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Effects of HZSM-5 addition during catalytic cracking of *n*-hexadecane on HY

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Additions of HZSM-5 to HY during cracking of *n*-hexadecane enhances formation of olefins in the range C_3–C_5, with concurrent suppression of hydrogen transfer processes. Ratios of branched to linear isomers are decreased for paraffins by addition of the pentasil, while the reverse is observed for olefinic products.

Keywords: Cracking; bimolecular processes; pentasil; zeolites

1. Introduction

In the petroleum industry, refineries conventionally use the faujasite Y zeolite in either a rare earth exchanged or ultrastable form for the production of high quality gasolines. Environmental concerns over the usage of lead additives as octane enhancers have forced refiners to seek alternative catalyst formulations to achieve high octane rating gasolines. Over the past five years, the addition of the shape selective zeolite ZSM-5 to the Y zeolite has been shown to improve gasoline octane ratings at the expense of yield.

Despite numerous studies reporting the cracking of gas-oils over Y/ZSM-5 combinations [1–6], the mechanism by which the pentasil additive promotes octane enhancement is still under debate. Relatively few studies have investigated the cracking behaviour of typical gas-oil components individually [7]. This approach, however, allows a detailed analysis of the reaction mechanisms occurring in the presence of zeolite combinations. In this study, the cracking of *n*-hexadecane over combinations of HY and HZSM-5 zeolites is reported.

2. Experimental

The feedstock *n*-hexadecane (99.8%) was obtained from Aldrich and used without further purification. The impurity present, branched C_{16} isomers, was considered in calculating product selectivities.

HY zeolite (CBV 760, Si/Al = 34.3) was provided by PQ zeolites, the Netherlands. HZSM-5 (Si/Al = 105) was provided by Snamprogetti, Milan, Italy. Catalysts were calcined at 500°C prior to use and sieved to mesh size 80/100.

All experiments were performed at 400°C and 1 atm pressure, using an integral, fixed-bed gas-phase plug-flow reactor with independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described in previous studies [8]. Catalysts were mixed with granules of washed sand, serving as a support matrix within the reactor. Blank experiments were performed to determine the extent of thermal cracking (less than 1% at longest times on stream). All thermal products were subtracted from yield of catalytic products.

In all experiments, 10 g of feed were injected over the catalyst at varying rates controlled by the feed-syringe pump. A catalyst to feed ratio of 0.057 was used for the HY zeolite. The amount of HZSM-5 was chosen to be approximately 5% by weight of the HY zeolite, giving a catalyst to feed ratio for the pentasil of 0.00285. Experiments were conducted on the individual zeolites and on their combination by mixing the corresponding masses of HY and HZSM-5 zeolites. Experiments were carried out over a range of times on stream (from 400 to 1200 s) to show that the observed effects were not significantly influenced by rates of catalyst decay.

Liquid products were analysed using a Hewlett Packard 5890A gas chromatograph with a Supelco capillary column (100 m × 0.25 mm i.d.) and flame ionisation detector. Gaseous products were also analysed on a similar chromatograph using a Chrompak capillary column (25 m × 0.32 mm i.d.). Identification of hydrocarbon products was assisted by the use of a Hewlett Packard 5890 gas chromatograph coupled to a 5970 mass selective detector.

3. Results and discussion

Cracking of *n*-hexadecane at 400°C was investigated on HY and HZSM-5 zeolites, both individually and in combination. For the zeolite combination, the percentage of HZSM-5 additive was held at 5% by weight, which is comparable to the levels used industrially in FCC units [1–3,6]. Fig. 1 shows the feed conversion as a function of time-on-stream for both the individual catalysts and also the HY/HZSM-5 combination. It can be seen that, in the presence of the pentasil, the degree of conversion is increased relative to the individual faujasite case. As would be expected, this increase is less than predicted by simple addition of the individual conversions.

Figs. 2a–2d show comparisons of the product distributions from reaction of the feedstock on HY and the faujasite/pentasil combination at 400°C and 800 s time-on-stream. Experiments carried out at other times-on-stream (from 400 to 1200 s) suggest that the observed phenomena are independent of run duration.

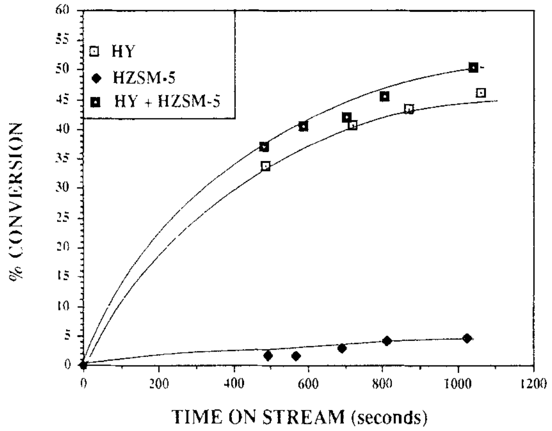

Fig. 1. Effects of time on stream and catalyst to feed ratios for hexadecane conversion on HY, HZSM-5 and the faujasite/pentasil combination at 400°C. Cat/feed ratios for reaction on HY = 0.057, HZSM-5 = 0.00285, zeolite combination = 0.0599.

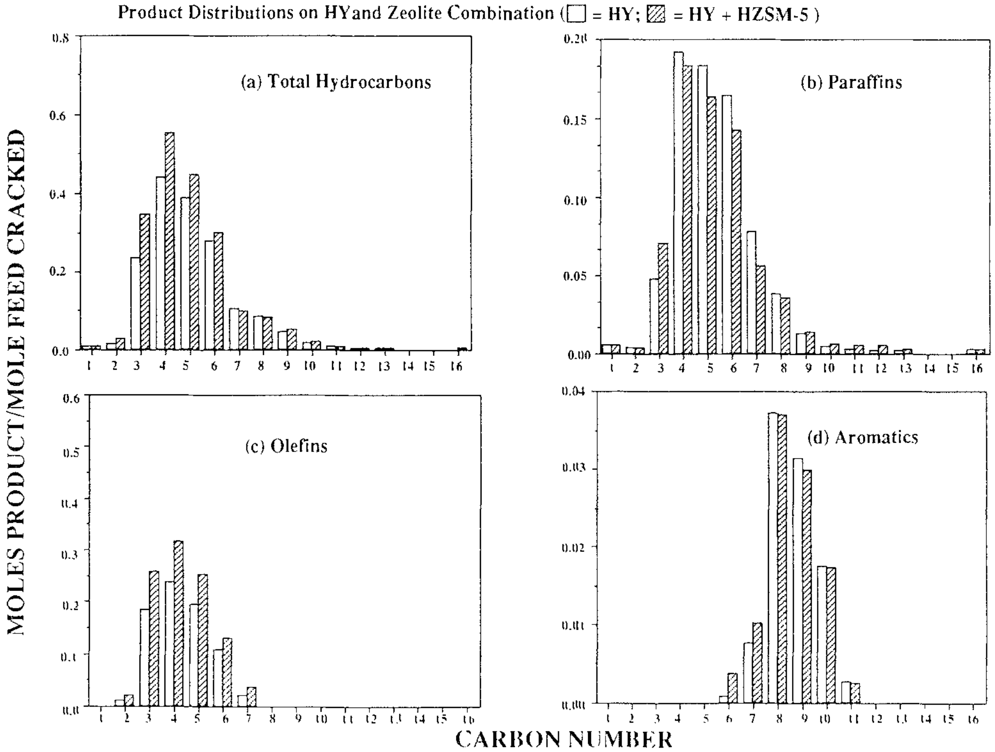

Fig. 2. Product distributions from reaction of feed on HY and zeolite combination at 400°C. Representative examples with cat/feed ratios as in fig. 1 and 800 s TOS. (a) Total hydrocarbons, (b) paraffins, (c) olefins, (d) aromatics.

The products observed from the cracking of *n*-hexadecane on both HY and HZSM-5 in isolation were typically acyclic paraffins and olefins, with small quantities of monoaromatic species. From fig. 2a, it is apparent that these products lie predominantly in the C_2–C_7 range, in agreement with previous studies [9,10]. A shift in selectivity towards lower carbon number for cracking over the HZSM-5 may be attributed to the low acid site density of this zeolite [9].

A noticeable increase in total hydrocarbon yield for C_3, C_4 and C_5 species is observed for cracking on the zeolite combination relative to the HY individually. Yields for other species remain essentially unchanged. By separating hydrocarbon product distributions into its paraffin, olefin and aromatic components as shown in figs. 2b, 2c and 2d respectively, the origin of changes in the product distribution may be traced.

Fig. 2b shows the product distribution for paraffinic species. A decreased yield of C_2–C_8 paraffins is noted upon addition of the pentasil. Such an observation may suggest that the pentasil additive acts to suppress bimolecular hydrogen transfer processes, which would otherwise occur readily on the HY zeolite. This is consistent with the proposal of Rajagopalan and Young [1]. In contrast, the olefin distribution (fig. 2c) shows increased yields of C_2–C_8 olefins in the presence of the HZSM-5. The marked increase in C_3 and C_4 olefins is consistent with many studies in which gas-oils have been cracked over faujasite–pentasil combinations [1–4,6]. Such olefinic species may be subsequently used as alkylate feed, thereby offsetting the decreased gasoline yield obtained [3–5]. The distribution of total aromatics (fig. 2d) shows there is little change in yields on addition of the pentasil to the base HY catalyst, apart from a significant increase in the amount of benzene formed. This is in agreement with many studies [2,3,6] on gas-oil cracking in which there is no reported net increase in aromatic yields.

By calculating the overall paraffin to olefin ratio (P/O) for products on the HY, HZSM-5 and on the zeolite combination, as shown in table 1, further evidence for the reduction of hydrogen transfer processes on the zeolite combi-

Table 1
Comparison of paraffin to olefin ratios for cracking products on HY, HZSM-5 and the zeolite combination

TOS (s)	HY		HZSM-5		HY + HZSM-5	
	cat/feed ratio	P/O	cat/feed ratio	P/O	cat/feed ratio [a]	P/O
490	0.0570	0.93	0.0028	0.58	0.0598	0.87
689	0.0570	1.01	0.0028	0.44	0.0598	0.81
710	0.0570	0.96	0.0028	0.57	0.0598	0.82
810	0.0570	1.04	0.0028	0.51	0.0598	0.82
1040	0.0570	1.06	0.0028	0.56	0.0598	0.84

[a] Cat/feed ratio for total catalyst used. Ratio Z/Y = 4.9% (wt/wt).

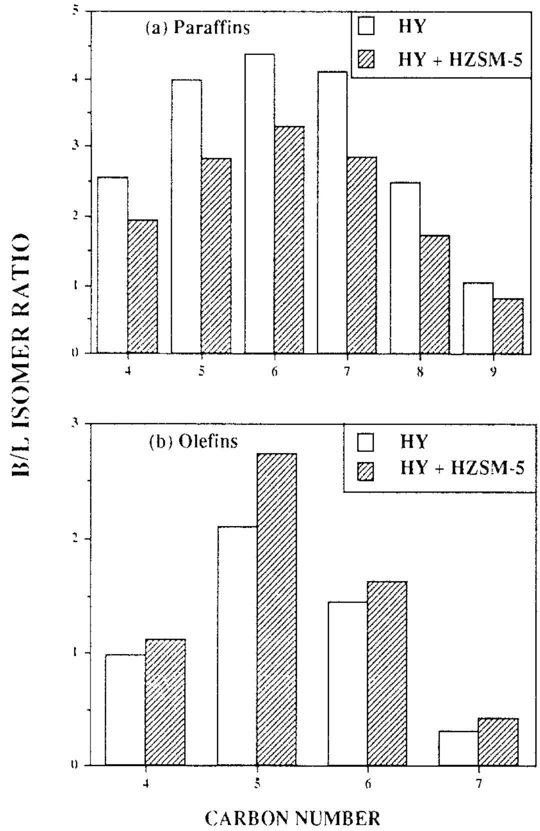

Fig. 3. Ratios of branched to linear isomers from reaction on HY and the faujasite/pentasil zeolite combination. (a) Paraffins, (b) olefins. Reaction conditions as in fig. 2.

nation is provided. For the individual Y zeolite, the P/O ratio is approximately 1, suggesting a high degree of hydrogen transfer, whilst on HZSM-5 it is approximately 0.5. Intermediate values obtained on the zeolite combination, together with the observed shifts in paraffin and olefin distributions, suggest that the strong tendency for conversion of olefins to paraffins via hydrogen transfer on the faujasite is reduced by the presence of the HZSM-5. It is apparent that these ratios for each system are not significantly influenced by time on stream showing that different rates of catalyst aging is not a significant factor.

Figs. 3a and 3b show the ratios of branched to linear isomers (B/L) for paraffins and olefins respectively. For all carbon numbers C_4–C_9, the ratio for paraffinic species on the zeolite combination is decreased relative to that found on the base faujasite zeolite (fig. 3a). This is contrary to many gas-oil studies in which increased branched to linear paraffin ratios are noted [3,6] There are, however, several studies in which reduced branching is noted in the presence of the pentasil additive [1,2]. It has been suggested that the addition of HZSM-5 leads to selective cracking of linear paraffin isomers in gas-oil feedstocks. The net result of pentasil addition may be a balance between preferential removal of linear paraffin isomers in the feedstock through cracking and their preferential formation as cracking products. For olefin products, there is an increased ratio of branched to linear isomers in the range C_4–C_7 with the zeolite combination, in agreement with published findings for the cracking of gas-oils [2–4].

4. Conclusions

The cracking of *n*-hexadecane as a typical gas-oil component on individual HY and HZSM-5, and also combinations of these has been investigated. On addition of HZSM-5 zeolite to HY increased yields of C_3–C_5 hydrocarbons are observed. This is attributable to a decrease in the yield of C_2–C_8 paraffins and a concurrent increased yield of olefins over the same range. Branched to linear isomer ratios for paraffins were found to decrease in the presence of the pentasil additive, whilst the reverse effect was noted for olefinic products.

Comparison of paraffin and olefin product distributions together with the overall paraffin to olefin ratio suggest that the HZSM-5 additive acts to suppress bimolecular hydrogen transfer processes, which would otherwise occur readily on the faujasite.

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