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On the Mechanism of Methanol Conversion to Hydrocarbons over HZSM-5

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Studies of methanol conversion over HZSM-5 using ^{13}C-labeled methanol in the presence of various olefins and aromatics revealed the importance of desorption limitation of reaction intermediates, as evidenced by extensive multiple labeling of polymethylbenzenes produced from unlabeled toluene. These studies also indicated that most of the ethylene produced from methanol is not a primary C_1 coupling product, but rather a secondary product derived from methyl attack on C_3^+ olefins, as evidenced by the predominant formation of singly labeled ethylene. A classical carbenium ion mechanism incorporating these findings is presented for the conversion of methanol to hydrocarbons over HZSM-5.

INTRODUCTION

Although there has been considerable speculation regarding the mechanism of methanol conversion to hydrocarbons over HZSM-5 (*1–5*), relatively few experiments have been designed to clearly differentiate between the various alternatives postulated. By studying the reaction of ^{13}C-labeled methanol in the presence of established reaction intermediates, we have been able to gather some novel insights into the overall methanol conversion process.

EXPERIMENTAL METHODS

Materials

^{13}C-Enriched methanol was obtained from Prochem (90 and 99% ^{13}C) and KOR isotopes (90% ^{13}C). The hexene used was from Aldrich (99%), the toluene was Baker reagent grade, and propylene was Matheson CP grade.

Catalysts

Three ZSM-5 catalysts were evaluated in this study: a small-crystal (~0.02 μm) and a large-crystal (~1 μm) ZSM-5 with Si/Al_2 ratios of 70 and 75, respectively, prepared according to the method of Argauer and Landolt (U.S. Patent 3,702,886), and a high-silica (Si/Al_2 > 200) small-crystal (<0.05 μm) ZSM-5 prepared without added aluminum via the method of Dwyer and Jenkins (U.S. Patent 3,941,871). All three zeolites were calcined to decompose occluded organics and subsequently ammonium ion exchanged to reduce sodium content to trace levels.

All catalysts were heated at 538°C for at least ½ h prior to use to generate the acid form.

Reactions

Reactions were conducted in a downflow Pyrex reactor contained in an electrically heated furnace. The liquid feeds were introduced into the reactor by means of a Sage syringe pump at atmospheric pressure. Reaction temperatures were in the range of 300–350°C.

The liquid mixtures used were: [^{13}C]methanol and toluene in a 1 : 1.4 molar ratio, and [^{13}C]methanol and hexene-1 in a 1 : 3.3 molar ratio. A slow stream of hydrogen was maintained throughout the reaction.

In one case, hexene-1 was introduced as a vapor in hydrogen, with the flow rate adjusted to provide 3 moles of olefin/mole of methanol fed. Propylene was charged as a

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gas at a ratio of 3.2 moles/mole of methanol.

Liquid products were collected in an ice water bath and gas samples were collected in gas tubes. Product analyses were performed on SP2100 capillary columns and on a Durapak column. Isotopic compositions of each compound were determined by gas chromatography–mass spectroscopy (GC–MS) on a Hewlett–Packard 5992 instrument at 70 eV.

The isotopic compositions were calculated using the procedure described by Biemann (*6*) beginning with the fully labeled hydrocarbon. Reference spectra of unlabeled compounds, corrected for natural abundance, were obtained on the 5992 spectrometer under conditions identical to those used for the labeling studies. Residuals were typically less than 2%.

RESULTS AND DISCUSSION

[^{13}C]Methanol Alkylation of Toluene

The alkylation of toluene by methanol to produce xylenes and other polymethylated aromatics represents one of the reactions known to be catalyzed by HZSM-5 (*7*). The corresponding reaction of ^{13}C-enriched methanol with excess toluene was now investigated under low-conversion conditions for three different HZSM-5 catalysts. These catalysts included a large-crystal (1 μm) ZSM-5 catalyst and a small-crystal (0.02 μm) form, both having approximately 70 : 1 SiO_2/Al_2O_3 ratios, as well as a small-crystal high-SiO_2/Al_2O_3 HZSM-5. The reaction products in all cases included a nonequilibrium mixture of xylene isomers, together with varying amounts of polymethylated aromatics, predominantly 1,2,4-trimethylbenzene (1,2,4-TMB) and durene (1,2,4,5-tetramethylbenzene). The product distributions observed at comparable toluene conversions for the three catalysts are shown in Table 1.

The nonequilibrium formation of xylenes, rich in the *para* isomer in the case of large-crystal HZSM-5 and *ortho* rich in the other two cases, can be understood in terms of diffusional control imposed by the large-crystal zeolite (*7*) favoring formation of the less bulky *para* isomer vs the kinetically controlled product distribution favoring production of the *ortho* isomer in the absence of strong diffusional control.

Desorption-Disguised Kinetics

The liquid products shown in Table 1 were analyzed by GC–MS and the isotopic enrichment in each compound determined. The ^{13}C distributions obtained are shown in Fig. 1.

Not surprisingly, the xylenes in all cases exhibited predominant enrichment by one labeled carbon atom, while the trimethylbenzenes were enriched by two carbon-

TABLE 1

Composition of Liquid Products Obtained from Reaction of Toluene[a] with [^{13}C]Methanol

Catalyst	T (°C)	WHSV[b]	Toluene (%)	p,m-Xylene (%)	o-Xylene (%) (% *ortho*)[c]	1,2,4-TMB (%)	Durene (%)
Large-crystal HZSM-5	350	18	85.2	9.5	1.0 (9.4)	2.6	<0.1
Small-crystal HZSM-5	300	19	85.1	5.9	5.0 (46)	1.5	0.75
High-silica HZSM-5	300	6	84.5	7.0	6.2 (47)	1.3	0.50

[a] Toluene/MeOH = 1.4/1.0 mole ratio: Composition given on a weight percentage basis.

[b] WHSV = weight hourly space velocity (g feed/g catalyst per hour).

[c] Percentage *ortho* isomer in xylene; equilibrium = 23% *ortho*.

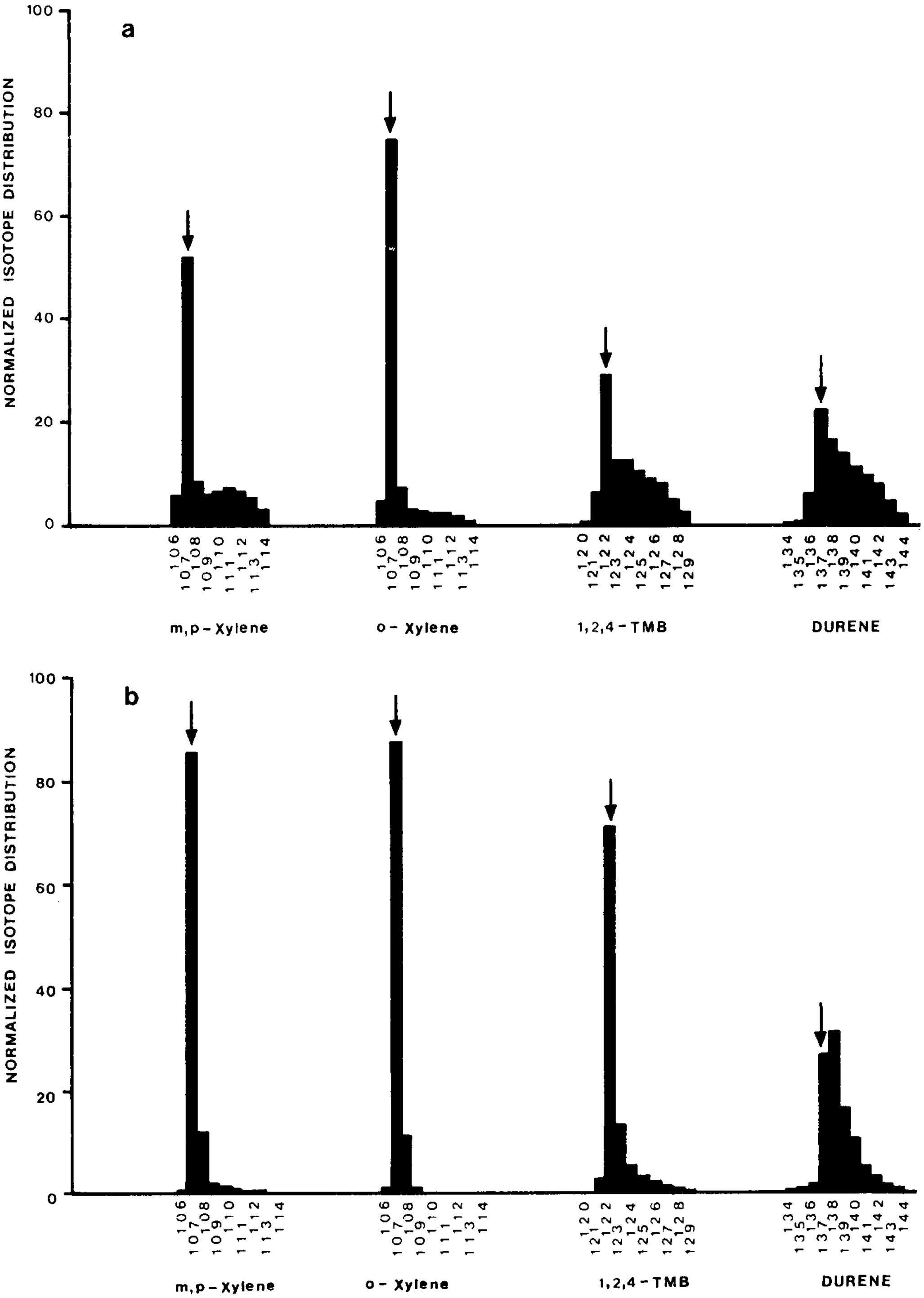
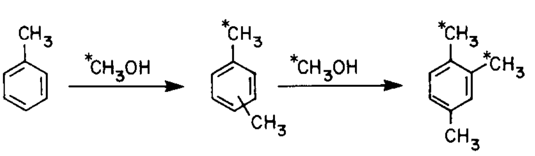


FIG. 1. Isotopic distribution of methylated aromatics. (a) Sample from large-crystal HZSM-5. (b) Sample from high-silica HZSM-5. ↓ denotes product expected by direct methylation.

13's, as anticipated from the direct methylation of aromatics.



However, what was surprising was the finding that some multiple labeling did occur in the xylenes, and even more so in the trimethylbenzenes and durene. The durene formed was most conspicuous, in that extensive multiple ^{13}C incorporation was observed, far beyond that expected for direct methylation. In fact, significant amounts of durene were formed in which all ten carbon atoms were labeled. Similarly fully labeled trimethylbenzenes and xylenes were also detected.

Formation of these multiply labeled aromatics can only arise via the self-condensation of labeled methanol, the well-known conversion of methanol to hydrocarbons over HZSM-5. Apparently, toluene and other aromatics formed via the methanol conversion process are not in equilibrium with the toluene contained in the feed or with those aromatics formed by alkylation of the unlabeled toluene under these reaction conditions.

The formation of multiply labeled aromatics, as well as the variation observed among the three HZSM-5 catalysts tested, can be rationalized on the basis of desorption-disguised kinetics (*8*). Intermediates formed inside ZSM-5 catalysts, especially in those catalysts having high acid site densities and large crystal sizes, do not readily desorb and diffuse out of the zeolite without undergoing further reaction. Thus, methanol which appears to be preferentially sorbed on the acid sites can react sequentially with intermediates formed from methanol itself all the way to durene prior to desorption from the zeolite.

The relative contribution of this desorption rate-limited methanol conversion pathway, as evidenced by the extent of multiply labeled aromatics formed (see Fig. 1), was greatest with the large-crystal catalyst and least in the case of the smaller-crystal high-silica/alumina HZSM-5. This qualitative difference is expressed in more quantitative terms in Table 2.

It is also interesting to note that the desorption-limited pathway made less of a contribution in the formation of *ortho-*

TABLE 2

Results of ^{13}C-Labeling Experiments: Toluene and [^{13}C]Methanol (1.4 : 1 Molar Ratio)

	Catalyst						
	Small-crystal HZSM-5			Large-crystal HZSM-5			High-silica HZSM-5
Toluene in product (wt%)	71.8	77.2	85.1	81.3	85.2	93.5	84.5
% ^{13}C in toluene	—	1.2	1.2	—	1.3	1.3	1.5
% ^{13}C in *m,p*-xylene	20.1	19.7	16.8	29.0	30.7	27.5	15.0
% ^{13}C in *o*-Xylene	17.8	14.2	13.3	22.9	19.8	16.2	14.1
% ^{13}C in 1,2,4-TMB	33.7	37.1	36.2	40.7	44.5	48.4	28.0
% ^{13}C in durene	43.0	47.8	50.0	48.2	50.6	57.1	44.7
% of product formed directly from MeOH							
m,p-Xylene	10	10	6	22	34	10	2
o-Xylene	7	2	2	14	10	5	1
1,2,4-TMB	19	24	22	29	34	40	7
Durene	25	32	36	33	37	47	21

TABLE 3

Isotopic Composition of Ethylenes

Catalyst	Added olefins	C=C (%)	C=^{13}C (%)	^{13}C=^{13}C (%)	^{13}C=^{13}C/^{13}C=C
Small-crystal HZSM-5	Propylene	49	27	24	0.91
Small-crystal HZSM-5	Hexene-1	72	20	8	0.42
High-silica HZSM-5	Hexene-1	84	14	2	0.14
MeOH coupling (theoretical)		1	18	81	4.5

xylene than in that of the other two xylene isomers, possibly indicative of *ortho*-xylene formation at or near the external surface of the zeolite.

Mechanism of Methanol Conversion—Source of Ethylene

One of the most intriguing questions associated with the methanol conversion process centers about the source of ethylene. To help resolve this question, the reaction of ^{13}C-labeled methanol in the presence of unlabeled olefins was investigated.

If ethylene were formed exclusively by direct combination of two C_1 fragments, whether carbene-like or not, all ethylene derived from labeled methanol would have to be doubly labeled. The presence of unlabeled olefins should not interfere in such a reaction, since any ethylene produced from these added olefins would be totally unlabeled.

When ^{13}C-labeled methanol was reacted over HZSM-5 (0.02 μm) in the presence of a 3 molar excess of propylene, a mixture of ^{13}C-labeled ethylenes was produced, as shown in Table 3.

The ratio of doubly labeled to singly labeled ethylene (0.9) was substantially lower than that expected for random coupling of 90% [^{13}C]methanol (4.5). This clearly indicates that some other pathway involving attack of methanol on olefins must be responsible for at least part of the ethylene produced. As in the case of toluene alkylation, the C_9 and C_{10} aromatics produced in the presence of unlabeled olefin were also found to be extensively multiple labeled due to desorption rate limitations.

The relative amount of double-labeled ethylene was substantially further reduced when hexene-1 was used as the trapping olefin, and even more so, when high-silica/alumina HZSM-5 was the catalyst (Table 3).

On the basis of these observations, we must conclude that most of the ethylene produced is not a primary reaction product from methanol, except possibly during a short initiation phase producing C_3^+ olefins. Initiation may indeed involve $C_1 + C_1$ bond formation, quite possibly via an oxonium ion rearrangement as has been proposed (*9*) or via a carbene insertion mechanism (*1*). However, this reaction becomes irrelevant once sufficient C_3^+ olefins have been formed. Once olefins exist, only methanol attack on these olefins is responsible for methanol conversion (*10*)[1] and subsequent ethylene formation via cracking of higher olefins. This is consistent with the reported autocatalytic (*11*) nature of the methanol reaction and the relative constancy of ethylene selectivity between 1% and 90% methanol conversion.

Consequently, we wish to propose the following mechanism for the methanol reaction over HZSM-5, based on classical, well-established carbenium ion chemistry. Superimposed thereon must be selective

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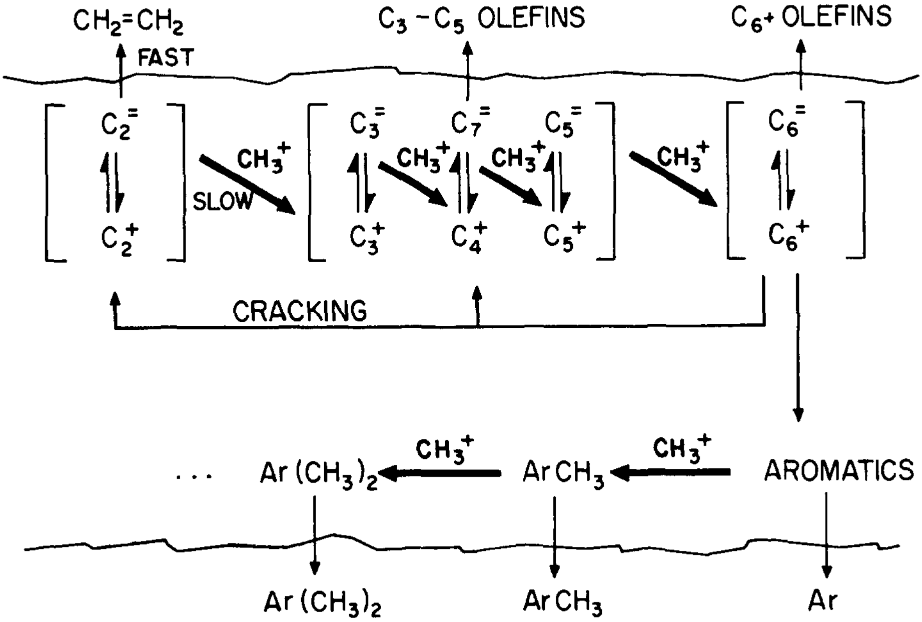
[1] As anticipated by such a propagation mechanism, the labeled butenes obtained from unlabeled propylene were predominantly (>90%) singly labeled.

desorption control characteristic of the acidic zeolite.



According to this mechanism, ethylene, which forms the least stable carbenium ion, desorbs most readily. Since it is also least susceptible to further electrophilic attack, it can be recovered as a major product even at high methanol conversions.

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