JOURNAL OF CATALYSIS **118**, 466–482 (1989)

Retained and Desorbed Products from Reaction of 1-Hexene over H–ZSM5 Zeolite: Routes to Coke Precursors

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Received January 27, 1989; revised April 14, 1989

Retained and desorbed products have been studied from the reaction of 1-hexene over H–ZSM5 zeolite at 353–593 K, with supplementary information using cyclopentadiene, cyclopentadiene dimer, and *n*-hexane. At 353–393 K the retained products from 1-hexene were paraffinic, and the associated dehydrogenation products (alkylbenzenes) were desorbed. The retained paraffins contained some chain branching and a distribution in Cn(C_8–C_{15}, C_{12} max) resulting from facile olefin oligomerization, cracking and isomerization. At >393 K unsaturated cyclic components were increasingly important in the retained products, with the evolutionary sequence, (alkyl)cyclopentadienes, (alkyl)indanes/indenes/tetralins, (alkyl)dihydronaphthalenes, leading to higher fused ring aromatics. Alkylbenzenes were by-products to this main sequence. Except for the (difficult) first steps, the residue-forming reactions from *n*-hexane followed those of 1-hexene. The reactions of cyclopentadiene and cyclopentadiene dimer indicated two distinct reaction paths leading to tetralin and methylindanes/indenes. From the dependence of residue weight and accessible pore volume on 1-hexene treatment conditions, it is concluded that the residue formed at 393–593 K was mainly within the pores: heating to ≥593 K caused this residue to migrate to the external zeolite surface where, free from size/shape selectivity restrictions, conversion into relatively involatile, higher molecular weight, products was possible. On H–ZSM5 which had been $SiCl_4$-treated to deacidify the external surface, the 1-hexene reaction at 513 K was the same as without $SiCl_4$ treatment. At 593 K, surface deacidification caused a large decrease in the proportion of higher aromatics, confirming that the latter are mainly formed at the external surface. © 1989 Academic Press, Inc.

INTRODUCTION

It has been known for some time that the reaction of lower olefins over catalysts such as REX zeolite (*1*) or amorphous silica–alumina (*2*) can give gaseous products which are predominately paraffinic, but only occasionally has a study been made (e.g., Ref. (*1*)) of the dehydrogenated (hydrogen donor) products which are a necessary and integral part of the reaction, and which remain associated with the catalyst. This is not a trivial matter: for instance, in the conversion of propylene over amorphous silica–alumina (*2*), only 1–35% of the total carbon was recovered as gaseous products.

A recent study of propylene oligomerization over H–ZSM5 zeolite (*3*) inferred from the relatively low discrimination against chain branching in the products that considerable pore blockage had occurred so that much of the product which was returned to the gas phase was formed at the external surface of the zeolite.

Clearly, a quite incomplete, and to some extent misleading, picture of the reaction chemistry of hydrocarbons on zeolites or other solid acid catalysts can be obtained if only the desorbed products are examined. Not only can retained products affect the size/shape selectivity of catalysts such as H–ZSM5, but they may also function as possible precursors to the formation of coke[1] and the general deactivation of the catalyst.

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[1] Following normal convention, we use the term "coke" to refer to relatively involatile, oligomeric or polymeric, hydrocarbonaceous residue of ill-defined chemical structure, formed on the catalyst as a result of hydrocarbon reactions. The H/C ratio and the extent of aromaticity and olefinicity depend on reaction conditions.

0021-9517/89 $3.00

A number of studies have been made of coke formation on acidic and bifunctional metal/acidic catalysts (*4*); it is known that coke formation depends on the catalyst and the reactant (*5–8*), but only limited information is available about the reaction pathway and the nature of the precursors.

With a Pt/Al_2O_3(Cl) naphtha-reforming catalyst at 788 K, Parera *et al.* (*9*) showed that the addition of cyclopentadiene or methylcyclopentadiene to the feed increased the rate of coke deposition, and that the coke contained, in addition to various polycyclic aromatic hydrocarbons, cyclopentadiene dimer (dicyclopentadiene), methylindane, and methylindene, which are plausible intermediates in the conversion of cyclopentadiene to polycyclic aromatics. This work indicates but does not prove that cyclopentadiene or methylcyclopentadiene are intermediates to coke formation if not deliberately added.

A more definitive indication of the role of cyclopentadiene in coke formation over Pt/Al_2O_3(Cl) catalysts has been given by Barbier *et al.* (*10*), with the amount of coke from cyclopentane at 673–743 K increasing as the concentration of cyclopentadiene in the evolved gases increased, and with the accessible platinum surface implicated as the necessary site for cyclopentane dehydrogenation.

In a recent study of coking of a silica–alumina/REX zeolite catalyst, it was reported (*11*) that the gaseous products from 1-hexene at 673 K contained C_3–C_5 cracked products, isomeric hexenes, C_6 alkanes and cycloalkanes, benzene, and alkylbenzenes, but no cyclopentadienes or indanes/indenes. On the other hand, cyclopentene reactant (more favorable for cyclopentadiene formation) gave gaseous products which contained cyclopentadiene and indanes/indenes. Nevertheless, cyclopentadiene was proposed as an important type of reaction intermediate in the formation of aromatic-type coke in both cases.

In the present work we have studied the gaseous and residue products formed in the reaction of 1-hexene over H–ZSM5 zeolite at 393–593 K, with supplementary data to 723 K. Extra reaction information was obtained using cyclopentadiene and cyclopentadiene dimer (dicyclopentadiene) as model reactants. Most emphasis was placed on the retained products and the reactions involved in their evolution.

An additional study was made of the reaction of *n*-hexane over H–ZSM5 in order to assess the residue-forming behavior of such a nonolefinic reactant in the absence of a metallic dehydrogenating function in the catalyst.

The importance of acidic sites on the external surface of the H–ZSM5 compared to internal sites was examined using surface-dealuminated H–ZSM5.

The limited channel dimensions of ZSM5 should result in some size/shape selectivity effects on the nature and location of the products. In this regard, it has already been reported (*12*) that in coke deposition during the reaction of *n*-heptane at 723 K, polyaromatic compounds were prevalent with HY-zeolite, whereas with H–ZSM5 alkylbenzenes and alkylnaphthalenes were prevalent.

EXPERIMENTAL

Materials

Zeolite H–ZSM5 was prepared and characterized by standard methods (*13*), giving two samples having SiO_2/Al_2O_3 molar ratios of 46/1 and 59/1. The ZSM5 consisted of hexagonally terminated lath-like crystal (average size ca. 2 μm) associated into aggregates (scanning electron microscopy).

1-Hexene was from Sigma, *n*-hexane, cyclopentadiene, and cyclopentadiene dimer were from Merck; the latter two were further purified by fractional distillation immediately before use.

Treatment Methods

Treatments were carried out using 1.0 g of zeolite supported as a thin (ca. 3 mm) bed in a down-flow reactor (Pyrex) in an air oven.

The zeolite sample was first pretreated *in situ* at 773 K in an oxygen stream (20 cm^3 min^{-1}) for 2 h, then flushed in a nitrogen stream at 773 K for 2 h, and cooled to room temperature in nitrogen. The sample was then treated with reactant vapor in nitrogen carrier gas by injecting liquid reactant into a heated vaporizer with a motor-driven syringe (carrier gas 20 cm^3 min^{-1}; reactant liquid delivery rate 0.27 cm^3 h^{-1}). At the end of the treatment time the sample was cooled to room temperature in a flow of nitrogen (15–30 min). Vaporizer and delivery lines were at 360 K, well above the temperature for complete vaporization of all reactants, and low enough for the rates of cyclopentadiene dimerization and cracking of cyclopentadiene dimer to be negligible.

Analytical Methods

The composition of the reactor effluent gas was analyzed in two ways: (i) via a sample valve for on-line GC analysis (Varian 3700 or Shimadzu 8A; heated valving and transfer lines; capillary column 12 m, type 25QC2-BP1-0.25; temperature-programmed mode 313–513 K), and (ii) by sorption of the organic components of the effluent stream onto Tenax GC 60/80 (20 mg) contained in a demountable transfer tube (3 mm i.d.) from which the components to be analyzed were thermally flash desorbed after introduction of the transfer tube into the sample compartment of a GC/MS system (Hewlett–Packard Model 5996; capillary column 25QC2-BP1-0.25).

The nature of the organic material contained within the catalyst was determined by either: (i) dissolution of the zeolite in dilute HF (4 *M*) with simultaneous solvent extraction (CH_2Cl_2) of the organic components (*6*) (treatment at 273 K, gentle shaking, 3–5 min), followed by GC/MS analysis after removal of the CH_2Cl_2 at room temperature, (ii) ^{13}C NMR CP MAS examination of the treated zeolite (Bruker MSL 400 NMR spectrometer at 100.6 MHz, contact time 2 ms, recycle time 10 s, MAS at 4 kHz, 2400–6000 spectra accumulated, spectra referenced to TMS).

Mass spectra were indexed by reference to literature spectra (EPA/NIH Mass Spectral Data Base, 1978), supplemented by spectra obtained with known reference compounds.

Surface deacidification. Surface deacidification of H–ZSM5 was via dealumination by treatment with $SiCl_4$ vapor at an elevated temperature (*14*), followed by treatment with 0.5 *M* HCl at 373 K for 12 h to remove nonframework aluminium, thorough washing with distilled water (absence of Cl^-), and drying at 373 K. Dealumination treatment was performed in a vertically mounted quartz tubular reactor using typically 1.0 g H–ZSM5. The $SiCl_4$ was introduced into a stream of dried argon (80 cm^3 min^{-1}) by a bubbler the temperature of which was controlled with an external bath. Before $SiCl_4$ treatment, the zeolite sample (protonic form, H–ZSM5) was pretreated *in situ* at the desired treatment temperature in dried argon for 2 h. In exploratory experiments, treatment times, treatment temperatures, and $p^0_{SiCl_4}$ values were varied in the ranges 0.5–60 min, 873–1023 K, and 1.04–53 kPa, respectively.

The efficiency of the surface deacidification treatment was assessed by comparing (i) the total acidity, estimated as the total Na^+-ion exchange capacity (exhaustive exchange at room temperature with 1 *M* $NaNO_3$ solution, titration of liberated acid), with (ii) the surface acidity, estimated as the monolayer methylene blue adsorption capacity (*15*) (equilibration of zeolite with aqueous methylene blue solution at room temperature for 48 h with intermittent shaking, aqueous supernatant concentrations estimated spectrophotometrically at 664 nm, monolayer adsorption estimated from Langmuir isotherm plot). The accuracy of the monolayer methylene blue adsorption method for the estimation of surface acidity was checked (for untreated H–ZSM5) by titration of the liberated acid, giving agreement to within 1%. Methylene blue is excluded from the channels of ZSM5 by size–shape selectivity effects.

If N_S is the number of surface acidic sites per gram of zeolite after deacidification and N_T is the total number of acidic sites per gram of zeolite after deacidification while N_S^0 and N_T^0 are the corresponding values before deacidification, N_B, the number of acidic site per gram of bulk zeolite equals $(N_T - N_S)$, and $N_B^0 = N_T^0 - N_S^0$; it is convenient to define degrees of deacidification D_S and D_B for the surface and the bulk, respectively, by $D_S = (N_S^0 - N_S)/N_S^0$ and $D_B = (N_B^0 - N_B)/N_B^0$. It is also convenient to define the surface specificity for deacidification, S_{DA}, by $S_{DA} = D_S/(D_S + D_B)$.

A detailed account of the quantitative aspects of this technique is given elsewhere (*16*). For the present purpose, conditions were chosen in order to give substantial surface deacidification selectivity with minimum deacidification of the zeolite interior (to preserve the reaction conditions in the zeolite channels unchanged so far as possible from the original zeolite). Treatment at 873 K for 1 min with $p^0_{SiCl_4} = 1.04$ kPa ($SiCl_4$ bubbler temperature 232 K) gave $S_{DA} = 98\%$, with $D_S = 61\%$ and $D_B = 1.1\%$. H–ZSM5 with $SiO_2/Al_2O_3 = 46/1$ was used.

Pore volume. Estimation by *t*-plot method (*17*) using data for nitrogen sorption at 77 K, obtained with a Carlo-Erba Sorptomatic 1800.

Organic residue content of treated zeolite. Oxidative burn-off of organic material, using a microbalance in which the sample (60 mg) was heated in air to 920 K to constant weight, with a linear temperature ramp of 10 K min^{-1}. In the manner described by Bibby *et al.* (*18*), correction was made for weight loss due to residual moisture in the sample from the shape of the weight loss/temperature profile, with all of the weight loss from room temperature to 520 K being ascribed to moisture, the validity of the latter being checked by weight loss measurements on organic-free zeolite.

RESULTS

Product Composition

To check if the HF dissolution technique had any effect on the sorbed reactant, blank experiments were carried out with silicalite or silica gel loaded with reactant. No reaction products could be detected.

Results obtained by the application of the zeolite dissolution/solvent extraction method to 1-hexene-treated H–ZSM5 zeolite samples are contained in Table 1, while Table 2 summarizes ^{13}C NMR CP MAS results for correspondingly treated samples. Table 1 also contains data from analysis of gaseous reaction products.

For comparison with the reaction of 1-hexene, the residue product obtained from the reaction of *n*-hexane over H–ZSM5 was studied at 513 and 593 K, and the results are summarized in Table 3.

Results for H–ZSM5 zeolite treated with cyclopentadiene and with cyclopentadiene dimer are contained in Tables 4 and 5, respectively, obtained for varying treatment temperatures and a fixed treatment time.

At the low treatment temperature of 393 K the product distributions from cyclopentadiene and cyclopentadiene dimer are relatively simple, and Fig. 1 shows the time evolution of the important individual products.

The zeolite dissolution/solvent extraction method with 1-hexene-treated, surface-dealuminated, zeolite samples gave results contained in Table 6 (513–593 K). Zeolite H–ZSM5 with a surface deacidification selectivity, S_{DA}, of 98% was used.

Void Fraction in Treated H–ZSM5 and Quantity of Organic Residue

The extent to which the organic deposit from 1-hexene blocked the pore volume of the zeolite was determined from the accessible pore volume of treated samples. The results are given in Fig. 2 as a percentage of the total pore volume for untreated H–ZSM5 (0.15 cm^3 g^{-1}) for both normal H–ZSM5 zeolite and for the surface-dealuminated zeolite. Figure 2 also contains values for the weight percentage of organic deposit contained by the treated zeolite.

TABLE I

Products from H-ZSM5 Treated with 1-Hexene[a,b]

Treatment temperature (K)	Products in zeolite[c] (wt% of product)							Products in gas (wt%)			
	Alkanes	Mono-olefins[p]	Alkylcyclo-pentadienes	Alkyl-benzenes	Alkyl-indanes/ indenes	Alkyl-naphthalene	Alkyl-phenanthrenes	Alkanes	Olefins[p]	Alkyl-benzenes	Higher aromatics
393	92(8–15)[d,e]	6(9–14)[e]	1(9)	1(9–10)	—	—	—	~25(≤5)[m] ~30(7–12)	~20(7–11)mo[l]	~25(7–12)	—
453	41(7–15)	6(8–15)	51(9–16)[f]	2(9–13)	—	—	—	~14(≤5)[m] ~3(8) ~3(8)co[n]	~80(7–15)mo	—	—
513	6(7–15)	—	83(10–17)[g]	10(8–13)[h]	1	—	—	~50(≤5)[m] ~10(6)	~5(7–9)mo ~20(7–12)co	~10(7–12)	~5(12–13)[o]
593	—	—	7(7–12)[i]	2(10–13)	39(11–17)[j]	40(11–15)[k]	12(14–17)[q]	~65(≤5)[m]		~25(6–11)	~10(10–14)[o]

[a] H-ZSM5, $SiO_2/Al_2O_3 = 46/1$.

[b] 1-Hexene treatment time ca. 30 min.

[c] GC–MS analysis of products from zeolite by dissolution/solvent extraction.

[d] Total carbon number range in brackets.

[e] Mainly C_{12}.

[f] Mainly C_{16}.

[g] Mainly C_{12}–C_{16}.

[h] Mainly C_{10}–C_{13}.

[i] Mainly C_7–C_9.

[j] Indanes and indenes in comparable amounts, mainly C_{16} and C_{17}.

[k] Mainly C_{12}–C_{14}.

[l] mo, monoolefin.

[m] Alkanes and olefins.

[n] co, cyclic olefin or diolefin.

[o] Mainly alkylnaphthalenes, small amounts of indanes, tetralins.

[p] *Not including reactant or other C_6 olefin isomer.*

[q] Including some tetrahydrophenanthrenes and some anthracenes.

TABLE 2

^{13}C NMR CP MAS Results for H-ZSM5[d] Treated with 1-Hexene

Treatment temperature (K)	Main peaks (ppm referenced to TMS[a,c]	Assignments[b]
353, 393	15, 24, 33, 40	Alkane carbon; chain branching
453	15, 24, 30, 33, 40	Alkane carbon; chain branching
	143	Olefinic carbon[e]
513	14, 19, 23, 30	Alkane, alkyl carbon; chain branching
	129, 145	Olefinic carbon[e]

[a] Spectra obtained at 100.6 MHz; 2400–6000 scans accumulated.

[b] By comparison with literature data (solution spectra).

[c] Spinning sidebands were also observed as rather broad peaks in the regions 50–80 ppm (353–513 K) and 165–190 ppm (513 K).

[d] H-ZSM5, SiO_2/Al_2O_3 = 59/1.

[e] 1-Hexene sorbed in (nonacidic) silicalite gave resonances at 113 and 139 ppm in the olefinic region: thus, the resonances at 129, 143, and 145 ppm cannot be due to unreacted 1-hexene.

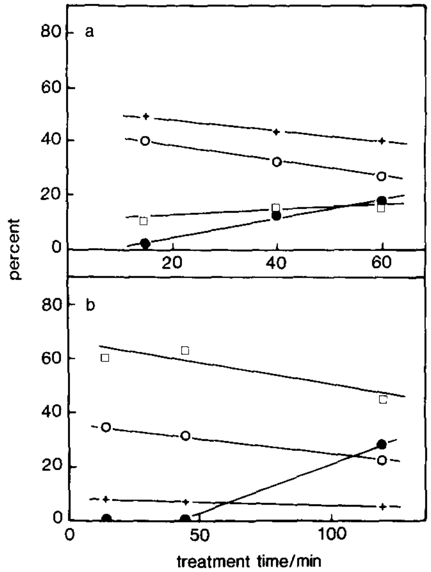


FIG. 1. Variation with treatment time of proportions of methylindanes, tetralin, and alkylbenzenes (normalized to total 100%) in the catalyst residue from the treatment of H-ZSM5 at 393 K with: (a) cyclopentadiene dimer; (b) cyclopentadiene. (□) 1- and 2-methylindanes; (+) 4- and 5-methylindanes; (○) tetralin; (●) alkylbenzenes. At 15-min treatment time, both reactants yielded only traces of products other than methylindanes and tetralin.

In the pore volume measurements, attention must be paid to possible error from desorption of some organic material during outgassing prior to nitrogen adsorption. An outgassing temperature of 393 K (1 h, final pressure ~6 × 10^{-2} Pa) was adopted because with an organic-free zeolite sample, moisture-equilibrated in air, this outgassing regime gave essentially the same pore volume as for outgassing at 523 K, and also that 393 K was the minimum temperature of any of the organic treatments (that is, if any organic desorption was to occur, it should

TABLE 3

Products from H-ZSM5 Treated with *n*-Hexane[a,b]

Treatment temperature (K)	Products in zeolite[c] (wt% of product)									
	Alkanes	Mono-olefins	Alkylcyclo-pentadienes	Alkyl-benzenes	Alkyl-indanes/ indenes	Alkyl-tetralins	Alkyl-naphthalenes	Alkyldihydro-naphthalenes	Alkyl-phenanthrenes	Other products
513	9(15–20)[d]	8(10–11)[e]	67(7–16)	16(10–16)	—	—	—	—	—	—
593	—	—	2(8–11)	18(8–12)	1(11)[f]	1(12)	22(11–14)[g]	2(11–12)	5(16–17)[h]	49[i]

[a] H-ZSM5, SiO_2/Al_2O_3 = 46/1.

[b] *n*-Hexane treatment time ca. 30 min.

[c] GC–MS analysis of products from zeolite by dissolution/solvent extraction.

[d] Total carbon number range in brackets.

[e] Alkylcyclohexenes.

[f] Indanes only.

[g] Mainly C_{13}.

[h] Including some tetrahydrophenanthrenes and some anthracenes.

[i] Alkyl-CPD-dimers (C_{15}–C_{19}) and alkyl-CPD-trimers (C_{21}–C_{23}).

TABLE 4

Products from H–ZSM5 Treated with Cyclopentadiene (CPD)[a,b]

Treatment temperature (K)	Residue (R) or gas (G)	Products (wt%)								
		Alkanes, cyclo-alkanes	Alkyl-benzenes	Alkyl-indanes	Alkyl-tetralins	Alkyl-naphthalenes	Alkyldihydro-naphthalenes	Alkyl-phenan-threnes	CPD-dimer	Other products
393	R[c]	—	23(7–11)[d,h]	42(10)[r]	19(10)[k]	2(15)	—	—	11	3[e]
	G	61(6–12)	39(6–10)	—	—	—	—	—	—	—
453	R	13(6)	8(6–11)[h]	58(10)	20(10)[k]	1(10)	—	—	—	—
	G	—	10(6–8)	8(9–10)[p]	7(10)[k]	—	—	—	42	33[f]
513	R	5(6)	29(6–10)[i]	18(9–10)[q]	10(10–12)[l]	18(10–13)[m]	12(11–13)[n]	—	—	8[g]
593	R	28(7–11)	18(7–9)[j]	1(10)[r]	—	34(10–13)[m]	1(11)	7(15–16)[o]	11	—

[a] H–ZSM5, $SiO_2/Al_2O_3 = 46/1$.

[b] CPD treatment time ca. 60 min.

[c] GC–MS analysis of products from zeolite dissolution/solvent extraction.

[d] Total carbon number range in brackets.

[e] Approx. comparable amounts of methylcyclopentadiene and dihydro-CPD-trimer.

[f] Approx. comparable amounts of indane, methyldihydroindane, trimethyltetrahydroindane methyldihydrotetralin, methylcyclopentadiene dimer, methylcyclopentene, plus small amounts of methylcyclopentadiene and 3-methylindene.

[g] Approx. comparable amounts of indane and 1-methylindene.

[h] Mainly methyl, C_4, C_5 substituents.

[i] Methyl, ethyl, C_3 substituents.

[j] Mainly methyl substituents.

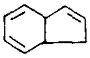
[k] Tetralin only.

[l] Mainly tetralin plus some dimethyltetralin.

[m] Mainly dimethylnaphthalenes.

[n] Mainly dimethyldihydronaphthalenes.

[o] Methyl substituents, and some anthracenes.

[p] Including some methylindene and C_1-C_3 derivatives of  or its nonaromatic double-bond shift isomer.

[q] Including some methylindene.

[r] Methylindane only.

have taken place during the nitrogen sweep at the treatment temperature at the end of the organic treatment). Nevertheless, some uncertainty remains about the validity of pore volume measurements made in this way for samples organic-treated at 393 K, and for these we have only retained pore volume values which are very low com-

TABLE 5

Products from H–ZSM5 Treated with Cyclopentadiene Dimer (Dicyclopentadiene)[a,b]

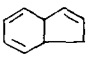
Treatment temperature (K)	Products in zeolite[c] (wt%)							
	Alkanes, cyclo-alkanes	Alkyl-benzenes	Alkyl-indanes	Alkyl-tetralins	Alkyl-naphthalenes	Alkyldihydro-naphthalenes	Alkyl-phenanthrenes	CPD
393	38(6–11)[d]	9(7–8)	28(10)[g]	24(10)[e]	1(10)	—	—	—
453	6(6)	10(7–10)	54(10–11)[f]	24(10)	6(10)	—	—	—
513	5(6)	28(6–10)	14(9–10)[f]	5(10–11)[f]	25(10–13)	23(11–13)	—	—
593	—	31(6–10)	—	—	42(10–13)[h]	13(11–12)[i]	7(15–17)[i]	7

[a] H–ZSM5, $SiO_2/Al_2O_3 = 46/1$.

[b] CPD-dimer treatment time ca. 60 min.

[c] GC–MS analysis of products from zeolite dissolution/solvent extraction.

[d] Total carbon number range in brackets.

[e] About one-third consists of methyl derivatives of  or its nonaromatic double-bond shift isomer.

[f] Mainly C_{10}.

[g] Methylindane only.

[h] Mainly methyl and dimethylnaphthalene.

[i] Methyl substituents and some anthracenes.

pared to those of untreated zeolite (that is, for which organic desorption is demonstrably negligible).

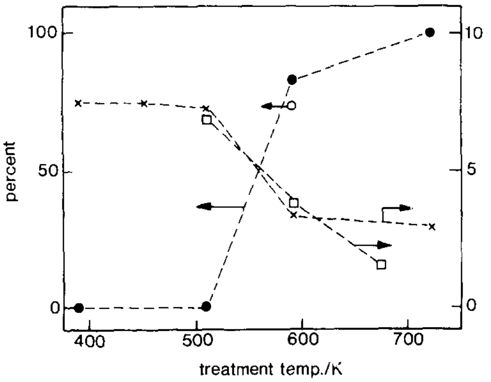


FIG. 2. Dependence of fraction of void space and amount of organic deposit on conditions of treatment of H–ZSM5 with 1-hexene. H–ZSM5, SiO_2/Al_2O_3 = 46/1: (●) percentage void space, treatment at indicated temperature for 60 min; (×) weight percentage organic deposit, treatment at indicated temperature for 60 min; (○) percentage void space, treatment at 513 K for 60 min followed by 593 K for 60 min. H–ZSM5, SiO_2/Al_2O_3 = 46/1, surface deacidified: (□) weight percentage organic deposit, treatment at indicated temperature for 60 min, surface deacidification at 873 K, $p^0_{SiCl_4}$ = 1.04 kPa, 1 min.

DISCUSSION

Treatment with 1-Hexene at ≤393 K

There is generally a reasonable agreement between the results contained in Tables 1 and 2 concerning the nature of the products retained by the H–ZSM5 after treatment with 1-hexene at ≤393 K. In agreement with van den Berg *et al.* (*19*) who used NMR to examine the oligomerization of $C_2^=$–$C_5^=$ olefins over H–ZSM5 at 300 and 375 K, the present work shows at 353 and 393 K reaction of 1-hexene led to retained material that was very largely paraffinic, C_8–C_{15}, with a distribution maximum at C_{12}. The present NMR data suggest some chain branching at both 353 and 393 K in agreement with previous data at 373 K (*19*). Table 1 shows that paraffinic and olefinic products with carbon number >6 were returned to the gas phase, together with cracked products with carbon number ≤5.

Although the retained alkane product at 393 K was dominated by the dimer C_{12}, the distribution of product carbon numbers in both retained and gaseous products clearly shows the occurrence of cracking together with oligomerization.

TABLE 6

Products from Surface-Deacidified H–ZSM5 Treated with 1-Hexene[a,b]

Treatment temperature (K)	U (H–ZSM5 untreated) or DA (H–ZSM5 deacidified)	Products[c] in zeolite (wt%)								
		Alkanes, cyclo-alkanes	Alkyl-cyclopenta-dienes	Alkyl-benzenes	Alkyl-indanes/indenes	Alkyl-dihydro-naphthalenes	Alkyl-tetralins	Alkyl-naphthalenes	Alkyl-phenanthrenes	CPD dimer
513	DA	8(7–9)	80(8–17)[d]	10(8–10)	2(11)	—	—	—	—	—
	U	6(7–15)	83(10–17)[e]	10(8–13)[f]	1	—	—	—	—	—
593	DA	—	24(8–10)	9(7–10)	36(11)[g]	3(11)	—	—	—	28
	U	—	7(7–12)[h]	2(10–13)	39(11–17)[i]	—	—	40(11–15)[j]	12(14–17)[k]	—

[a] S_{DA} = 98%, starting material H–ZSM5, SiO_2/Al_2O_3 = 46/1.

[b] 1-Hexene treatment time ca. 30 min.

[c] GC–MS analysis of products from zeolite dissolution/solvent extraction.

[d] Total carbon number range in brackets.

[e] Mainly C_{12}–C_{16}.

[f] Mainly C_{10}–C_{13}.

[g] Including small amount of C_{11} indene.

[h] Mainly C_7–C_9.

[i] Indanes and indenes in comparable amounts.

[j] Mainly C_{12}–C_{14}.

[k] Including some tetrahydrophenanthrenes and some anthracenes.

The substantial amounts of alkylbenzenes (C_7–C_{12}) in the gas phase product from 1-hexene at 393 K (Table 1) is, we suggest, closely linked to alkane formation, with the alkylbenzenes being the end products of hydrogen abstraction reactions required for the conversion of olefins to alkanes. The thermodynamic feasibility of this may be demonstrated by considering an archetypal reaction from 1-hexene (e.g., proceeding via acid-catalyzed hydride transfer and cyclization)

$$4C_6H_{12} \rightleftharpoons C_6H_6 + 3C_6H_{14} \qquad (1)$$

for which the equilibrium constant, K_p, at 393 K is 3.3×10^6 (literature data (*20*)).

The retention of the paraffinic product with the catalyst and the rejection of the associated dehydrogenation products into another phase are the opposite of those encountered in normal conjunct oligomerization/polymerization from olefins (*21*) and are probably because the pore structure of the H–ZSM5 (ca. 0.59-nm-diam channels) is sterically more accessible to the paraffinic products than to the aromatics. By contrast, oligomerization/reaction of ethylene over REX zeolite (ca. 0.8-nm diam windows to 1.3-nm diam cages) at 422–486 K (*1*) resulted in paraffins being returned to the gas phase, and the bulkier aromatics exclusively retained in the zeolite. Even so, the disposition of hydrogen donor and hydrogen acceptor products with H–ZSM5 is variable and dependent on reaction conditions: for example, the data of Table 1 show that at higher temperatures and as their carbon number range becomes lower, alkanes appear increasingly in the gaseous product.

Treatment with 1-Hexene at >393 K

Table 1 shows that as the treatment temperature increased above 393 K, higher molecular weight, unsaturated, cyclic products became of increasing importance in the retained component. In particular, alkylcyclopentadienes were the major residue product at intermediate temperatures (453 and 513 K), but were not detected as gaseous products. At 593 K alkylnaphthalenes and alkylindanes/indenes (and lesser amounts of alkylphenanthrenes) were the main residue products while in the gaseous products at this temperature alkylnaphthalenes and alkylbenzenes were the most significant components apart from cracked products.

That cyclopentadienes are an important class of intermediate is in general agreement with the conclusions of Barbier *et al.* (*10*) (reaction of cyclopentane over Pt/Al_2O_3(Cl) and of Mercier des Rochettes *et al.* (*11*) (reaction of cyclopentene over silica–alumina/REX zeolite).

However, it is now clear that, with an olefin rectant (e.g., 1-hexene), H–ZSM5 can readily form cyclopentadienes at temperatures more than 200 K below those at which they were observed from cyclopentene over the silica–alumina/REX zeolite (*11*), and that a C_5-cyclic olefin is not a required reactant. We ascribe the previous failure to observe cyclopentadienes from 1-hexene (*11*) to reliance on analysis of only the gaseous product.

The formation of cyclopentadienes from 1-hexene over H–ZSM5 probably proceeds via adsorbed (alkyl)cyclopentenyl carbocations (in effect, protonated cyclopentadienes), which have been identified by Vedrine *et al.* (*22*) by UV spectroscopy following the adsorption/oligomerization of $C_2^=$–$C_4^=$ olefins at room temperature on H–ZSM5. Starting with 1-hexene, oligomerization, cracking, skeletal isomerization, and double-bond shift are all facile acid-catalyzed reactions, and the formation of alkylcyclopentadienes may be formulated via cyclization from an alkylpentadienyl carbocation, the latter being formed via diolefin. Because cracking accompanies oligomerization (cf. cracked products returned to the gas phase, Table 1), a range of sizes is expected for the alkyl substituent, while extensive chain branching in the olefinic precursors may occur leading to more than one alkyl substituent.

The formation of cyclopentadiene from

cyclopentene by a hydrogen donor/acceptor process

$$2\ \text{cyclo-}C_5H_8 \rightleftarrows \text{cyclo-}C_5H_6 + \text{cyclo-}C_5H_{10} \quad (2)$$

is thermodynamically favorable at these temperatures (equilibrium constant for reaction (2) equals 3.1 at 450 K; literature data (*20*)).

Alkylbenzenes occur at all temperatures but in relatively modest amounts (Table 1): their mode of occurrence does not parallel that of higher aromatics.

There are two possible routes to the formation of alkylbenzenes which would operate independently. The alkylcyclopentadienyl carbocation is known from UV spectroscopy (*22*) to undergo ring expansion at 373 K on H–ZSM5 to an alkylcyclohexenyl carbocation, and this can undergo further hydrogen abstraction at 373–473 K to generate alkylbenzene (*22*). Alternatively, alkylbenzenes may be formed by ring opening from alkylindanes/indenes (*23*). The mode of formation of naphthalenic and higher aromatics will be discussed subsequently.

Treatment with n-Hexane

The results in Table 3 for the composition of the residue from treatment of H–ZSM5 with *n*-hexane are broadly comparable with those from 1-hexene at similar temperatures (Table 1). The main differences are the recovery of some alkylcyclopentadiene dimers and trimers from the *n*-hexane reaction and the somewhat reduced amounts of higher aromatics and increased amounts of alkylbenzenes from n-hexane. Nevertheless, *n*-hexane clearly enters a similar reaction sequence as generated from 1-hexene, the initial step probably being hydride abstraction

$$X^+ + C_6H_{14} \rightarrow C_6H_{13}^+ + X\text{–}H \quad (3)$$

where the initiating species X^+ originates either from the olefin impurity or from a surface proton.

The reactivity of *n*-hexane at these temperatures is consistent with previous reports (*30*) for the catalytic conversion of *n*-hexane over H–ZSM5 at 673 K. Of course, reaction (3) is relatively difficult, so that the conversion of *n*-hexane is much less facile than 1-hexene and does not occur at lower temperatures.

Treatment with Cyclopentadiene and with Cyclopentadiene Dimer

The main products from the treatment of H–ZSM5 (393–593 K) with cyclopentadiene or cyclopentadiene dimer were alkanes/cycloalkanes (hydrogen acceptor products), alkylbenzenes, alkylindanes (largely methylindanes), tetralins (largely tetralin itself), and higher aromatics. In addition, some cyclopentadiene dimer was produced from the reaction of cyclopentadiene, and some cyclopentadiene from the reaction of cyclopentadiene dimer.

As the treatment temperature was increased (393–593 K, Tables 4 and 5), indanes decreased to negligible proportions in the residue, while higher aromatics (naphthalenes and phenanthrenes) increased from very low levels to become the main residue products. Alkylbenzenes were substantial residue products over the whole reaction temperature range, tending to increase somewhat in proportion at higher temperatures.

Particularly at higher temperatures, products tended to occur as alkyl derivatives of the parent of each class as a result of alkylation reactions. Cracking reactions generate a range of alkylating agents, while cracking in the alkyl substituents (cf. Ref. (*23*)) also leads to a range of substituent sizes, and probably contributes to the often dominant methyl substituents in the naphthalenes, dihydronaphthalenes, and phenanthrenes.

Methylindanes and tetralin. At short times (e.g., 15 min) at 393 K, only traces of products other than methylindanes and tetralin were found. The data in Fig. 1a, when extrapolated to zero treatment time, show that the initial products from the reac-

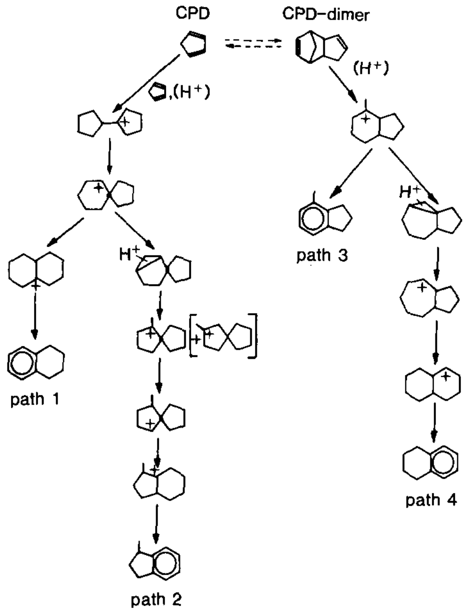


FIG. 3. Outline of acid-catalyzed skeletal conversions for the formation of methylindane isomers and tetralin from cyclopentadiene (CPD) and cyclopentadiene dimer (CPD-dimer). Except for the starting and terminal species, unsaturation is not explicitly shown, but double-bond migration will be facile. Most skeletal conversions involve more than one elementary step. For the involvement of protonated cyclopropane intermediates (rather than primary carbonium ions), and for cyclo-C_7 carbonium ions, see review in Ref. (*29*).

tion of cyclopentadiene dimer consisted of tetralin (~50%) and methylindanes of which ~85% was 4- and 5-methylindane. However, the initial products from cyclopentadiene (Fig. 1b) consisted of tetralin (~35%) and methylindanes of which ~90% was 1- and 2-methylindane.

From both of these reactants, alkylbenzenes only appeared at higher treatment times in the manner of secondary products, suggesting that they were formed from C_5-ring opening in methylindanes/indenes.

The migration of a methyl group between the C_6 and C_5 rings in the indane/indene system in the presence of a Brønsted acid catalyst would be expected to be difficult, so the fact that different methylindane isomers were formed as initial products from cyclopentadiene and from its dimer, strongly suggests that they were formed by basically different reaction paths, although in both cases tetralin was an initial coproduct. In each case, the appropriate methylindane isomers and tetralin appear in a manner indicating common precursors (in particular, at this temperature 1- and 2-methylindanes are not initially formed to a significant extent from teralin, or visa versa), and on this basis Fig. 3 summarizes reasonable reaction pathways. (cf. Ref. (*29*) for involvement of protonated cyclopropane intermediates, and for cyclo-C_7 carbonium ions).

The formation of C_6-ring-substituted methylindanes from (protonated) cyclopentadiene dimer would be expected for a methyl substituent originating from the bridging methylene, and the manner of ring opening at the methylene bridge in Fig. 3 follows the mechanism for the conversion of α-pinene to dipentene (*21*) and norbornane to methylcyclohexane (*24*) and was suggested previously (*11*).

A spiro (4, 5)-C_{10} intermediate (cf. Fig. 3, path 2) has been suggested previously for the acid-catalyzed conversion of cyclopentene to octahydronaphthalene (*25, 11*) and, by analogy, for cyclopentadiene to tetralin (*10*). However, in the cyclopentene-based system (catalyst silica–alumina/REX zeolite, 573–723 K) it was proposed (*11*) that a C_5-substituted methylindane skeleton (as methyltetrahydroindane) was formed by ring contraction in an immediate precursor to octahydronaphthalene. In the present cyclopentadiene system (catalyst H–ZSM5) at 393 K, an analogous process is not responsible for the formation of C_5-substituted methylindane (cf. Fig. 3, path 2), although it may well become possible at higher temperatures.

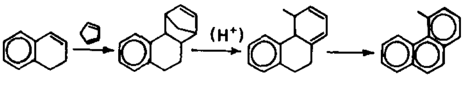
Reaction paths 1/2 and 3/4 (Fig. 3) are both accessible to cyclopentadiene and to cyclopentadiene dimer via the monomer–dimer interconversion (known to occur uncatalyzed and to be catalyzed by a range of catalyst types (*26*)).

Higher aromatics. Higher aromatics relating to the naphthalene or phenanthrene/anthracene systems tend to occur as alkyl (mainly methyl) derivatives (cf. Tables 4 and 5). The origin of the alkyl substituents is partly obscured by the likely occurrence of alkylation/side-chain cracking reactions (vide supra) which cannot be avoided at the higher temperatures required for the formation of higher aromatics. Nevertheless, at least with the phenanthrene/anthracene products, the most likely pathway for their formation (see below) necessarily requires the formation of a methyl substituent.

Naphthalenes can be formed from corresponding tetralins (or an immediate tetralin precursor, cf. Fig. 3) by conventional stepwise hydrogen abstraction reactions (*21*), and the intermediate (alkyl) dihydronaphthalenes, in fact, occur as significant products (Tables 4 and 5).

It is possible to formulate two general pathways for the formation of products of the phenanthrene/anthracene type (or larger) in a cyclopentadiene-based system. One depends on Diels-Alder cyclopentadiene addition and the second involves the conversion of methylindane/indene or tetralin related precursors via a spiro(4, 5)-C_{10} intermediate or its analog (cf. path 2, Fig. 3).

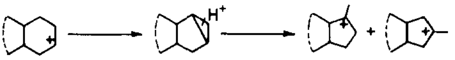
Starting with Diels-Alder cyclopentadiene trimer, the scheme outlined in Fig. 4a leads to methylanthracene. The steps involving ring opening at the bridging methylenes are the same as in path 3, Fig. 3, while the enlargement of the C_5 ring involves the same process as in path 4, Fig. 3. Furthermore, Diels-Alder addition of cyclopentadiene may occur at an isolated double bond, for instance from dihydronaphthalene



(4)

and is a general way in which a methyl-substituted C_6 ring may be added.

A spiro(4, 5)-C_{10} intermediate or its analog provides a general route for the generation of fused C_6 rings (*21*), and an archetypal reaction may be represented in Fig. 4b, starting for example with a C_5-ring-substituted carbocation from the methylindane/indene system (cf. path 2, Fig. 3). In this case, the relative stability of the tertiary carbonium ion at the methyl substituent in the indicated position would predicate the reaction toward methylphenanthrene rather than a methylanthracene. If the C_5 ring carried no methyl substituent, an analogous reaction may be written but without this discrimination between methylphenanthrene and methylanthracene products. Reference to Tables 4 and 5 shows that phenanthrene products were favored. This type of reaction has been suggested (*27*) for fusion to a C_6-ring carbocation, involving prior ring contraction to the starting structure in Fig. 4b, e.g.,



(5)

At the relatively high temperature required for the formation of higher aromatics, reaction (5) would be expected to occur, and

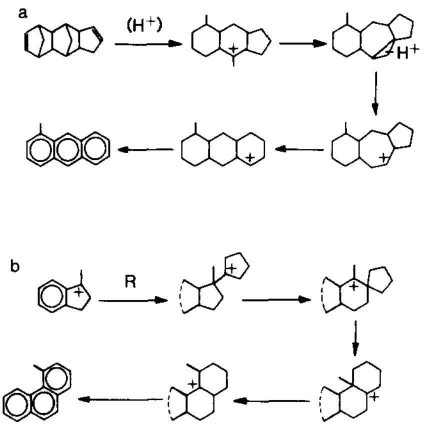


FIG. 4. Outline of acid-catalyzed skeletal conversions for the formation of tricyclic-fused ring aromatics from (a) cyclopentadiene trimer and (b) methyl-substituted C_5-ring carbocation (e.g., from the methylindane/indene system: reactant R could be cyclopentadiene or cyclopentene). Except for the starting and terminal species, unsaturation is not explicitly shown, but double-bond migration will be facile. Most skeletal conversions involve more than one elementary step.

this provides another general pathway for further C_6-ring-forming reactions from partly hydrogenated (incompletely dehydrogenated) aromatic precursors.

Zeolite Pore Blockage and Residue Location

The data in Fig. 2 show that the residue formed from 1-hexene at 393–513 K rendered the pores inaccessible to nitrogen sorption. In this temperature range the residue content of the zeolite was about 7.5 wt% and, assuming a residue density of 0.90 g cm^{-3} (average value for the main residue constituents), this corresponds to a specific residue volume of 0.083 cm^3 g^{-1} which is 55% of the specific pore volume (0.15 cm^3 g^{-1}). It is concluded therefore that the residue in this temperature range was nonuniformly distributed in the ZSM5 grains, being concentrated toward and on the outer surface so as to block the entire pore volume.

At 593–718 K (Fig. 2) the accessible pore volume was 85–100% of the total pore volume, while the residue content of the zeolite was about 3 wt%. Clearly this residue must have existed largely on the external surface of the zeolite and in a manner which left most of the entrances to the internal pore system open, since the rate of nitrogen adsorption equilibration was about the same as for untreated (residue-free) zeolite.

The data in Fig. 2 also show that if a residue was first deposited at 513 K (resulting in zero accessible pore volume), and the 1-hexene treatment temperature was then increased to 593 K, the resultant accessible pore volume was then about the same as would have been obtained by treatment entirely at 593 K: that is, increasing the treatment temperature from 513 to 593 K had caused the initial deposit to migrate so as to unblock the pore system.

We have no definitive evidence from which to decide if the pore-blocking residue formed at 393–513 K was in the pores, on the external surface or partly both. However, the following argument suggests that most was in the pores. Of the components identified in Table 1 for the residue formed at 393–513 K, most have 1 atm boiling points below about 550 K, and many are <500 K. Because of this, significant amounts of these components would not have accumulated at a free surface (e.g., external zeolite surface), so their retention with the zeolite implies their accumulation in the pores. We confirmed this argument by noting the difficulty, relative to the 1 atm boiling point, of removing organic compounds sorbed nonreactively into the pores of silicalite. The phenomenon of strong sorption into pores of molecular dimensions has been discussed quantitatively (*28*).

On the basis of the above conclusion, we propose that the unblocking of the pore system of 1-hexene-treated H–ZSM5 at ≥593 K was due to migration of residue out of the pores to the external surface where part was lost by evaporation, and part was converted into higher molecular weight, relatively involatile, products (retained on the external surface). These higher products were mainly higher alkylaromatics—e.g., C_{11}–C_{17} alkylnaphthalene and C_{15}–C_{17} alkylphenanthrenes at 593 K (Table 1)—and were presumably formed at the external surface rather than in the pores because of size/shape selectivity restrictions in the pores. Such restrictions are greatly relaxed in wide pore zeolites such as X- or Y-zeolites, which is clearly why with the latter higher aromatics were readily formed at high temperatures within the pores as well as on the external surface (*6*).

Treatment of Surface-Deacidified H–ZSM5 with 1-Hexene

The data in Table 6 for the reaction of 1-hexene show that at 513 K surface deacidification had no significant effect on the distribution of products in the residue: in both cases alkylcyclopentadienes were the strongly dominant component. On the other hand, at 593 K a very large difference in the component distribution was found:

surface deacidification resulted in a large decrease in the proportion of higher aromatics (naphthalenes and phenanthrenes/anthracenes) in the residue and an increase in the proportion of alkylcyclopentadienes. A similar trend with respect to higher aromatics was observed for the gaseous products, although at much lower levels of occurrence.

This difference in the content of alkylnaphthalenes and related compounds with surface deacidification confirms the model in which they are mainly formed on the external surface of the zeolite from alkylcyclopentadiene precursors. The latter can be formed from the 1-hexene reactant both within the pores and at the external surface. At lower temperatures the alkylcyclopentadienes merely accumulate in the pores. However, at higher temperatures (e.g., 593 K) they will be converted at the external surface (provided adequate acidic sites are present) free from size/shape selectivity restrictions to higher aromatics, for which purpose those alkylcyclopentadienes formed within the pores migrate to the external surface.

On this basis, it would be expected that deacidification of the external surface would reduce the amount of aromatic residue held externally, and this is confirmed by the data in Fig. 2 for residue produced at 673 K.

Reactions with 1-Hexene—Comments and Conclusions

Compared to the reactions from the cyclopentadiene/dimer system, the principal product classes from 1-hexene cover a wider range of carbon numbers, originating in larger and more numerous substituent groups. This probably arises from the facile oligomerization/cracking reactions of 1-hexene over H–ZSM5 which generate a spectrum of olefinic reactants which also can function as alkylating agents and hydrogen acceptors.

A relatively high concentration of hydrogen acceptor species clearly facilitates dehydrogenation to the final aromatic products, and this is probably the reason for the near absence of partly hydrogenated aromatics (e.g., tetralin and dihydronaphthalene) in the products from 1-hexene although these were readily found under comparable conditions in the products from the cyclopentadiene/dimer system, and the increased proportion of indenes relative to indanes found from 1-hexene reactant probably has its origin in a similar way.

That substantial indanes/indenes product only appeared at 593 K from 1-hexene, but was a major product at 393–513 K from the cyclopentadiene/dimer reactant system, we attribute to an expected increase in the rate of indanes/indenes formation resulting from the increased concentration of cyclopentadiene precursor when the latter is fed as reactant.

In general terms, a comparison between the products formed from 1-hexene and those from cyclopentadiene/dimer clearly indicates a reaction route for 1-hexene which passes via cyclopentadienes, indanes/indenes/tetralines, and by partly hydrogenated aromatics, leading to fused ring aromatic products. The main feature of the various steps have been discussed previously (cf. Figs. 3 and 4; reactions (4) and (5)). A rather complex network of reactions is involved, and this is summarized in Fig. 5 for product aromatics as high as fused ring tricyclics.

Two further explanatory comments are useful in relation to the reaction scheme in Fig. 5. First, although alkylcyclopentadienes may, in principle, form a nonaromatic coke via fulvene-type compounds using acid-catalyzed reactions, significant amounts of fulvene derivatives were not detected, leading to the conclusion that this route was not important under the present conditions. Second, it is also possible, in principle, for bicyclic aromatics to be formed in acid-catalyzed reactions from alkylbenzenes, the immediate precursor to ring closure being an alkylbenzene with an alkyl group, C_n ($n > 4$), and with the re-

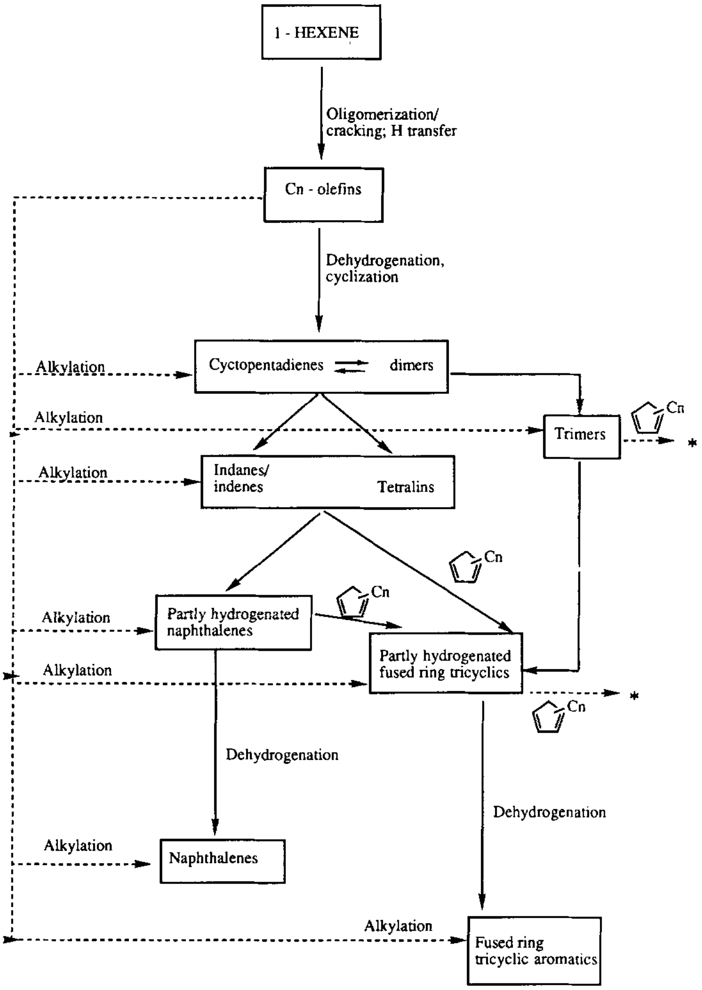


FIG. 5. Main features of reaction scheme for conversion of 1-hexene to fused ring tricyclic aromatics (phenanthrenes/anthracenes). Subsidiary products from hydrogen donor or acceptor reactions not shown explicitly. Entry points to paths leading to fused ring tetracyclic aromatics are indicated with *.

quired alkylbenzenes being formed by cyclization from, say, hexene dimer. However, under the present conditions alkylbenzenes were never more than quite modest components in the residue products (cf. Table 1): thus, although a contribution from this route cannot be totally ruled out, we believe that, on balance, its contribution could not have been other than relatively small.

Size/shape selective effects appear to operate in the formation of higher aromatics from 1-hexene over H–ZSM5. Products in the naphthalene and phenanthrene/anthracene systems were mainly formed at 593 K on the external surface of the zeolite. Phenanthrene (or any of its alkyl derivatives) could not be accommodated within the H–ZSM5 channel structure nor could, for instance, 1-methylanthracene (but 2-methylanthracene could be accommodated). Furthermore, there would be steric impediments within the channels to the processes in Fig. 4 and in reaction (4), made more severe when, as in the case with products from 1-hexene, the species are fairly heavily alkylated. This effect also operates in the naphthalene system. While naphthalene and, for instance, 2-methylnaphthalene are readily accommodated within the channels, more extensive alkylation leads to molecules which cannot be so accommodated, nor could the corresponding processes for their formation occur (cf. Fig. 3).

Results presented in previous sections indicated that alkylcyclopentadienes were formed from 1-hexene and accumulated within the H–ZSM5 channels. While the reaction of cyclopentadiene itself to yield tetralin or 1-methylindane could probably proceed within the channel structure (particularly using the channel intersections), it seems very probable that the conversion of alkylcyclopentadienes to the corresponding alkyltetralins or alkylindanes/indenes could not occur within the channels, but would require prior migration of the alkylcyclopentadienes to the external surface of the zeolite.

Finally, attention should be drawn to the hydride-transfer processes which are vital components of most of the reactions elaborated in previous sections. There is already evidence (*31*) that higher molecular weight (presumably unsaturated) hydrocarbon condensation products formed in acid-catalyzed reactions act as co-catalysts by mediation in hydride-transfer (e.g., as hydride "hand-on" intermediates). This would imply some degree of auto-catalysis and the existence of a quasi-induction period (as originally observed (*31*)), but the nature of our experiments precluded the observation of an induction period, even if present. Nevertheless, the existence of some such assisted hydride-transfer pathway may enable the residue-forming reaction on a solid acid catalyst to be propagated to a greater product depth than would otherwise be possible with normal limitations on transport through the product layer.

ACKNOWLEDGMENTS

The authors are grateful to T. Mole for advise in the preparation of the manuscript, to K. G. Wilshier and T. Behrsing for assistance with the reactor system, and to H. K. A. Jaeger and G. W. West for providing electron microscopy and NMR, respectively. The authors are also grateful to one of the referees for kindly providing some additional mechanistic insights.

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