# On the H-ZSM-5 Catalyzed Formation of Ethylene from Methanol or Higher Olefins

R. M. DESSAU

*Mobil Research and Development Corporation, Central Research Laboratory, Princeton, New Jersey 08540*

The distributions of olefins formed in the HZSM-5 catalyzed total conversions of methanol and heptene-1 were examined at low partial pressures as a function of contact time. The results clearly indicated that ethylene was only obtained at long contact times, and then via secondary reequilibration of the primary kinetic olefinic products, propylene and butenes. © 1986 Academic Press, Inc.

## INTRODUCTION

One of the most intriguing problems still the subject of much controversy is the mechanism for hydrocarbon formation from methanol and, particular, the production of ethylene (for recent reviews see Ref. (*1*)). Despite an abundance of mechanistic hypotheses, the formation of C—C bonds from a one-carbon species, methanol, remains a mystery. Even the question of whether ethylene is the first olefin produced from methanol remains controversial (*2*), although simplistically one might expect two-carbon species to be formed before larger molecules are produced.

In this communication, we would like to present some new data on ethylene formation from methanol and from a related reaction, heptene cracking. We will also propose a mechanism, fully consistent with these and earlier observations, that will explain the large variations in ethylene yields previously observed.

Ethylene selectivities, under conditions that do not favor aromatization, typically are under 10%, with propylene exceeding ethylene by factors as high as 5 or more (on a weight basis) (*3*). In contrast, a partial conversion MTG process in the presence of added water can produce as much as 28% ethylene, with ethylene exceeding propylene by a factor of almost 2 (*4*).

In contrast to previous work, our investigation was deliberately conducted at very low partial pressures (1–10 Torr), conditions we have found to severely limit olefin reequilibration. By suppressing olefin equilibration, we were able to observe the true kinetic products of these reactions.

## EXPERIMENTAL METHODS

The catalysts used included an HZSM-5 having a silica/alumina ratio of about 70 and an $\alpha$ activity of about 140, and a high silica/alumina (1670 : 1) HZSM-5, having an $\alpha$ of 6.

Methanol and heptene-1 (which was percolated through alumina prior to use) were introduced into the nitrogen stream for vaporizers maintained at −22 to −37°C, depending on the partial pressure desired. Butenes were added via vaporizers maintained at −78°C. Reactant partial pressures were in the range of 1–10 Torr.

Reactions were conducted at 400 and 450°C as noted. Reaction products were analyzed by on-line gas chromatography on a 15-ft. *n*-octane/Durapak column. A Bentone column was also used to confirm the absence of dimeric products from heptene.

## RESULTS AND DISCUSSION

*Heptene cracking.* The HZSM-5 catalyzed cracking of olefins at 275°C was studied by Garwood (*5*), who found ethylene to be produced in only trace quantities (<0.1%) from hexene or decene. The near-
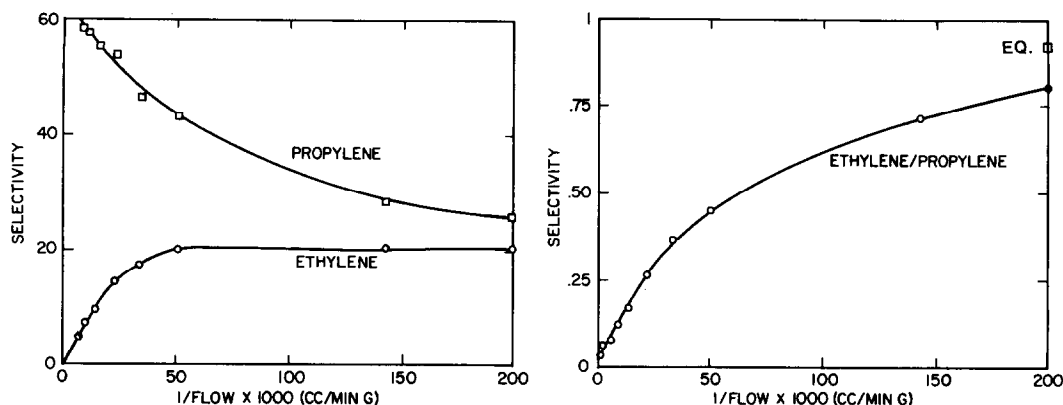
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FIG. 1. Product selectivity (weight basis) as a function of contact time in heptene cracking.

absence of ethylene in the primary cracking products of alkenes at 350–405°C was recently confirmed by Abbot and Wojciechowski (6).
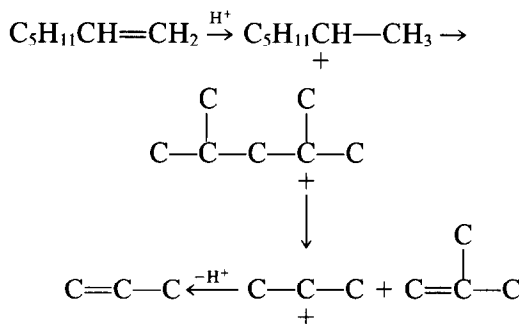
We have now reinvestigated heptene-1 cracking at 400°C and, more importantly, at high dilution (1–2.5 Torr in $N_2$), so as to minimize olefin equilibration and formation of paraffins and aromatics. Reaction severity was varied by changes in flow rates. Conversion of heptene was virtually complete under even the fastest flow rate examined (equilibrium concentration of heptene under these dilute conditions was estimated to be very small). The products obtained at various severities are shown in Table 1 and Fig. 1.

This yield of ethylene, as well as the ratio of ethylene to propylene, was found to increase with increasing reaction severity. A gradual increase of ethylene selectivity from approximately 2 to >20% was observed, at which point the olefin distribution approached equilibrium composition.

*Kinetic vs thermodynamic product.* At low reaction severities, the distribution of olefins from heptene is primarily determined by kinetic factors. On the basis of cracking studies over dual-functional catalysts[1] (7), the kinetic cracking products

[1] Hydrocracking heptane over Pt/HZSM-5 at 240°C produced approximately equimolar amounts of propane and isobutane.

from heptene would be expected to be predominantly propene and butenes, via the sequence

$$C_5H_{11}CH{=}CH_2 \xrightarrow{H^+} C_5H_{11}\overset{+}{C}H{-}CH_3 \rightarrow$$

$$C{-}\overset{\overset{\displaystyle C}{|}}{C}{-}C{-}\overset{\overset{\displaystyle C}{|}}{\underset{+}{C}}{-}C$$

$$\downarrow$$

$$C{=}C{-}C \xleftarrow{-H^+} C{-}\underset{+}{C}{-}C + C{=}\overset{\overset{\displaystyle C}{|}}{C}{-}C$$

As the residence time of the products increases, the olefin distribution shifts toward equilibrium, and hence toward more ethylene. Ethylene clearly is not a primary cracking product of any significance, but is formed principally by secondary reequilibration of primary olefinic products.

*Methanol conversion.* The HZSM-5 catalyzed conversion of methanol was investigated under similar conditions to those used for heptene cracking (400°C and ~8 Torr methanol in $N_2$). Reaction severity was again varied by changing flow rates.

Methanol conversion to hydrocarbons was essentially complete under all flows examined. The product distribution was similar to that produced from heptene under comparable conditions. The products obtained at various degrees of reaction severity are shown in Table 2 and Fig. 2.

TABLE 1

Product Yields From Heptene-1 Cracking

Catalyst: HZSM-5
Temperature: 400°C
Heptene pressure: ~1 Torr
Total pressure: 1 atm $N_2$

| Flow[a] | $C_2^{=\,b}$ | $C_3^=$ | $\Sigma C_4^=$ | $C_3^=/C_2^=$ |
|---|---|---|---|---|
| 530[c] | 2.3 | 50.7 | 34.9 | 22 |
| 350[c] | 3.6 | 49.6 | 32.1 | 14 |
| 150 | 5.0 | 58.4 | 28.1 | 11.6 |
| 105 | 7.5 | 57.5 | 26.4 | 7.7 |
| 70 | 9.9 | 55.3 | 23.8 | 5.6 |
| 45 | 14.5 | 53.8 | 21.5 | 3.7 |
| 30 | 17.5 | 46.5 | 18.9 | 2.7 |
| 20 | 20.1 | 43.3 | 16.3 | 2.2 |
| 7 | 20.8 | 28.6 | 11.5 | 1.4 |
| 5 | 20.4 | 25.8 | 10.2 | 1.26 (equil = 1 : 1) |

[a] In cm³/min g.
[b] Weight percentage.
[c] 2.5 Torr heptene.

TABLE 2

Product Yields from MeOH Conversion

Catalyst: HZSM-5
Temperature: 400°C
MeOH Partial pressure: ~8 Torr
Total pressure: 1 atm $N_2$

| Flow[a] | $C_2^{=\,b}$ | $C_3^=$ | $\Sigma C_4^=$ | $C_3^=/C_2^=$ |
|---|---|---|---|---|
| 4700[c] | 1.17 | 50.6 | | 43 |
| 3250[d] | 1.39 | 47.2 | | 34 |
| 2200 | 2.07 | 49.4 | | 24 |
| 1520 | 2.72 | 54.6 | | 20 |
| 1040 | 2.97 | 50.6 | | 17 |
| 700 | 3.10 | 49.4 | | 16 |
| 500 | 4.44 | 56.7 | 26.3 | 13 |
| 335 | 5.70 | 56.4 | 26.8 | 10 |
| 230 | 8.27 | 54.0 | 26.1 | 6.5 |
| 155 | 9.38 | 54.1 | 24.0 | 5.8 |
| 100 | 12.3 | 51.1 | 22.0 | 4.2 |
| 70 | 16.7 | 44.0 | 20.8 | 2.6 |
| 45 | 19.3 | 38.4 | 17.6 | 2.0 |
| 30 | 21.5 | 34.3 | 16.3 | 1.60 |
| 20 | 23.3 | 31.5 | 14.4 | 1.35 |
| 11 | 21.7 | 24.8 | 8.1 | 1.14 |
| 8 | 21.8 | 23.0 | 6.3 | 1.07 |
| 5 | 21.4 | 20.1 | 6.7 | 0.94 |
| Equil. | | | | 0.96[e] |

[a] In cm³/min g.
[b] Weight percentage produced.
[c] At >90% $CH_2$ conversion.
[d] At ~95% $CH_2$ conversion.
[e] Calculated for 100% conversion of MeOH at 8 Torr to 65% olefins and 35% paraffins plus aromatics.

As we observed in heptene cracking, the yield of ethylene, as well as the ethylene/propylene ratio, increased with reaction severity. At low severity, yet under conditions of complete methanol conversion to hydrocarbons, the weight ratio of ethylene to propylene was less than 0.04, whereas ratios as high as 1.0 were obtained at higher severities.

The high silica/alumina (1670 : 1) HZSM-



FIG. 2. Product selectivity (weight basis) as a function of contact time in methanol conversion.
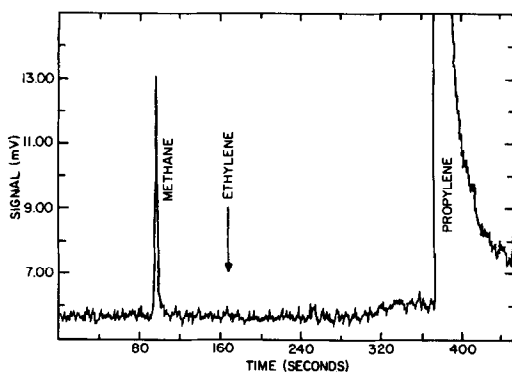
FIG. 3. On-line GC analysis of methanol conversion products.

5 catalyzed partial conversion of methanol was also examined under the low-pressure conditions (8 Torr, 400°C) shown to suppress olefin reequilibration.

The main products observed at 21% $CH_2$ conversion were propylene (43.4 wt% selectivity), butenes (17.7%), pentenes (15.4%), hexenes (10.1%), and methane (1.1%). No *measurable amount of ethylene was detected* (see GC trace shown in Fig. 3).

The yields of ethylene produced over this catalyst at 450°C, under conditions of total methanol conversion, are shown in Fig. 4.
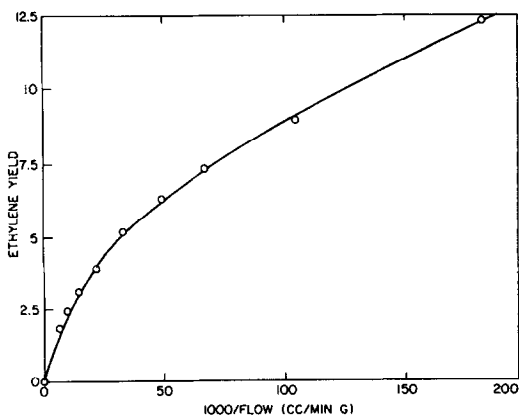
Ethylene yields increased dramatically with contact time, as did the relative yields of ethylene to propylene (Fig. 5). Whereas the relative yield of ethylene increased with reaction severity, the relative yields of butenes and pentenes both decreased with contact time and gradually approached equilibrium concentration (Fig. 5).

*Mechanism of methanol conversion and ethylene formation.* The results shown above indicate that ethylene is *not* the initial observable olefin produced from methanol, but is formed by secondary reequilibration of the primary olefinic products, propylene and butene. Ethylene formation in reactions conducted at higher pressures, even at low conversions, is predominantly the result of thermodynamic control. Ethylene yields higher than equilibrium can be obtained under diffusion-controlled conditions, where olefin equilibration occurs inside the zeolite crystal, due to the apparent greater rate of diffusion of ethylene out of the acidic zeolite. Thus ethylene selectivities from methanol, under conditions of high olefin production, were greatest for small pore zeolites (erionite, zeolite T), lower for intermediate pore zeolites (ZSM-5), and least for large pore zeolites (X, Y) (8).



FIG. 4. Ethylene yield (weight percent) as a function of contact time for complete methanol conversion at 450°C.
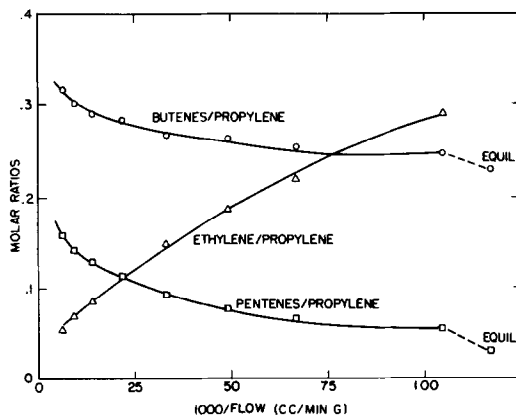


FIG. 5. Molar olefinic product ratios as a function of contact time for complete methanol conversion at 450°C.

This conclusion, that ethylene is not the primary product, is totally consistent with our observation regarding methanol conversion over dual-functional catalysts. In the presence of hydrogen and a platinum hydrogenation function, which served to intercept olefinic products as they were formed, the yield of propane greatly exceeded that of ethane by factors as high as 30.

In view of the now well-established finding that the methanol reaction is autocatalytic and catalyzed by added olefins (9), carbon atoms of which can be incorporated into the ethylene produced (10), we would like to propose the following mechanism:

METHANOL CONVERSION PATHWAY

$$CH_3OH \xrightarrow{H^+} CH_3^+ + H_2O$$
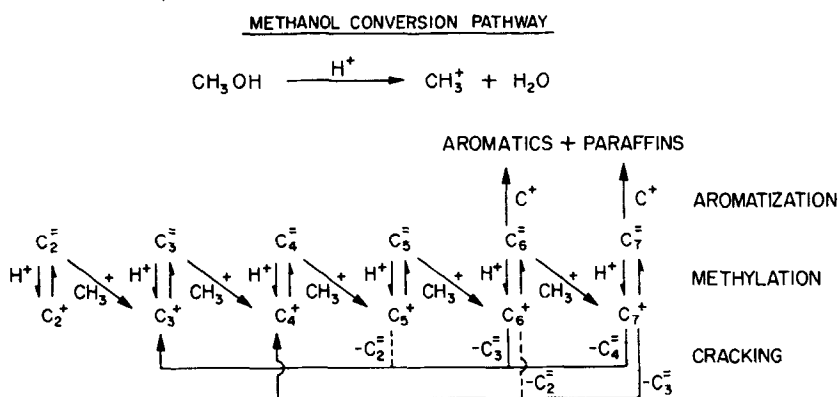
The use of low methanol partial pressure reaction conditions in this study allowed us to examine the true kinetic products of the reaction by suppressing the rate of olefin equilibration relative to that of methanol conversion. Low partial pressures reduced the concentration of alkyl carbenium ions on the catalyst, by shifting that equilibrium toward the free olefin, whereas the concentration of methyl cations from methanol remained relatively unaffected.

$$H^+{}^-Z + RCH{=}CH_2 \rightleftharpoons R{-}\underset{+}{CH}{-}CH_3\,{}^-Z$$

$$H^+{}^-Z + CH_3OH \rightleftharpoons CH_3^+\,{}^-Z + H_2O$$
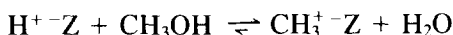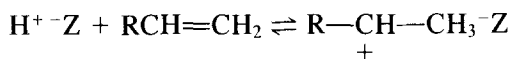
*Olefin methylation.* The very rapid direct methylation of olefins by methanol was confirmed by conducting the methanol conversion reaction in the presence of an equimolar amount of butenes at low partial pressures. At 450°C, pentenes were the major products obtained and relatively little propylene was observed at low conversions. Thus, with butene-1 as the reactant, the molar product composition observed was: propylene (0.027), butenes (1.00), pentenes (0.21), hexenes (0.084), and heptenes (0.011); and with isobutene as the reactant, the composition was: propylene (0.005), butenes (1.00), pentenes (0.24), hexenes (0.045), and heptenes (0.005). Individually, both methanol and butene were relatively unreactive under these reaction conditions.

Under the low-pressure and high-temperature reaction conditions, methylation of olefins by methanol is extremely rapid and faster than olefin equilibration. Only these conditions permit observation of primary kinetic products uncomplicated by secondary olefin equilibration.

*Conclusions.* The only question remaining in the mechanistic scheme presented is where the first olefin molecule comes from. This is analogous to asking where the first peroxide comes from in autooxidation reac-

tions.[2] It is of importance only during the relatively limited initiation phase of the reaction, which is responsible for producing little of the total product observed.

According to the mechanism we propose, as little as one molecule of ethylene or other olefin formed during the initiation phase could be sufficient to catalyze methanol conversion. All olefins produced after that derive from repeated methylation, oligomerization, and cracking.

Ethylene may well be the initial olefin formed during the initiation phase, but this ethylene represents only a tiny fraction of the total ethylene produced under most conditions. The bulk of the ethylene generally observed is formed by reequilibration of higher olefins. The mechanism for ethylene formation during this rather limited initiation phase remains speculative, and irrelevant to the overall mechanism of methanol conversion to hydrocarbons.

## ACKNOWLEDGMENTS

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[2] Chain branching, as commonly understood, is characterized by the formation of more than one new active center for each one reacting. That is the case for both autooxidation and methanol conversion. Note that in the sequence: propylene + 3 methanol = hexene = 2 propylene, two olefin molecules capable of reacting with methanol are produced from one initial olefin.