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The Catalytic Isomerization of 1-Hexene on H-ZSM-5 Zeolite: The Effects of a Shape-Selective Catalyst

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The isomerization of 1-hexene on 60/80-mesh ZSM-5 zeolite was studied in the temperature range 200–280°C, and the results were compared with those previously obtained for HY at 200°C. The observed products were formed through a variety of processes including double bond shift, *cis–trans* isomerization, skeletal rearrangement, cracking, hydrogen transfer, polymerization, and coke formation. By applying the time-on-stream theory, the products were classified as primary, secondary, or both according to their optimum performance envelope curves on product selectivity plots. At all levels of conversion, *cis-* and *trans*-2-hexene were found to be the principal products. The ratio of the initial selectivities of *cis-* to *trans*-2-hexene at 200°C was 0.54, significantly closer to the equilibrium value than previously found for HY zeolite. A possible explanation is given, relating to the difference in pore structure of these zeolites. The ratio of the initial rate of deprotonation to that of hydrogen shift in the hexyl carbenium ion was found to decrease with temperature. At 200°C this ratio was greater than that observed on HY. Skeletal rearrangement, polymerization, cracking, and hydrogen transfer reactions were all found to increase with temperature. At 200°C the total contribution from these processes accounts for significantly less product than on HY. All products of skeletal rearrangement were observed to be secondary. The formation of 2,3-dimethyl-1-butene appears to be restricted on ZSM-5 due to the size of this molecule. Skeletal rearrangement of 1-hexene gives *cis*-3-methyl-2-pentene and *trans*-3-methyl-2-pentene as secondary products. These isomers are also formed as initial products by double bond shift of the principal impurity present in our feed, 2-ethyl-1-butene. Coke formation decreases with increasing temperature. The composition of the coke indicated that it initially consists mainly of adsorbed olefins. No aromatic products could be detected and polymerization appeared to be restricted to the formation of dimers. The small amount of paraffinic products found, and the lack of cyclization and dehydrogenation to aromatic structures appear to be related to the pore size of ZSM-5.

INTRODUCTION

The double bond of olefins can be isomerized through an ionic mechanism by both acidic and basic catalysts (*1, 2*), and as the product selectivity depends on the catalyst, several reaction schemes have been proposed. In the case of acid catalysts, the differences have been related to either the acidity of the catalyst, or to geometrical constraints during the formation of intermediate complexes on the surface (*2*).

The new synthetic zeolite ZSM-5 presents unique characteristics in certain carbenium ion reactions (*3–7*). The property known as shape selectivity has been observed in catalysis on ZSM-5 for various reactions, including xylene isomerization (*3*), aromatic alkylation (*4*), synthesis of hydrocarbons from alcohols (*5, 6*), and cracking of hydrocarbons (*4, 7*).

In a previous paper (*8*), a detailed analysis of the reactions of 1-hexene on HY at 200°C was reported. The present work was undertaken with a view to revealing any significant differences between the catalytic effects of ZSM-5 and HY zeolites. In particular, the aim was to determine whether variations in product distribution could be rationalized solely in terms of zeolite pore

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structure, or whether it is necessary to postulate major differences in the active sites present.

In the present work, the reactions of 1-hexene on ZSM-5 at 200, 250, and 280°C were studied and selectivity curves obtained for the major and minor products, as well as for the residual coke. The reaction network was established for this system and results compared with those previously obtained (*8*) for HY under similar conditions.

THEORY

A theoretical treatment of the decline in the concentration of active sites with time-on-stream, t, has enabled three classes of catalyst decay to be defined according to the value of a decay parameter, N (*9*). Each class gives characteristic curves when the integral reactant conversion, $\overline{X}_R$, is plotted against run duration, t_f. Class I catalysts ($N < 1$) give complete integral conversion at sufficiently long time-on-stream for any constant catalyst to reactant ratio. Class II catalysts ($N = 1$) give different limiting values of integral conversion at long times-on-stream at various ratios of catalyst to reactant. Maximum integral conversion is observed at a certain time on stream for each catalyst to reactant ratio for class III catalysts ($N > 1$).

For each reaction product, the time average yield sampled from $t = 0$ to t_f can be plotted against $\overline{X}_R$. These plots can be enveloped by a single curve, the optimum performance envelope (OPE), which describes the selectivity behavior of a product as t_f approaches zero. This allows the behavior of six types of product to be described by characteristic curves, illustrated in Fig. 1. A product is regarded as primary if its formation has not been preceded by any intermediates in the gas phase, although many intermediate species may have existed on the catalyst surface. A secondary product is derived from a primary product in a similar sense. The initial selectivity of a product, given by the slope of the OPE at zero conversion, is nonzero for a primary product and zero for secondary or subsequent products.

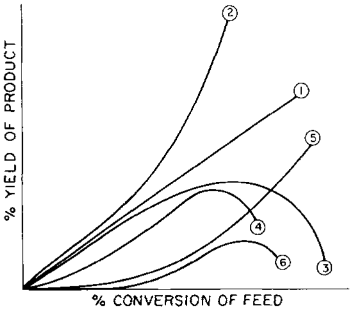


FIG. 1. Theoretical optimum performance envelope (OPE) curves of various products for all three classes of catalyst. The OPE's shown refer to the following products: (1) a stable primary product, (2) a stable primary plus secondary product, (3) an unstable primary product, (4) an unstable primary plus secondary product, (5) a stable secondary product, and (6) an unstable secondary product.

NOMENCLATURE

1H	1-Hexene
c- or *t*-2H	*cis*- or *trans*-2-Hexene
(*c* + *t*)-3H	(*cis* + *trans*)-3-Hexene
n-Ha	*n*-Hexane
2E1B	2-Ethyl-1-butene
3M1P	3-Methyl-1-pentene
c- or *t*-3M2P	*cis*- or *trans*-3 Methyl-2-pentene
3MPa	3-Methylpentane
c- or *t*-4M2P	*cis*- or *trans*-4 Methyl-2-pentene
2M1P	2-Methyl-1-pentene
2M2P	2-Methyl-2-pentene
4M1P	4-Methyl-1-pentene
2,3DM1B	2,3-Dimethyl-1-butene
2,3DM2B	2,3-Dimethyl-2-butene
3,3DM1B	3,3-Dimethyl-1-butene
1P	1-Pentene
(*c* + *t*)-2P	(*cis* + *trans*)-2-Pentene
2M1B	2-Methyl-1-butene
2M2B	2-Methyl-2-butene
2MBa	2-Methylbutane
1B	1-Butene
c- or *t*-2B	*cis*- or *trans*-2-Butene
iB	Isobutene
iBa	Isobutane
Pre	Propylene
*n*Pa	*n*-Pentane
Pra	Propane
Ee	Ethylene
Ea	Ethane
C_n	Hydrocarbons with carbon number *n*
C_n^{I}	Paraffins with carbon number *n*
C_n^{II}	Olefins with carbon number *n*

TABLE 1

The Composition of 1H Feed

Compound	Weight percentage
1H	97.78
c-2H	0.153
t-2H	0.432
2E1B	1.55
n-Ha	0.060
3M1P	0.020
iB	0.010
Total	99.995

EXPERIMENTAL

1-Hexene of 97.78% purity, obtained from Aldrich, was used without further purification. The composition of the feed is given in Table 1. The preparation and characterization of the ZSM-5 zeolite have been reported elsewhere (*10, 11*).

H-ZSM-5 was prepared from ZSM-5 (Si/Al ratio 80) by ion exchange with 0.5 *M* ammonium nitrate solution. A sample with mesh size 60/80 was steamed for 24 h at 200°C.

Four catalyst to reactant ratios were used at 200°C (0.026, 0.075, 0.195, 0.386 by weight); three at 250°C (0.026, 0.075, 0.195); three at 280°C (0.026, 0.075, 0.195). Blank runs were carried out at 280°C to ensure that the glass used to dilute the catalyst was inert.

All experiments were performed using an integral, fixed bed, gas phase, plug flow reactor with independently controlled three zone heater. The experimental apparatus and procedures were similar to those described in previous studies (*12, 13*).

Liquid and gaseous products were respectively analyzed by a Varian model 3700 and a Carle SX 1156 gas chromatograph, using conditions described previously (*8*). Identification of products was facilitated by use of a Finnigan 1020 automated GC/MS. The analysis of heavier products was carried out by first subjecting an accumulated mixture of all products to vacuum distillation to concentrate the high-molecular-weight components.

After each run the reactor was purged with dry nitrogen gas using a set flow rate at the reaction temperature for 15 min. Residual material in the reactor was regarded as coke. The reactor temperature was increased to 500°C, while dry, and carbon dioxide-free air was passed over the catalyst. The weight of water collected in a tube of drierite allowed the hydrogen content of the coke to be calculated. The weight of carbon dioxide absorbed by a tube containing Ascarite gave the carbon content of the coke. Complete combustion to carbon dioxide was ensured by passing the combusted product stream through a reactor packed with copper oxide at 350°C.

RESULTS

The integral conversion of 1H was calculated allowing for a weight percentage of 97.78% present in the original feed (Table 1). Plots of integral conversion against time on stream showed that this is a class II system in the temperature range studied. A similar result has been obtained (*8*) for isomerization of 1H on HY zeolite at 200°C.

Selected OPE curves and selectivity plots are presented in Fig. 2. Yields of *c*-2H and *t*-2H were obtained by subtracting the amounts initially present in the feed. In cases where there was a measurable amount of the minor products in the feed, the original weight percentage is shown directly on the vertical axis at zero 1H conversion. The total weight percentages of coke obtained are plotted as a function of 1H conversion in Fig. 3 for each temperature studied.

By comparison with Fig. 1, the morphologies such as those illustrated in Fig. 2 allow each product to be classified as primary or secondary, stable or unstable. Table 2 shows this classification for products at 200 and 280°C on ZSM-5. Assignment of product type previously obtained for isomerization of 1H on HY (*8*) is also shown, together with classification of reaction type.

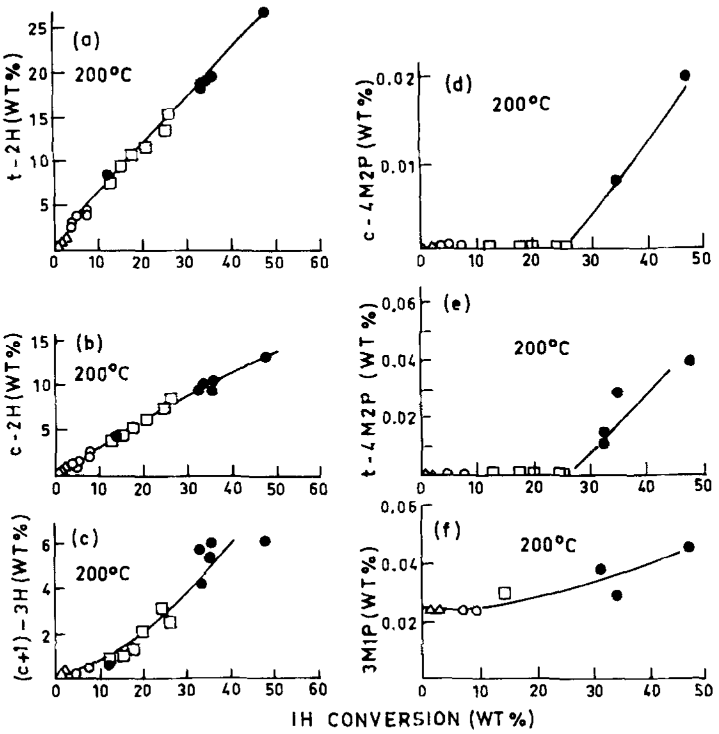


FIG. 2. Examples OPE curves at 200°C for (a) *t*-2H, (b) *c*-2H, (c) (*c* + *t*) 3H, (d) *c*-4M2P, (e) *t*-4M2P, (f) 3M1P; c/o 0.026 (△); 0.075 (○); 0.195 (□); 0.386 (●).

The initial selectivities of the primary products obtained on ZSM-5 at 200 and 280°C are given in Table 3, with results obtained for HY at 200°C included for comparison.

DISCUSSION

Table 2 shows that most of the reactions which occur on ZSM-5 in the temperature range studied are very similar to those found previously on HY (*8*) while the rate of conversion of 1H on HY is 90 times that on ZSM-5. The following sections discuss the formation of various products, with particular emphasis on the differences observed in the reactions of 1H on the two zeolites.

Double Bond Shift

In the temperature range 200–280°C, the major products were *c*-2H, *t*-2H, and (*c* + *t*)-3H, these contributing over 95% of the total at 50% 1H conversion. This is comparable to the 94.75% double bond shift contribution obtained on HY.

Both *cis* and *trans* 2H were found to be primary products on ZSM-5, indicating formation of both isomers directly from 1H.

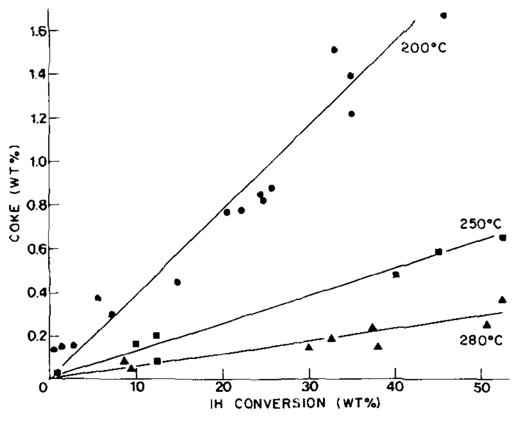


FIG. 3. The OPE curves of total coke at 200°C (●), 250°C (■), and 280°C (▲).

TABLE 2

Reaction Products in the Isomerization of 1H

Product	Product type[a]			Reaction type[b]
	HY(200°C)	ZSM-5(200°C)	ZSM-5(280°C)	
t-2H	IU	IU	IU	DBS
c-2H	IU	IU	IU	DBS
(*c* + *t*)3H	(1 + 2)S	(1 + 2)S	(1 + 2)S	DBS
c-3M2P	2S	2S	2S	SR
t-3M2P	2S	2S	2S	SR
c-4M2P	2S	2S	2S	SR
t-4M2P	2S	2S	2S	SR
2,3DM1B	2S	N	2S	SR
2M2P	2S	N	2S	SR
3M1P	2S	2S	2S	SR
1P	(1 + 2)S	1S	1S	(P + C)
(*c* + *t*)2P	2S	2S	1S	(P + C)
t-2B	2S	2S	1S	(P + C)
c-2B	2S	2S	1S	(P + C)
2M1B	2S	N	2S	(P + C)
2M2B	2S	N	2S	(P + C)
1B	1U	N	N	(P + C)
iB	1U	2S	1S	(P + C)
Pre	1U	2S	1S	(P + C)
3MPa	1S	N	N	HT
2MBa	(1 + 2)S	2S	2S	HT
iBa	1U	2S	1S	HT
*n*Pa	N	2S	2S	HT
Ea	1U	N	N	HT
Pra	1U	N	N	HT
n-Ha	2S	2S	2S	HT
Coke	(1 + 2)S	1S	1S	P + C + CZ[c]

[a] The product type is classified with respect to 1H; 1, primary; 2, secondary; S, stable; U, unstable; N, not found in the range of conversion studied.

[b] DBS, Double bond shift; SR, skeletal rearrangement; HT, hydrogen transfer; C, cracking; P, polymerization; (P + C), polymerization followed by cracking; Cz, cyclization.

[c] Cyclization probably does not occur on ZSM-5.

This type of process has previously been suggested for the isomerization of 1-butene on NaY (*14*). Formation of *t*-2H isomers by consecutive reactions has been suggested for isomerization of 1-butene on silica-alumina (*15*) but cannot apply here as one of the isomers would then be seen as a secondary product.

At thermodynamic equilibrium at 200°C the ratio of *c*-2H to *t*-2H has been experimentally determined as 0.39 (*16*). A different ratio indicates that the reaction is kinetically controlled, with values above 0.39 showing a higher relative rate of production of the *cis* isomer. The literature contains numerous studies on olefin isomerization. Preferential formation of the *cis* isomer on zeolites (*8*, *17*), amorphous silica-alumina (*13*, *18*), and alumina (*18*) has been well documented. On both HY zeolite and silica-alumina, initial ratios close to unity are reported by most authors.

The initial *c*-2H/*t*-2H ratios calculated from the initial selectivity of these isomers are given in Table 4 for ZSM-5 and HY. Figure 4 shows the variation in this ratio at

TABLE 3

The Initial Selectivities for Primary Products in the Isomerization of 1H

Product	Initial selectivity			Reaction type[a]
	HY(200°C)[b]	ZSM-5(200°C)	ZSM-5(280°C)	
t-2H	0.500	0.620	0.638	DBS
c-2H	0.415	0.335	0.267	DBS
(*c* + *t*)-3H	0.062	0.030	0.090	DBS
1P	0.00032	0.00080	0.0022	(P + C)
1B	0.00070	—	—	(P + C)
iB	0.0051	—	0.0012	(P + C)
Pre	0.00060	—	0.00070	(P + C)
c-2B	—	—	0.00050	(P + C)
t-2B	—	—	0.0010	(P + C)
(*c* + *t*)-2P	—	—	0.00040	(P + C)
2MBa	0.00033	—	—	HT
iBa	0.00028	—	0.00038	HT
Pra	0.0060	—	—	HT
Ea	0.0014	—	—	HT
Coke	0.0055	0.0340	0.0050	P, C, CZ
Total				
DBS	0.977	0.985	0.995	
HT	0.00801	0	0.00038	
P + C	0.00672	0.00080	0.0050	
Coke	0.0055	0.0340	0.0050	

[a] Symbols for reaction type have the same meaning as those in Table 2.

[b] Results taken from Ref. (*8*).

200°C over a wide range of conversion for both ZSM-5 and HY. It is apparent that, while the *cis/trans* ratio decreases toward the equilibrium value with conversion for both zeolites, the ratio is significantly lower for ZSM-5 over a wide range. This is probably the result of different spatial constraints at the active sites during the formation of the transition state leading to the individual isomers in the two zeolites. HY belongs to the faujasite class of zeolites, which are large pore zeolites having channels with diameters (9–12 Å) much larger than the cross section of the 2H isomers. ZSM-5,

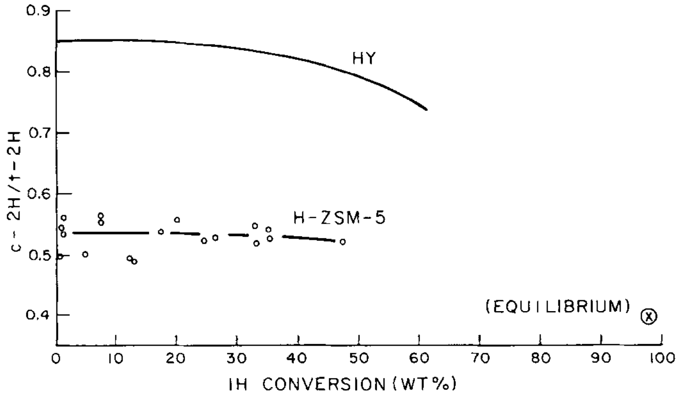


FIG. 4. The ratios of *c*-2H to *t*-2H on ZSM-5 and HY at 200°C. Results for HY taken from Ref. (*8*).

TABLE 4

Ratios of Initial Selectivities for Isomerization of 1H on ZSM-5 and HY

Catalyst	$\frac{(c+t)\text{-2H}}{(c+t)\text{-3H}}$	Equilibrium[a]	$\frac{c\text{-2H}}{t\text{-2H}}$	Equilibrium[a]
ZSM-5 (200°C)	31	2.82	0.54	0.39
ZSM-5 (250°C)	18	2.65	0.50	0.44
ZSM-5 (280°C)	10	2.63	0.42	0.44
HY[b] (200°C)	15	2.82	0.83	0.39

[a] Results taken from Ref. (*16*).

[b] Results taken from Ref. (*8*).

however, has pore structures and dimensions which are significantly different from those in faujasites. The elliptical channels in ZSM-5 have diameters (5–6 Å) in a range approaching the kinetic diameters of straight chain paraffins (4.3 Å) (*19*). This property has led to wide interest in reactions of hydrocarbons in this zeolite which are said to be controlled by shape selectivity (*20*). Diffusional inhibition of olefins has also been observed in ZSM-5, with the severity of inhibition increasing markedly as substituents are placed on an unbranched olefin (*21*). It may be possible, then, that the reason for *cis/trans* ratios closer to equilibrium in ZSM-5 is associated with initial spatial requirements of the transition state followed by equilibration encouraged by diffusional limitations. There is a high probability that a particular 2H molecule, once formed, will undergo repeated collision with the channel walls, leading to repeated adsorption at active sites, before escaping from a ZSM-5 zeolite particle.

From the initial selectivities for *c*-2H, *t*-2H, and (*c* + *t*) 3H the initial rate of deprotonation (to form 2H) is estimated to be about 31 times faster than the rate of hydrogen shift (to form 3H) at 200°C. This compares with a ratio of 15 for HY at the same temperature (*8*). Table 4 shows that as the temperature increases so does the ease of hydrogen shift compared to deprotonation.

Skeletal Rearrangement

As shown in Table 1, 2E1B is the principal impurity present in the feed. In the temperature range studied the amount of 2E1B decreased rapidly from its initial value of 1.55% to a constant value of 0.1% at 10% 1H conversion. At the same time, *c*-3M2P and *t*-3M2P show a rapid initial increase over a similar range, until the total amount of 3M2P isomers present was 1.6%. After this point, the amounts of these isomers increased slowly at rates determined by the temperature. This shows that, although double bond shift of 2E1B is the primary source of 3M2P, it is also formed from sources such as 2H and 3H by skeletal rearrangement. On HY at 200°C (*8*) *c*-3M2P and *t*-3M2P were also found to be the principal products formed from the impurity 2E1B. However, the reaction products from 2E1B on ZSM-5 did not appear to include 2M1P and 3MPa, which were found as primary products on HY.

The relative rate of skeletal rearrangement to double bond shift appears to be much lower in ZSM-5 than HY. At about 50% conversion, the total percentage of products formed by skeletal rearrangement is five times smaller on ZSM-5 at 200°C. Skeletal rearrangement of 2H or 3H leads to branched olefins, and as these molecules would have larger kinetic diameters than the linear molecules from which they are formed, their formation may be severely restricted by the pore dimensions in ZSM-5. This may account not only for the lower total amount of skeletal rearrangement, but may also explain the absence of 2,3DM1B at 200°C. This di-substituted olefin was found as a secondary product on HY (*8*) when the total 1H conversion reached ~10%, and in amounts exceeding the yields of other products of skeletal rearrangement at ~50% total conversion. On ZSM-5, however, the size of this molecule may tend to restrict its formation and subsequent diffusion through the narrower channels. Even at 280°C, this product does not appear until ~40% total conversion, and then in amounts less than observed on HY at 200°C at similar total conversion.

This interpretation is supported by studies on the cracking of hexane isomers (*4*). At 350°C the first-order rate constant for cracking *n*-Ha on ZSM-5 was approximately 100 times larger than for 2,3-dimethylbutane. In the absence of steric constraints using amorphous silica-alumina or a Y zeolite the rate constants reflected the intrinsic reactivity of the molecules, and 2,3-dimethylbutane was more reactive than *n*-Ha. The absence of 2M2P on ZSM-5 at 200°C might be expected in the range of conversions studied, as it is not detected on HY until the total conversion exceeds ~35%.

The absence of other possible products, such as 4M1P, 2,3-DM2B, or 2M1P, is probably due to both thermodynamic factors and low stability of intermediate carbenium ions, as has been discussed elsewhere (*1, 2, 8*). The formation of 3,3-DM1B on ZSM-5 would appear to be particularly unlikely. Its formation would require the unfavorable conversion of a tertiary to a secondary carbenium ion (*8*). In addition, as adsorption studies have shown that neopentane is rejected by ZSM-5 because its kinetic diameter (6.2 Å) exceeds the pore dimensions (*19*), it is probably that 3,3-DM1B is too large to form in this zeolite.

Polymerization and Cracking: Olefins

Figure 2 shows some selectivity plots of alkenes with less than six carbon atoms. Fewer compounds of this type are formed at 200°C on ZSM-5, compared to HY. Their total weight percentage yield was less than half that on HY at ~50% 1H conversion.

As no methane, ethane, or ethylene was found in the products it appears unlikely that C_4 or C_5 alkenes could be formed directly from a C_6 carbenium ion, and a polymerization-cracking mechanism seems probable. Formation of two Pre molecules from a C_6 carbenium ion appears possible, by initial cracking to give one Pre molecule and a propyl carbenium ion, which could subsequently deprotonate to give a second Pre molecule. Although abstraction of a hydride ion leading to Pra appears possible, this paraffin was not observed. In contrast, Pra was formed in excess of Pre on HY at all levels of conversion (*8*).

Almost all the identified compounds with seven or more carbon atoms were olefins, both straight chain and branched. Heptenes, octenes, nonenes, decenes, undecenes, and duodecenes were all found by GC/MS. Alkenes with more than 12 carbon atoms, polyenes, or cyclic structures were not detected. With the possible exception of Pre, and the hexenes, it appears probable that most of the olefins are formed as a result of addition of a hexene molecule to a hexyl carbenium ion to form a dimer, followed by cracking. This would account for the presence of C_3–C_9 and C_{12} olefinic species. The C_{10} and C_{11} olefins may be formed by addition of C_4 and C_5 olefins to hexyl carbenium ions.

Coke

Coke can be defined as the material which remains on the catalyst surface after a postreaction stripping purge with an inert gas for a specific period of time at the reaction temperature. Figure 3 shows that at all three reaction temperatures studied, coke appears to be a stable primary product, suggesting it is formed from 1H. It is evident that the amount of coke decreases with increasing temperature at all levels of 1H conversion. The material remaining on the catalyst surface after reaction has a C/H ratio in the range 0.42–0.66. These observations are consistent with the idea that the coke consists mainly of adsorbed olefins.

Table 5 shows that at 200°C and ~50% 1H conversion, the amount of coke formed on ZSM-5 (1.65%) exceeds that formed on HY (0.43%). However, the amount of coke formed on ZSM-5 per unit weight of catalyst is about half that for HY.

Studies on the isomerization of 1B on HY (*22*) and 1H on HY (*8*) have shown that cyclization and aromatization occur. Infrared studies on 1H adsorption (*23*) have

TABLE 5

Coke Produced during Isomerization of 1H

Catalyst	1H Conversion (%)	Weight percentage of coke	Weight of coke/weight of catalyst
ZSM-5(200°C)	49.93	1.65	0.0425
ZSM-5(280°C)	51.98	0.25	0.0129
HY[a](200°C)	54.09	0.43	0.0822

[a] Results taken from Ref. (*8*)

demonstrated that polymerization and dehydrogenation begin to occur to form conjugated polyene structures at 150°C, and on heating at 260°C, cyclization has occurred to form hydrogen-deficient aromatic ring structures. Low quantities of alkylated benzenes and naphthalenes and alicyclic compounds have been detected by GC/MS after reaction of 1B on HY in the range 250–400°C (*22*), suggesting that coke precursors in this system possess cyclic structures.

On ZSM-5, however, both the C/H ratios and the absence of aromatic fragments, polyenes and few, if any, alicyclics suggest that cyclization with subsequent dehydrogenation of polymeric species does not occur.

A comparative study (*24*) of coke formation in ZSM-5 and mordenite, with mixtures of hexane and alkyl benzenes as reactant, showed that significantly less coke was formed in ZSM-5. It was concluded that the difference must lie in the size of the pores, ZSM-5 being a 10-ring, mordenite a 12-ring structure. Differences in coke formation were attributed to spatial constraints, the alkylaromatics being prevented from reacting further to produce coke (by cyclization, hydrogen transfer, repeated alkylation, etc.) in the smaller ZSM-5 pore.

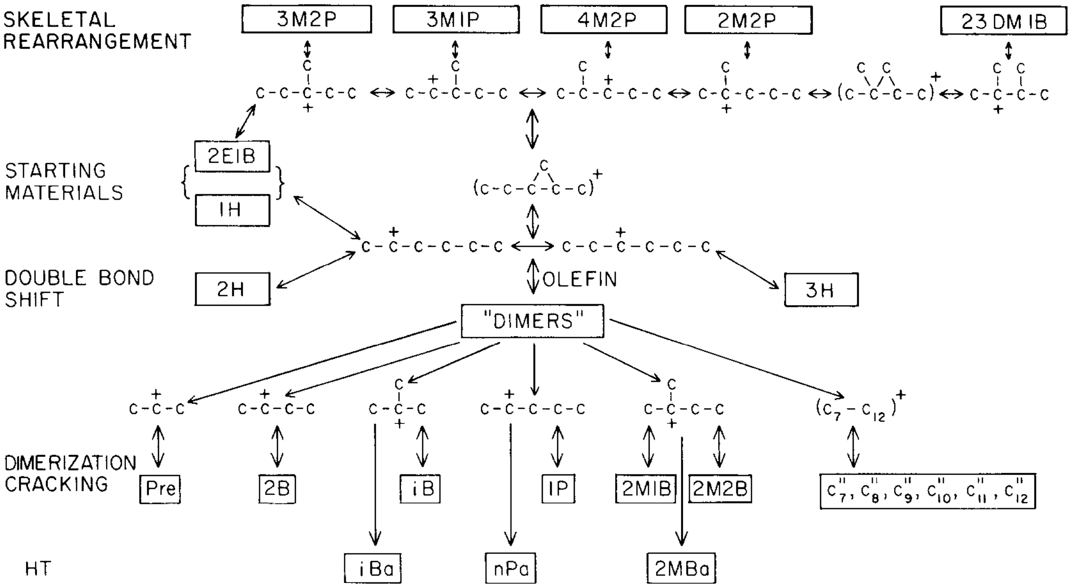
It has also been found that, for the conversion of methanol to hydrocarbons on ZSM-5, carbonaceous residues were formed primarily on the outer surfaces of the zeolite crystallites, producing a high resistance to aging (*6*). For offretite and mordenite, in contrast, the channels are large enough to accommodate carbonaceous residues, leading to a drastic loss of catalytic activity and very fast aging.

Polymerization and Cracking; Paraffins

In general, the reactions of olefins on solid acid catalysts can result in the formation of polymerization and cracking products with high amounts of paraffinic hydrocarbons (*22, 25*). The main products of the reactions of the lower olefins above 100°C are iBa and 2MBa, whatever the starting olefin may have been.

Our selectivity curves indicate that at 200 and 280°C the paraffins formed are stable secondary products, except iBa which is primary at the higher temperature. A major difference between reactions of 1H on ZSM-5 and HY is the amount of low-molecular-weight paraffins formed. At 200°C the initial selectivity of hydrogen transfer reactions on ZSM-5 is zero, and even at 280°C it is still significantly less than on HY. At 50% 1H conversion and 200°C, hydrogen transfer products with six or less carbon atoms are ~40 times more plentiful on HY, compared to ZSM-5. The material of higher molecular weight (C_7–C_{12}) produced on ZSM-5 consists almost entirely of olefins, while the dominant species formed on HY at 200°C in the C_9–C_{12} range were paraffins (*8*).

The origin of saturated hydrocarbons is probably the cracking of polymeric species on the catalyst surface. Carbenium ions formed in this way may either lose a proton to form an alkene, or produce a saturated paraffin molecule by hydrogen transfer. In the previous section it was noted that the residual coke on ZSM-5 appeared to consist of adsorbed olefins. In contrast, studies of 1H isomerization on HY zeolite have shown that polymerization, cyclization, and dehydrogenation occur to produce a coke with substantial aromatic character. As no hydrogen gas was detected in the product from either ZSM-5 or HY, the source of hydrogen required to form paraf-



SCHEME I. Reaction network for isomerization of 1-hexene.

fins is coke or its precursors. Although transfer of hydrogen from coke or precoke species to alkenes would lead to molecules of greater stability (paraffins, and aromatic structures with their associated resonance stabilization energy), the rate of paraffin formation will depend on the availability of suitable hydrogen donors on the surface, which in turn may depend on the cyclization and aromatization of the polymeric species. Thus the lack of paraffins produced on ZSM-5 is probably due to the difficulty in forming cyclic structures leading to extended aromatics because of the restrictions imposed by pore dimensions in this zeolite.

CONCLUSIONS

A detailed analysis of the major and minor products of the isomerization of 1H over ZSM-5 zeolite has elucidated the overall reaction network shown as Scheme I. Variation between the observed products on this catalyst and those in an earlier study on HY can be ascribed entirely to the differences in pore structure in these zeolites.

The principal products, *c*-2H, *t*-2H, and (*c* + *t*)-3H are formed by double bond shift on both catalysts. The ratio of *c*-2H to *t*-2H is nearer the equilibrium value on ZSM-5 than that observed on HY, at all levels of 1H conversion. This may be due to the spatial constraints imposed on the active sites in the ZSM-5 structure and the more severe restrictions to diffusion and consequently more thorough equilibration of species trapped in the pore structure.

The ratio of the initial rate of deprotonation to that of hydrogen shift in the hexyl carbenium ion was found to decrease with temperature, and at 200°C was greater than that on HY.

The reason why *cis* and *trans* 2H should be more equilibrated than the 2-3H hydrogen shifted product needs more investigation. Perhaps we are observing the effects of surface configuration in the vicinity of the active sites.

All products of skeletal rearrangement of 1H were found to be secondary. At 50% 1H conversion, the relative rate of double bond shift to skeletal rearrangement on ZSM-5 at 200°C was significantly higher than on HY. The decreased tendency for skeletal rearrangement, and the low amounts of 2, 3DM1B observed, were attributed to steric constraints in ZSM-5.

The contribution from cracking and polymerization products at 200°C and 50% 1H conversion consists mainly of alkenes and is significantly smaller than that found on HY. Polymerization was limited on ZSM-5 to dimer formation, and no aromatic molecules were detected in contrast to the products on HY.

Coke was observed to be a primary product and its formation decreased with temperature at all levels of 1H conversion. Analysis of the C/H ratio indicated that mainly olefins are present in the coke on ZSM-5. The size of the pores in ZSM-5 probably inhibits cyclization and dehydrogenation to form the extended aromatic structures which are thought to form in large pore zeolites such as HY.

The initial selectivity for and total yield of paraffinic products with six or fewer C atoms is very small compared to HY at 200°C. Even at 280°C, paraffins were less prevalent on ZSM-5 than on HY at 200°C. No paraffins in the range C_7–C_{12} were detected using ZSM-5, whereas saturated hydrocarbons were previously found to be dominant in the C_9–C_{12} range with HY. The lack of paraffin formation on ZSM-5 may be related to the deficiency of cyclic hydrogen donor species produced in the ZSM-5 structure because of spatial constraints.

All in all ZSM-5 differs from HY in yielding fewer aliphatics, no aromatics, and fewer branching isomerizations. We attribute all these phenomena to differences in the steric properties of the two zeolites and not to any properties of the active sites per se.

REFERENCES

1. Pines, H., "The Chemistry of Catalytic Hydrocarbon Conversions," Chaps. I and II. Academic Press, New York, 1981.
2. Germain, J. E., "Catalytic Conversion of Hydrocarbons," Chapter IV, Academic Press, New York/London, 1969.
3. Olson, D. H., and Haag, W. O., U.S. Patent 4,159,282, (1979).
4. Chen, N. Y., and Garwood, W. E., *J. Catal.* **52,** 453 (1978).
5. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
6. Dejaifve, P., Auroux, A., Gravelle, P. C., Védrine, J. C., Gabelica, Z., and Derouane, E. G., *J. Catal.* **70,** 123 (1981).
7. Kaeding, W. W., Chu, C., Young, L. B., and Butter, S. A., *J. Catal.* **69,** 392 (1981).
8. Ko., A. N., and Wojciechowski, B. W., *Int. J. Chem. Kinet.* **15,** 1249 (1983).
9. Wojciechowski, B. W., *Catal. Rev.-Sci. Eng.* **9,** 79 (1974).
10. Argauer, R. J., and Landolt, G. R., U.S. Patent 370288G (1982).
11. Costa, E., Sotelo, J. L., Gutiérrez, M. L., Uguina, M. A., Ovejero, G., and Torregrosa, J., *Rev. R. Acad. Cienc. Exactas Fis. Nat. Madrid* **73,** 92 (1975).
12. Best, D., and Wojciechowski, B. W., *J. Catal.* **47,** 11 (1977).
13. Corma, A., and Wojciechowski, B. W., *J. Catal.* **60,** 77 (1979).
14. Lombardo, E. A., Sill, G. A., and Hall, W. K., *Adv. Chem. Ser.* **102,** 346 (1971).
15. Lucchesi, P. J., Baeder, D. L., and Longwell, J. P., *J. Amer. Chem. Soc.* **81,** 3235 (1959).
16. Maurel, R., Guisnet, M., and Bove, L., *Bull. Soc. Chim. Fr.* 1975 (1969).
17. Sinitsyna, O. A., Moskovskaya, I. F., and Topchieva, K. V., *Kinet. Katal.* **21,** 728 (1980).
18. Brouwer, D. M., *J. Catal.* **1,** 22 (1962).
19. Flanigen, E. M., Bennett, J. M., Grose, R. W., Cohen, J. P., Patton, R. L., Kirchner, R. M., and Smith, J. V., *Nature (London)* **271,** 512 (1978).
20. Derouane, E. G., and Gabelica, Z., *J. Catal.* **65,** 486 (1980).
21. Haag, W. O., Lago, R. M., and Weisz, P. B., *Faraday Discuss. Chem. Soc.*, 317 (1982).
22. Langmer, B. E., *J. Catal.* **65,** 416 (1980).
23. Eberly, P. E., *J. Phys. Chem.* **71,** 1717 (1967).
24. Walsh, D. E., and Rollman, L. D., *J. Catal.* **56,** 195 (1979).
25. Bolton, A. P., and Weeks, T. J., *Trans. Faraday Soc.* **70,** 1676 (1974).