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Cracking and Isomerization of Hydrocarbons with Combinations of HY and HZSM-5 Zeolites

Z. ZAINUDDIN, F. N. GUERZONI, AND J. ABBOT

Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

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Catalytic reactions of *n*-octane on sequential combinations of HY and HZSM-5, as well as on random mixtures of the zeolites, have been examined. Theoretical product distributions have been calculated for reactions on these catalyst combinations by assuming relative contributions based on the individual product distributions as well as the conversions on the individual components. Effects due to interactions of products of one catalyst with the other in a binary combination can be identified by comparing theoretical and observed product distributions. Predicted values from this approach provide a good approximation when considering the product distributions in terms of total hydrocarbons formed at each carbon number. Significant differences are found between observed and predicted values in the relative proportion of paraffins and olefins at a particular carbon number, and also in the ratios of branched to linear paraffin isomers. Reaction processes attributable for these deviations have been identified as hydrogen transfer processes, particularly on HY, and paraffin isomerization on HZSM-5.

INTRODUCTION

There have been numerous studies of cracking and isomerization reactions of pure hydrocarbons on individual zeolite catalysts (*1–5*). Kinetic phenomena relating conversions of feedstocks to variables such as catalyst to feed ratios and reaction times have been extensively studied. These studies have taken into account factors such as aging characteristics of the catalyst, as active sites are poisoned, and competitive adsorption on the available sites, which may give rise to product inhibition. Product selectivity has also been examined for many systems, providing details of initiation processes at low conversion and also at higher conversions revealing secondary reaction phenomena, where primary products participate in further reactions. Such investigations have been extended to include studies of simple mixtures of hydrocarbons (*6–8*) on individual catalysts, as well as very complex gas oils (*9*) which contain hundreds of individual components.

Although commercial cracking catalysts are composed of a mixture of solid components which can exhibit catalytic activity (*10–12*), there have been few detailed studies which have attempted to relate the resultant effect of the composite catalyst to that of the individual components. For the past two decades cracking catalysts have contained a form of Zeolite Y. More recently there has been interest in addition of a small proportion of a second zeolite component, in particular the pentasil HZSM-5 (*13–22*). There have, however, been very few reported studies of reactions on individual hydrocarbons on binary zeolite mixtures. For example, in a study by Buchanan (*22*), the cracking of C_6–C_{10} normal paraffins and olefins on combinations of zeolites was investigated. It was reported that the pentasil additive plays an active role in the isomerization and cracking reactions of olefin species, while the reactivity toward paraffins is limited.

In the present study we have examined the behaviour of *n*-octane under cracking conditions in the presence of faujasite–pentasil combinations (HZSM-5 to HY ra-

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tios ranged from 0.3 to 1.8) at 400°C. Previous studies on cracking with zeolite combinations have generally focused on the effect of the presence of a second zeolite on the product distribution obtained on a single zeolite. Our aim is to develop a methodology based on adding together product distributions from individual catalysts. This should permit us to identify additional effects in which the products from reaction on one zeolite interact with the other zeolite. The use of *n*-octane as a feedstock is well suited for this purpose, as the cracking distributions obtained are simple enough to be analyzed in detail.

EXPERIMENTAL

The feedstock, *n*-octane (99.7%), was obtained from Aldrich and used without further purification. Impurities in the feedstock were *n*-hexane (0.2%), 2-methylheptane (0.08%), and isopentane (0.02%).

HY zeolite (97.3% exchanged) was prepared from NaY (Linde Lot No. 45912, SK40; Si/Al = 2.4) by repeated exchange with 0.5 *M* ammonium nitrate solution. HZSM-5 (Si/Al = 105) was provided by SNAM Progretti S.P.A. (Milan, Italy). Details of synthesis and characterization of the pentasil have been reported previously (*23*). Catalysts were calcined at 500°C before use, and experiments were performed on catalysts of mesh size 80/100.

All experiments were performed by 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 (*24*). All reactions were carried out at 400°C and 1 atm pressure. Catalysts were mixed with granules of washed sand which served as an inert support matrix within the reactor. Blank experiments at long times on stream showed that thermal conversion of *n*-octane at 400°C was negligible (<0.5%). Liquid products were analyzed using a Hewlett–Packard 5890A gas chromatograph with a 50-m capillary column and flame ionization detector. Gaseous products were also analysed using a Hewlett–Packard gas chromatograph of the same type with a Chrompak capillary column (25 m × 0.32 mm i.d.). Data handling was facilitated using a DAPA software package. Identification of hydrocarbon products was assisted by use of a Hewlett–Packard 5890 gas chromatograph coupled to a 5970 mass selective detector.

RESULTS AND DISCUSSION

Conversion of n-Octane on Individual Zeolites and Catalyst Combinations

In this study we have examined the cracking and isomerization processes which occur during reaction of *n*-octane on the Zeolites HY and HZSM-5 at 400°C both individually and in combinations. At this temperature, the contribution from thermal cracking processes was found to be negligible, confirming the previous studies (*24, 25*). Our approach has been to relate observed effects of particular combinations of these zeolites to the predicted combined contributions from the individual catalysts under the same conditions. In theory, any discrepancy between the observed and the predicted effects of a combination should be explainable in terms of the influence of the presence of the second catalyst on the products from the first, or vice versa.

In this study we have attempted to reach general conclusions regarding combination effects which are independent of process conditions such as time on stream or the level of conversion examined. For catalysts of different types, such as a faujasite and a pentasil, intrinsic activity and decay characteristics can differ very significantly (*26–28*). This is illustrated in Fig. 1 which shows plots of conversion of *n*-octane at 400°C against time on stream for three catalyst to feed ratios for each catalyst. In this work we chose to make comparisons under conditions where the activity of the individual catalyst (as measured by cumulative conversion of *n*-octane) was equivalent. This condition can be taken as points of intersection of curves in Fig. 1, correspond-

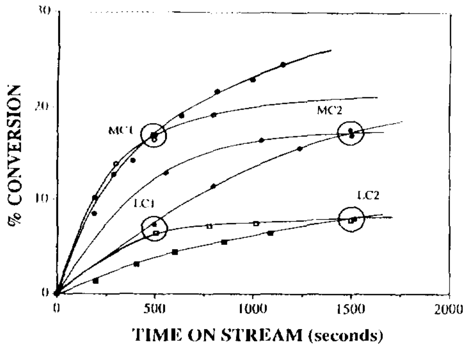

FIG. 1. Effect of time on stream and catalyst to feed ratio for conversion of *n*-octane on HY and HZSM-5 at 400°C. Catalyst to feed ratio: On HY, □ = 0.0101, ◇ = 0.0579, ○ = 0.0900; on HZSM-5: ■ = 0.0101, ◆ = 0.0179, ● = 0.0310.

ing to a specific time on stream. Four such points have been identified in that figure. These have been labeled LC1 and LC2 (corresponding to low conversion at two distinct values of time on stream) and MC1 and MC2 (corresponding to medium conversion levels). Taking conditions at each of these four points in turn, we have compared the behavior of individual catalysts (HY and HZSM-5) with that of various combinations of the zeolites always using the same time on stream, the amount of *n*-octane feedstock, and the amount of catalyst introduced. At low conversions of *n*-octane, it is also valid to state that the individual catalyst to reactant values are approximately equal to those presented to the isolated catalysts. This assumption of course becomes less valid as levels of conversion are increased. We have therefore restricted our study to low and medium conversion (<20%). It should be noted that the results obtained herein are obtained using a fixed bed reactor with integral averaged conversion. This is quite distinct from the industrial case, in which deactivated catalysts convert products and never actually contact the feed.

Three types of combinations of zeolites were selected for study. The first combination consisted of HY followed by HZSM-5 in sequence in the reactor, designated [Y → Z]. The second combination, [Z → Y], used a sequence in the reverse order. The third combination consisted of a random mixture of HY and HZSM-5, designated [RANDOM], and this would correspond to the combination used in most previous investigations using gas–oil mixtures (*13–21*). Table 1 shows the total conversion of *n*-octane corresponding to each of the four points LC1, LC2, MC1, and MC2. In each case, as expected, the conversion of *n*-octane with a catalyst combination is greater than that on an individual zeolite, but the total conversion is always less than the sum of the individual conversions, designated by (Y + Z). The difference observed lies in the fact that for second order reactions as is the case for catalytic cracking, the crackability (defined as conversion/(100-conversion)) is additive and not the conversion (*29*). This may be expected, considering that doubling the catalyst to feed ratios for any given catalyst generally produces less than twice the conversion (*30*). Alternatively, for a sequential mixture of zeolites, it could be inferred that the products from reactions on the first component may cause more rapid aging than the reactant itself. In Table 1, [Y] and [Z] refer to the conversion of *n*-octane on the individual faujasite and pentasil catalysts, respectively, using identical amounts of catalysts and times on stream as for each of the catalyst combinations reported.

Product Distributions on Individual Catalysts

Product distributions from reactions of *n*-octane on HY and HZSM-5 at 400°C at equivalent levels of conversion are shown in Fig. 2. Distributions from cracking of linear paraffins on individual HY and HZSM-5 catalysts have been previously reported (*2, 31*). It is apparent that acyclic olefins and paraffins are the dominant products. The maximum in the distribution of total hydrocarbons was shifted to lower molecular size on HZSM-5 relative to that on HY in each case examined (*2, 31*) as illustrated for LC1 in Fig. 2a. A similar trend was observed con-

TABLE 1

Observed and Calculated Conversions of *n*-Octane on Zeolites at 400°C

Run conditions	Percentage conversion for catalyst configurations							
	[Y]	[Z]	(Y + Z)	[Y → Z]	[Z*][a]	[Z → Y]	[Y*][a]	[RANDOM]
LC1	6.5	7.0	13.5	11.8	5.3	10.2	3.2	13.4
LC2	7.9	8.0	15.9	10.6	2.7	9.7	1.7	11.2
MC1	17.1	17.0	34.1	30.6	13.5	22.4	5.4	33.5
MC2	16.9	18.0	34.9	29.1	12.2	21.6	3.6	32.1

[a] [Z*] and [Y*] give the calculated conversion of *n*-octane on the second component of the [Y → Z] and [Z → Y], respectively.

sidering the distributions of saturated products according to carbon number (Fig. 2b). In particular, it can be seen that at the same levels of *n*-octane conversion, C_1, C_2, and C_3 paraffins are formed in greater abundance on HZSM-5 compared to HY. Figure 2c shows that the abundance of olefinic products on HY is lower than that on HZSM-5. This can be explained in terms of the increased tendency toward hydrogen transfer processes on the faujasite compared to the medium pore pentasil (*19*). This is also revealed by the much higher tendency to produce aromatic products on HY, as illustrated in Fig. 2d.

Figures 3 and 4 show the ratios of branched to linear (B/L) isomers for product C_4–C_6 paraffins and C_4 and C_5 olefins, re-

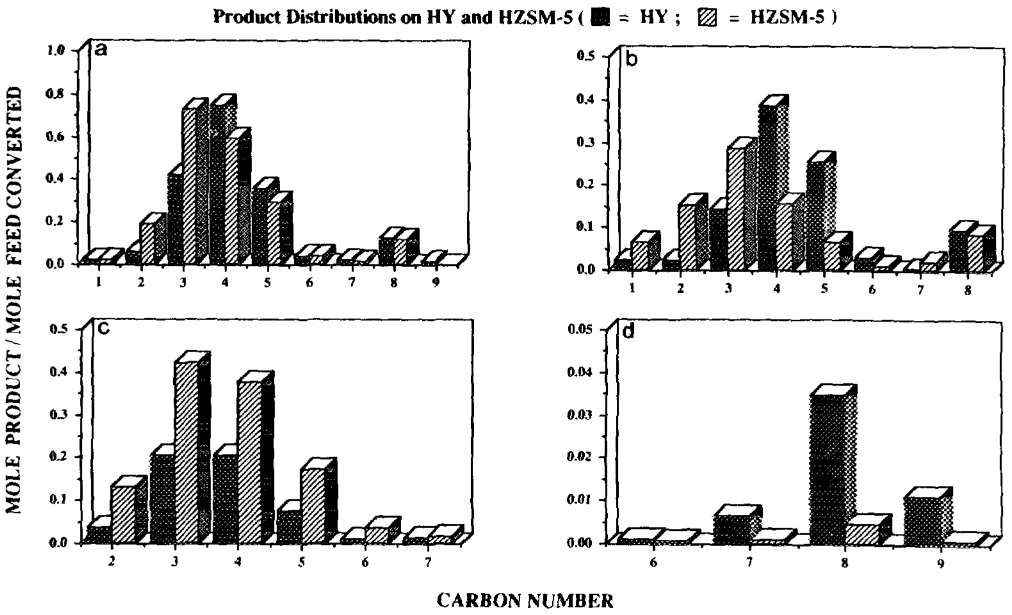

FIG. 2. Product distributions from catalytic reaction of *n*-octane on HY and HZSM-5 at 400°C. (Representative examples from conditions LC1, LC2, MC1, and MC2). (a) Total hydrocarbons (LC1), (b) paraffins (LC2), (c) olefins (MC2), (d) Aromatics (MC1).

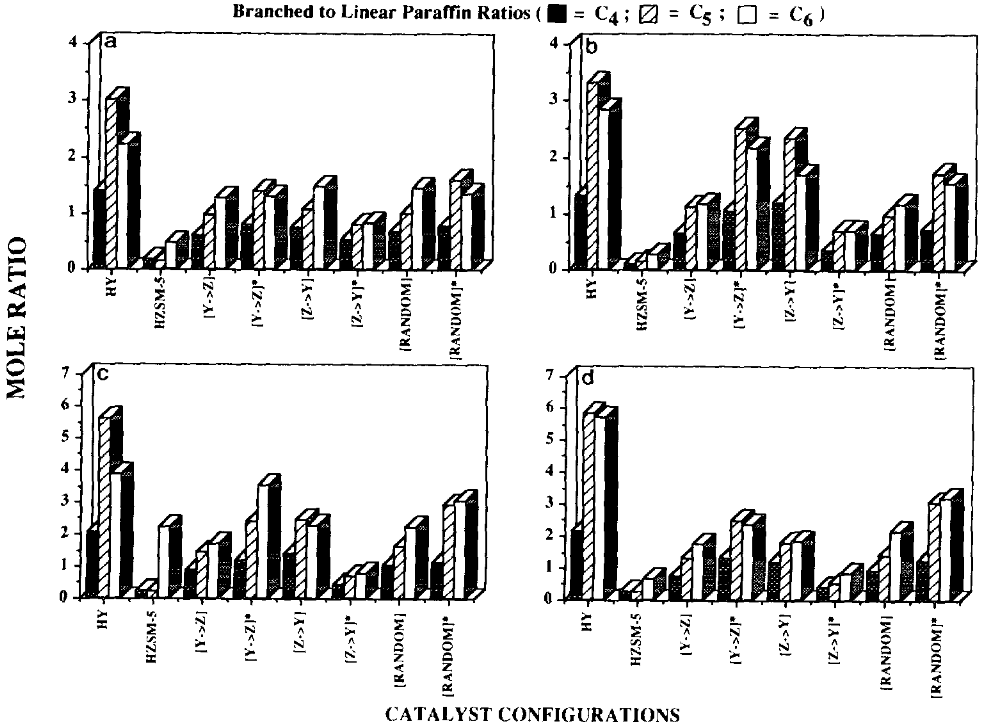

FIG. 3. Ratios of branched to linear paraffins (C_4–C_6) from individual catalysts and catalyst combinations. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

spectively. It is apparent that for reaction of *n*-octane on the individual zeolites (Fig. 3) there are significant differences in the branched to linear ratios of paraffin products. Branched paraffins are dominant on HY while the linear isomers are preferentially formed on HZSM-5 (6). Figure 4 shows that for C_4 and C_5 olefins the branched to linear ratios show less variation than for the corresponding saturated products, with values generally in the range 1 to 2.5. It can be seen that there is a higher tendency to form branched C_4 olefins on HZSM-5 (B/L ratios 1.38–1.46) compared to HY (B/L ratios 0.92–1.02). A similar trend is also found for the C_5 olefins. Ratios of branched to linear isomers for products formed on combinations of catalysts are also shown in Figs. 3 and 4, and these are discussed in subsequent sections.

Reactions on Sequential HY Followed by HZSM-5

The total conversions of *n*-octane when passed over HY together with HZSM-5 are given in Table 1. In each case (LC1, LC2, MC1, and MC2), knowing the conversion of *n*-octane under the same conditions without the presence of HZSM-5, it is possible to calculate the total conversion of *n*-octane on the pentasil component, designated [Z*] in Table 1. In the first instance, it can be assumed that product distributions from reaction of *n*-octane on HZSM-5 on the combination [Y → Z] are the same as those observed on HZSM-5 alone. Taking into account the calculated conversion of *n*-octane on each zeolite component of the sequence, it is then possible to compute predicted distributions of products for reaction on the catalyst sequence [Y → Z]. These predicted

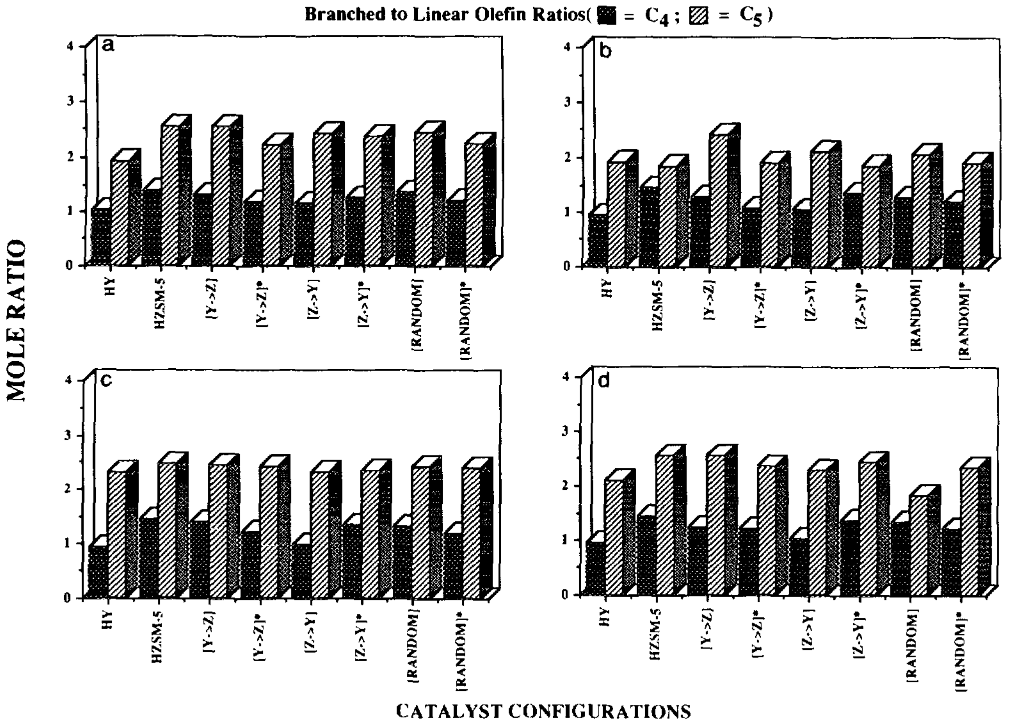

FIG. 4. Ratios of branched to linear olefins (C_4 and C_5) from individual catalysts and catalyst combinations. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

distributions assume that only *n*-octane reacts on the second catalyst component of the sequence (in this case, HZSM-5) and that the catalyst reaction products formed on HY pass through the pentasil unchanged. These predicted product distributions are designated [Y → Z]*. By comparing these predicted distributions with those actually observed, it is possible to infer the extent to which the assumptions made, concerning the interactions on the second zeolite, are correct. Variations between observed and predicted distributions can then be explained in terms of interactions and additional reaction processes.

Figures 5–8 show comparison between observed and predicted distributions (i.e., [Y → Z] and [Y → Z]*) corresponding to each of the four reaction conditions. Separate comparisons have been made for total hydrocarbons (Fig. 5), paraffins (Fig. 6), olefins (Fig. 7), and aromatics (Fig. 8). Inspection of Fig. 5 clearly shows that the observed distributions for total hydrocarbons produced are generally well represented by the predicted values.

Comparison between the observed and the predicted values of C_3, C_4, and C_5 paraffins (Fig. 6) shows that in every case, extensive hydrogen transfer processes, which would lead to significant additional paraffins in this range, do not occur on ZSM-5. This is confirmed by a similar inspection of the results for the corresponding olefins (Fig. 7), which does not reveal extensive depletion of olefins present within the distribution. Further inspection of this figure shows that while C_2 and C_4 olefins are very close to predicted values, there are losses in C_3 olefins, with gains in C_5, C_6, and C_7 olefins, while higher olefins were not detected. These observations can be explained by as-

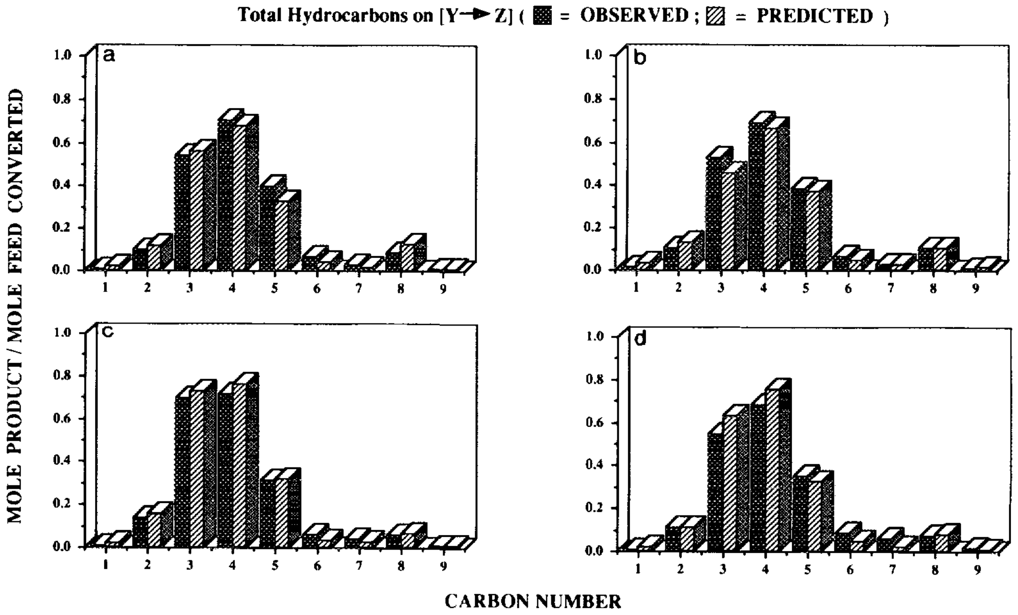

FIG. 5. Total hydrocarbon distributions from catalytic reaction of *n*-octane on the sequential catalyst [Y → Z]. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

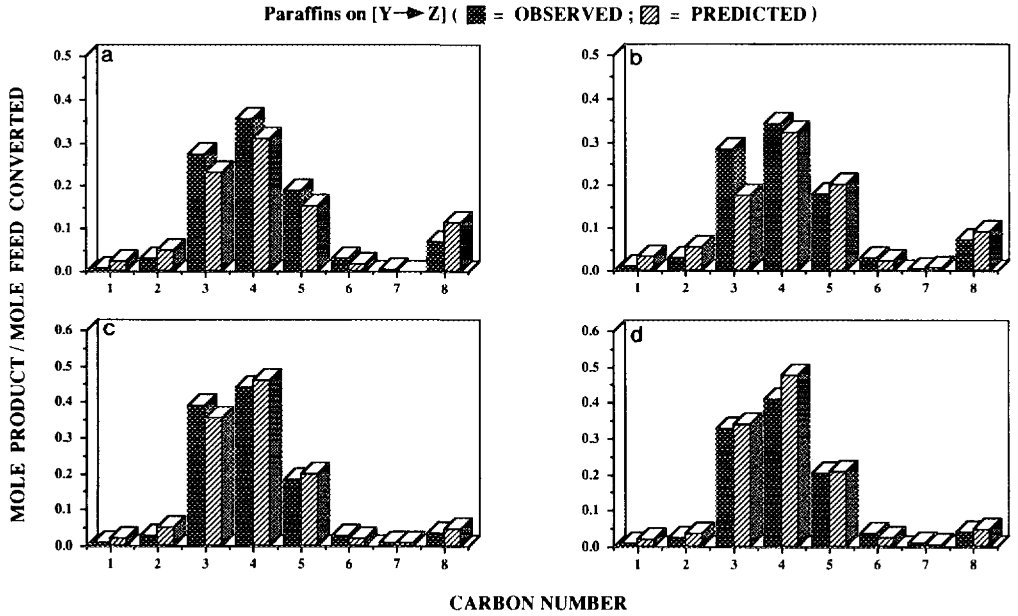

FIG. 6. Paraffin distributions from catalytic reaction of *n*-octane on the sequential catalyst [Y → Z]. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

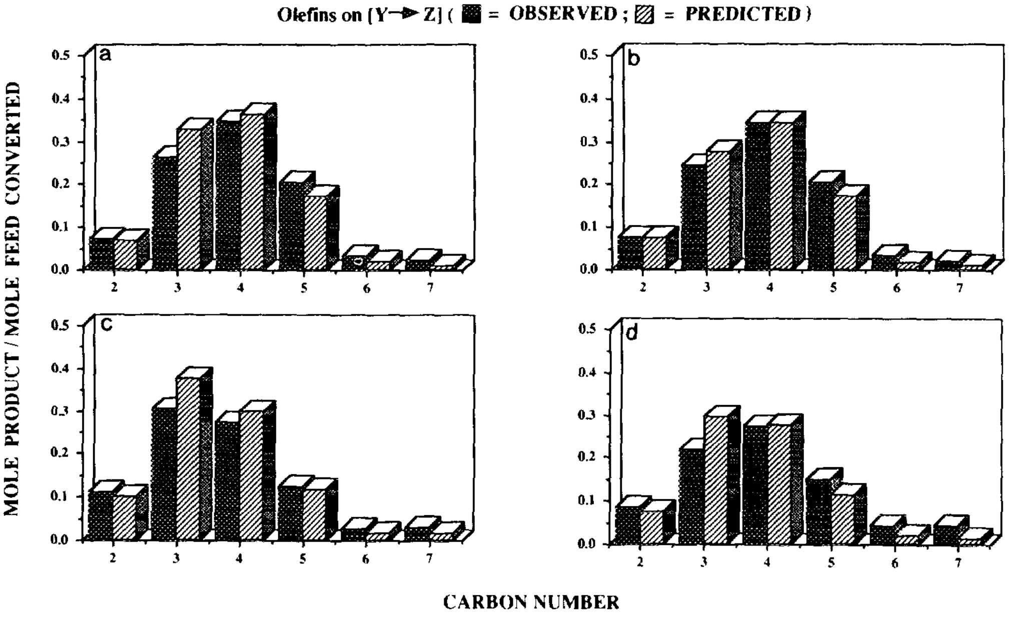

FIG. 7. Olefin distributions from catalytic reaction of *n*-octane on the sequential catalysts [Y → Z]. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

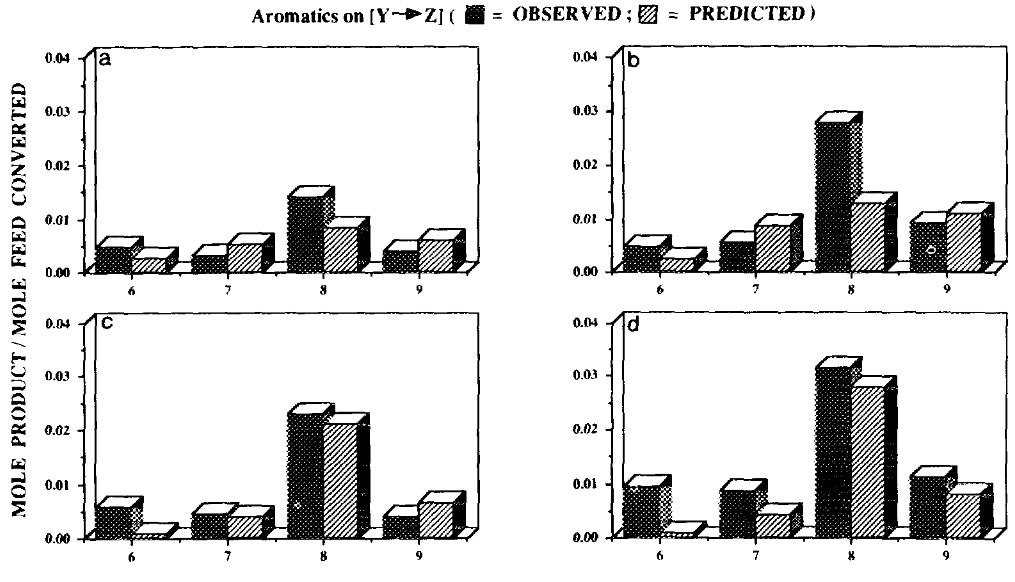

FIG. 8. Aromatic distributions from catalytic reaction of *n*-octane on the sequential catalyst [Y → Z]. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

suming that the olefins produced on ZSM-5 from cracking of *n*-octane, and those entering as products from reactions on HY, can participate in a dimerization-cracking process (*32, 33*), which can result in a redistribution of the olfein species present. These processes eventually result in a net loss in propylene, net gains in C_5, C_6, and C_7 olefins, and little net change in the butenes. Figure 4 shows that the ratios of branched to linear C_4 and C_5 olefins for [Y → Z] are close to predicted values ([Y → Z]*), with the observed ratios consistently slightly larger than those obtained by calculation. This indicates that while the dimerization-cracking processes may alter the distribution of molecular size of olefins present, there is little net influence on isomer distribution at each carbon number. The consistent agreement between observed and predicted values for the proportion of ethylene may suggest that the C_2 olefin does not extensively participate in the dimerization processes, possibly due to instability of the C_2 carbenium ion.

Once formed, a carbenium ion produced from a dimerization processes can crack via β-scission processes, to give smaller olefins, or desorb directly as a C_6 or C_7 olefin. Alternatively, cyclization can lead to formation of additional aromatic species. From Fig. 8, it is evident that, in particular, the amount of benzene produced on this sequential combination is higher than that predicted by simple addition of the distributions. At the same time Fig. 6 shows consistently higher values for production of C_6 and C_7 paraffins than predicted. Possibly some C_6 and C_7 carbenium ions are available for hydrogenation during concurrent formation of aromatics, and these give rise to the saturated products. The depletion in C_8 paraffins as shown in Fig. 6 can be explained in terms of the instability of the corresponding carbenium ion (i.e., it cracks before it can either desorb as an olefin or participate in hydrogen transfer to produce a C_8 paraffin).

Figure 3 shows that the ratios of branched to linear C_6 paraffins for the combination [Y → Z] are lower than those predicted on the basis of simple addition of distributions, [Y → Z]*. However, if it is assumed that additional C_6 paraffins formed on HZSM-5 (Fig. 6) by hydrogen transfer are predominantly linear, the observed branched to linear ratios can be rationalized. The observed and predicted values of these ratios are given in Table 2. Adjusted values represent the predicted values that have been recalculated to meet the observed values, based on the assumption that any additional paraffins are formed through hydrogen transfer process, and any loss of paraffins can be attributed to selective cracking of branched saturated isomers.

The total amounts of C_3, C_4, and C_5 paraffins do not markedly differ from the predicted values, which assumes products emerging from reaction on the Y zeolite are unchanged on HZSM-5. The absence of extensive hydrogen transfer processes, which could give rise to additional paraffin formation from olefins produced on Y has already been noted. The lack of additional small cracking fragments (C_1 and C_2) also suggests that these paraffins do not undergo significant cracking on passing through the pentasil (Fig. 6). It is therefore interesting to note that, in contrast to the corresponding olefins, the ratios of branched to linear paraffins for C_4 and C_5 are significantly lower than predicted in each case by comparing values obtained for [Y → Z] and [Y → Z]* in Fig. 3.

In contrast to the C_6 paraffin isomers previously discussed, the required adjustment in the branched to linear isomer ratio in favor of linear C_4 and C_5 saturated products to coincide with the observed distributions cannot be explained merely in terms of hydrogen transfer with selective production of linear paraffins. In the cases where additional paraffins are observed, (Fig. 6, LC1 and LC2) the amounts are insufficient to account for the observed branched to linear ratio, as illustrated in Table 2. In the other cases (MC1 and MC2), there is in fact an apparent reduction in the amounts of C_4 and

TABLE 2

Ratios of Branched to Linear Paraffins from the Catalytic Reaction of *n*-Octane on the Sequential Catalysts {Y → Z} at 400°C

Run conditions	C_6			C_5			C_4		
	Observed	Predicted	Adjusted	Observed	Predicted	Adjusted	Observed	Predicted	Adjusted
LC1	1.26	1.28	0.55[a]	0.98	1.38	0.90[a]	0.59	0.79	0.62[a]
LC2	1.17	2.15	1.21[a]	1.12	2.50	2.13[b]	0.64	1.05	0.92[a]
MC1	1.19	3.53	1.18[a]	1.44	2.39	2.13[b]	0.89	1.17	1.08[b]
MC2	1.72	2.34	0.82[a]	1.30	2.47	2.35[b]	0.75	1.29	0.96[b]

[a] Calculation assumes excess paraffins formed by selective hydrogen transfer to give linear paraffins.
[b] Calculation assumes loss of paraffins through selective cracking of branched isomers.

C_5 paraffins formed. Neither can the observed branched to linear ratios for C_4 and C_5 paraffins after contact with HZSM-5 be explained easily by selective cracking of the branched saturated isomers. Cracking reactions of small branched paraffins such as isobutane and isopentane on HZSM-5 (*34–36*) give high selectivity toward formation of C_1 and C_2 fragments, whereas Fig. 6 shows that additional amounts of these products are not observed.

It appears that in order to explain the observed branched to linear ratios for C_4 and C_5 paraffins, isomerization of the branched paraffins must occur on HZSM-5. However, previous studies of reactions of individual branched paraffins on HZSM-5 show that the predominant reaction process is cracking rather than isomerization, as shown in Table 3. For example, reaction of isobutane (*34*, *36*) on HZSM-5 at 400°C shows a selectivity for formation of *n*-butane of less than 20%. In our study, reaction of 2-methylpentane at 400°C shows a selectivity of 0.4% for production of *n*-hexane. These results suggest that isomerization rather than cracking becomes the preferred reaction mode when the feed contains a high proportion of olefins. The isomerization of branched paraffins on HZSM-5 represents the first significant difference between predicted and observed behavior.

Other reported investigations, particularly with isobutane, have shown that a significant selectivity for paraffin isomerization to produce *n*-butane is observed for reactions on Y zeolites in some cases (*37*). High selectivities toward isomerization have been observed using solid superacid catalysts (*38*, *39*), in particular for catalysts re-

TABLE 3

Selectivities of Cracking and Isomerization of Branched Paraffins on HZSM-5

Feed	Temperature (°C)	Selectivity			Reference
		Cracking	Total isomerization	Isomerization to linear isomer	
Isobutane	400	1.0	0	0	(*34*)
Isobutane	500	0.95	0.5	0.5	(*34*)
Isobutane	400	0.83	0.17	0.17	(*36*)
2-Methylpentane	500	0.967	0.025	0	(*28*)
3-Methylpentane	500	0.922	0.066	0	(*28*)
2-Methylpentane	400	0.960	0.040	0.004	This study

ported to have an appropriate balance in the amounts of strong Brønsted and Lewis acid sites. It is possible that the change in selectivity in favor of isomerization of branched paraffins for the system under present consideration may be associated with formation of Lewis sites due to adsorption of product olefins at Brønsted sites in HZSM-5. Lewis acid sites alone do not appear to be active in most hydrocarbon transformations *(40–43)*. However, coupling of Lewis sites and Brønsted sites can apparently result in significant changes in both acidity *(41)* and activity.

The second significant difference between observed and predicted distributions for the sequence [Y → Z] relates to the amounts of methane and ethane formed (Fig. 6). In each case, it is apparent that there is significantly less of these C_1 and C_2 fragments observed than would be predicted by addition of individual distributions. Again, it can be inferred that reactions of *n*-octane on HZSM-5 are perturbed when the feedstock contains a significant proportion of olefins. The observed reductions in methane and ethane are consistent with the proposal *(44)* that the cracking pathway via direct protonation of the paraffin becomes less significant in the presence of olefins, in favor of a bimolecular cracking mechanism. This reasoning can explain the reduction in the proportion of ethane formed (Fig. 6). For methane, however, the absolute amounts present after the product mixtures emerge from reactions on the sequence [Y → Z] is less than that entering the HZSM-5 stage of the sequence (Fig. 9). This implies not only that there is a reduction in cracking processes via protonation yielding methane, but that now there is also evidence for reaction of methane itself on this catalyst to form other products. This is unexpected, as methane is generally regarded as a stable product of cracking.

It has been shown that although higher paraffins ($>C_3$) can undergo reaction over HZSM-5, methane and ethane are themselves unreactive when passed through the catalyst as a pure feedstock *(45)*. The present results show, however, that it is possible for methane to be converted into other products when passed over a zeolite catalyst in the presence of other hydrocarbons. Recent studies *(46–48)* have shown that methane and ethylene can undergo coupling reactions to produce higher hydrocarbons on solid superacid catalysts, and it is possible that our observed losses in methane and ethane are due to coupling reactions involving unsaturated species. Alternatively, it is possible that methane may be involved in a reversible reaction in which interaction with an adsorbed carbenium ion at a Brønsted site produces a pentacoordinated carbonium ion, as proposed by Kanai *et al.* *(49)*.

The results presented for the sequential catalyst [Y → Z] corresponding to the four conditions show that the general conclusions are independent of time on stream and conversion levels. This was also found to be the case for the combinations discussed in subsequent sections. However, due to space limitations, results presented in the following sections are representative.

Reaction on Sequential HZSM-5 Followed by HY

Examples of observed product distributions for reaction of *n*-octane on the zeolite sequence [Z → Y] are presented in Figs. 10 and 11. As for the previous catalyst sequence, predicted distributions are also presented ([Y → Z]*), using conversions in Table 1 and the appropriate distributions of products on individual zeolites as illustrated in Fig. 2. As for the [Y → Z] sequence, the predicted distributions of total hydrocarbons according to carbon number also provide reasonable approximations to the observed values, as shown in Fig. 10. Again, it is possible to focus on differences in the various observed and predicted product distributions, particularly those for paraffins, olefins, and aromatics, to describe any possible additional reactions and interactions as products formed on HZSM-5 pass over the Y zeolite.

A feature which is apparent from inspec-

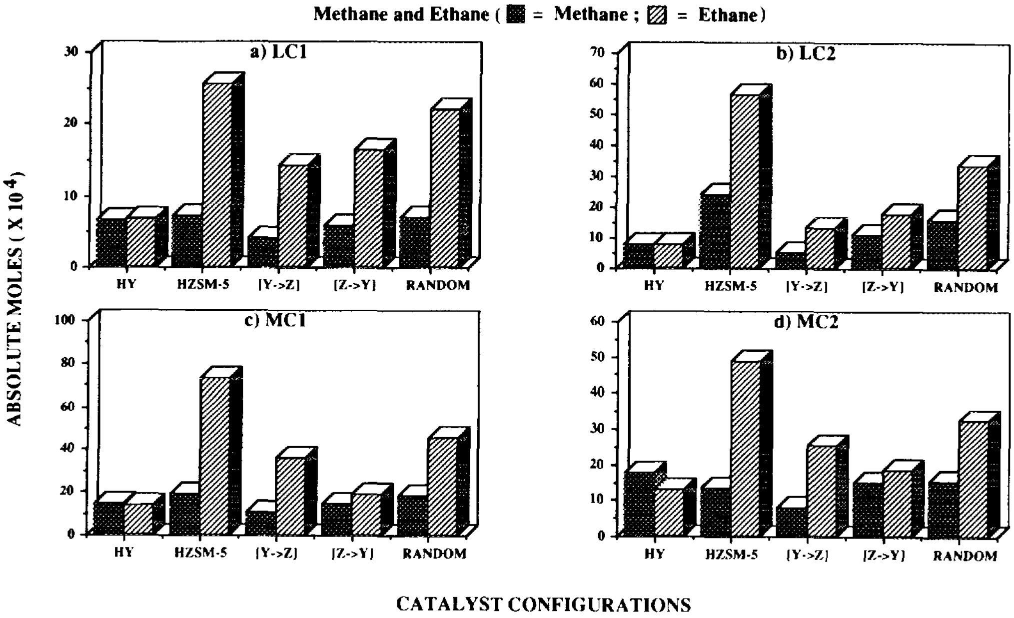

FIG. 9. Molar amounts of methane and ethane produced from catalytic reaction of *n*-octane at 400°C. (a) LC1, (b) LC2, (c) MC1, (d) MC2.

tion of these distributions is that the amounts of C_3–C_6 paraffins are generally in excess of the predicted values, as illustrated in Fig. 10b. In contrast, the observed amounts of olefins in this range are significantly less than those predicted (Fig. 10c). This is indicative of significant additional hydrogen transfer processes occurring on the Y zeolite, particularly involving product olefins formed on the HZSM-5. For this catalyst configuration, the extent of these processes is, in fact, sufficient to explain the observed branched to linear ratios for paraffins in the range C_4–C_6, as shown in Fig. 3, by comparing the results obtained on the sequences [Z → Y] and [Z → Y]*. The predicted ratios are lower than those actually observed on the assumption that products formed on the ZSM-5 pass through the Y zeolite unchanged. Table 4 shows the limiting adjusted values of these ratios, assuming that all additional C_4, C_5, and C_6 paraffins formed on HY through hydrogen transfer to olefins result in formation of the corresponding branched saturated isomers. In all cases, the adjusted values are already higher than the corresponding observed value, so that it is not necessary here to invoke a paraffin isomerization process on the faujasite, as proposed for reaction on the pentasil for the [Y → Z] sequence previously discussed.

Figure 11 shows that there is significant additional formation of aromatics using the [Z → Y] sequence, shown here for LC1 and MC2, comparing calculated values for simple addition of product distributions. This can be rationalized in terms of reactions of olefinic species formed on the HZSM-5 in the first stage of the sequence, through cyclization and hydrogen transfer processes on HY to produce aromatic species as well as the saturated products already discussed. Figure 4 shows that the observed branched to linear ratios for C_5 olefins are very close to the predicted values, while the observed ratios for the C_4 olefins are generally somewhat lower than those predicted. This may

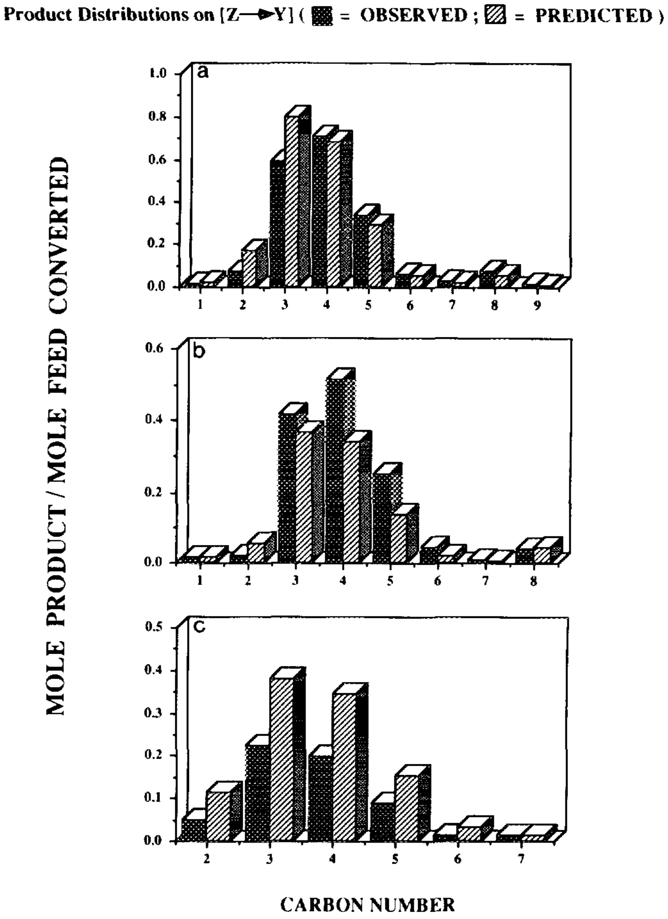

FIG. 10. Product distributions from catalytic reaction of *n*-octane on the sequential catalyst [Z → Y] at MC2; (a) Total hydrocarbons, (b) paraffins, (c) olefins.

be explained by assuming that the hydrogen transfer process occurring on the faujasite was selectively directed toward the branched C_4 olefins yielding branched isomers of the corresponding paraffins. This assumption was fairly well justified by the excess C_4 paraffins observed compared to predicted values (Fig. 10b) and the larger observed ratios of branched to linear isomers of C_4, C_5, and C_6 paraffins (Fig. 3).

As noted previously for reaction on the sequence [Y → Z], reaction of *n*-octane on the sequence [Z → Y] also shows an interesting result for formation of methane and ethane (Fig. 10b). There is consistently less of the C_1 and C_2 paraffin fragments observed then predicted by calculation. Figure 9 shows that, as for methane on the catalyst sequence [Y → Z] catalyst, these reductions are not simply due to reduced C_1 and C_2 paraffin formation on the second catalyst of the sequence, but an actual reduction in the amounts finally emerging due to reactions on the Y zeolite. Again, it seems that methane and ethane undergo reaction with other hydrocarbons when the mixture comes into contact with the second catalyst component. Therefore it can be concluded that it

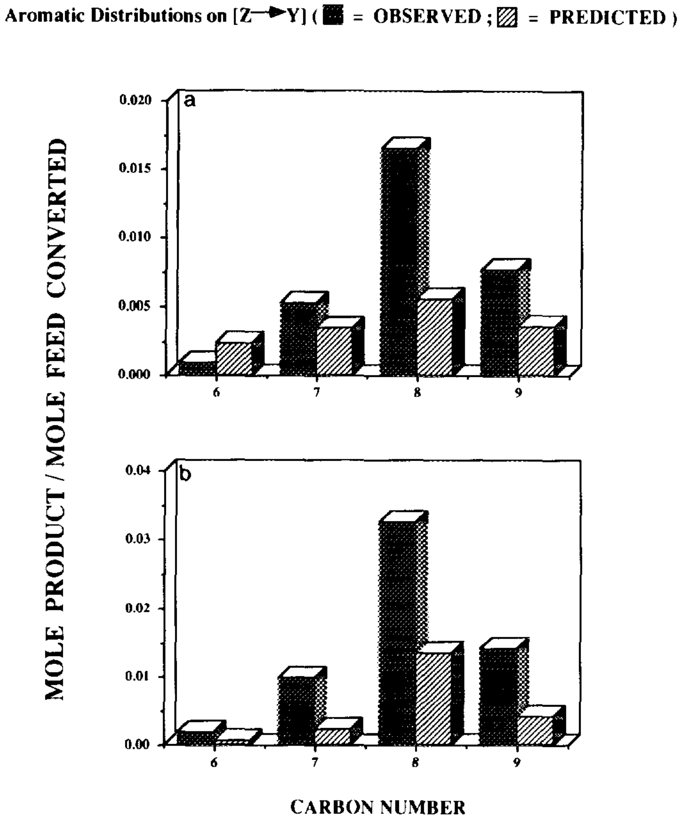

FIG. 11. Aromatic distributions from catalytic reaction of *n*-octane on the sequential catalyst [Z → Y]; (a) olefins (LC1), (b) aromatics (MC2).

is not the specific type of zeolite that is responsible for this observed phenomenon, but rather the influence of other hydrocarbons present in the mixture.

Reactions on Random Mixtures of HY and HZSM-5

The random mixtures of HY and HZSM-5 used corresponded to amounts of HY and HZSM-5 which produced equal conversions of *n*-octane under the same conditions. The total conversions of *n*-octane observed for reaction on these random mixtures of catalysts are given in Table 1. It was found that a simple averaging of distributions for total products on the individual catalysts according to carbon number again provides a very reasonable representation of the observed distribution (Fig. 12a). This shows that, as for the sequential combinations previously considered, the overall distribution of total hydrocarbon products by carbon number is well represented by the sum of the individual contributions on the isolated catalysts. It might be thought that a random mixture of particles of HY and HZSM-5 could be regarded as a large number of repeated [Y → Z] and [Z → Y] sequences. If that were the case, then we might expect the overall effect to result in a summation of the influences already discussed in the simple binary sequences.

Figure 12b shows that the observed amounts of paraffins in the range of C_3–C_6

TABLE 4

Ratios of Branched to Linear Paraffins from the Catalytic Reaction of *n*-Octane on the Sequential Catalysts [Z → Y] at 400°C

Run conditions	Branched to linear ratios								
	C_6			C_5			C_4		
	Observed	Predicted	Adjusted	Observed	Predicted	Adjusted	Observed	Predicted	Adjusted
LC1	1.46	0.83	2.24	1.07	0.79	1.59	0.74	0.51	1.09
LC2	1.69	0.69	2.59	2.33	0.69	2.85	1.20	0.35	1.58
MC1	2.44	0.78	3.05	2.42	0.69	3.45	1.41	0.44	2.16
MC2	1.83	0.82	3.22	1.78	0.54	1.82	1.17	0.41	1.14

are in excess of predicted values. This can again be correlated with reduced amounts of olefins (Fig. 12c) and increased amounts of aromatics (Fig. 12d). This appears to show that HZSM-5 does not suppress the hydrogen transfer process occurring on HY (*19*). Rather, the excess formation of small olefins observed by addition of HZSM-5 to a Y cracking catalyst is for the direct contribution of olefin products from reaction on the pentasil. An indication of the related tendency to undergo hydrogen transfer is provided by paraffin to olefin ratios at similar conversion levels. Ratios are presented in Table 5 corresponding to C_4, C_5, and C_6 for the three binary catalyst systems. It is

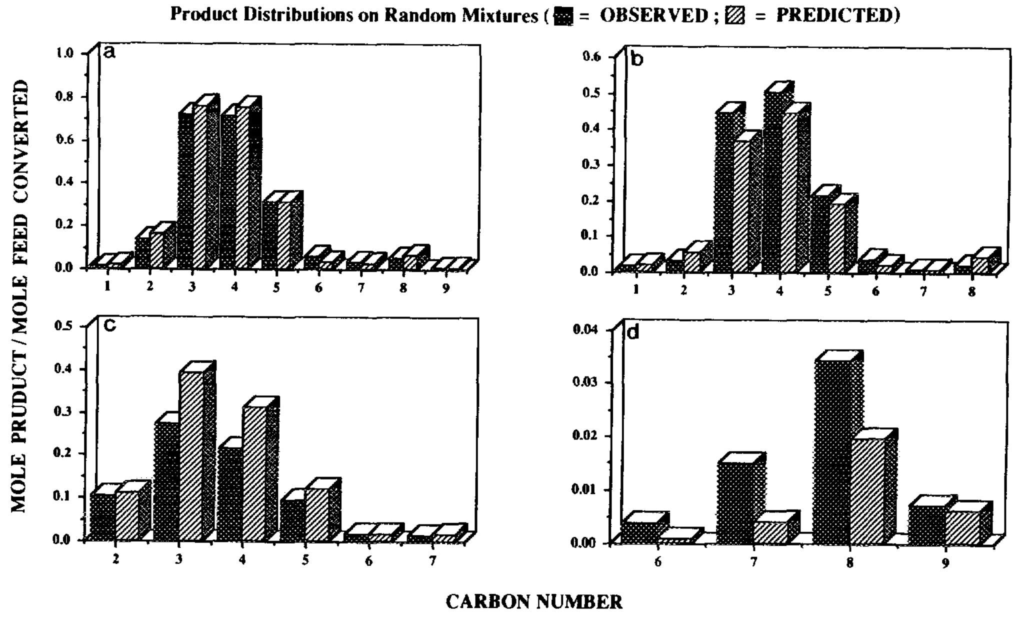

FIG. 12. Product distributions from catalytic reaction of *n*-octane on the random mixture of HY and HZSM-5 at MC1; (a) total hydrocarbons (b) paraffins, (c) olefins (d) aromatics.

TABLE 5

Paraffin to Olefin Ratios from Catalytic Reaction of *n*-Octane on Combinations of HY and HZSM-5, at 400°C

Run conditions: Catalyst configurations	Paraffin to olefin ratio					
	LC1			MC1		
	C_4	C_5	C_6	C_4	C_5	C_6
[Y → Z]	1.02	0.91	0.89	1.60	1.48	0.93
[RANDOM]	1.14	1.08	1.39	2.33	2.30	1.96
[Z → Y]	1.18	1.21	1.9	3.03	4.00	4.76

apparent that values are highest for the [Z → Y] sequence, lowest for the [Y → Z] combination, and intermediate for [RANDOM] mixtures.

For the random mixtures, the ratios of branched to linear olefins (Fig. 4) are close to predicted values given by [RANDOM]*. A comparison of these ratios for *all* systems studied shows that the variations in observed values are not large, with somewhat higher values for the [Y → Z] sequence than for either [Z → Y] or [RANDOM]. Figure 3 shows much more overall variation in branched to linear ratios for saturated products, depending on the particular catalyst or catalyst combination. The observed branched to linear ratios for paraffins on the mixture [RANDOM] are consistently smaller than the predicted values [RANDOM]* as given in Table 6.

Figure 12b shows that the proportions of methane and ethane produced on a random mixture of HY and HZSM-5 are less than those predicted. Figure 9 shows that the actual amounts of these products lie between those detected from reaction on the individual catalysts. In contrast to the sequential combinations, the amount of methane formed is not reduced below that formed on HY itself.

The results reported herein are in conflict with those of Buchanan (*22*), who suggests that the cracking of *n*-octane on ZSM-5 alone is negligible. We find significant reaction of the linear feedstock, in accord with previous studies (*42*). Such differences can be attributed to the use of different reaction conditions. The conclusions with regards to the pentasil additive acting to enhance isomerization processes, particularly for olefinic

TABLE 6

Ratios of Branched to Linear Paraffins from the Catalytic Reaction of *n*-Octane on the Random Mixture of HY and HZSM-5 [RANDOM] at 400°C

Run conditions	Branched to linear ratios								
	C_4			C_5			C_6		
	Observed	Predicted	Adjusted	Observed	Predicted	Adjusted	Observed	Predicted	Adjusted
LC1	0.68	0.78	0.47[a]	0.99	1.59	1.34[a]	1.43	1.35	2.28[c]
LC2	0.65	0.72	0.34[b]	0.96	1.72	0.67[b]	1.18	1.55	1.04[b]
MC1	1.06	1.13	0.88[a]	1.61	2.91	1.93[a]	2.22	2.91	0.63[a]
MC2	0.93	1.20	1.14[b]	1.40	3.04	1.97[a]	2.11	3.18	0.67[a]

[a] Calculation assumes excess paraffins formed by selective hydrogen transfer to give linear paraffins.

[b] Calculation assumes loss of paraffins through selective cracking of branched isomers.

[c] Calculation assumes excess paraffins formed by selective hydrogen transfer to give branched paraffins.

species, are however in accordance with those made by Buchanan (*22*).

CONCLUSION

Overall distributions of cracking products by carbon number from reaction of a linear paraffin on combinations of HY and HZSM-5 can be reasonably described by the addition of product distributions on individual catalysts, weighted according to the relative amounts present. The observed distributions of paraffins, olefins, and aromatics composing a product group at any particular carbon number show more widespread deviations from calculated product ratios. This arises particularly from hydrogen transfer processes which occur on the faujasite, leading to more extensive formation of paraffins and aromatics at the expense of olefins.

Isomerization reactions of both olefin and paraffin cracking products are promoted by the presence of HZSM-5. The presence of the pentasil produces higher concentrations of branched olefin isomers. There is also evidence that preferential isomerization of branched paraffins can occur when high concentrations of product olefins are also present, whereas cracking is favored at low olefin concentrations.

The latter observation demonstrates that the behavior of a particular reactant within a complex mixture may not be easily predictable from studies where that reactant is introduced as a pure feedstock. This also applies to the observed disappearance of ethane and methane when contacted with a fresh zeolite sample as a minor component of a complex hydrocarbon mixture.

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