

Naphtha Reforming over Catalysts Containing a Ferrisilicate Zeolite of the Pentasil Type

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ABSTRACT

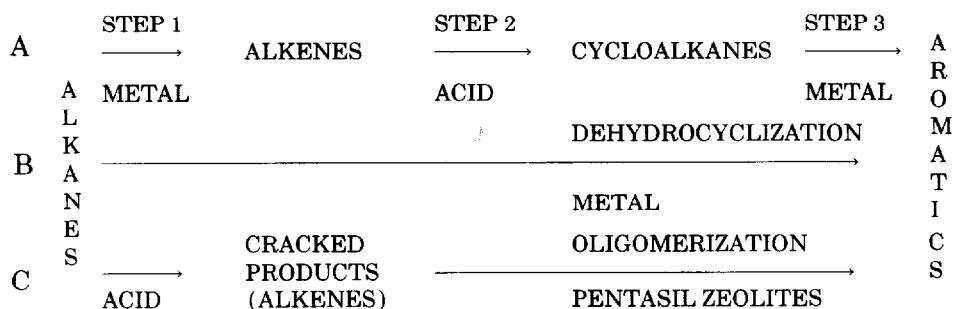
A moderately acidic ferrisilicate zeolite of the pentasil type has been used to promote the support acidity of both mono- and bimetallic naphtha reforming catalyst formulations. The added zeolite (1-10 wt.%) enhances the number of isomerization sites and also catalyses the oligomerization of the cracked products into aromatics. The oligomerization activity is maximal when the reaction is carried out with recycling of gaseous products.

INTRODUCTION

Although conventional commercial reforming catalysts are based on halogen-promoted acidic aluminas, a number of zeolite-based catalysts have also been reported and patented [1-6]. Processes such as selectoforming [7], M-forming [8,9] and cyclar [10], which are based on zeolite-containing catalysts, produce high octane gasoline blend stocks or aromatics through different pathways. In selectoforming octane improvement is achieved by the cracking of n-alkanes, whereas in M-forming it is achieved through alkylation of light aromatics [11]. The M2-forming and cyclar processes produce additional aromatics by oligomerization of light olefins.

The two important reactions that lead to aromatics during naphtha reforming are naphthene dehydrogenation and alkane dehydrocyclization. Of these, the dehydrocyclization (DHC) of alkanes is the slower reaction and the efficiency of reforming catalysts is largely dependent on their ability to catalyse this reaction. A schematic representation of the various routes leading to the production of aromatics is presented in Scheme 1.

Three different routes have been proposed. Route A is the conventional route proposed by Mills et al. [12], and route B has been proposed in more recent



publications [13–15]. Our own studies [16] have indicated that the mono-functional route (route B) is the more important with C_6 n-alkanes and the bifunctional route could also be important with C_8 alkanes. For conventional catalysts, route C is not expected to be operative; it is applicable mainly to zeolite-containing catalysts.

In this study, we observed that the addition of small amounts (1–10 wt.%) of a moderately acidic ferrisilicate zeolite of the pentasil type to conventional reforming catalyst formulations increased the aromatics yield either (i) by increasing the number of acid sites required to catalyse step 2 of route B or (ii) by oligomerizing the cracked fragments into aromatics according to route C.

EXPERIMENTAL

Materials

Ferrisilicate zeolite

The synthesis and characterization of the ferrisilicate zeolite (FeZ) has been described previously [17]. The acid-washed zeolite had an $SiO_2:Fe_2O_3$ ratio of 90.

Reforming catalysts

The required amounts of the ferrisilicate zeolite were physically blended with powdered alumina hydrate (boehmite), extruded, dried (338 K) and calcined (823 K) to make the support for the catalysts. This support material was then loaded with the required amounts of the platinum salt and hydrochloric acid from aqueous solutions by a wet impregnation technique. The details of the catalysts used are reported in Table 1.

Procedures

The reforming reactions were carried out in commercial high-pressure reactors (Catatest, Geomecanique, France, and Twin Reactor, MetrimpeX, Hungary). Generally, 20–30 g of catalyst were used in the tests, and the catalysts

TABLE 1

Description of catalysts

Catalyst	FeZ (wt.%)	Platinum (wt.%)	Rhenium (wt.%)	Chloride (wt.%)	S_{BET}^* (m ² /g)
M0	0	0.6	—	1.0	232
M4	4	0.6	—	1.1	229
M5	5	0.6	—	1.1	250

* S_{BET} : specific surface area, determined by the BET method.

were pre-sulphided at 643 K to a level of 0.06 g of sulphur per gram of the catalyst using the hydrocarbon feed spiked with dimethyldisulphide. The clean feedstocks, n-hexane and the commercial naphtha cut had sulphur contents of 1 and 4 ppm, respectively.

RESULTS

When reforming a wide cut naphtha (343–413 K cut), the most difficult fraction to aromatize is the C₆ fraction. The aromatizing efficiency of a reforming catalyst can hence be measured qualitatively by its ability to dehydrocyclize n-hexane to benzene. The reforming of n-hexane over monometallic catalysts is reported in Table 2. The reaction was carried out under low-severity conditions, suitable for monometallic catalysts, in a single-pass mode and the data refer to a time-on-stream of 25 h. It is seen that distinct improvements in the

TABLE 2

n-Hexane reforming* on platinum catalysts with and without zeolites

Conditions: $P = 20 \text{ kg cm}^{-2}$, $\text{WHSV} = 1.3 \text{ h}^{-1}$, hydrogen:hydrocarbon molar ratio = 6.

Catalyst	Temperature (K)	Product distribution (wt.%)							C ₅₊ yield (wt.%)	Benzene selectivity (S _B)
		C ₁ +C ₂	C ₃ +C ₄	C ₅	i-C ₆	n-C ₆	Bz	C ₇ +Ar		
M0	753	15.6	33.1	18.5	21.5	7.3	3.9	0.1	51.3	5.6
	773	19.4	38.2	16.3	13.5	4.5	7.5	0.4	42.3	9.6
M4	753	12.4	37.0	15.8	22.9	7.2	4.6	0.1	50.6	6.9
	773	15.6	51.7	12.3	8.7	3.0	8.3	0.2	32.6	9.2
M5	753	12.8	37.7	14.6	22.5	7.5	4.7	0.1	49.5	6.7
	773	15.3	52.5	13.2	8.0	2.7	7.9	0.2	32.2	9.7

*Single-pass operation; data refer to time-on-stream = 25 h.

TABLE 3

Reforming of naphtha by different modes of operation

Conditions: $T = 753 \text{ K}$; $P = 1.8 \text{ MPa}$, $\text{WHSV} = 2 \text{ h}^{-1}$, hydrogen:hydrocarbon molar ratio = 6.

Catalyst	Mode of operation	Product/feed composition (wt.%)															Aromatics (wt.%)	C_{5+} (wt.%)
		C_6			C_7			C_8			C_9			Aromatics (wt.%)	C_{5+} (wt.%)			
		P	N	A	P	N	A	P	N	A	P	N	A					
M0	Recycle	Feed	-	1.0	-	7.2	12.9	3.8	36.0	23.7	6.5	15.9	2.7	0.4	10.7	94.7		
	Product	1.3	0.2	1.1	7.8	1.0	15.5	26.5	1.3	31.3	3.6	-	3.9	51.8				
	AA	-	-	1.1	-	-	11.7	-	-	24.8	-	-	-	3.5	41.1			
M4	Recycle	Feed	-	1.0	-	7.2	12.9	3.8	36.0	23.7	6.5	15.9	2.7	0.4	10.7	85.2		
	Product	1.7	0.3	2.9	0.2	0.4	23.1	0.1	0.2	37.8	-	-	3.1	66.9				
	AA	-	-	2.9	-	-	19.3	-	-	31.3	-	-	-	2.7	56.2			
M4	Single-pass	Feed	-	0.2	-	3.7	8.3	4.8	31.1	26.2	13.8	7.5	4.4	-	18.7	71.6		
	Product	1.8	0.1	1.4	0.2	0.2	15.4	0.0	-	38.0	-	-	2.9	57.8				
	AA	-	-	1.4	-	-	10.6	-	-	24.2	-	-	2.9	39.1				

aromatic yields occur when the ferrisilicate zeolite is incorporated (catalysts M4 and M5).

The C_{5+} yields decrease on addition of the zeolite owing to the greater cracking activity of the zeolite. The benzene yields increase on increasing the zeolite level (up to 5%) at 753 K, although at 773 K the optimal zeolite content is ca. 4%. An interesting observation is that although the total gas (C_1 – C_4) yields are higher on zeolite catalysts, the yields of C_1 and C_2 (dry gases) are lower on these catalysts. Further, at 753 K, the zeolite catalysts (M4 and M5) produce more isohexanes than the alumina-only (M0). Apparently, at the lower temperature (753 K), the moderate acidity incorporated by the addition of zeolites increases the isomerization activity. However, at 773 K, the cracking reactions predominate and the isohexane yields are lower.

The results of the reforming of a commercial naphtha cut (383–413 K) are reported in Table 3. The experiments were carried out under both recycle and single-pass modes. The data reported were obtained during 48–52 h of operation. The composition of the feeds used in each experiment is also reported in Table 3. The difference between the aromatic contents of the product and the corresponding feed are also listed as ΔA . These values represent the aromatics produced by the catalyst.

DISCUSSION

The results of the reforming of the 383–413 K cut from straight-run naphtha under both recycle and single-pass modes (Table 3) indicate that with the 4% zeolite-containing catalyst (M4), operation under recycle conditions produces more C_{5+} and aromatics than in the single-pass mode. There is a 17.1% increase in total aromatics yield and a 13.6% increase in the C_{5+} yield when operating in the recycle mode compared with the single-pass mode.

In both the recycle and single-pass modes, the hydrogen:hydrocarbon molar ratio was kept constant ($=6$), and the moisture level also was kept constant (about 20 ppm). The hydrocarbon content of the recycle gas was higher (about 20%) with the zeolite-containing catalyst than with the non-zeolite-containing catalyst (10%). This results in the hydrogen partial pressure being lower with the zeolite-containing catalyst. As the total pressure was kept constant at 1.8 MPa (18 kg cm^{-2}), the partial pressure of hydrogen would have been 1.27 and 1.41 MPa, respectively, for the zeolite- (M4) and alumina-based (M0) catalysts. Separate partial pressure experiments showed that a reduction in partial pressure of 0.14 MPa cannot bring about the observed large increases in aromatic yields.

The aromatics found in the product constitute the feed aromatics and those formed by the transformation of the naphthenes and alkanes. If we assume that all the naphthenes that disappeared from the feed ended up as aromatics, then we can find the amount of alkanes that underwent aromatization. The

efficiency of a naphtha reforming catalyst can be measured in terms of the amount of alkanes converted into aromatics. Such an evaluation of the catalysts M0 and M4 (in the recycle and single-pass modes) for the formation of C₈ aromatics is illustrated below:

C₈ aromatics in feed, 6.5%

C₈ naphthenes in feed, 23.7%

C₈ naphthenes in product, 1.3%

C₈ naphthenes converted, $(23.7 - 1.3) = 22.4\% = 21.2\%$ aromatics

Fraction of the feed naphthenes converted, $22.4/23.7 = 0.95$

Aromatics in product, 31.3%

Aromatics from feed + naphthene conversion, 27.7%

Therefore, aromatics from alkanes, $31.3 - 27.7 = 3.6\% = 3.87\%$ alkanes

Alkane content of feed, 36.0%

Fraction of alkanes converted into aromatics, $3.87/36 = 0.11$

Hence we can write the following equation for aromatics formation:

$$C_8 A_p = 1.0 A + 0.95 N + 0.11 P$$

where A_p represents the aromatics in the product and A, N and P represent the aromatics, naphthenes and alkanes in the feed.

Similar calculations for catalyst M4 give the following equations:

$$M4 \text{ (recycle): } C_8 A_p = 1.0 A + 0.99 N + 0.27 P$$

$$M4 \text{ (single pass): } C_8 A_p = 1.0 A + 0.98 N + 0.0 P$$

Therefore, it is seen that the zeolite-containing catalyst operating in the recycle mode converts more alkanes (17%) than the non-zeolite-containing catalyst (11%). The extra conversion of alkanes is mainly due to the oligomerization of the cracked products. In the absence of recycling, the alkanes are only cracked into lighter products and not converted into aromatics. This becomes evident when we compare the performance of the zeolite-containing catalyst (M4) with the alumina-only catalyst (M0). Although the aromatics production with the zeolite-containing catalyst (M4) in the single-pass mode is the same as that with the non-zeolite-containing catalyst (M0) (41.1% for M0 and 39.1% for M4), the C₅₊ yields are lower on the zeolite-containing catalyst (71.6% for M4 and 94.7% for M0). Therefore, for heavy naphthas zeolite addition has no advantage if the catalyst is operated in the single-pass mode.

CONCLUSIONS

The incorporation of small amounts of a ferrisilicate zeolite of the pentasil type in naphtha reforming formulations can enhance the yield of aromatics, probably by oligomerization of the cracked fragments. The enhancement is

significant when the reactor is operated in the recycle mode as in commercial practice.

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