the catalysts used in the study are presented in Table 1. The metal oxide contents of the catalysts are nearly the same ($\sim 3\%$). Loading of the oxides decreases slightly both the surface area (S_{BET}) and adsorption of n-hexane suggesting probably some pore-size modification or pore mouth blockage. The total acidity is also slightly reduced. XRD patterns did not suggest any damage to the zeolite due to metal loading and calcination.

3.1. Influence of promoter on product yields

A comparison of product yields obtained over H-ZSM-5 and promoted H-ZSM-5 catalysts is presented in Table 2. The comparative study was carried out at atmospheric pressure in N₂ (n-hexane: N₂ (mole) = 1.5). The conversion of n-hexane (n-C₆) was 100% over all the catalysts at the temperature of the study (793 K). From the point of aromatics production, the catalysts can be arranged in increasing order of activity as follows: Cr₂O₃/H-ZSM-5 < Fe₂O₃/H-ZSM-5 < H-ZSM-5 < Ga₂O₃/H-ZSM-5 < ZnO/H-ZSM-5. Zn- and Ga-oxides promote the aromatization reaction while Cr- and Fe-oxides decrease the aromatization. The lower yield of aromatics is accompanied by an increase in the yield of C₂–C₄ saturates (Table 2). The increased production of saturates is probably due to the greater hydrogenation activity possessed by these promoters (Cr- and Fe-oxides) which, in all likelihood, are present as lower valent reduced species under the reaction conditions. The promoters Zn and Ga produce less saturates and more olefins than H-ZSM-5. Increased yields

Table 2
Product distribution over metal promoted H-ZSM-5 catalysts ^a

Product distribution (wt%)	H-ZSM-5	Ga ₂ O ₃ / H-ZSM-5	ZnO/ H-ZSM-5	Fe ₂ O ₃ / H-ZSM-5	Cr ₂ O ₃ / H-ZSM-5
C ₁	0.6	3.5	3.9	2.8	4.3
C ₂ (=)	3.0	6.0	7.3	1.4	3.5
C ₂	15.8	13.9	13.3	10.0	15.6
C ₃ (=)	3.3	3.4	4.5	6.4	3.7
C ₃	31.9	18.4	17.7	37.0	36.0
i-C ₄	1.7	2.0	1.1	7.3	3.3
n-C ₄	1.8	2.2	1.2	7.9	4.5
C ₄ (=)	1.7	2.6	1.8	3.8	1.8
C ₅ –C ₈ (alip)	1.0	0.9	0.3	2.4	7.0
Benzene	8.5	12.5	14.9	3.8	3.9
	(0.23) ^b	(0.26)	(0.31)	(0.18)	(0.19)
Toluene	16.9	20.1	19.2	8.0	8.1
	(0.44)	(0.43)	(0.40)	(0.39)	(0.41)
Xylenes	8.3	9.2	9.5	5.7	6.1
	(0.21)	(0.20)	(0.19)	(0.28)	(0.31)
Ethyl benzene	0.8	0.6	0.3	0.5	0.4
C ₈ ⁺	4.7	4.7	5.0	3.0	1.8
	(0.12)	(0.10)	(0.10)	(0.15)	(0.09)
ΣAromatics	39.2	47.1	48.9	21.0	20.3

^a Reaction conditions: 793 K, 1 atm, WHSV = 2 h⁻¹, TOS = 1 h, N₂: n-C₆ (mole) = 1.5. n-C₆ conversion was 100% in all experiments.

^b Values in the brackets are the ratios of the components in total aromatics. The break-up of aromatics at equilibrium (800 K) in the case of toluene-disproportionation is: C₆ = 0.32; C₇ = 0.41; C₈ = 0.23 and C₈⁺ = 0.04, and in the case of xylene-disproportionation it is C₆ = 0.06, C₇ = 0.24, C₈ = 0.41 and C₈⁺ = 0.29 [24].

of aromatics and lower yields of saturates over Ga and Zn promoted H-ZSM-5 have been reported by earlier workers during the aromatization of lower alkanes and alkenes [7,8]. The promoting action of both Ga- and Zn-oxides has been attributed to their ability to dehydrogenate alkanes and the production of allylic species. The yield of CH₄ is higher in the case of all the promoted catalysts than over H-ZSM-5. Presumably, the reduced forms of the promoters possess some hydrogenolysis activity. Kanai and Kawata [13,14] have also observed higher yields of aromatics during the aromatization of n-hexane over H-ZSM-5 doped with ZnO and Ga₂O₃.

In the case of Ga₂O₃ promoted H-ZSM-5 Kanai and Kawata [13] have reported an aromatic yield enhancement of about 50% on loading 3 wt% Ga₂O₃ (from Fig. 1 in Ref. [13]) during the aromatization of n-hexane. On the other hand, Ono et al. [11] have reported 2 and 3 fold yield (aromatic) enhancements by Ga₂O₃ during the aromatization of n-pentane and propane respectively. Kanai and Kawata [13] have also reported that selectivity to aromatics is partly determined by the nature and location of the Ga-ions. They have observed that selectivity to aromatics decreases in the order: Galloaluminosilicate > Ga-exchanged H-ZSM-5 > Ga₂O₃/H-ZSM-5 > H-ZSM-5. Besides, Kanai [14]

has also reported that pretreatment temperature influences the aromatics selectivity of Ga₂O₃/H-ZSM-5. In the case of ZnO promoted catalysts also, the enhancement of aromatization selectivity depends on the substrate. For example, during the aromatization of butane, the aromatics selectivity increased 6-fold on incorporation of ZnO into H-ZSM-5 [9], though the increase was only 2-fold during the aromatization of butene-1 [15]. The 20–25% enhancement in aromatics yield on the addition of Ga and Zn oxides reported by us is rather small in comparison to the literature reports presented above. Apparently, many factors such as the concentration and method of loading the promoters, the properties (SiO₂/Al₂O₃; crystallite size) of the base H-ZSM-5, the process parameters, the duration of the run and the nature of the substrate determine the level of enhancement of aromatics selectivity by the promoters, Ga₂O₃ and ZnO.

Based on an estimate of the H₂-produced at zero-aromatics selectivity, Kanai and Kawata [13,14] have concluded that over H-ZSM-5, the aromatization proceeds through the cracking of n-hexane, while it proceeds mainly through the dehydrogenation of n-hexane to n-hexene and subsequent cracking of the hexene to lower olefins over Ga₂O₃/H-ZSM-5. Both types of cracking reactions take place over ZnO/H-ZSM-5. Both the ZnO and Ga₂O₃ promoted catalysts operate by a bifunctional mechanism, the ZnO and Ga₂O₃ promoters taking part in both the initial dehydrogenation of n-hexane and also in the dehydrogenation of the cyclic oligomeric species into aromatics.

It is interesting to note that, even though n-hexane is used as the feed, the major product is toluene (Table 2). An examination of the Eqs. (10 to 13; Table 3) reveals that the change in free energy (ΔG_r) accompanying the formation of

Table 3
Reactions in the aromatization of n-hexane

No.	Reaction	ΔG_r (Kcal)	Equilibrium conversion (x)		
			1 bar	1 bar (H ₂)	15 bar (H ₂)
1	n-C ₆ → n-C ₆ [≡] + H ₂	4.83	0.214	0.073	0.005
2	n-C ₆ [≡] → C ₃ [≡] + C ₃ [≡]	-8.27			
3	n-C ₆ → C ₃ [≡] + C ₃ [≡]	-7.81	0.996	0.998	0.970
4	n-C ₆ → C ₂ [≡] + C ₄ [≡]	-7.83			
5	C ₃ [≡] + H ₂ → C ₃ [≡]	-4.37	0.755	0.906	0.995
6	C ₄ [≡] + H ₂ → C ₄ [≡]	-5.13	0.804	0.938	~ 1
7	2C ₃ [≡] → n-C ₆ [≡]	8.27	0.003	0.002	0.027
8	C ₃ [≡] + C ₄ [≡] → n-C ₇ [≡]	8.19			
9	2C ₄ [≡] → n-C ₈ [≡]	8.11			
10	n-C ₆ → Bz + 4H ₂	-20.24			
11	2n-C ₆ → Bz + 2C ₃ [≡] + 3H ₂	-32.42			
12	2n-C ₆ → Tol + C ₂ [≡] + C ₃ [≡] +	-37.82			
13	2n-C ₆ → Xyl + 2C ₂ [≡] + 3H ₂	-40.32			
14	2Tol → Bz + m-Xyl	2.90			
15	m-Xyl → TMB + Tol	0.05			

Saturates denoted by “-” and olefins by “≡”; C₄[≡] to C₈[≡] refer to 1-olefins; Bz = benzene; Tol = toluene; Xyl = m-xylene; TMB = 1,2,4-trimethylbenzene.

Table 4
Influence of added gas and pressure on the aromatization of n-hexane

Product distribution (wt%)	H-ZSM-5						ZnO/ H-ZSM-5	Ga ₂ O ₃ / H-ZSM-5
	Atmospheric			15 bar			Atmospheric	
	n-C ₆	n-C ₆ + N ₂	n-C ₆ + H ₂	n-C ₆	n-C ₆ + N ₂	n-C ₆ + H ₂	n-C ₆ + H ₂	n-C ₆ + H ₂
C ₁	1.0	0.6	1.9	8.1	8.1	6.1	8.4	9.7
C ₂ (^o)	4.0	3.0	3.4	4.7	5.0	4.1	1.3	0.8
C ₂	16.8	15.8	13.8	27.4	23.4	33.6	22.0	12.6
C ₃ (^o)	3.1	3.3	4.0	4.4	4.7	4.4	0.8	0.7
C ₃	33.8	31.9	36.2	15.2	16.6	12.5	21.8	23.8
i-C ₄	1.6	1.7	2.7	0.7	1.3	3.7	0.6	2.1
n-C ₄	2.1	1.8	4.8	0.9	1.6	5.0	2.0	3.7
C ₄ (^o)	1.2	1.7	1.2	0.1	0.2	1.0	0.6	0.3
C ₅ –C ₈ (alip)	1.0	1.0	0.8	2.3	2.1	1.3	0.5	1.1
Benzene	8.9	8.5	7.1	6.9	6.1	6.1	12.3	10.2
Toluene	16.0	16.9	12.8	11.4	11.4	9.9	15.4	19.0
Xylenes	7.3	8.3	6.7	5.7	6.7	4.8	9.3	12.2
Ethylbenzene	0.7	0.8	0.6	0.7	0.9	0.3	0.3	0.6
C ₈ ⁺	2.5	4.7	4.0	11.5	11.9	7.2	4.7	3.2
ΣAromatics	32.4	39.2	31.2	36.2	37.0	28.3	42.0	45.2

Reaction conditions: 793 K, WHSV = 2h⁻¹, N₂ (or H₂): n-C₆ (mole) = 1.5, TOS = 1 h.

an aromatic molecule increases in the order m-xylene < toluene < benzene. However, at the conditions of the experiment, the aromatic molecules produced will undergo rapid isomerization/disproportionation reactions (14 and 15; Table 3) and the product pattern obtained is mainly due to these reactions. An examination of the break-up of the different components in the aromatics fraction (Table 2) reveals that the distribution of aromatics is reasonably similar to what one would expect from the disproportionation of toluene (see footnote of Table 2). Even though toluene is the major aromatic product over all the catalysts, the small variations in the distribution of aromatics observed over the different catalysts (Table 2) suggest that the interconversion of aromatics is influenced by the promoters presumably via changes in the acidity and pore size characteristics.

3.2. Influence of added gas and total pressure on product yields

The product yields obtained over H-ZSM-5 at atmospheric pressure and 15 bars (total pressure) in the absence and presence of added gases (n-C₆: gas (mole) = 1.5) are reported in Table 4. Besides, the results obtained over ZnO and Ga₂O₃ promoted catalysts in the presence of H₂ (1 bar) are also reported in the table. As the reaction involves olefinic intermediates, one would expect a large decrease in the yield of aromatics when H₂ is added and on increasing the total pressure. In the case of H-ZSM-5, the addition of N₂ increases the yield of aromatics while H₂-addition decreases the yield. Increasing the pressure de-

creases the yield of C₆–C₈ aromatics, but has little influence on total aromatics yield when no added gas is present. When N₂ is present (at 15 bar), the yield of total aromatics is only marginally more, but significantly less when H₂ is present (Table 4). The Ga₂O₃ and ZnO promoted catalysts also produce less aromatics in the presence of H₂ than in the presence of N₂ (Tables 3 and 4), the effect being more pronounced in the case of Zn. The increase in aromatics production on addition of N₂ is probably a consequence of the inert gas dilution effect which increases the equilibrium conversion values for many of the olefin and aromatics production reactions such as 1 to 4 and 10 to 13.

Table 3 indicates that the dehydrogenation of n-hexane (reaction 1) is much less thermodynamically favoured than the cracking of n-hexane and n-hexene (reactions 3–4) at 800 K. Besides, the former reaction is very much suppressed by added H₂ and high pressure than the cracking reactions (Table 3). The hydrogenation of the intermediate C₃–C₄ olefins (reactions 5 and 6; Table 3) is also very much enhanced by H₂ and high pressures. However, as the aromatics-production reactions are the most favoured (reactions 10–13) at the operating conditions, their production is understandable. Aromatics are believed to be formed (over zeolites) from alkene-oligomers by successive deprotonation and hydride transfer reactions [16]. These reactions occur rapidly on the surface of H-ZSM-5 and the intermediate alkenes are rapidly converted as fast as they are formed. Besides, these reactions are probably not sensitive to added molecular H₂. Additionally, steric factors inside the pores of ZSM-5 might also favour the stabilization of the oligomers (reactions 7 and 9; Table 3) as ψ -cyclic intermediates and their rapid dehydrogenation to aromatics. The formation of ψ -cyclic intermediates has been suggested by Derouane et al. [17] in the reforming of n-paraffins over Pt-KL.

Overall, as aromatics production is a dehydrogenation reaction, a decrease in aromatics yield on addition of H₂ or increasing the pressure is expected purely from thermodynamic reasons. However, due to the large number of reactions and the complexity of the reaction network it is not possible to predict the extent to which the added H₂ will reduce the aromatics yield. Though reports on the influence of H₂ on the aromatization reaction over ZSM-5 catalysts are limited, they do confirm our observations [18,19]. The decrease in aromatics production over the ZnO and Ga₂O₃ promoted catalysts is not more than that observed over H-ZSM-5 suggesting that the initial dehydrogenation of n-hexane (reaction 1; affected by H₂) may not be the important (rate determining) reaction in the aromatization of n-hexane over ZSM-5 based catalysts.

3.3. Influence of promoters on catalyst deactivation

In the aromatization of alkanes over H-ZSM-5, the yield of aromatics is significant only beyond 753 K. Typically, temperatures in the range 773–813 K are preferred. At these high temperatures, coke deposition and catalyst deactiva-

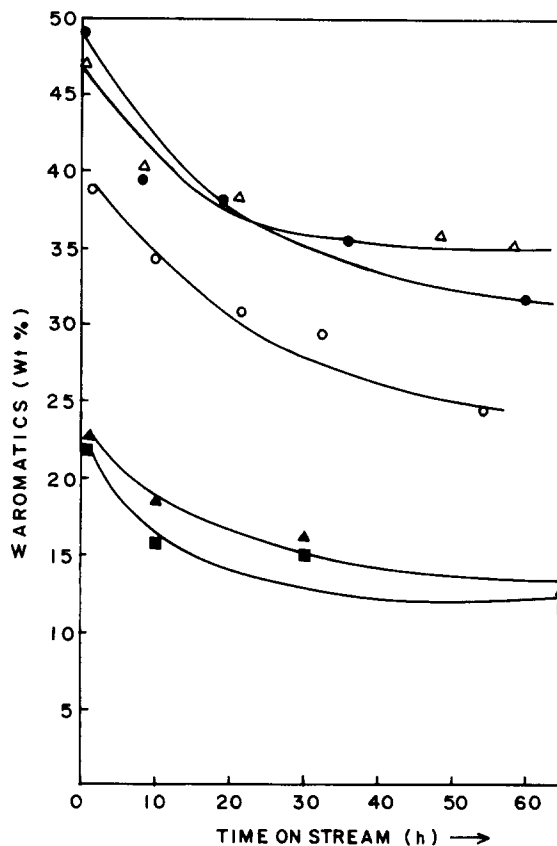


Fig. 1. Influence of duration of run on yield of aromatics over promoted H-ZSM-5 catalysts. (Temperature = 793 K; WHSV = 2.0 h⁻¹; N₂: n-C₆ (mole) = 1.5; pressure = atmospheric). (○) H-ZSM-5; (●) ZnO/H-ZSM-5; (△) Ga₂O₃/H-ZSM-5; (▲) Cr₂O₃/H-ZSM-5; (■) Fe₂O₃/H-ZSM-5.

tion are rapid. By virtue of its special pore dimensions and poor H-transfer ability, H-ZSM-5 generally deactivates slower than other zeolites through coke lay down. Even so, deactivation rates are rapid, limiting the economic attractiveness of this process.

The influence of promoters on the deactivation rate (aromatics-loss) are presented in Fig. 1. The experiments were carried out in N₂ (n-C₆: N₂ (mole) = 1.5) at atmospheric pressure. The catalysts generally deactivate rapidly in the beginning and then the deactivation becomes less rapid. Visual inspection of Fig. 1 shows that the rate of deactivation is different over the different catalysts. To get a better appreciation of the deactivation rate, the aromatic yields at different times on stream were fitted into the Voorhies' equation [20] $k = At^{-n}$; n is the deactivation coefficient for the loss of aromatics. The values of n for the different catalysts are presented in Table 5 along with the coke content of the catalysts at the end of the run. It is noticed that the coke contents

Table 5
Influence of promoters on deactivation rate and coke lay down

Catalyst	Deactivation coefficient (n) ^a	Coke (wt%) ^b
H-ZSM-5	0.085	10.5
Ga ₂ O ₃ /H-ZSM-5	0.068	11.3
ZnO/H-ZSM-5	0.092	15.5
Cr ₂ O ₃ /H-ZSM-5	0.170	10.0
Fe ₂ O ₃ /H-ZSM-5	0.139	9.0

Reaction conditions: 793 K, 1 atm, WHSV = 2 h⁻¹, N₂: n-C₆ (mole) = 1.5, TOS = 60 h.

^a Deactivation coefficient (for total Aromatics) determined by fitting into the Voorhies' equation [20].

^b After a time on stream of 60 h.

are related to the amount of aromatics produced by the catalysts and not to the deactivation coefficients. The orders of aromatics production and coke deposition are nearly the same: Zn > Ga > H > Cr ~ Fe. This is probably due to the fact that both coke (polyunsaturated compounds) and aromatics have com-

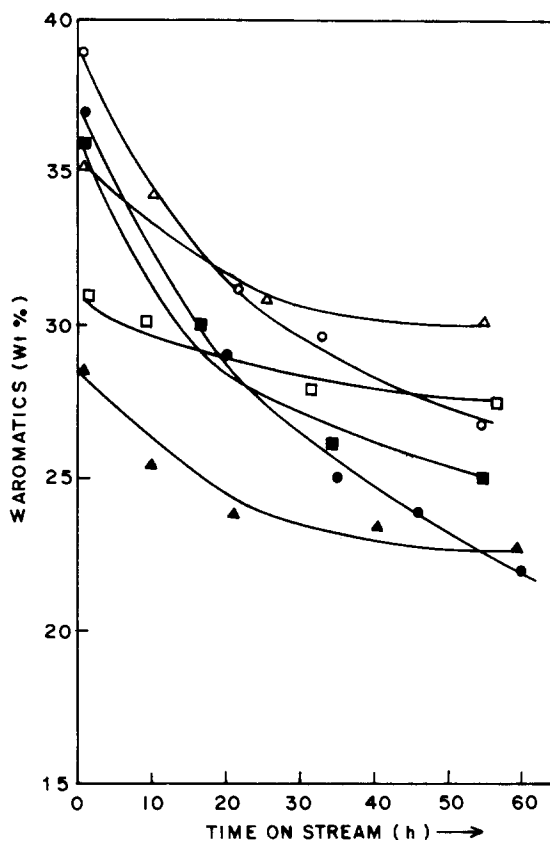


Fig. 2. Influence of duration of run on yield of aromatics over H-ZSM-5 in the presence of added gases. (Temperature = 793 K; WHSV = 2.0 h⁻¹; Gas: n-C₆ (mole) = 1.5). (Δ) n-C₆ (atm); (□) n-C₆ + H₂ (atm); (○) n-C₆ + N₂ (atm); (■) n-C₆ (15 bar); (▲) n-C₆ + H₂ (15 bar); (●) n-C₆ + N₂ (15 bar).

Table 6
Influence of pressure and added gases (H_2 or N_2) on the deactivation rate and coke lay down

Pressure	Deactivation coefficient (n) ^a			Coke (wt%) ^b		
	n-C ₆	n-C ₆ + N ₂	n-C ₆ + H ₂	n-C ₆	n-C ₆ + N ₂	n-C ₆ + H ₂
Atmospheric	0.045	0.085	0.032	9.4	10.5	5.7
15 bar	0.087	0.112	0.053	12.3	11.9	10.0

Reaction conditions: 793 K, WHSV = 2h⁻¹, N₂ (or H₂): n-C₆ (mole) = 1.5, TOS = 60h.

^a Deactivation coefficient (for total Aromatics) determined by fitting into the Voorhies' equation [20].

^b After a time on stream of 60h.

mon precursors. The deactivation coefficient is large for the poor promoters, Fe₂O₃ and Cr₂O₃ (Table 5). ZnO/H-ZSM-5 deactivates faster than H-ZSM-5 while Ga₂O₃/H-ZSM-5 deactivates slower. The more rapid deactivation of ZnO has already been reported [21]. It has been suggested to be due to the reduction of ZnO to Zn metal during the reaction and its loss as vapour [21]. It appears more likely that the deactivation in the case of ZnO/H-ZSM-5 in our experiments is due to more rapid coke deposition (Table 5) brought about by the reduced Zn species.

3.4. Influence of added gas and total pressure on catalyst deactivation

Fig. 2 and Table 6 present the results of the influence of added gas and total pressure on the deactivation of the catalysts. The results indicate that deactivation rate and coke deposition are lowered by the presence of H₂. N₂, however increases the deactivation rate. The deposition of coke over zeolite catalysts during hydrocarbon transformation has been extensively investigated [22,23]. The type of coke and its toxicity has been reported to be different on different zeolites. H-rich (soft) coke has been found to be less toxic than the harder graphitic coke. The coke formed on ZSM-5 has been shown to be richer in hydrogen than the coke formed over mordenite or USY [23]. Apparently, the hydrogen externally added during the aromatization reaction over the ZSM-5 catalysts helps in increasing the hydrogen content (softness) of the coke, thereby reducing its toxicity to the reaction. It is also possible that the added H₂ decreases the coking rate by decreasing the concentration of the polyunsaturated coke-precursors.

Increasing the pressure of the reaction increases both deactivation rate and coke deposition. Apparently, at higher pressures, large molecular products are produced, through condensation/polymerization reactions deactivating the active centers more rapidly by increased coke deposition.

4. Conclusions

The aromatization of n-hexane over H-ZSM-5 is enhanced by the promoters ZnO and Ga₂O₃, while Fe₂O₃ and Cr₂O₃ decrease the aromatization. Both ZnO

and Ga₂O₃ containing catalysts deactivate less. Significant production of aromatics occurs over the catalysts even in the presence of H₂ at 15 bars (total pressure). Addition of H₂ decreases deactivation and coke deposition. It appears that the aromatization of n-hexane over ZSM-5 based catalysts takes place via cracking of n-hexane into C₃ and C₄ olefins, the oligomerization of the olefins into μ -cyclic intermediates inside the pore system and the subsequent dehydrogenation via deprotonation and H⁺ transfer reactions.

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