

APCAT 2230

Reforming of pyrolysis gasoline over platinum–alumina catalysts containing MFI type zeolites

K. Madhusudan Reddy, S.K. Pokhriyal, P. Ratnasamy and S. Sivasanker

National Chemical Laboratory, Pune-411 008 (India)

(Received 4 January 1991, revised manuscript received 3 December 1991)

Abstract

Reforming of pyrolysis gasoline, a highly olefinic feed, has been carried out over Pt–alumina catalysts containing small amounts of MFI type zeolites. The incorporation of these zeolites helps in lowering the coke deposition on the catalysts, thereby increasing their life. Further, the products are virtually free of aliphatics. Due to the large concentration of aromatics in the feed, significant aromatic gain is obtained only at low pressures of operation.

Keywords: reforming, pyrolysis gasoline, platinum–alumina, zeolites, ZSM-5.

INTRODUCTION

Pyrolysis gasoline (PG) is obtained during the manufacture of light alkenes by the steam cracking of naphtha and other hydrocarbon materials. Generally, the yield of PG is about 15–25 wt.-% of the naphtha feed. Thus, large quantities of this material are available in the industry. PG is rich in aromatics making it a good source for benzene, toluene and xylenes (BTX). However, direct extraction of BTX by solvents is difficult due to the presence of alkenes and dialkenes (Bromine no. of PG=60–90) which tend to slip into the aromatic fraction and also damage the solvent. Therefore, pyrolysis gasoline is first hydrogenated (in two stages) and then extracted for aromatics. Extraction of aromatics by solvents, apart from being expensive, often results in the loss of 1–5 wt.-% aromatics during the extraction process. Usually the raffinate is further reformed to obtain more BTX. The direct reforming of PG over conventional reforming catalysts is not feasible due to their rapid deactivation by the alkenes present in the feed.

Two important characteristics of medium pore pentasil zeolites like ZSM-5 are shape selectivity [1] and resistance to coke deposition [2]. The former property forms the basis of commercial processes like catalytic dewaxing [3] and shape-selective catalytic cracking [4]. The low coke-forming tendency of ZSM-5 should also make it useful as a catalyst for the upgrading of highly

Correspondence to: Dr. S. Sivasankar, National Chemical Laboratory, Pune-411 008, India. Fax (+91-212) 334761.

olefinic feedstocks with high coking characteristics. A number of reports of the use of ZSM-5 and other shape-selective zeolites for reforming naphtha fractions have been published [5-7] and patented [8-11]. However, the use of ZSM-5 in reforming pyrolysis gasoline has not been documented in the open literature.

In this paper, we report the results of our studies on the reforming of pyrolysis gasoline, using catalysts containing pentasil zeolites of the MFI type.

EXPERIMENTAL

ZSM-5 and its Fe-isomorph, (Fe)ZSM-5, were prepared from solutions containing tetrapropylammonium ions according to procedures described elsewhere [12,13]. The NH_4^+ -forms were obtained by ion exchange of the sodium-forms using 1 M NH_3NO_3 solution. They were then calcined in static air for 4 h at 773 K to obtain the H-forms. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and average crystallite size of ZSM-5 were 84 and 0.2 μm , respectively. The $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio of (Fe)ZSM-5 was 108 and its average crystallite size was 0.5 μm .

Catalyst extrudates (1.5 mm diam. \times 3 mm length) were prepared by blending alumina hydrate (Catapal B, Vista Chemical Co., USA) and the required amount of the zeolites. These extrudates were dried at 383 K and calcined at 773 K for 6 h. The extrudates were next soaked in HCl (0.01 M) to enable a Cl⁻ pick up of about 0.8 wt.-% following published procedures [14]. The Cl-loaded extrudates were dried at 473 K for 3 h and then impregnated with 0.6% platinum using a dilute solution of H_2PtCl_6 . Finally, the extrudates were dried at 383 K and calcined at 773 K for 6 h. The final chlorine content of the extrudates was between 1 and 1.1 wt.-%.

Estimation of chlorine was carried out by extraction procedures described earlier [14]. The acidity measurements were carried out on the zeolites by temperature-programmed desorption (TPD) of adsorbed ammonia [13]. Metal dispersion studies of the finished catalysts were carried by the adsorption of hydrogen as per published procedures [15]. The metal dispersions of the catalysts used in this study were in the range $90 \pm 5\%$.

Pyrolysis gasoline was obtained from two different commercial sources. As PG is highly unstable due to the olefinic and diolefinic material present in it, different fresh batches of PG obtained from two sources were used in these studies. The typical compositions of the two feed stocks are presented in Table 1. PG2 is a slightly higher boiling material than PG1, and is also more olefinic. It also contains about 4.4 wt.-% of dicyclopentadiene. The resulting feed compositions will, therefore, be reported along with the product compositions.

The catalytic reactions at atmospheric pressure were carried out in a fixed bed down-flow integral silica reactor using 2 g of the catalyst. The high-pressure reactions were carried out in a fixed bed, down-flow stainless steel reactor (Catatest, model B supplied by M/S Geomecanique, France). The catalyst

TABLE 1

Typical properties of the feedstocks (pyrolysis gasoline fractions) used

Feed	PG1	PG2
(1) Composition (wt.-%):		
C ₅ -C ₈ -aliphatics ^a	23.25	20.29
Benzene	58.20	44.20
Toluene	14.05	18.01
C ₈ aromatics	0.23	8.53
C ₉ +	4.26 ^b	8.97 ^b
(2) Boiling range		
IBP (K)	325	318
FBP (K)	428	451
(3) Bromine number		
	20.50	79.00
(4) Sulphur (ppm)		
	34.0	160.0
^a Break up of aliphatics:		
	(PG1)	(PG2)
C ₅ (saturated)	0.52	1.13
(unsaturated)	2.61	7.67
C ₆ (saturated)	5.68	2.25
(unsaturated)	1.42	0.52
C ₇ (saturated)	6.79	4.04
(unsaturated)	4.02	2.94
C ₈ (saturated)	1.71	1.27
(unsaturated)	0.50	0.47

(Dialkenes: traces only, not estimated)

^bDicyclopentadiene: PG1, 0.0%; PG2, 4.38%.

charged was 20 g. Both in atmospheric and high pressure runs, the catalyst was first activated in dry air at 723 K for 4 h, cooled to room temperature in a flow of nitrogen, and then reduced at the reaction temperature (usually above 723 K) and the desired pressure in flowing hydrogen for 3 h prior to injection of the feed. The reactions were carried out at different temperatures (753-793 K), pressures (0.1-1.0 MPa) and space velocities (WHSV = 1-4 h⁻¹). As the aromatic contents of the feedstocks were high, experiments were carried out at 0.1 to 1.0 MPa to avoid thermodynamic limitations on the aromatic content of the product.

The products were analysed by gas chromatography (HP 5880 A) using a PONA capillary column (Cross linked methyl silicone, 0.5 mm × 50 m long).

RESULTS AND DISCUSSION

The results of the reforming of pyrolysis gasoline from two different sources are presented in Table 2. Reforming of feedstocks derived from two sources

TABLE 2

Reforming of pyrolysis gasoline from different sources over ZSM-5 (5%)-Pt (0.6%)-Cl (1.1%)-Al₂O₃

Conditions: pressure, 0.45 MPa; WHSV, 2.5 h⁻¹; H₂/HC (mol ratio), 7.0 (773 K), 8.0 (753 K); TOS 20 h

Temperature (K)	773		753	
	Feed 1 (wt.-%)	Product 1 (wt.-%)	Feed 2 (wt.-%)	Product 2 (wt.-%)
C ₁ -C ₆	11.00	15.96	15.99	30.23
Aliphatics ^a in BTX range	8.18	0.10	3.67	0.11
Benzene	73.78	75.29	37.59	41.11
Toluene	7.02	8.30	15.22	17.09
Xylenes	0.02	0.35	3.38	3.31
Styrene	-	-	5.61	-
Ethyl benzene	-	-	1.45	5.74
C ₉ + (including dicyclopentadiene)	-	-	17.09	2.41
(Δ C ₈ aromatics)	-	+3.12	-	+4.02)

^aAlkenes: Feed 1, 3.41%; Feed 2, 2.34%; No alkenes in products.

using a ZSM-5 (5 wt.-%) containing catalyst leads to increased yields of aromatics for both feedstocks. At the pressure (0.45 MPa) studied, there was a slow deactivation of the catalyst with time. The results reported in the Table 2 refer to a time on stream of 20 h.

The interesting aspect of the results is the negligible amount of BTX range aliphatics in the products, even though the feeds themselves have large quantities of these hydrocarbons. In the case of PG1, for example, the feed contained 8.18 wt.-% aliphatics in the BTX-boiling range, while the product contained only 0.10 wt.-% aliphatics. The small amount of aliphatics present in the product makes it possible to obtain BTX with high purity by a simple fractionation step. Thus, reforming over ZSM-5 containing catalysts could make the production of aromatics from pyrolysis gasoline a much simpler operation than the multistep processes presently in commercial practice.

The role of the zeolite on yield of products and ageing of catalyst

The results of the reforming of pyrolysis gasoline (PG) over a conventional mono-metallic catalyst and one containing 5 wt.-% ZSM-5 are reported in Table 3. The data were obtained at atmospheric pressure over a period of ten hours. Both Pt-alumina and the zeolite containing Pt-alumina catalyst pro-

TABLE 3

Reforming of pyrolysis gasoline: comparison between Pt-Alumina and ZSM-5-Pt-Alumina catalysts

Conditions: temperature: 763 K, pressure: 0.1 MPa, WHSV: 2.25 h⁻¹, H₂/HC (mol ratio): 6.

Component	Feed	Pt-Al ₂ O ₃ -Cl ^a			Pt-Al ₂ O ₃ -Cl+ZSM-5 ^b		
		Products at TOS ^c			Products at TOS ^c		
		1.5	5.5	10.0	1.5	5.5	10.0
C ₁ -C ₂	0.00	0.35	0.32	0.23	1.05	1.18	1.66
C ₃	0.00	0.64	0.55	0.41	5.78	5.40	6.21
C ₄	0.00	0.73	0.62	0.49	3.87	3.70	3.71
C ₅	3.13	3.83	5.13	5.37	0.91	1.12	1.84
C ₆	7.10	7.13	6.48	6.73	1.92	3.45	3.94
Aliphatics ^c in BTX ^f	13.02	5.57	7.49	9.68	0.43	1.31	1.67
Benzene	58.20	64.33	62.98	58.76	66.80	64.52	61.04
Toluene	14.05	12.18	11.70	13.48	15.91	15.94	16.59
C ₈ aromatics	0.23	0.54	0.50	0.60	1.56	1.62	1.74
C ₉ ^{+d}	4.26	4.69	4.21	4.24	1.76	1.77	1.61
Σ aromatics	76.74	81.74	79.39	77.08	86.03	83.85	80.98
Δ aromatics ^c	-	5	2.65	0.34	9.20	7.11	4.24
Δ BTX ^c	-	4.57	2.70	0.36	11.79	9.60	6.89

^a0.5 wt.-% Pt and 1.1 wt.-% Cl.

^b0.6 wt.-% Pt, 1.0 wt.-% Cl and 5.0 wt.-% ZSM-5.

^cAlkenes = 4.52 wt.-% in BTX aliphatics in feed, negligible alkene content in products.

^dMostly aromatics.

^eTOS = Time-on-stream (h).

^fBTX = Benzene, toluene, ethylbenzene and xylenes.

duce extra aromatics. However, the aromatic gain is negligible (0.34%) after 10 h in the case of the conventional catalyst (Pt-alumina), while it is significant (4.24%) in the case of the zeolite containing catalyst. The Pt-alumina catalyst is found to transform far less C₆ and aliphatics in the BTX (benzene, toluene, ethylbenzene and xylenes) boiling range than the zeolite containing catalyst. The increased conversion of C₆-C₉ aliphatics results in more aromatics and C₁-C₄ gas fraction. The increased production of aromatics, particularly BTX, in the case of the zeolite containing catalyst could be due to (a) enhanced dehydrocyclisation of the C₆-C₈ alkanes/alkenes fraction, (b) dealkylation of C₉ aromatics and (c) oligomerization of the cracked hydrocarbon fragments over ZSM-5. However, from an examination of the composition of the aromatic fraction, it is not possible to identify the relative importance of the three routes in increasing the aromatics yield.

A comparison of the ageing rates of Pt-alumina and ZSM-5 containing Pt-

alumina is made in Fig. 1. Plots of total aromatic gain and aliphatic content in the BTX range with time-on-stream have been made for the two catalysts. Pt-alumina deactivates more rapidly than the zeolite catalyst. The reasons for the slower deactivation of the zeolite catalyst are (1) the resistance of ZSM-5 to accumulate coke inside the pores and (2) the ability of ZSM-5 to crack away the coke precursors preventing them from building up on the catalyst surface. The coke contents of the zeolite containing catalyst at the end of 52 h on stream was 4.3 wt.-%, while that of the Pt-alumina catalyst at the end of 12 h on stream was 8.7 wt.-%. As both feeds contained large amounts of sulphur (Table 1), it is possible that sulphur also affected their activities and deactivation rates. Generally, sulphur is a poison for the metallic function and its contribution is likely to be similar in deactivating the metallic components of both the zeolite and the conventional catalyst. Again, sulphur has been reported to increase the acidities of both alumina [16] and zeolites [17] including ZSM-5 [18]. Similarly, platinum metal is also believed [19] to be stabilized better on ZSM-5. However, in the case of the catalysts reported here, the amount of platinum inside the zeolite channels (in close interaction with the zeolite) is likely to be small as the catalyst preparation involved impregnation with anions (PtCl_6^{2-}) and the stabilization of platinum by ZSM-5 may not be a significant factor. Due to the contradictory effects of sulphur on the metal and

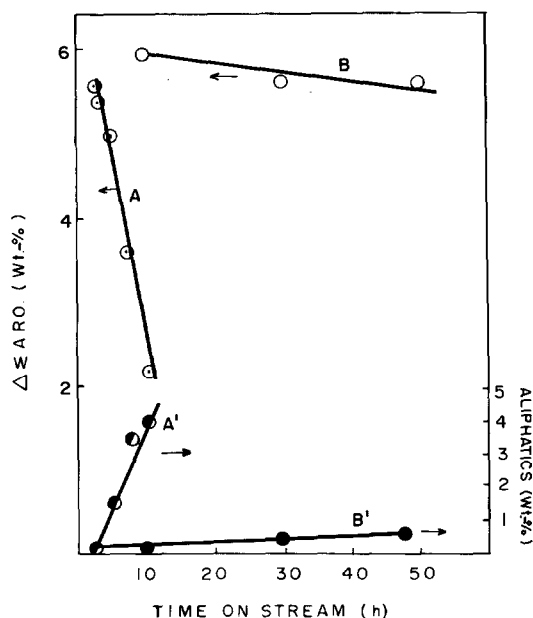


Fig. 1. Comparison of ageing rates between Pt-Al₂O₃ and ZSM-5-Pt-Al₂O₃ catalysts. A,A': Pt-Al₂O₃; B,B': ZSM-5 (5 wt.-%)-Pt-Al₂O₃. Feed: PG1, Temp. (K): 773, Press. (MPa): 0.45, WHSV (h⁻¹): 2.25, H₂/oil (mole ratio): 6.

the supports, its influence on the two sets of catalysts can not be clearly spelt out.

Influence of zeolite content on product yields

The influence of varying the zeolite content on product yields is presented in Fig. 2. These studies were carried out at 1 MPa. The yield of C_1-C_4 gases increases as the zeolite content is increased, and the concentration of aliphatics boiling in the BTX-range decreases. The aromatic yield increased on addition of the zeolite upto about 5 wt.-% beyond which it decreases. The reason for the loss of aromatics at higher zeolite levels (10 wt.-%) is probably due to the rapid cracking of the cycloalkanes produced by the hydrogenation of aromatics at the high pressure (1 MPa) used. While hydrogenation is a fast reaction, cracking is a slow one and the destruction of aromatics is determined by the rate of cracking of the cycloalkanes, the cracking rate being dependent on the available number of acid sites (zeolite content).

Influence of zeolite acidity

The next part of the study relates to the comparison between ZSM-5 and (Fe)ZSM-5 as additives. TPD profiles of ammonia adsorbed on the ZSM-5 and (Fe)ZSM-5 samples used in these studies were obtained by adsorbing ammonia at 298 K over the samples degassed at 773 K for 6 h in vacuum (about

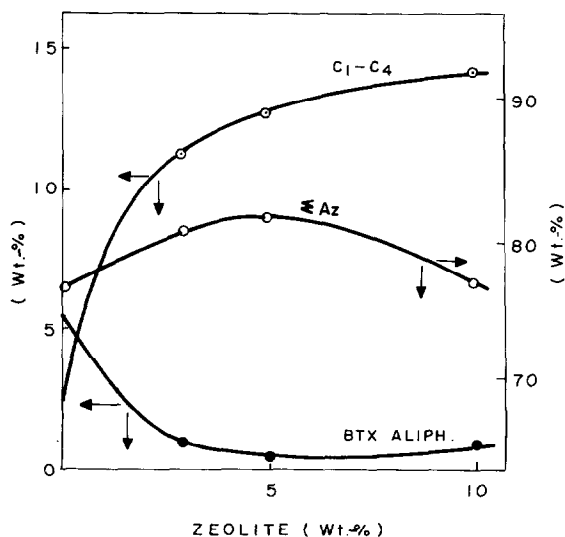


Fig. 2. Influence of zeolite content on product distribution. Feed: PG1, Press. (MPa): 1.0, WHSV (h^{-1}): 2.25, Temp. (K): 753, H_2 /oil (mole ratio): 6.

10^{-3} Pa) upto a pressure of $4 \cdot 10^4$ Pa, degassing the physically adsorbed ammonia at 298 K for 600 s, and desorbing at a programmed heating rate of 10 K/min in a helium flow of 10 ml min^{-1} . The desorbed gases were continuously monitored by a TCD (Shimadzu GC 6A). The studies revealed two low-temperature peaks (< 473 K) and one high-temperature peak (> 473 K), attributed, respectively, to weakly adsorbed and strongly chemisorbed ammonia. The highest temperature of the peak maximum was 698 K for ZSM-5 and 628 K for (Fe)ZSM-5. As the desorption temperature is proportional to the strength of adsorption, the Fe-isomorph possesses weaker acid sites than the Al-form. The number of the acid sites in the two samples were, however, nearly the same as the areas of the high-temperature peaks were similar [13]. Two catalysts each containing 10 wt.-% of (Fe)ZSM-5 and ZSM-5 were examined in these studies. Both (Fe)ZSM-5 and ZSM-5 containing catalysts produce additional aromatics, the yield of the aromatics being more in the case of the ZSM-5 catalysts (Table 4). Further, the stability of the ZSM-5 containing catalyst is better and the BTX range aliphatics are lower. Both (Fe)ZSM-5 and ZSM-5 catalysts deactivate, the aliphatic content going up from 2.63 at 1 h on stream

TABLE 4

Reforming of pyrolysis gasoline: comparison of ZSM-5 and (Fe)-ZSM-5 catalysts

Conditions: temperature: 773 K, pressure: 0.1 MPa, WHSV: 2.25 h^{-1} , H_2/HC (mole ratio): 6, composition of catalyst: zeolite, 10 wt.-%; Pt, 0.6 wt.-%; Chlorine, 1.1 wt.-%; Al_2O_3 , 88.3 wt.-%.

Component	Feed (wt.-%)	ZSM-5		(Fe)-ZSM-5	
		Product distribution at TOS ^a		Product distribution at TOS ^a	
		1	10	1	10
C ₁ -C ₂	-	1.72	1.20	0.78	0.86
C ₃	-	5.71	3.67	3.07	2.50
C ₄	-	3.01	1.98	2.42	2.06
C ₅	3.37	0.64	0.52	3.17	3.32
C ₆	7.80	1.65	3.64	4.80	7.10
Aliphatics in BTX ^b	12.92	0.62	2.03	2.63	4.41
Benzene	57.43	62.2	62.4	63.80	62.09
Toluene	14.20	19.26	18.62	15.05	13.57
C ₈ aromatics	0.27	2.60	2.90	1.63	1.10
Others	4.01	2.59	3.04	2.65	2.99
Σ BTX ^b	71.90	84.06	83.02	80.48	76.76
Δ BTX ^b	-	12.16	11.12	8.58	4.86

^aTOS = Time-on-stream (h).

^bBTX = Benzene, toluene, ethylbenzene and xylenes.

to 4.41 at 10 h on stream in the case of (Fe)ZSM-5 and from 0.62 to 2.03 in the case of ZSM-5.

Influence of dicyclopentadiene in the feed

In addition to the light alkenes and dialkenes present in PG, generally, dicyclopentadiene (DCP) is also present in the heavier fractions. DCP is a very reactive hydrocarbon and transforms itself into coke rapidly over catalysts, particularly at high temperatures. The results of the studies on the influence

TABLE 5

Influence of dicyclopentadiene (DCP) content on cracking activity and BTX gain

Catalyst: ZSM-5(5%)-Pt(0.6%)-Cl(1.1%)-Al₂O₃, conditions: temperature: 73 K, WHSV: 2.0 h⁻¹, H₂/HC (mole ratio): 7, pressure: 0.6 MPa, TOS (h): 20, Feeds: PG2 fractionated to contain different levels of DCP.

DCP in feed (wt.-%)	Percent cracking of aliphatics in BTX range	Aromatics gain (wt.-%)
0.0	99.5 (74) ^a	2.7 (10.0)
2.38	99.0	0.7
8.11	87.0 (45)	0.3 (6.8)

^aThe bracketed values refer to data at 0.1 MPa and TOS of 7 h.

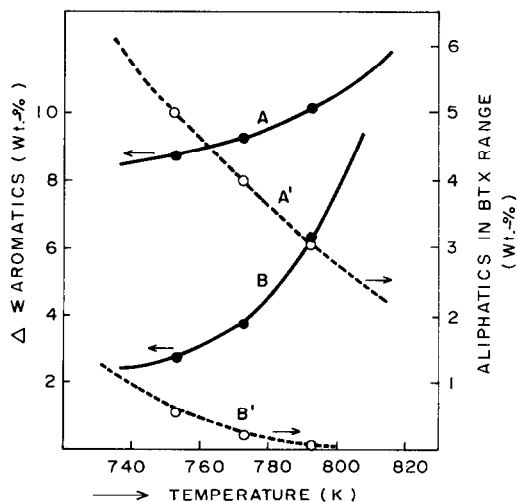


Fig. 3. Influence of temperature on product distribution. A,A': 0.1 MPa, B,B': 1.0 MPa. Catalyst: ZSM-5(5%)-Pt-Al₂O₃, see Tables 6 and 7 for process parameters.

TABLE 6

Pyrolysis gasoline reforming: effect of temperature

Catalyst: ZSM-5 (5%)-Pt(0.6%)-Cl(1.1%)-Al₂O₃, conditions: WHSV: 2.0 h⁻¹, pressure: 0.1 MPa, H₂/HC (mole ratio): 6.0, TOS: 2 h.

Component	Feed (wt.-%)	Product distribution at temp. (K)		
		753	773	793
C ₁ +C ₂	-	0.32	0.54	0.70
C ₃	-	1.05	1.70	1.71
C ₄	-	1.04	1.47	1.58
C ₅	1.35	2.21	2.33	2.95
C ₆	6.69	5.94	5.01	4.04
C ₇	12.95	5.00	3.76	2.82
Benzene	59.47	66.92	67.40	68.35
Toluene	14.12	14.78	14.59	13.94
C ₈ arom.	0.23	0.87	1.05	1.60
Others	5.18	1.85	2.15	2.31
Σ BTX	73.82	82.57	83.05	83.89

TABLE 7

Influence of temperature in the reforming of pyrolysis gasoline

Catalyst: ZSM-5 (5%)-Pt(0.6%)-Cl(1.1%)-Al₂O₃, conditions: WHSV: 2.5 h⁻¹, pressure: 1.0 MPa, H₂/HC (mole ratio): 6.0, TOS: 5 h.

Component	Feed (wt.-%)	Product distribution at temp. (K)		
		753	773	793
C ₁ +C ₂	-	0.12	0.17	0.22
C ₃	-	9.02	9.40	8.00
C ₄	-	2.61	2.71	2.10
C ₅	3.26	1.23	0.78	0.42
C ₆	6.06	1.01	0.13	0.23
Aliphatics in BTX range	7.94	0.54	0.20	0.05
Benzene	67.94	68.60	69.49	71.53
Toluene	13.70	14.95	15.25	15.81
Xylenes	0.17	1.02	0.81	0.81
Others	0.94	0.90	0.96	0.80
Σ BTX	81.81	84.57	85.55	88.15
Δ BTX (+)	-	2.76	3.74	6.34

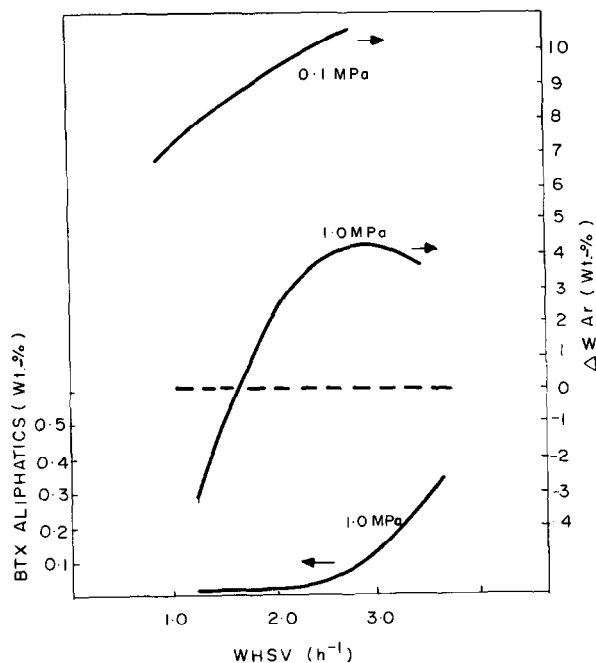


Fig. 4. Influence of feed-rate (WHSV) on product distribution, Catalyst: ZSM-5(5%)-Pt-Al₂O₃, Temp. (K): 773 K, H₂/oil (mole ratio): 6.

TABLE 8

Influence of WHSV on the reforming of pyrolysis gasoline

Catalyst: ZSM-5(5%)-Pt(0.6%)-Cl(1.1%)-Al₂O₃, conditions: temperature: 773K, pressure: 0.1 MPa, H₂/HC: 6.0, TOS: 2.0 h.

Component	Feed (wt.-%)	Product distribution at WHSV (h ⁻¹) (wt.-%)		
		0.90	1.69	2.25
C ₁ +C ₂	-	1.08	0.76	0.53
C ₃	-	2.43	1.47	1.08
C ₄	-	2.21	1.65	1.25
C ₅	3.24	3.47	5.15	3.21
C ₆	6.97	6.92	5.85	6.86
C ₇	12.89	3.99	4.50	4.94
Benzene	55.05	61.78	63.12	63.72
Toluene	13.81	12.31	12.39	13.88
Xylenes	0.27	1.47	0.82	0.85
Others	7.78	4.52	4.11	3.68
Σ BTX	69.13	75.56	76.33	78.46

of DCP on the activity of a ZSM-5 containing catalyst are presented in Table 5. The cracking activity of the catalyst and BTX gain are lowered by DCP. However, a higher pressure reduces the deactivating influence of DCP on cracking. For example, when a large amount of DCP is present in the feed, the cracking activity is 87% even after 20 h on stream at 0.6 MPa pressure, while the activity is only 45% at a time-on-stream (TOS) of 7 h at 0.1 MPa (Table 5). However, the decrease in aromatics gain primarily due to the deactivation of the metal sites is significant even at 0.6 MPa pressure.

Influence of process parameters

The influence of temperature on BTX gain and BTX range aliphatics content at two different pressures are shown in Fig. 3. The catalyst used was a 5 wt.-% ZSM-5 containing Pt-alumina. The detailed product analyses are presented in Tables 6 and 7. Increasing the temperature increases the yield of the aromatics and decreases the BTX range aliphatics at both 0.1 MPa and 1.0 MPa. This effect of pressure can be understood by examining the Tables 3, 6 and 7 and Fig. 1 and 4, which compare activities at different pressures and temperatures and times-on-stream. As expected, because of thermodynamic limitations, increasing the pressure decreases aromatics gain while improving the life of the catalyst. At the same time, higher pressures favour the cracking of BTX range aliphatics.

The influence of WHSV on the reforming of pyrolysis gasoline at a pressure of 0.1 MPa is presented in Table 8. The content of BTX range aliphatics in the product increases with WHSV. This is to be expected, as cracking reactions are slow and the rate prone to decrease with decreasing contact time. The yield of aromatics, however, increases with increasing WHSV in the short WHSV range studied. Fig. 5 compares the influence of WHSV at two pressures viz., 0.1 and 10 MPa. The higher pressure results are more interesting. At low space velocities (< 1.5) there is actually an aromatic loss caused by the hydrogenation of the aromatics and their subsequent cracking by the zeolite. Even though hydrocracking reactions are slow, the large availability of cycloalkanes (hydrogenated aromatics) at higher pressures results in destruction of significant amount of aromatic compounds at low WHSV's (high contact times). At moderate WHSV's (1.5-2) there is an increase in the aromatic gain, though at still higher WHSV's (> 2.5) the aromatic gain decreases due to decrease in the reforming and other reactions responsible for aromatic production.

CONCLUSIONS

Pyrolysis gasoline is rich in alkenes and it is not possible to reform it using conventional reforming catalysts, which tend to deactivate rapidly. The addition of small amounts of ZSM-5 reduces the deactivation of reforming catalysts

and permits the reforming of pyrolysis gasoline. The pressures have to be kept low enough to achieve a significant increase in the concentration of aromatics.

ACKNOWLEDGEMENT

This work was partly funded by UNDP.

REFERENCES

- 1 P.B. Weisz, *Pure Appl. Chem.*, 52 (1980) 2091.
- 2 L.C. Rollmann and D.E. Walsh, *J. Catal.*, 56 (1979) 139.
- 3 R.H. Perry, F.E. Davis and R.B. Smith, *Oil Gas J.*, 76 (1978) 81.
- 4 N.Y. Chen, W.E. Garwood and F.G. Dwyer, in H. Heinemann (Editor), *Shape selective catalysis in industrial applications*, Marcel Dekker, New York, 1989, p. 85.
- 5 G.V. Bickle, G.V. Bhaskar, D.D. Do and N.J. Beltramini, *Appl. Catal.*, 47 (1989) 59.
- 6 N.Y. Chen and W.E. Garwood, *Catal. Rev. Sci. Eng.*, 28 (1986) 185.
- 7 S. Sivasanker, K.J. Waghmare, S.R. Padalkar, P. Ratnasamy and K.R. Murthy, *Appl. Catal.*, 33 (1988) 127.
- 8 C.J. Plank, E.J. Rosinski and E.J. Givens, *US Patent 4 141 859* (1979).
- 9 C.J. Plank, E.J. Rosinski and E.J. Givens, *US Patent 4 276 151* (1981).
- 10 S. Sivasanker and P. Ratnasamy, *EP. 382 960* (1990).
- 11 S. Sivasanker and P. Ratnasamy, *US Patent 4 950 385* (1990).
- 12 S.B. Kulkarni, V.P. Shiralkar, A.N. Kotasthane, R.B. Borade and P. Ratnasamy, *Zeolites*, 2 (1982) 313.
- 13 P. Ratnasamy, R.B. Borade, S. Sivasanker and V.P. Shiralkar, *Acta. Phys. Chem.*, 31 (1985) 137.
- 14 S. Sivasanker, A.V. Ramaswamy and P. Ratnasamy, in B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Editors), *Preparation of Catalysts*, Elsevier, Amsterdam, 1979, p. 185.
- 15 L. Spenadel and M. Boudart, *J. Phys. Chem.*, 64 (1960) 204.
- 16 P. Ratnasamy, A.V. Ramaswamy and S. Sivasanker, *J. Catal.*, 61 (1980) 519.
- 17 H.G. Karge and J. Rasko, *J. Colloid Interface Sci.*, 64 (1978) 522.
- 18 K.M. Reddy, Thesis, University of Poona, May 1990.
- 19 O.V. Bragin, E.S. Shpiro, A.V. Peobrazhensky, S.A. Isaev, T.V. Vasina, B.B. Dyusenbina, G.V. Antoshin and Kh.M. Minachev, *Appl. Catal.*, 27 (1986) 219.