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Reaction Pathways for the Conversion of Methanol and Olefins on H-ZSM-5 Zeolite

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The conversions of methanol, dimethyl ether, ethylene, propene, 1-butene, and 3,3-dimethyl-1-butene by reaction on various H-ZSM-5 catalysts at 370–380°C demonstrate the importance of a carbenium ion mechanism in the formation of various aliphatic (C_1–C_6) and aromatic (C_6–C_{10}) hydrocarbons. C_2–C_4 olefin reactions occur in a way very similar to the classical conjunct polymerization of olefins. The initial step in the formation of aromatics is a "concerted" cycloaddition of an olefin and a carbenium ion which is favored by the unique structural properties of the zeolite. From correlations between the Si/Al ratio and yields in aromatics and C_4 aliphatics, it is proposed that strong acid sites are responsible for the dehydrocyclization of C_{6+} olefins into aromatics. Some evidence is also presented for alkylation reactions. Some of the unique properties of H-ZSM-5 are apparently due to the combination of strongly acidic and molecular sieving properties.

INTRODUCTION

Well-established and large-scale industrial processes that utilize zeolite-based catalysts are catalytic cracking, some hydrocracking processes, and paraffin isomerization. Recently, a number of new families of molecular sieves has been discovered among which the ZSM-5 family, developed by Mobil Corporation, has been the starting point to unique catalysts for a variety of processes. Apart from the methanol-to-gasoline process (*1*, *2*) which is not yet of commercial application, the major processes which are the closest to becoming firmly established commercially are the isomerization of xylenes (*3*), the disproportionation of toluene (*4*), and the synthesis of ethylbenzene (*5*, *6*).

When methanol or ethanol (*1*, *2*) and lower olefins (*7*, *8*) are converted to higher compounds on the protonated form, H-ZSM-5, of the zeolite, aromatic hydrocarbons may represent more than 30–35% of the total hydrocarbon yield with a neat selectivity toward the formation of C_7 and C_8 aromatics. It was also noticed that ethylbenzene could be partially converted to benzene (*9*), the proposed mechanism being that ethylene cracked from the ethylbenzene is "reassembled" into benzene. Both the industrial interest and the mechanistic aspects have then stimulated the present investigation which aims to clarify among others some of the possible reaction pathways leading to aromatic hydrocarbons.

Our investigation of the methanol conversion on the H-ZSM-5 zeolite, by gas chromatography (*2*, *14*) and ^{13}C-NMR (*2*, *11*, *14*), led us to propose a carbenium ion mechanism to account for the formation of higher aliphatics and aromatics (*2*). Some additional support for such a mechanism is found in a detailed characterization of the Brønsted and Lewis acidic properties of the zeolite (*10*) by infrared spectroscopy, electron spin resonance, microcalorimetry, and in the recent proposal that acidic zeolites behave as ionizing solvents (*13*).

By dehydration, methanol is succes-

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sively converted into dimethyl ether and a C_2 surface species from which ethylene can be desorbed. This surface species is thought to be a carbenium-ion-like intermediate which by further reaction with methanol or gaseous ethylene can yield C_3 and C_4 surface species. The latter may then undergo oligomerization, isomerization, cyclization, dehydrogenation (to aromatics), and hydrogenation (to saturated aliphatics) leading to the final products. Molecular sieving effects (*16*) and selective cracking (*7, 16*) by this type of material have been firmly assessed. Our proposal is close to that recently put forward by Ahn *et al.* (*20*) but it certainly is basically different from that of Anderson *et al.* (*21*). Our mechanism also differs from the carbene-type and from the radical mechanism put forward by other groups (*1, 15*).

In this paper, we first describe how a carbenium ion mechanism accounts in part for the high selectivity into aromatic hydrocarbons obtained from the conversion of methanol. Second, it is shown that reactions between lower olefins provide additional support for reaction pathways involving carbenium ion–olefin additions. Finally, alkylation reactions which are also catalyzed by acid sites are considered.

EXPERIMENTAL

Materials

Methanol, dimethyl ether, ethylene, propene, but-1-ene, 3,3-dimethyl-but-1-ene, and benzene were high-purity-grade commercially available reagents and were used without further purification.

Catalysts

The catalysts were prepared as previously described (*2*). Four different types of H-ZSM-5 zeolites were obtained, depending on the method used for protonation (*32*). Chemical analyses are given in Table 1. Average crystallite sizes for all catalysts were almost identical and in the range 2.5–3.5 μm as measured by electron microscopy.

TABLE 1

H-ZSM-5 Samples Used

ZSM-5 samples	Acidification	Chemical formula[a]
H-ZSM_1-5	0.5 *N* HCl	$Na_{0.1}H_{4.7}Al_{4.8}Si_{91.2}O_{192} \cdot 12H_2O$
H-ZSM_2-5	2 *N* HCl	$Na_{0.2}H_{3.2}Al_{3.4}Si_{92.6}O_{192} \cdot 16H_2O$
H-ZSM_3-5	NH_4NO_3[b]	$Na_{0.2}H_{4.6}Al_{4.8}Si_{91.2}O_{192} \cdot 14H_2O$
(Na, H)-ZSM_4-5	None	$Na_{0.3}H_{0.9}Al_{1.2}Si_{94.8}O_{192} \cdot 17H_2O$

[a] Data obtained from chemical analyses of Na and Al, the number of Si + Al atoms per unit cell being taken equal to 96, according to Ref. (*18*).

[b] Followed by decomposition at 500°C.

Apparatus and Procedure

A fixed-bed continuous-flow microreactor was used with 0.1 g of catalyst. The vapor phase of the thermostated liquid reagents was carried through the catalytic bed by using nitrogen as vector gas. Gaseous reagents were mixed directly with the nitrogen flow to achieve the desired space velocity. The reactor temperature was 370°C. After 20 min, the reaction products were analyzed on-line by gas chromatography using flame-ionization detection and two separation columns in sequence, namely, polar diglycerol on a Chromosorb column followed by a squalane column. Temperature programming was from 40 to 100°C leading to an elution time of about 150 min for C_9 compounds such as 1,2,4-trimethylbenzene. Although convenient, this analytical approach has some limitations. The main one certainly consists in the lack of separation of the *meta*- and *para*-xylene isomers. Calibration (retention times and response factors) was performed with pure compounds as standards, leading to satisfactory carbon balances for the products with respect to the amount of C atoms in the reagents. This indicated that coking of the catalyst was not important. In the case of ethylene, however, discrepancies were eventually observed showing the deposition of carbonaceous species on the zeolite.

RESULTS

The Conversions of Methanol and Dimethyl Ether

At 370°C, methanol (and dimethyl ether) are converted with a rather considerable selectivity to higher hydrocarbons: about ten products (mainly the lower aliphatics, xylenes, and toluene) account for 85% of the hydrocarbons formed. Moreover, *meta*- and *para*-xylene represent about 65% of the aromatic hydrocarbons of which the others are mainly 1,2,4-trimethylbenzene (10.5%), ethyl-toluenes (8.4%), and toluene (7.4%). Table 2 shows a typical analysis of the products.

TABLE 2

Selectivity in the Methanol Conversion over H-ZSM-5 Zeolite

Catalyst: H-ZSM_1-5 (0.102 g), Methanol WHSV: 10.27 hr^{-1}, Conversion[a]: 81.2%, Temp.: 372°C

Products	Distribution (%)[b]
Propene and propane	32.1
Ethene and ethane	18.1
But-1-ene and isobutene	7.8
But-2-enes	8.1
Isobutane	7.7
m- + *p*-Xylenes	6.2
Isobutane	3.8
Other products	16.2

Selectivity into Aromatic Hydrocarbons for the Methanol Conversion on H-ZSM-5 Zeolite

Catalyst: H-ZSM_1-5 (0.102 g), Methanol WHSV: 10.27 hr^{-1}, Conversion[a]: 81.2%, Aromatization[c]: 9.5%, Temp.: 372°C

Products	Distribution (%)[d]
Benzene	Tr
Toluene	7.4
Ethylbenzene	4.2
m- + *p*-Xylene	65.3
o-Xylene	4.2
(*m* + *p*)-Ethyltoluenes	8.4
1,2,4-Trimethylbenzene	10.5

[a] In carbon atoms.

[b] Percentages (in carbon atoms) in total amount of hydrocarbons obtained.

[c] Percentage (in carbon atoms) of aromatics in total amount of hydrocarbons.

[d] Percentage (in carbon atoms) in total amount of aromatics.

In an investigation of the aromatization mechanism, the most significant information is obtained from the variation in the distribution of hydrocarbons as a function of the degree of conversion (see Fig. 1). Olefins are the major products at low conversion. For conversions higher than 50%, the amount of olefins decreases abruptly while paraffins (mainly i-C_4 and i-C_5) and aromatics appear simultaneously. It is concluded that the initial products are olefins which are, in turn, converted to higher hydrocarbons by hydrogen transfer and cyclization reactions (i.e., dehydrocyclization).

Table 3 and Fig. 2 shows that aromatics are essentially obtained by reactions between the lower olefins (ethylene, propylene, and butenes) formed with high yields in the early stages of the reaction. It is worth noting that the C_2 hydrocarbon concentrations (of which ethylene is the major compound (*1*) stays constant up to a degree of aromatization of 20%, while the propene concentration first increases (up to 33% of the hydrocarbons formed) and further decreases when aromatics are formed. At a

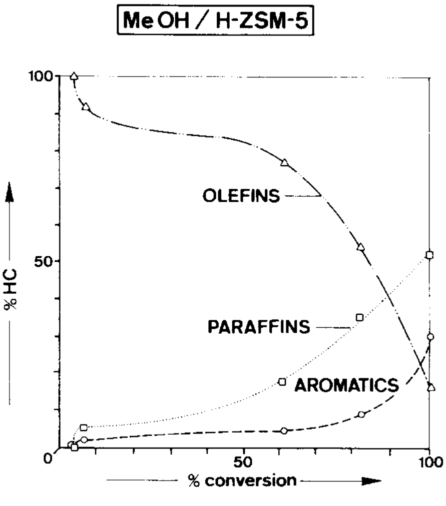

FIG. 1. Zeolite-catalyzed methanol conversion; olefins, paraffins, and aromatics concentrations vs degree of conversion (370°C).

TABLE 3

The Conversion of Methanol with H-ZSM-5 Zeolites of Various Si : Al Ratio

	Catalyst								
	H-ZSM$_4$-5	H-ZSM$_4$-5	H-ZSM$_4$-5	H-ZSM$_3$-5	H-ZSM$_2$-5	H-ZSM-5 (Ref. (*1*))	H-ZSM$_1$-5	H-ZSM$_1$-5	H-ZSM-5 (Ref. (*1*))
Si : Al	79	79	79	19	27.2	—	19	19	—
Temperature (°C)	372	372	372	378	380	371	372	372	371
WHSV (hr^{-1})	11	2	0.7	11	11	—	10[f]	10	—
LHSV (hr^{-1})	—	—	—	—	—	108	—	—	1
Methanol[a]	51.4	32.6	18.0	4.0	10.3	31.9	6.6	11.0	—
Dimethyl ether[a]	44.9	60.7	21.6	2.0	10.6	46.3	7.5	7.8	—
Hydrocarbons[a]	3.7	6.7	60.4	94.0	79.1	21.8	85.5	81.2	100.0
Aromatics[b] (wt%)	0.5	2.1	4.6	4.8	5.4	6.6	6.7	9.1	41.1
Olefins[b] (wt%)									
Ethylene[c] and ethane	13.6	15.9	13.2	17.6	16.9	13.6	13.5	18.1	2.2
Propene and propane	33.0	31.9	35.6	36.1	35.5	29.2[d]	34.5	32.1	17.2[e]
Butenes	49.9	43.3	21.9	20.5	19.5	15.8	19.2	15.9	1.3
Pentenes	3.0	3.7	6.0	5.7	6.2	—	5.5	4.6	—
C_4 saturated aliphatics									
Isobutane	0	0	2.8	4.5	4.4	6.5	7.1	8.0	18.7
n-Butane	0	0	0	1.2	1.3	1.3	1.5	1.7	5.6

[a] Weight percentages in the total product fraction (H_2O excepted).

[b] Weight percentages in the total amount of hydrocarbons.

[c] No separation between these C_2 compounds. Note however that the amount of ethane should be small (Table 4 of Ref. (*1*)).

[d] 26.7% of propene.

[e] 1.0% of propene.

[f] Conversion of dimethyl ether.

very low degree of aromatization, the butenes are the major products (50% of the hydrocarbons); however, they disappear very sharply when saturated aliphatics (mainly isobutane) and aromatics appear. The C_{5+} olefins show a maximum in concentration (6% in the products) when aromatization is at about 5%. A similar reaction pattern is obtained from the data shown in Fig. 3, where the amounts of C_3 and C_4 olefins relative to ethylene (of which the concentration is almost constant for degrees of aromatization below 20%) are plotted as a function of the total yield in toluene and xylenes. It further demonstrates that the C_7 and C_8 aromatic compounds are directly obtained from the lighter olefins, namely, from propene and butenes.

Although these data were obtained using different zeolite catalysts, it is believed that this interpretation is sound in view of the analogy with the data reported earlier (*1*). It is also supported by the data plotted in Fig. 4 which show that the aromatic and C_4 aliphatic product concentrations depend closely on a well-defined parameter, namely, the percentage of aluminum ions in lattice cationic sites. The latter should somehow reflect the acidity of the catalyst.

The Conversion of Olefins

The reactions of ethylene, propene, but-1-ene, and 3,3-dimethyl-but-1-ene have also

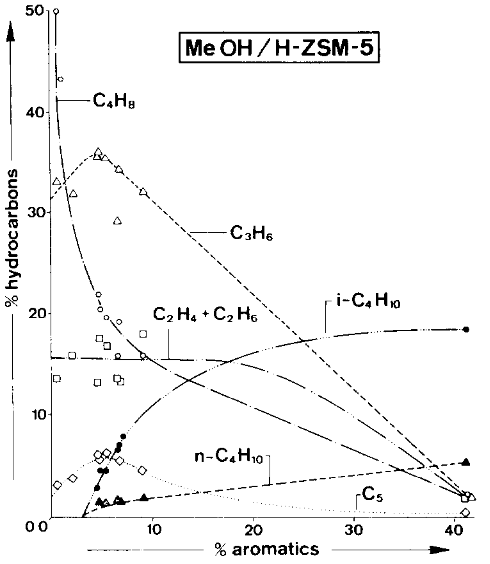

FIG. 2. Zeolite-catalyzed methanol conversion (370°C); C_2–C_5 olefins and C_4 paraffins concentrations vs degree of aromatization.

been investigated on the H-ZSM-5 catalyst in conditions identical to those used for the methanol conversion.

Experimental data are summarized in Table 4 and confirm the results already obtained from the methanol conversion. The major olefinic products are propene and butenes while the aromatic hydrocarbons essentially consist of xylenes and toluene. In order to present the data of Table 4 in a uniform manner, as different olefins were used, the aromatics distributions are calculated as relative amounts with respect to the yields of *para-* and *meta*-xylene observed in each case.

The same data also show that, in the same temperature and space velocity conditions, propene is much more reactive than ethylene, in agreement with previous data (*20–22*).

The Alkylation of Benzene by Dimethyl Ether

In order to investigate the importance of alkylation reactions, which should occur on such an acidic catalyst (*17*), the reaction of dimethyl ether in the presence of net excess of benzene ($p_{C_6H_6}/p_{CH_3OCH_3} = 10$) has been studied. As shown in Table 5, a large amount of C_{7+} aromatics is formed of which the major products (toluene, xylenes) are showing the occurrence of direct benzene methylation.

It is also worth noting the unusual occurrence of large amounts of ethyltoluene, ethylbenzene, and propylbenzene.

DISCUSSION

The Carbenium Ion Mechanism

The analogies between the conversion of methanol and ethanol (*2*) led us to propose (*2, 14, 19*) a carbenium ion mechanism for the upgrading of the hydrocarbon chain and the formation of higher hydrocarbons based on a common initial intermediate, i.e., ethylene, as produced by the dehydration of methanol and/or dimethyl ether or of course ethanol.

However, patent literature (*22*), recent data (*20, 21*) and our present data (see Table 4) definitely prove the lower reactivity of ethylene when compared to propylene or methanol in the same reaction condi-

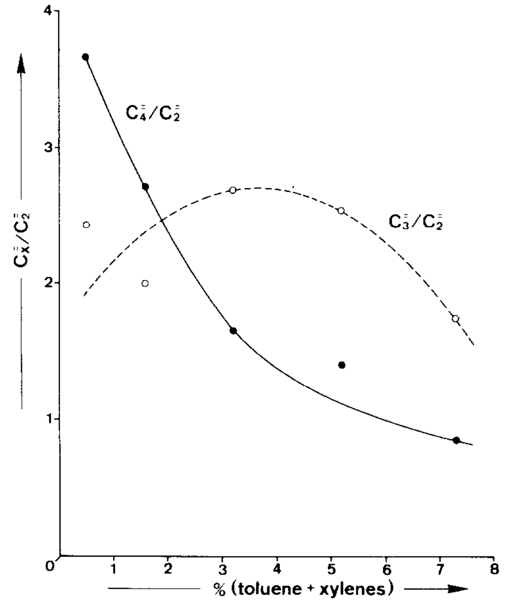

FIG. 3. Zeolite-catalyzed methanol conversion (370°C); relative amounts to ethylene of propene and butenes vs the total yield in toluene and xylenes.

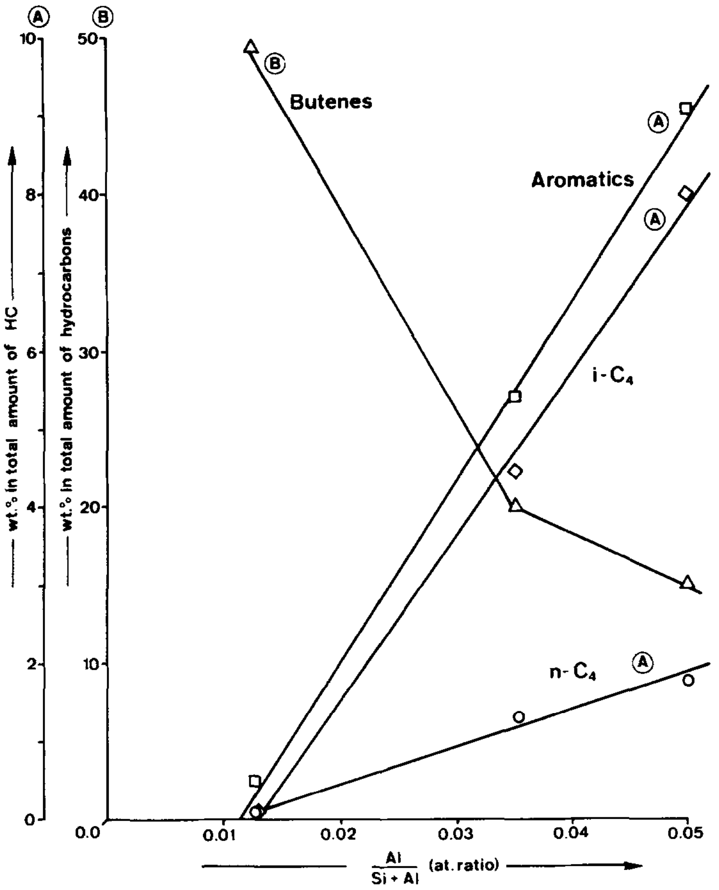

FIG. 4. Zeolite-catalyzed methanol conversion; butenes, isobutane, butane, and aromatics concentrations as functions of the Al/(Si + Al) ratio. (T = 370–380°C; WHSV = 10–11 hr^{-1}.)

tions. Therefore, it is most unlikely that *gaseous* ethylene is part of the consecutive reaction network as originally proposed (*2, 14, 19*).

Infrared, NMR, and thermogravimetry data (*23*) support the proposal that ethylene, being protonated by Brønsted acidic sites, can form a carbeniumlike surface species, which can react further with the formation of higher-molecular-weight oligomers.

It is now believed that a suitable and descriptive reaction sequence is that of Scheme I which accounts for all the related experimental results.

An ethyl-carbenium ion[2] is formed initially, which can either desorb as ethylene or react with methanol or dimethyl ether (leading to ethylmethyl ether) or ethylene (to form a butenyl-carbenium ion). The former data and our results (*1, 20–23*) imply clearly that:

(i) further reaction of the ethyl-carbenium ion with either methanol (or dimethyl ether) or ethylene is faster than its desorption as gaseous ethylene;

(ii) the desorption of ethylene is faster than its reactive chemisorption;

(iii) a C_2-surface species may play, as described, an important role as common intermediate.

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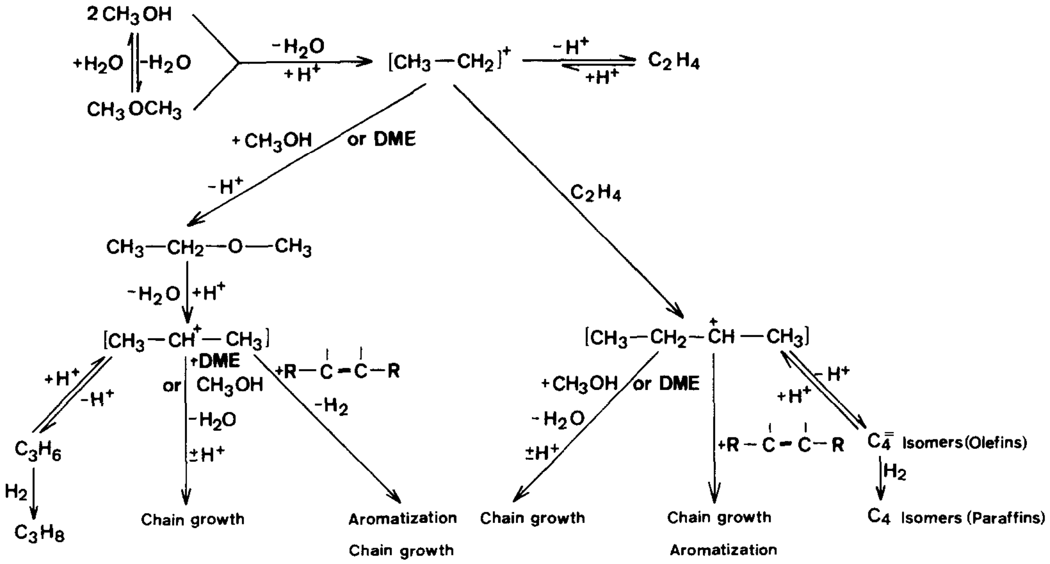
[2] By this term we mean to describe and refer to a CH_3–$CH_2^{\delta+}$–$O^{\delta-}$–R surface species which may be an intermediate between an ethyl-carbenium ion, a surface ethoxy group (CH_3–CH_2–O–zeolite), or an ethoxy group in a molecule adsorbed on the zeolite surface.



SCHEME I

This scheme also accounts for the observation that lower olefins can be synthesized in larger relative amounts on other materials of lower acidity (*20*) or on ZSM-5-based catalysts provided that their acidity is moderated by various promoters or by water addition in the methanol feed or by steaming of the catalyst (*24*).

Propene and butene are formed from the C_2-surface species. A similar mechanism may hold for the formation of the higher-molecular-weight olefins. For example, a C_5 olefin may be formed from a C_4-surface species by reaction with methanol and dehydration or from a C_3-surface species by ethylene addition.

The data in Table 4 also imply that the lower olefins may react, *in the absence of water* (which may sometime be present as a cofeed compound or because of an alcohol dehydration), by a C_1-step increase of the hydrocarbon chain: ethylene gives mainly propylene and propylene forms essentially butenes. This, of course, points out the existence of cracking reactions which are of importance if the acidity of the zeolite is not moderated.

Propylene could be formed from ethylene according to the following schematic reaction:

$$3\ C_2H_4 \rightarrow [C_6H_{12}] \rightarrow 2\ C_3H_6$$

and propylene could lead to butene by

$$4\ C_3H_6 \begin{cases} \nearrow 3\ C_4H_8 \\ \searrow 2\ C_4H_8 + 2\ C_2H_4 \end{cases}$$

the above reactions being quoted as examples only.

The occurrence of carbenium-ion-type reactions can also be ascertained by using other reactants. For example, in the same reaction conditions, we have observed that 3,3-dimethyl-but-1-ene is readily isomerized to 2,3-dimethyl-but-1-ene (by a methyl rearrangement) and 2,3-dimethyl-but-2-ene (through both methyl and double-bond migrations) and cracked to form large amounts of light olefins (mainly propene and butenes, 19 and 46%, respectively). A carbenium ion mechanism also explains these observations as shown in Scheme II. The carbenium ion from 3,3-dimethyl-but-1-ene is rearranged by a methyl shift into a more stable tertiary cation. The latter, by proton release, leads to the two olefinic C_6 isomers while, by cracking, propene is

TABLE 4

The Conversion of Olefins over H-ZSM-5 Zeolites[a]

	Reagent					
	Ethylene	Ethylene	Propene	But-1-ene	3,3-Dimethyl-but-1-ene	Methanol
Catalyst (0.1 g)	H-ZSM$_1$-5	H-ZSM$_1$-5	H-ZSM$_1$-5	H-ZSM$_2$-5	H-ZSM$_1$-5	H-ZSM$_1$-5
Temperature (°C)	373	372	372	379	370	372
WHSV (hr^{-1})	4.24	4.24	6.96	6.63	—	10.27
Conversion degree (%)[b]	1.7	9.2	58.0	44.8	—	81.3
C_2–C_5 olefins distribution[c] (%)						
Ethylene	95.5	92.2	3.0	1.9	1.4	25.7
Propene	1.4	4.1	50.0	27.9	18.9	45.3
Butenes	0.1	3.0	38.4	59.1	45.6	22.5
Pentenes	0.0	0.7	8.6	11.1	34.1	6.5
Aromatics distribution[d] (%)						
Benzene	—	0.8	2.0	5.5	3.9	0.3
Toluene	33.3	22.9	27.1	27.5	15.2	7.5
Ethylbenzene	26.7	16.7	12.8	10.3	11.3	3.7
m× + *p*-Xylenes	40.0	41.3	43.1	45.0	36.9	65.7
o-Xylene	—	2.5	2.5	0.7	0.5	3.7
m- + *p*-Ethyltoluenes	—	14.6	9.7	6.9	15.1	8.2
o-Ethyltoluene	—	1.2	0.1	—	0.2	—
1,2,4-Trimethylbenzene	—	—	0.8	1.4	2.2	10.8
Isopropylbenzene	—	—	1.0	1.2	8.6	—
n-Propylbenzene	—	—	—	—	5.5	—
C_{10} aromatics	—	—	0.8	1.5	0.5	—
Relative amounts of xylenes[e]						
Benzene	0.0	2.0	4.5	12.2	10.7	0.4
Toluene	83.3	55.6	62.8	61.1	41.4	11.5
$C_3^=/C_4^=$	17.1	1.4	1.3	0.5	0.4	2.0
o-Xylene	0.0	6.1	5.9	1.5	1.4	5.6
Ethylbenzene	66.7	40.4	28.8	22.9	30.8	5.6
$(C_5^= \times C_3^=)/(C_4^=)$	0.0	0.33	0.29	0.09	0.31	0.59
m- + *p*-Ethyltoluenes	0.0	35.4	22.6	15.3	40.9	12.5
1,2,4-Trimethylbenzene	0.0	3.0	1.9	3.1	5.9	16.5
$C_5^=/C_4^=$	0.0	0.24	0.22	0.19	0.75	0.29
Isopropylbenzene	0.0	0.0	2.4	2.7	23.4	0.0
[(3-Methyl-but-1-ene) + $C_5^=$]/$C_4^=$	0.0	0.2 10^{-3}	16.10^{-3}	13.10^{-3}	43.10^{-3}	7.10^{-3}

[a] $C_2^=$ = ethylene; $C_3^=$ = propene; $C_4^=$ = butenes; $C_5^=$ = pentenes. Italic values indicate the presence of alkylation reactions.

[b] Conversion degree (in % of C atoms) to hydrocarbons different from the initial olefin and its isomers.

[c] C_2–C_5 olefins distribution in C atoms normalized to 100% for ($C_2^=$ + $C_3^=$ + $C_4^=$ + $C_5^=$).

[d] Distribution of aromatics (in C atoms); the total amount of aromatics is normalized to 100%.

[e] Relative amounts of a given aromatic compound (in C atoms) divided by the amount of *m*- + *p*-Xylenes obtained in this experiment: $R_x = 100 \cdot$ ((amount A_x in % C atoms)/amount of *m*- + *p*-xylenes in % C atoms)).

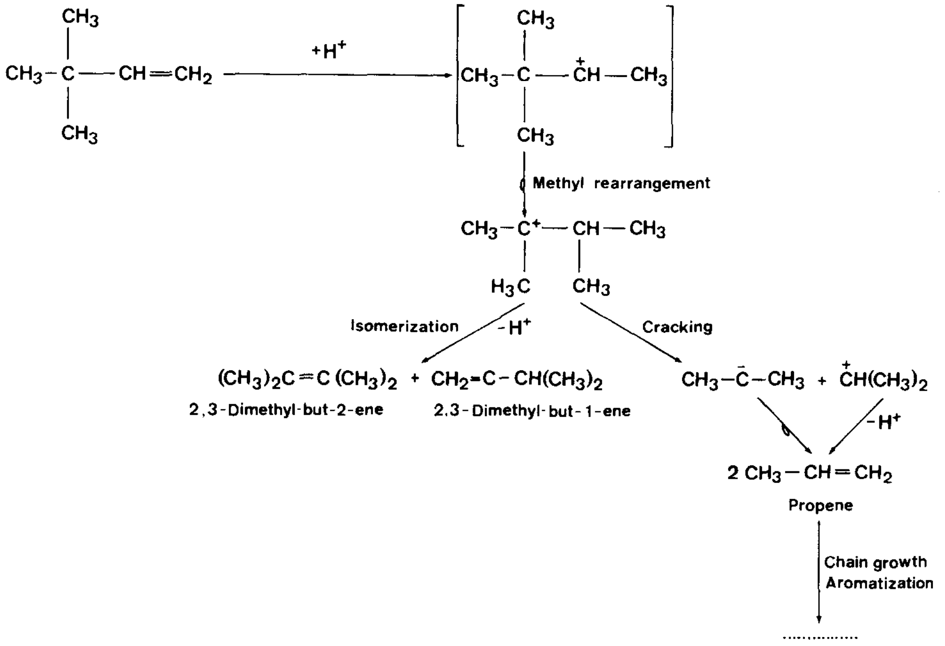
formed. Propene can, of course, be converted to butene as previously mentioned.

The Carbenium Ion Aromatization Mechanism

The upgrading of the hydrocarbons can be explained by ionic polymerization of the C_2–C_4 olefins. If, however, the catalyst has active centers for aromatization, other competitive reactions are also likely to occur. These are:

(i) the condensation of an olefin and a carbenium ion which by dehydrocyclization can form cyclic C_{6+} hydrocarbons;

(ii) hydrogen-transfer reactions between these cyclic hydrocarbons and light olefins leading to aromatics and saturated C_2–C_5 hydrocarbons.

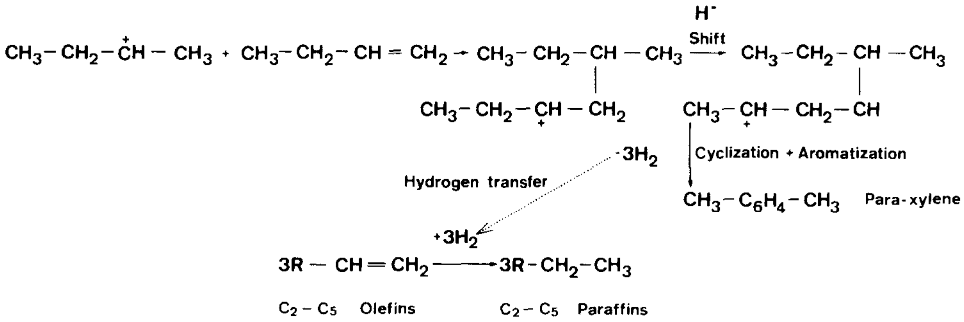


SCHEME II

They are shown in scheme III.

Such a scheme is in line with previous proposals (*25, 26*) accounting for the formation of higher-molecular-weight olefins and paraffins, and aromatics, by reaction of C_2–C_4 olefins on synthetic zeolite catalysts. These conversions may be thought to occur in terms close to the classical "conjunct" polymerization of olefins as observed in strongly acidic media (*27, 28*).

The shape-selective character of the H-ZSM-5 zeolite (*16*) will certainly favor such condensation–cyclization reactions since the catalyst's spatial structure shows long intercrossed channels (*18*). It has been shown most recently that organic molecules are adsorbed in an "end-to-end" configuration in the pores of such a material and that, at maximum, two C_2–C_5 molecules are accommodated per "intersecting element" (*29*); the latter does not hold for C_6 compounds which are too large already. It can be understood, therefore, that an olefin ($\leq C_5^=$) and a carbenium ion ($\leq C_5^+$) can meet rather easily at such intersections, reacting together in a "conjunct" cycloaddition as described above, leading to maximum to a C_{10} oligomer. It also accounts, in



SCHEME III

TABLE 5

Alkylation of Benzene by Dimethyl Ether[a]

Alkylated aromatics (%)[b]			
Toluene	68.1	Ethylbenzene	4.2
m- + *p*-Xylenes	21.8	*p*-Ethyltoluene	1.0
o-Xylene	0.8	Isopropylbenzene	1.0
1,3,5-Trimethylbenzene	0.1	*n*-Propylbenzene	1.5
1,2,4-Trimethylbenzene	1.0	C_{10} aromatics	0.2
1,2,3-Trimethylbenzene	0.3		

[a] Reaction conditions: Catalyst, 0.097 g of H-ZSM$_2$-5; Temp., 377°C; partial pressures, 9.64 Torr dimethyl ether; 94.96 Torr benzene.

[b] Percentage in C atoms.

addition, for the upper limit at C_{10} of the major compounds produced in various organic compound conversions and for the high "constraint index" (*1*) of this material.

Such oligomerization and aromatization mechanisms also describe the formation of polycyclic compounds, aromatics, and polyalkylnaphthalenes, which may act as coke precursors (*30*). These will not occur inside the ZSM-5 structure as the pores and "intersecting element" sizes limit the upper dimension of the products which can be formed, explaining thereby the high resistance of ZSM-5 to coking, in agreement with previous data (*31*).

The experimental data obtained from the conversion of methanol agree with such a scheme. Indeed, paraffins and aromatics appear simultaneously while the concentration of olefins (which are essentially propene and butenes) decreases abruptly.

Aromatization reactions from butenes also occur easily. The butenes are initially the main products but they disappear very sharply when xylenes (by reaction between butene and butene carbenium ions) and toluene (by reaction between propene and butene carbenium ions, or butene and propene carbenium ions) are formed. Figure 5 shows reaction pathways and possible combinations for the formation of C_6–C_8 aromatic compounds by reaction between the major C_2–C_4 olefins and their corresponding carbenium ions. In Table 6, all the possible condensations between C_2–C_5 olefins and their carbenium ions have been examined. The various olefins can react with others (as indicated in the same column) leading to a given aromatic compound. Both primary and secondary carbenium ions are considered in these schemes, although it is recognized that reactions involving secondary carbenium ions will be favored because of the larger stability and occurrence of the latter.

Assuming that the probability for the formation of a given aromatic hydrocarbon is roughly proportional to the number of available reaction paths, the major aromatic compounds should be toluene, xylenes, ethyltoluenes, and 1,2,4-trimethylbenzene. Benzene, propylbenzene, isopropylbenzene and mesitylene would be present in low concentrations. Such a distribution agrees with the experimental observations and further reinforces the role played by the molecular sieving properties of the zeolite which are needed to favor "concerted" cycloaddition reactions.

A more complicated situation is encountered for the conversion of olefins. It can however be rationalized and simplified in the following way. Consider that the conversion of hydrocarbons, and specifically olefins, on the H-ZSM-5 zeolite is the result of consecutive reactions. One can expect that at intermediate conversions the concentration of a given aromatic compound in the products should be proportional to its rate of formation (provided that it does not undergo drastic shape-selective reforming) and in accordance with basic reaction kinetics. In such an approximation, the concentration of a given aromatic compound should be proportional to the absolute concentrations (not quoted in Table 4) of the parent olefins as measured in the reaction products. Hence:

(Xylenes): $R_{\text{xylenes}}/(\text{butenes})^2$
(Toluene): $R_{\text{toluene}}/(\text{propene})(\text{butenes})$
(Ethylbenzene: $R_{\text{ethylbenzene}}/(\text{pentenes})(\text{propene})$
(Ethyltoluene): $R_{\text{ethyltoluene}}/(\text{pentenes})(\text{butenes})$

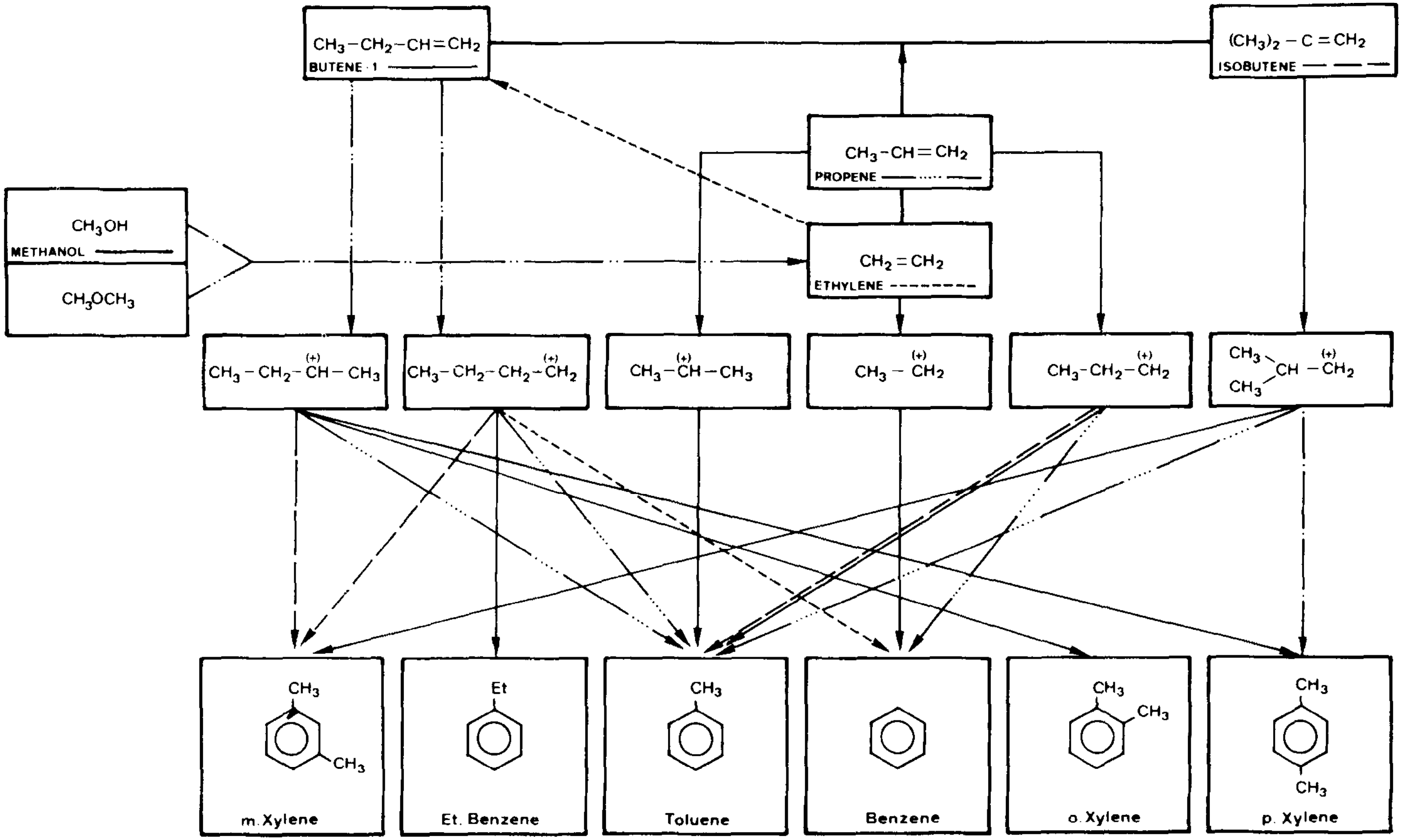


FIG. 5. Reaction network for the formation of aromatic hydrocarbons by initial "concerted" cycloadditions of C_2–C_4 olefins and their carbenium ions.

TABLE 6

Reaction Pathways for the Formation of Aromatic Compounds from C_2–C_5 Olefins and Their Carbenium Ions

				Olefins				
Aromatics	Ethylene	Propene	But-1-ene	Isobutene	Pent-1-ene	Pent-2-ene	2-Me-1-butene	3-Me-1-butene
Benzene	1-butene	propene	ethylene	—	—	—	—	—
Toluene	1-pentene 2-Me-1-butene	1-butene isobutene	propene	propene	ethylene	ethylene	ethylene	ethylene
Et-benzene	—	1-pentene 2-pentene	1-butene	—	propene	—	—	—
o-Xylene	—	1-pentene 2-Me-1-butene 3-Me-1-butene	1-butene	—	—	propene	propene	—
m-Xylene	—	1-pentene 3-Me-1-butene	isobutene	1-butene	propene	propene	propene	propene
p-Xylene	—	2-Me-1-butene	1-butene	isobutene	—	—	—	propene
1,2,4-3Me-benzene	—	—	1-pentene 3-Me-1-butene	2-Me-1-butene 3-Me-1-butene	—	1-butene	1-butene isobutene	1-butene
1,2,3-3Me-benzene	—	—	2-Me-1-butene	—	—	—	1-butene	—
1,3,5-3Me-benzene	—	—	—	1-pentene 2-pentene	—	isobutene	—	—
o-Et-toluene	—	—	1-pentene 2-pentene	—	1-butene	1-butene	—	—
m-Et-toluene	—	—	3-Me-1-butene 1-pentene 2-pentene	1-pentene 2-pentene	isobutene	—	—	1-butene
p-Et-toluene	—	—	2-pentene 2-Me-1-butene	—	1-butene	—	1-butene	—
Propylbenzene	—	—	1-pentene	—	1-butene	—	—	—
Isopropylbenzene	—	—	3-Me-1-butene	—	isobutene	—	—	1-butene
1245-Durene	—	—	—	—	—	1-pentene 2-pentene	1-pentene 2-pentene	—
1235-Durene	—	—	—	—	—	2-Me-1-butene 3-Me-1-butene	3-Me-1-butene	—
1234-4Me-benzene	—	—	—	—	—	—	2-Me-1-butene	—

[a] Me = methyl, 3Me = trimethyl, 4Me = tetramethyl, Et = ethyl, 1245-durene = 1,2,4,5-tetramethylbenzene, 1235-durene = 1,2,3,5-tetramethylbenzene, 1234-4Me-benzene = 1,2,3,4-tetramethylbenzene.

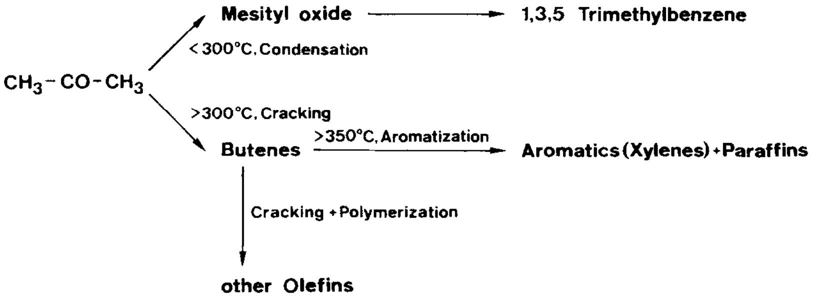
with R_Z equal to the rate of formation of compound Z. In order to account for side effects due to variable degrees of conversion, theoretical concentrations calculated in this manner can be normalized relative to the total amount of xylenes. They are quoted in Table 4 (see ratios of lower part of Table 4, relative amounts to xylenes).

The calculated values reflect the trend in the experimental variations and thus confirm the aromatization mechanism involving as an initial step the condensation of an olefin and a carbenium ion. Discrepancies, however, are observed for ethylbenzene and ethyltoluenes which seem to be present at too high a concentration in the conversion of ethylene, while the ethylbenzene yield from the conversion of methanol is too low. In the latter case, the methyl-aromatic concentrations appear too high. Such anomalies can be explained by alkylation reactions which will be dealt with later.

Such an aromatization pathway also accounts for the acetone conversion data at different temperatures as reported by Chang and Silvestri (*1*). Under 300°C, acetone is converted by an ionic mechanism of ketonic condensation. The major aromatic product (86 to 100% of the total amount of aromatics) is 1,3,5-trimethylbenzene, which is usually not detected in the methanol conversion reaction. At about 300°C, a new reaction route becomes competitive: butenes are formed following cracking of acetone and the concentration of C_4 olefins in the products increases, whereas the amount of mesitylene falls abruptly (see Fig. 6). When aromatization is favored, i.e., at temperatures above 350°C, the concentration of butenes sharply decreases and aromatic compounds (essentially xylenes), other than mesitylene, are detected in large amounts. There is then strong evidence for a change in the reaction mechanism above 350°C: the ketonic condensation becomes negligible and cracking occurs. This leads to butenes which, by the carbenium ion mechanism previously described, are converted to paraffins, olefins, xylenes, and other aromatics. Scheme IV summarizes these conclusions.

Figure 4 shows the dependence of the concentrations of the C_4 and aromatic hydrocarbons as a function of Si/Al ratio. Product concentrations are taken from Table 3. They were gathered for the data mentioned in Fig. 4 at nearly identical space velocities, i.e., WHSV = 10–11 hr^{-1}. Such a plot may be used to reinforce the idea that strong acid sites are responsible for the dehydrocyclization of the low-molecular-weight olefins into aromatics.

It is indeed observed that the relative concentrations of the aromatics and the C_4 paraffins increase as functions of the Al/(Si + Al) ratio while that of the butenes decrease (in agreement with the mechanism described in Scheme III). At the same time, the maximum heat for ammonia adsorption increases (*32*): it is of about 123 kJ mol^{-1} for a material with Al/(Si + Al) = 0.0125 (H-ZSM$_4$-5), reaching 150 kJ mol^{-1} or more when this ratio reaches 0.050 (H-ZSM$_1$-5).



SCHEME IV

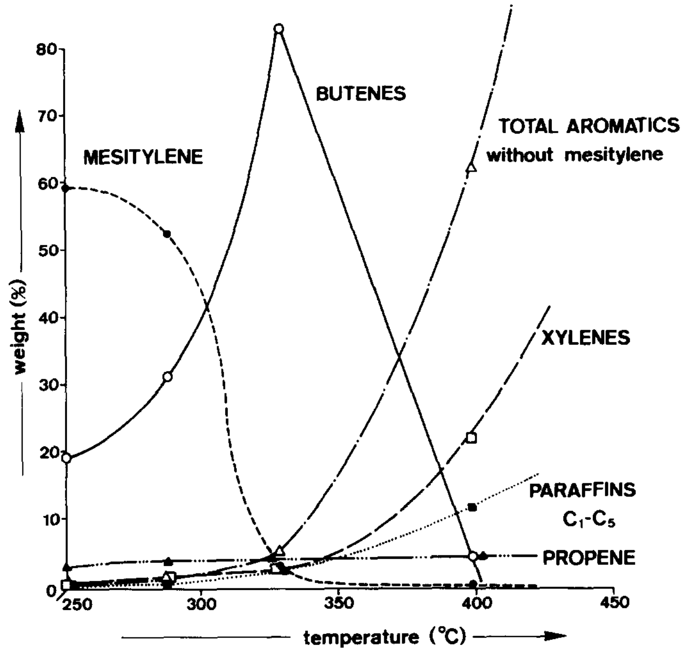


FIG. 6. Zeolite-catalyzed acetone conversion; yield structure vs temperature (LHSV = 8 hr^{-1}, data from Ref. (*1*)).

The additional fact that the concentrations of aromatics and C_4 paraffin products do extrapolate at zero for an Al/Si + Al) ratio of about 0.011 seems to confirm the proposal that not all sites are equivalent (*32*); the proportion of strong acidic sites in H-ZSM-5 should increase with Al content according to the present data and a material with a Si/Al ratio greater than 90 should not show a high aromatization activity.

This proposal agrees with the observation of Ahn *et al.* (*20*) who report that materials of lower acidity show less aromatics formation. It is also substantiated by data available in the patent literature which show clearly that moderating the acidity of H-ZSM-5 catalysts decreases their aromatization activity (*24*).

The Importance of Alkylation Reactions

As shown in Table 5, benzene is readily alkylated by carbenium ions. Alkylation reactions for an aromatic compound are electrophilic substitutions and are, consequently, expected to occur on an acidic catalyst (*17*) which will favor the formation of carbenium ions. In addition, aromatic electrophilic substitutions are "activated" if alkyl substituents are already present on the aromatic ring, as is the case for toluene and xylenes.

Alkylation also occurs in the conversion of methanol and olefins by the H-ZSM-5 zeolite and competes with the reaction pathway described before for the formation of aromatics (Fig. 5 and Table 6). It accounts, namely, for the discrepancies in the aromatic selectivities indicated in Table 4. The most striking example is that of 1,2,4-trimethylbenzene which is a low-yield product in the conversion of olefins and is present in much larger amounts when methanol is reacted. It stems essentially, in the latter case, from the alkylation of xylenes (which are the major aromatics) by CH_3^+ species. In the same way for the ethylene conversion, alkylation by $C_2H_5^+$ accounts for the too-high concentration in ethyl-aromatic products (ethylbenzene and ethyltoluenes). It is worth adding, finally, that alkylations by higher carbenium ions ($C_3H_7^+$, $C_4H_9^+$, etc.) have no net effect. They would produce alkyl-aromatics too bulky with respect to the structural properties (shape and size of the pores and channels) of the zeolite (*16*).

CONCLUSIONS

Aside from well-assessed reactions (such as isomerization, polymerization, dehydrogenation, and shape-selective cracking) which are known to occur on acidic zeolites, the present work demonstrates the important role played by a carbenium ion mechanism in the formation of higher aliphatic and aromatic hydrocarbons from C_1 to C_4 feeds.

The initial step in the formation of aromatics is a "concerted" cycloaddition of an olefin and a carbenium ion which is favored by the unique structural properties of the zeolite. The predicted distribution for the aromatic hydrocarbons (nature and relative amounts) is remarkably well reflected in the experimental data and discrepancies can be accounted for by the occurrence of alkylation reactions.

It is proposed that some of the unique properties of the acidic forms of the ZSM-5-family zeolites result from the combination of strongly acidic and molecular sieving properties.

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