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Studies on the Conversion of Methanol and Other Small Molecules over H-ZSM-5: Yield Studies and the Use of ^3H NMR in a Reexamination of Routes to Ethylene Production

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Routes to ethylene production involving ethyl aromatic intermediates have been investigated in the conversion of methanol to gasoline over the zeolite H-ZSM-5. Yield studies and tritium NMR have shown that some of the postulated steps either do not occur or give ethyl aromatic products in very low yields. Furthermore, yields of ethylene from such ethyl aromatics are too low to be significant in methanol conversion over H-ZSM-5.

INTRODUCTION

In the conversion of methanol to gasoline over the "Mobil" catalyst, H-ZSM-5, alkenes are recognized as being important intermediates (*1*). While some authors claim that ethylene is not the most reactive (*2*) of these, the mechanism of its formation has received much attention. The purpose of this paper is to conduct a critical review of evidence bearing on these proposed mechanisms and to present results of some new experiments relevant to ethylene production.

Dessau and LaPierre (*3*) have studied the methylation of propylene using ^{13}C methanol and found that the resulting ethylene contained less ^{13}C than would be expected if the product were derived entirely from methanol. The amount of doubly labeled ethylene was further reduced when hexene-1 was used as the trapping olefin. They concluded that most of the ethylene was produced, not as a primary product, except during a short initiation phase, but as a product of cracking of built-up alkenes.

In a recent paper, Dessau (*8*) has presented convincing evidence for the involvement of propylene and butenes in the production of ethylene by the route involving long contact times on the catalyst and involving secondary reequilibration of the primary kinetic olefinic products.

Mole (*2*) has presented evidence showing that ethylene is produced by two different routes when methanol is converted over H-ZSM-5 at 280°C. By using ^{13}C-labeled methanol mixed with propylene and observing the relative abundances of $^{13}C_2H_4$, $^{12}C^{13}CH_4$, and $^{12}C_2H_4$, he has shown that the ethylene produced contains less ^{13}C than expected if it were produced from $^{13}CH_3OH$ alone, and more than expected if produced from an equilibrated $^{13}C/^{12}C$ pool. He interprets this as indicating two routes: one, the "direct" route, involves condensation of two molecules of methanol via an oxonium ion-ylide mechanism, and the other, "indirect" route, is assigned to the cracking of some product produced by methylation of a nonlabeled substrate by the labeled methanol. Two suggestions are made as to the nature of this substrate.

(i) Propylene may be methylated to butene which is then cracked to ethylene. (This route accounts for the observed autocatalysis of ethylene production.)

(ii) Toluene, a compound known to be present in the products from converting methanol, may be methylated at the side-chain carbon producing ethylbenzene which is known to crack yielding ethylene.

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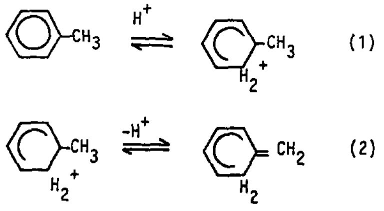
Mole and co-workers favor (*2*) the aromatic route (ii) and describe (*4*) an experiment in which a mixture of Ph-$^{13}CH_3$/$^{12}CH_3OH$ is passed over H-ZSM-5 at ca. 300°C and yields ethylene, some 6% of which contains one ^{13}C atom in the molecule. This result is quoted as evidence in favor of side-chain methylation of toluene-forming ethylbenzene which cracks to ethylene.

Other studies of significance in this discussion are summarized below:

(iii) A mixture of toluene and D_2O passed over H-ZSM-5 at 325°C gave mainly d_5 toluene (*4*), implying facile exchange of ring protons. When the temperature was raised to 460°C, however, significant amounts of more highly deuterated toluene appeared, implying that deuterium was entering the methyl group.

(iv) *p*-Xylene was found (*4*) to become deuterated in both ring and methyl sites at 330°C. This reactivity greater than that of toluene was attributed to a higher susceptibility of the more completely methylated aromatic, and also to the lower rate of diffusion of xylene in the catalyst pores. A mechanism proposed for these exchange reactions is summarized by reactions (1) and (2) (see Scheme 1).



SCHEME 1

Reaction (1) would lead to deuteration in the ring whereas reaction (2) accounts for incorporation of deuterium into the methyl group under more strenuous conditions. It was suggested (*4*) that the exomethylene group produced by reaction (2) could be subject to electrophilic attack by methylating agents to give ethylbenzene which is known to crack to ethylene.[2]

Support for the above reaction scheme is adduced from the ^{13}C study outlined in (ii), and the observation mentioned above. This result is difficult to reconcile with the observation, mentioned in (iii), that very little exchange occurs even at 325°C between the methyl protons of toluene and D_2O. Thus, reaction (2), involving as it does loss of protons from the methyl group, appears not to occur at this temperature. The model may be modified to avoid this difficulty by suggesting methylation of toluene to form xylenes before commencing a reaction such as (2), it being known (*4*) that *p*-xylene exchanges deuterium at a lower temperature as described above. Evidence (*4*) showing that scrambling of isotopically labeled carbon atoms between ring and side-chain positions occurs when methanol mixed with ^{13}C benzene is passed over H-ZSM-5 at 310°C is presented. The ethylene formed in this reaction was shown to contain a high percentage of $^{13}C^{12}CH_4$. The authors suggest alkylation of benzene followed by ring to side-chain scrambling and finally deethylation as a route to ethylene production.

These isotopic results can be accommodated in a scheme, proposed by Mole (*4*) and modified as described above, of the form shown in Scheme 2.

In the next section we present new experimental results relevant to this scheme and some comment.

EXPERIMENTAL

(*a*) *Catalyst Preparation*

The sodium form of ZSM-5 (DSIR #1) was supplied to us by the Chemistry Division of the DSIR. Details of preparation and characterization of this material have been published (*6*). This material was calcined by raising the temperature from 200 to 450°C in 50°C steps over 24 h to remove the organic template (propylamine). This material gave an aluminium content of

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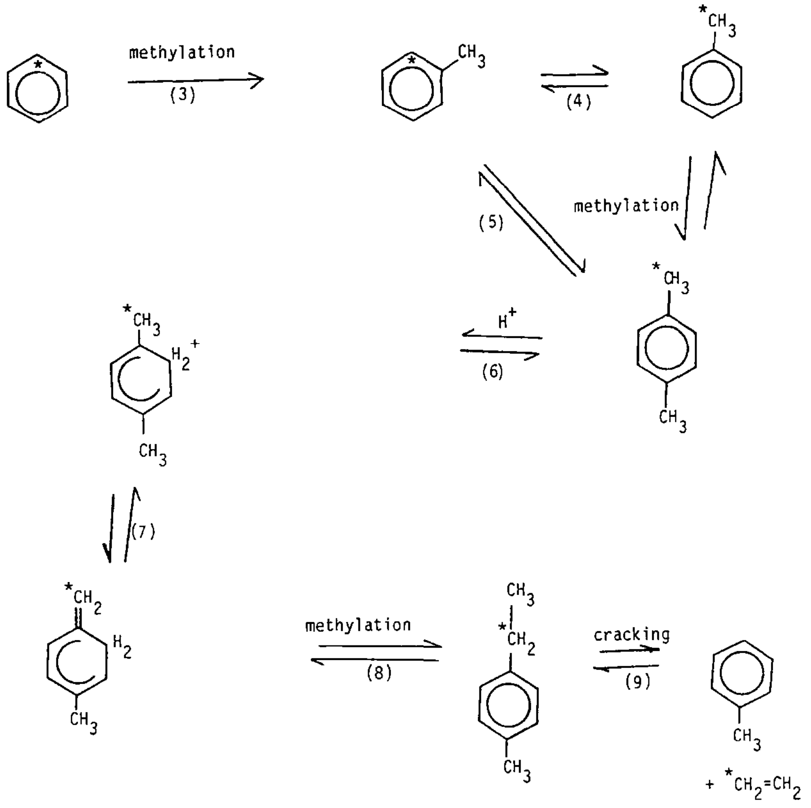
[2] A route involving side-chain methylation of xylene was also suggested by Dr. Mole in an informal seminar at Auckland University in August 1984.



Scheme 2

2.7 Al atoms per unit cell as determined by atomic absorption spectroscopy. Na^+ ions were exchanged by washing with 0.1 mol liter^{-1} ammonium nitrate until no further Na^+ was released (as determined by atomic absorption). The catalyst was heated to 400°C in a stream of nitrogen for 24 h to remove ammonia.

(*b*) *Equipment*

The equipment used in this study has been described more fully in an earlier publication (*5*). Pelletized H-ZSM-5 (0.42 g) was supported on a glass frit in a glass microreactor tube set in aluminium block heaters (capable of being thermostated to ±2°C from room temperature to 500°C). The methanol to gasoline (MTG) convertor was mounted onto a Varian 1800 GLC in such as way as to prevent any possibility of condensation problems that could otherwise be expected if the convertor was removed from the GLC. A 10-port valve was used for sampling the reactor effluent through a fixed volume 1-ml sample loop. The 10-port valve also provided the facility for backflushing columns and control of the flow of vector gas (nitrogen) from 0 to 30 ml min^{-1} through the reactor. A multispeed syringe pump drive, quite separate from the convertor used syringes with long needles passing through a septum in the top of the convertor.

The following columns were used for the various analyses:

(a) The first included durapak *n*-octane on porasil C (80–100 mesh) in a stainless-steel column 2 m × 2 mm i.d.; carrier gas N_2, 30 ml min^{-1}; temperature program, 10°C hold 3 min (subambient), ramp 40°C

min^{-1} to 60°C, hold. This column was used for light gas analyses giving excellent separation up to C_4, including ethane/ethylene separation.

(b) The second included 5% AT-1200 + 1.75% Bentone 34 on Chromosorb W-AW (100/200 mesh) in a stainless-steel column 2 m × 2 mm i.d.; carrier gas N_2, 30 ml min^{-1}; temperature program, 75°C hold. This column was used for aromatics and gave baseline separation of all xylenes and ethyl toluenes.

The effluent of the GLC column was split 1 : 10. The larger stream was fed to a 5-ml brass ion chamber, coupled to a Cary electrometer, for radioactivity measurements, and the remainder to an FID for mass measurements.

Tritium NMR spectra were recorded using a JEOL FX-60 spectrometer operating at 64 MHz (*7*).

RESULTS AND DISCUSSION

(*a*) *Side-Chain Methylation of Toluene*

The possibility that side-chain methylation of toluene to form ethylbenzene as an intermediate in the production of ethylene has been investigated using titrium tracing and tritium NMR studies as well as yield studies on methylation products, as follows.

Conversion of [*methyl-^3H*]*toluene.* Toluene labeled with tritium in the side chain at a level of ca. 74 mCi/ml was passed over H-ZSM-5 at 370°C and a MHSV of 0.35 h^{-1}. Tritium NMR studies on the product showed no detectable signals at a chemical shift corresponding to ring tritium atoms. The detection limit was estimated to be about 0.5% of the peak height obtained for the methyl-^3H resonance.

This result confirms the inertness to the exchange of side-chain hydrogens reported by Mole *et al.* (*4*) at 325°C, and indicates that reaction (2) is not observed under these conditions.

An important further implication is that carbon scrambling between ring and side chain, as postulated by Mole *et al.* (*4*) (see (iv) above) is shown to be most unlikely for toluene under these conditions, since such carbon scrambling would necessarily imply some hydrogen scrambling. This rules out reaction (4), for toluene, at temperatures up to 370°C.

Alkylation of toluene. Methylation of toluene was studied by passing methanol and toluene mixtures (24 : 1 mole ratio) over H-ZSM-5 at 370°C and a search for ethylbenzene in the product was made. Yields of methylated and ethylated products obtained from methanol/toluene mixtures are compared with those from methanol alone in Table 1 for five different runs.

It is clear that, while the yields of xylenes, trimethylbenzenes, and ethyltoluenes are strongly enhanced by the addition of toluene, there is no increase in ethylbenzene yields within experimental error. We conclude that side-chain methylation of toluene does not occur under these conditions.

In conducting this experiment a large excess of toluene was used as evidenced by the fact that the toluene yield was some three times as great as that seen in the pure methanol conversion. If toluene were to methylate to ethylbenzene in the conversion of pure methanol as claimed (*4*), then such a reaction would have been more pronounced under the conditions pertaining in our experiment.

Alkylation of benzene. A possibility that should be considered is that the small yield of ethylbenzene might be due to high yield cracking of ethylbenzene yielding ethylene and benzene. This possibility was investigated as follows.

Mixed benzene and methanol were passed over the catalyst under the same conditions as above. Yields of products are given in Table 2. Large increases in the yields of methylbenzenes on adding benzene and also a fivefold increase in the yield of ethylbenzene are seen.

We have shown previously (*10*) that when pure ethylbenzene is passed over H-ZSM-5 under conditions similar to those

TABLE 1

Alkylation of Toluene by Methanol over H-ZSM-5

	I		II		III		IV		V	
Feedstock	Methanol	Methanol/ toluene	Methanol	Methanol/ toluene	Methanol	Methanol/ toluene	Methanol	Methanol/ toluene	Methanol	Methanol/ toluene
					Reaction conditions					
T (°C)	370	370	370	370	370	370	370	370	370	370
Methanol conversion (%)	100	100	100	100	100	100	100	100	100	100
Feed rate MHSV (h^{-1})	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Mole ratio of mixed feed	—	24 : 1	—	24 : 1	—	24 : 1	—	24 : 1	—	24 : 1
					Hydrocarbon distribution (wt%)					
Aliphatics (C_1–C_7)	69.83	58.87	76.77	56.67	72.92	62.38	74.37	58.94	78.61	56.25
Ethylbenzene	0.22	0.21	0.27	0.20	0.22	0.20	0.24	0.20	0.25	0.21
p-Xylene	2.34	3.70	2.12	3.60	2.22	3.42	2.19	3.65	2.02	3.71
m-Xylene	5.30	8.39	4.54	8.16	5.00	7.64	4.92	8.18	4.52	8.34
o-Xylene	2.30	3.67	1.96	3.58	2.16	3.36	2.13	3.59	2.03	3.65
p-Ethyltoluene	0.22	0.31	0.28	0.30	0.24	0.28	0.23	0.31	0.22	0.30
m-Ethyltoluene	0.62	0.79	0.77	0.84	0.65	0.80	0.66	0.83	0.61	0.81
o-Ethyltoluene	0.06	0.08	0.05	0.17	0.09	0.09	0.06	0.08	0.06	0.09
Mesitylene	1.06	1.33	0.41	1.77	1.01	1.28	0.87	1.34	0.65	1.49
Pseudo-cumene	10.40	16.66	8.61	17.81	11.41	14.61	10.69	16.13	8.19	17.56
Hemimellitene	0.67	0.89	0.35	1.19	0.61	0.85	0.61	0.90	0.53	0.97
Durene	3.63	4.52	3.78	5.45	3.18	3.76	2.81	4.66	1.71	4.96
Other aromatics	1.18	0.57	0.68	0.85	0.27	1.37	0.28	1.18	0.59	1.67

Note. Because small changes occur in catalysts selectivity with time and catalyst history, each methanol run was conducted immediately after a methanol run. The procedure was repeated five times (I . . . V) on different days so that some variation occurred from day to day and it is not meaningful to average results over the whole array. Rather, the selectivities for each methanol/toluene run should be compared with those of the adjacent methanol run. Data are expressed as weight percentages (wt%) after subtracting yields of toluene. Corrections have been made for varying flame ionization detector (FID) sensitivities of different hydrocarbons.

above (370°C and MHSV 0.4 h^{-1}) 40 wt% of it remains unconverted.

It is clear from these two results that ethylbenzene can survive our reaction conditions and appear in the product mix when it is formed in the reaction.

We conclude that side-chain methylation of toluene to ethylbenzene as a route to ethylene is ruled out under the conditions of our experiment.

(*b*) *Side-Chain Methylation of p-Xylene*

Tritium NMR and yield studies have been used to investigate the possibility of side-chain methylation of xylenes, as follows.

Conversion of [2-^{3}*H*]*m-xylene*. *m*-Xylene labeled in position 2 to a level of ca. 63 mCi/ml was passed over freshly regenerated H-ZSM-5 at 370°C and MHSV of 0.36 h^{-1}. The product was analyzed by radio-GLC which showed some 34% of the feed had isomerized forming approximately equal amounts of *o*- and *p*-xylenes. Small amounts of toluene and trimethylbenzenes were also found. Tritium NMR spectra of the mixed xylene products showed that a large amount of tritium was now incorporated in the methyl groups. This finding is in accord with the enhanced reactivity reported by Mole *et al.* (*4*) for xylenes compared to toluene and supports the inclusion of (6) in the reaction scheme. Carbon scrambling as in (5) is not excluded by this evidence as it was in (4) in the case of toluene.[3]

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[3] Such carbon scrambling between ring and side-chain positions can be explained by the known benzylic cation–tropylium ion equilibration.

It is noteworthy, however, that Hwu (*9*) found that when ^{14}C-labeled benzene and methanol were converted at 368°C no radioactivity was detected in nonaromatic products. This suggests that yields of light gases, including ethylene, from reactions which involve such aromatic/alkyl scrambling processes, will be small under conversion conditions.

TABLE 2

Alkylation of Benzene and *p*-Xylene by Methanol over H-ZSM-5

Feedstock:	Methanol (I)	Methanol/benzene (II)	Methanol (III)	Methanol/*p*-xylene (IV)
		Reaction conditions		
T (°C)	370	370	370	370
Methanol conversion(%)	100	100	100	100
Feed rate MHSV (h^{-1})	0.36	0.36	0.36	0.36
Mole ratio of mixed feed	—	20 : 1	—	27 : 1
		Hydrocarbon distribution (wt%)		
Aliphatics (C_1–C_7)	73.10	34.30	79.85	76.23
Benzene	—	—	0.34	0.33
Toluene	2.77	11.37	2.19	2.12
Ethylbenzene	0.38	2.05	0.31	0.34
p-Xylene	2.59	6.01	—	—
m-Xylene	5.56	13.10	—	—
o-Xylene	2.46	5.99	—	—
p-Ethyltoluene	0.42	0.69	0.30	0.34
m-Ethyltoluene	1.03	1.66	0.80	0.86
o-Ethyltoluene	0.13	0.10	0.05	0.04
Mesitylene	0.27	0.54	0.83	0.58
Pseudo-cumene	8.36	15.94	11.43	14.82
Hemimellitene	0.13	0.64	0.45	0.49
Durene	2.07	3.41	2.74	2.83
Other aromatics	0.59	3.82	0.71	1.03

Note. Data are expressed as weight percentages (wt%) after subtracting yields of benzene for runs (I) and (II) and all xylenes for runs (III) and (IV). Corrections have been made for flame ionization detector (FID) sensitivities of different hydrocarbons.

Alkylation of p-xylene. An attempt was made to study the products from a mixed *p*-xylene/methanol feed under the same conditions as those described for the toluene/methanol study. Unlike toluene, pure xylenes (without added methanol) are highly reactive over H-ZSM-5 at 370°C and suffer isomerization, accompanied by some 10% disporportionation and cracking. These reactions occur to such an extent as may obscure the products formed from xylene/methanol mixtures which might be attributed to methylation reactions and make interpretation of yields uncertain. Nevertheless, we present results for conversion of *p*-xylene/methanol mixture in Table 2 in which yields are expressed as weight percents on a xylene-free basis, all conversions of methanol being 100% complete.

Apart from isomerization products the yield pattern is dominated by products of ring methylation reactions notably pseudo-cumene. The yields of ethyltoluenes, all initially small (<1 wt%) are only slightly changed, yields of two isomers being raised and one lowered. Of these the largest increment in yield on adding *p*-xylene is that of *m*-ethyltoluene (0.80 wt% → 0.86 wt% or $\Delta = 0.06$ wt%). This is a small change compared to the increments for ring methylation, e.g., pseudo-cumene (11.43 wt% → 14.82 wt% or $\Delta = 3.39$ wt%).

It is interesting also to compare these increments with those found for ring ethylation by methanol as shown for benzene/methanol in Table 2. Ethylbenzene yields are 0.38 wt% → 2.05 wt% or $\Delta = 1.67$ wt%.

Thus any side-chain methylation of xy-

TABLE 3

Yields of Ethylene from Ethyl Aromatics Compared with Those from Methanol and *n*-Heptane

Feedstock:	Methanol	*n*-Heptane	Ethylbenzene	*p*-Ethyltoluene
Reaction conditions				
T (°C)	380	380	380	380
Conversion (%)	100	80	61	64
Feed rate MHSV (h^{-1})	0.36	0.36	0.36	0.36
Ethylene yield (wt%)	5.3	1.4	3.3	4.8

lenes appears to be unimportant compared with ring alkylation as a source of ethyl aromatics.

(*c*) *Ethyl Aromatics as Precursors for Ethylene*

We have shown that side-chain methylation of toluene to form ethylbenzene does not occur and further that a similar reaction with xylene to yield ethyltoluene gives, at most, very low yields.

Ethylbenzene does, however, occur as a minor product (some 0.35 wt%) among the products of converting methanol and might be considered as a precursor for ethylene.

Ethyltoluene yields from converting methanol are some three times larger than those for ethylbenzene.

Yields of ethylene obtained by passing ethylbenzene and *p*-ethyltoluene (without added methanol) over H-ZSM-5 were studied and compared with those from conversion of methanol and heptane (see Table 3).

These results show that ethylbenzene and *p*-ethyltoluene give yields of ethylene (3.3 and 4.8 wt%) which is in agreement with Mole *et al.* (who reported 4.5 wt%). This is not as high as those from methanol (5.3 wt%) and not much higher than those from *n*-heptane (1.4 wt%).

Remembering that these two ethyl aromatics occur at abundance levels of 0.22 and 0.62 wt%, respectively, in products of conversion of methanol, they will not yield significant quantities of ethylene in methanol conversions if they crack to the extent shown above. The maximum ethylene yields we may assign to such routes to ethylene may be estimated as via ethylbenzene 0.22 wt% × 3.3 wt% = 0.006 wt% and via ethyltoluene 0.62 wt% × 4.8 wt% = 0.03 wt%. The observed yield of ethylene from methanol is 5.3 wt% (see Table 3). Mole (*2*) has shown that 40–90% of this is formed by the indirect route. Thus it is clear that, under the conditions of our experiments, yields of ethylene formed via ethylbenzene or via ethyltoluene fall short of yields assigned (*2*) to the indirect route by two orders of magnitude.

(*d*) *Other Possible Routes to Ethylene Involving Aromatics*

p-Xylene conversion. As ethylbenzene is not produced by methylation of toluene over H-ZSM-5, some alternative route must be postulated to accommodate the tracer experiment (*4*) in which [*methyl*-^{13}C]toluene/methanol mixtures yield some labeled ethylene. It has been shown that xylenes are more reactive than toluene and might conceivably be a source of ethylene.

Conversion of *p*-xylene over the catalyst at 380°C at MHSV of 0.44 h^{-1} gave the following light gas products: methane 0.07%, ethane 0.04%, and propane 0.46%, but not detectable amounts of ethylene. This rules out *p*-xylene as a precursor for ethylene.

Disproportionation of toluene. An alternative route to ethylene, using disproportionation of toluene to benzene and xylene, might be proposed following our observation that some 6% of such disproportionation occurs when toluene is passed over the catalyst at 370°C and MHSV of 0.44 h^{-1}. This reaction is usually attributed to *trans*-alkylation via benzylic cations, but if the methyl group were to leave the aromatic ring during disproportionation and transfer via the catalyst surface to another ring this could provide an opportunity for this mobile and reactive species to be sequestered by methylation in systems where methanol is present. Since Mole *et al.* (*4*) observed only 6% of the ethylene to be monolabeled with ^{13}C in his experiment with labeled toluene, our unorthodox proposed disproportionation route might well account for this degree of labeling in the ethylene.

The route to ethylene via C_4–C_6 alkenes proposed by Dessau avoids these difficulties and leaves only the problem of accounting for the 6% of the ethylene which is monolabeled-formed for [*methyl*-^{13}C]toluene/methanol observed by Mole.

CONCLUSIONS

1. Methylation of the methyl group of toluene to form ethylbenzene does not occur when methanol is passed over H-ZSM-5 at 370°C in mixture with toluene. Hence ethylbenzene cannot be regarded as an intermediate in forming ethylene from toluene during methanol conversion. In the case of added xylenes, methylation produces mainly polymethyl aromatics, changes of yields of ethyl aromatics being small.

2. Xylenes are more reactive than toluene with respect to exchange of side-chain hydrogen atoms and also with respect to disproportionation reactions. Whereas it is possible to invoke carbon scrambling reactions between ring and methyl carbons from xylenes over H-ZSM-5, these are ruled out for toluene at 370°C.

3. Ethyl aromatics, when converted alone, give yields of ethylene lower than those for methanol. Coupling this fact with the very low yields of ethyl aromatics in methanol conversion, it is possible to rule out ethyl aromatics as giving significant yields of ethylene in such conversions.

4. Many hydrocarbons convert giving appreciable yields of ethylene (e.g., *n*-heptane) and there are probably many substances found in gasolines produced by methanol conversion which make a contribution to ethylene yields under conversion conditions. These reactions may be formulated as occurring via olefinic intermediates. Ethyl aromatics do not give higher yields of ethylene than do many other hydrocarbons making it unnecessary to specify ethyl aromatics as the only or even the main precursors for ethylene formed by the "indirect" route.

Consideration of the above evidence leads us to conclude that the indirect route to ethylene production is not dominated by ethyl aromatic intermediates. The homologation of olefins by methanol (*2*) appears to be a route more in line with our observations and with the evidence recently presented by Dessau (*8*).

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