

Conversion of Methanol to Hydrocarbons

II. Reaction Paths for Olefin Formation Over HZSM-5 Zeolite Catalyst

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Methanol was converted to hydrocarbons, primarily olefins, and water over a low-activity HZSM-5 zeolite catalyst with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1600/1. Mixtures of methanol and individual C_2 - C_4 olefins were also used to simulate conditions in the catalyst bed at low conversions. Facile methylation of olefins with methanol to produce the next higher olefinic homolog was observed. Ethylene was the major primary hydrocarbon produced from methanol at low conversion. The olefin mixtures isolated under various conditions of reaction were fitted to the chain-growth kinetics as described by the Flory equation. Good to excellent correlation coefficients were found at low and medium conversions of methanol. This is consistent with a stepwise growth in molecular weight of the olefins, starting with propylene, by alkylation of the olefins with methanol. However, since ethylene is produced by a different mechanism, it does not fit the Flory equation. At higher temperatures and conversions, the olefins undergo scrambling or thermodynamic equilibration reactions also producing olefin mixtures with good correlation coefficients. Under the latter conditions, a distinction between the stepwise growth and thermodynamic equilibration reactions cannot be made since both contribute to the product mixture.

I. INTRODUCTION

Methanol is converted to water and a mixture of hydrocarbons containing up to 10 carbon atoms over ZSM-5 type zeolite catalysts (1-4). It is evident that a considerable number of steps are needed to accomplish this starting with a single-carbon reagent. Olefin formation, alkylation, oligomerization, cracking, aromatization, and disproportionation reactions have been proposed, based primarily on the various products isolated (4-6). At low conversions, olefins predominated while aromatic and paraffinic products appeared at high conversion (5, 6).

The formation of the initial carbon-carbon bond and/or the first hydrocarbon(s) from methanol or methyl ether is of special interest since herein lies one of the unique and valuable characteristics of this class of zeolite catalysts. Venuto and Landis (7) and Chang and Silvestri (4) have proposed carbene or carbenoid intermediates. Kaed-

ing and Butter have suggested that ethylene is the primary hydrocarbon formed, probably from prior formation of methyl ethyl ether (MEE) (5). The latter then undergoes a known, very rapid, acid-catalyzed elimination of methanol from the protonated species to give ethylene. Higher olefins could be produced by subsequent alkylation of ethylene with methanol to give propylene, then butylene, etc. or by olefin oligomerization (5). Derouane has proposed that higher ethers, such as propyl methyl ether, are produced from MEE by addition of an active C_1 intermediate (8). Subsequent elimination of methanol from the protonated ether would thereby produce propylene and higher olefins from their corresponding higher alkyl ethers as primary hydrocarbon products. Van Hooff and co-workers have proposed that trimethyl and subsequently higher trialkyl oxonium ions are formed which could produce the higher olefins by alcohol elimination (9).

A common feature of all these mechanisms includes the stepwise increase in molecular weight of the aliphatic products by sequential addition of one reactive carbon unit. The simplest reactive single-carbon intermediates can be a methyl carbenium ion or even carbene itself. More recently, the mechanism for hydrocarbon formation from methanol over ZSM-5 catalyst has been reviewed (4).

In order to focus attention on the early events which occur in the zeolite catalyst, starting with methanol, a variety of approaches have been used to repress formation of the higher molecular weight products. Selectivity to C_2 - C_4 olefins is usually enhanced by operation at low conversion achieved by use of deactivated catalysts, high space velocity, and by judicious selection of temperature, inert diluents, etc. (4, 5, 10). We have observed that very high selectivities to olefins were obtained by using ZSM-5 class zeolite catalysts with high silica/alumina ratios starting with methanol, light olefins, or a mixture of both.

The Flory equation (11) was used to analyze and interpret the relative amounts of products produced with these catalysts. An objective was to gain additional information about the reaction mechanism for production of ethylene, propylene, and the higher molecular weight olefins.

II. EXPERIMENTAL METHODS

Reagent grade methanol (99+%) was used without further purification. Methods for preparation of ZSM-5 have been described previously (12, 13). The hydrogen form of ZSM-5 was prepared by drying the original crystals at 125°C, calcining at 500°C followed by exchanging the sodium ion with an aqueous ammonium salt solution. The ammonium form was then converted to the hydrogen form by calcination.

A. Material Balance Runs

Five grams of catalyst, diluted with 4 vol of low-surface-area quartz chips, was centered in a fixed-bed, continuous flow, elec-

trically heated, cylindrical quartz reactor, 1.1×15 cm, containing a centered quartz thermowell. Temperatures were measured at three positions in the catalyst bed. The reaction temperature recorded was the highest reading in the bed. Methanol was delivered by a metering pump to a vaporizer.

The vapor from the reactor was passed successively through cold water and dry-ice traps. The remaining gas was measured by a wet test meter or collected in a tower by displacement of brine or water for subsequent analysis. The liquid in the dry-ice trap was warmed to ambient temperature and the gas evolved was collected in a Teflon bag. The liquid remaining was combined with the condensate in the water-cooled trap and the organic and water phases were separated, weighed, and analyzed by GC. A silica gel column was used to analyze gases, a 5% SP-1200/5% Bentone on Supelcoport column was used for the organic liquid, and a Porapak QS column was used for the aqueous phase. Reaction products were collected for 1-h periods during steady state conditions.

Individual isomers were identified for the C_2 - C_4 products. Aromatic compounds could be easily detected. Individual C_5 and higher aliphatic products were lumped according to retention times established by certain representative pure standards. Material balances of ± 1 -3% were usually obtained. Methanol conversion is defined as the methanol consumed divided by methanol fed to the reactor multiplied by 100 for conversion to percentage. Methyl ether was converted to methanol equivalent and considered as unconverted methanol.

B. On-Line Analysis Runs

HZSM-5 (2 g), silica-to-alumina ratio of 1600 to 1, pelletized to 14/20 mesh, and diluted with 4 g of quartz chips, was packed in a downflow metal reactor constructed of 316 S.S. with an internal diameter of $\frac{3}{8}$ in., a centrally located thermal well, and an 8-in. metal preheater section. The reactor was

heated by a two-zone furnace. Reactor temperature was recorded at the top of the catalyst bed by a thermocouple in the thermal well. Aqueous methanol, 57.2% by weight, or pure water was metered by an Isco pump. Ethylene or propylene was fed by tank pressure and regulated by a Supelco low-flow needle valve. The total reactor effluent was diluted with nitrogen carrier gas at a rate of 40 cc/min, mixed at the reactor outlet and transported through tubing at 200°C to an automatic gas sampling valve connected to a Hewlett-Packard (HP) gas chromatograph, with a flame ionization detector. The total hydrocarbon products were analyzed with a 12-ft. column of *n*-octane on Poracil. A constant volume, 1-cc gas sample was injected from the sampling loop onto the GC column. For each set of conditions, at least three samples were taken over a period of 2 to 3 h to ensure reproducible, steady-state operation. The CO or CO₂ content was checked by a silica gel column on a separate GC with a thermal conductivity detector, whenever reaction conditions were changed. They were always well below 1% of hydrocarbon products. The GC results were integrated and analyzed by a HP LAS 3354 computer. For runs with low conversions of starting mate-

rial, the chromatograms were carefully re-analyzed on a HP 2648A graphic terminal with expanded sensitivity to ensure proper peak integration and identification of trace products. Small amounts of paraffin were lumped with the corresponding olefin to make the Flory calculations.

III. RESULTS AND DISCUSSION

A. Products from Methanol with ZSM-5 Class Zeolites

Effects of catalyst activity. Reaction products obtained from methanol or methyl ether over a series of ZSM-5 zeolite catalysts with silica/alumina ratios ranging from 35 to 1600 are summarized in Table 1. The catalytic activities of the zeolites are directly associated with the framework alumina content (14). Values derived by the alpha-test, which measures the relative cracking rates of *n*-hexane, are also shown (14). In Run A (Table 1), where ZSM-5 with the lowest alpha value was used (lowest activity), the major products observed were low molecular weight olefins. As the activities of the zeolites increased, Run B to F, the aromatic fraction and paraffinic products also increased to finally become large components. The selectivity change of light

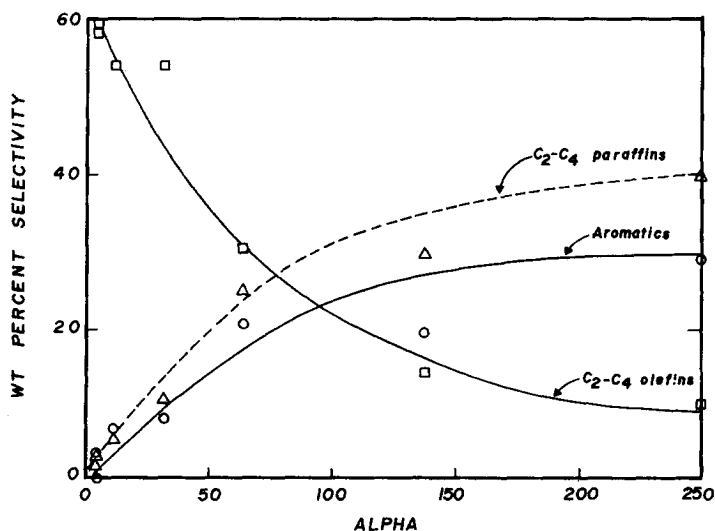


FIG. 1. Selectivities of olefins, aromatics, and paraffins as a function of catalyst activities, determined by alpha values. □, C₂ to C₄ olefins; ○, aromatics including benzene, toluene and xylenes; △, C₂ to C₄ paraffins.

TABLE I
Conversion of Methanol to Hydrocarbon Products over HZSM-5 with Various SiO₂/Al₂O₃ Ratios
100% Methanol Conversion^a

	Run							
	A	B	C	D	E	F	G	H
Mole ratio, SiO ₂ /Al ₂ O ₃	1600	500	298	140	70	35	1600	1600
Alpha ^b	5	12	32	64	138	250	5	5
Starting material	MeOH	MeOH	MeOH	MeOH	MeOH	MeOH	ME ^f	ME/N ₂ ^g
Space time, sec ^c	2.5	2.5	2.5	2.5	2.5	2.5	3.9	1.3
Product selectivity (wt%)								
CO, CO ₂ , CH ₄	3.2	2.1	0.7	1.3	1.0	4.8	1.0	0.6
Olefins								
C ₂ H ₄	5.2	9.9	7.3	6.4	2.8	2.0	2.7	1.8
C ₃ H ₆	32.1	20.1	20.1	7.4	3.7	1.5	31.0	33.8
C ₄ H ₈	22.0	23.9	26.5	26.7	8.0	6.7	23.6	23.6
Total	59.3	53.9	53.9	30.5	14.5	10.2	58.3	59.2
Paraffins								
C ₂ H ₆	0.1	0.3	0.2	0.4	0.4	1.3	0.1	0
C ₃ H ₈	0.7	1.5	2.9	6.6	8.4	13.9	0.4	0.2
C ₄ H ₁₀	2.6	3.8	7.8	18.2	21.0	24.6	1.6	1.6
Total	3.4	5.6	10.9	25.2	29.8	39.8	2.1	1.8
C ₅ ^d	12.1	17.3	14.2	10.9	12.5	3.7	16.2	15.4
C ₆	6.5	4.2	4.0	2.9	4.0	0.5	12.5	15.4
C ₇	6.6	6.2	4.1	2.0	3.4	0.2	5.9	5.0
C ₈ +	5.2	3.9	3.9	6.9	15.0	11.8	5.1	2.6
BTX ^e	3.7	6.8	8.3	20.3	19.7	29.1	—	—
Total	100.1	100.0	100.0	100.0	99.9	100.0	100.0	100.0

^a Reaction temperature: 450°C, except Run E at 400°C, WHSV of methanol: 4.0–4.3. Under these conditions, methanol and ME conversion to hydrocarbons was 100% in every run. WHSV = weight of starting material fed per unit weight of catalyst per hour. ME = methyl ether.

^b A measure of acidity (Ref. (14)).

^c Space time was calculated from catalyst volume divided by the volumetric flow rate of reactants converted into gas at STP conditions.

^d In this fraction, the olefin and paraffin compositions are not separated.

^e Benzene, toluene, and xylenes.

^f WHSV = 3.8, ME = methyl ether.

^g WHSV ME = 3.8, N₂ = 4.4.

olefins, paraffins and aromatics as a function of alpha is also shown in Fig. 1. This result demonstrates that olefins are the primary hydrocarbon products produced from methanol and that olefins were subsequently converted to aromatics and paraffins under more vigorous reaction conditions by use of more active catalysts (4, 10).

Effect of nitrogen diluent. The hydrocarbon products obtained from methyl ether,

over ZSM-5, SiO₂/Al₂O₃ = 1600/1 are shown in Runs G and H of Table 1. In the latter, nitrogen, an inert diluent, was used to change the space-time parameter. Runs A, G, and H (Table 1), show that similar products were obtained starting with either methanol or methyl ether. Interconversion between methanol and methyl ether plus water proceeds more rapidly than formation of hydrocarbons (15). Propylene and butylene were the major olefinic products

TABLE 2

Methanol Conversion to Hydrocarbons by HZSM-5
SiO₂/Al₂O₃, 1600/1, at Different Temperatures^{a,b}

	Run				
	I	J	K	L	M
Temp. °C	327	332	356	380	389
MeOH conversion	0.03	0.5	2.0	17.0	31.2
Hydrocarbon product selectivity (wt%)					
CH ₄	26.5	21.4	16.3	3.8	2.5
Olefins					
C ₂ H ₄	50.0	32.8	28.9	9.2	6.5
C ₃ H ₆	23.5	27.4	25.5	32.5	30.5
C ₄ H ₈	0	10.1	13.4	20.8	21.0
Total	73.5	70.2	67.8	62.5	58.0
Paraffins					
C ₂ H ₆	0	0.6	0.6	0.1	0.1
C ₃ H ₈	0	0	0.6	0.3	0.3
C ₄ H ₁₀	0	2.1	1.7	2.6	2.4
Total	0	2.7	2.9	3.0	2.8
C ₅	0	5.8	9.2	15.7	15.6
C ₆	0	0	3.8	14.9	10.9
C ₇	0	0	0	0	6.1
Others	0	0	0	0	4.2
Total	100.0	100.1	100.0	99.9	100.1

^a These data were obtained by on-line analytical method (see Experimental).

^b Fifty seven percent methanol in water was fed through the catalyst at WHSV of 1.8.

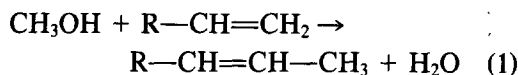
observed and the former even increased slightly as contact time was reduced at the expense of ethylene (Run H).

Effect of reaction temperature on methanol conversion and products with HZSM-5 SiO₂/Al₂O₃, 1600/1. By carefully controlling the reaction temperature and using 57.2 wt% methanol in water, hydrocarbon product distributions were observed at very low to medium methanol conversions by on-line analytical methods (Table 2). At 327°C (Run I), methanol conversion was 0.03%. Ethylene (50% selectivity) and propylene (23.5%) were the only olefinic hydrocarbons observed by GC analysis adjusted for high sensitivity. Methane selectivity was 26.5%. As the reaction temperature increased up to 389°C (Run M), a gradual increase in methanol conversion was observed, as expected. Concurrently, selectivities to ethylene and methane decreased and formation of larger hydrocarbons with more than 4 carbons increased.

The high selectivity to ethylene at low conversion (Runs I or J) demonstrated that ethylene was a primary hydrocarbon product produced from methanol. The high methane selectivity at low conversion (Runs I, J, and K) may be a result of an independent and constant thermal or catalyzed decomposition of methanol or methyl ether (16). Propylene selectivities were relatively constant over this wide conversion range.

B. Reaction of C₂-C₄ Olefins and Methanol Over HZSM-5, SiO₂/Al₂O₃, 1600/1

In order to simulate the composition of products at an early stage of the reaction and observe the alkylation of olefins by methanol to produce the next higher homolog:



mixtures of various olefins, methanol, and water as a diluent were used (Table 3). By judicious selection of temperature, it was also desired to gain some insight on the reactivities of methanol or hydrocarbons alone and various combinations. Many replicates were made at each set of conditions by the on-line method of analysis for each representative point shown to confirm reproducibility (see Experimental Section).

In Run N (Table 3), mixtures of aqueous methanol and ethylene were used over HZSM-5, SiO₂/Al₂O₃, 1600/1, at 332°C. The methanol conversion to hydrocarbons was 19% and the net ethylene conversion was 16%. The major product was propylene, 42%. Under similar conditions, aqueous methanol alone was very unreactive (Run O). Methanol conversion was less than 1%. Ethylene diluted with water (Run P) was also unreactive. Net ethylene conversion was less than 1% and the major product was butene, 73%. These results clearly indicated that the rate of reaction of methanol with ethylene was significantly faster than

TABLE 3

Reactions of Olefins and Methanol over HZSM-5, SiO₂/Al₂O₃, 1600/1^a

	Run					
	N	O ^b	P	Q	R	S
Temperature, °C	332	332	332	312	312	300
Reactants	MeOH/C ₂ H ₄ /H ₂ O	MeOH/H ₂ O	C ₂ H ₄ /H ₂ O	MeOH/C ₃ H ₆ /H ₂ O	C ₃ H ₆ /H ₂ O ^d	1-C ₄ H ₈ /H ₂ O
WHSV	1.0/0.3/0.8	1.0/0.8	0.3/2.0	1.0/0.1/0.8	0.1/2.0	0.1/2.0
Space time, sec ^c	3.4	3.9	2.4	3.8	2.6	2.6
Conversion						
MeOH ^d	19	0.5	—	11.3	—	—
Olefin ^e	16	—	0.2	39.9	6.5	66.3
Hydrocarbon product selectivity (wt%)						
CH ₄	0.4	21.4	0	0.3	0	0
C ₂ H ₆	0.3	0.6	0	0	0	0
C ₂ H ₄	SM ^f	32.8	SM ^f	7.7	0.8	0.3
C ₃ H ₈	0.5	0	0	3.9	7.7	0.6
C ₃ H ₆	42.0	27.4	27.0	SM ^f	SM ^f	18.3
C ₄ H ₁₀	3.4	2.1	0	4.3	0	4.3
C ₄ H ₈	19.9	10.1	73.0	42.4	30.3	SM ^f
C ₅	13.6	5.8	0	24.3	13.0	38.8
C ₆	10.6	0	0	10.4	48.2	21.2
C ₇	6.9	0	0	3.6	0	} 16.3
Others	2.5	0	0	3.3	0	

^a The data in this table were obtained by the on-line analytical method (see Experimental).^b Run O is identical to Run J of Table 2.^c Space time was calculated from catalyst volume divided by the volumetric flow rate of reactants converted into gas at STP conditions.^d Methanol conversion was calculated based on the difference of the CH₂ equivalent of methanol or methyl ether in the feed and product effluent.^e Conversions based on weight percent of starting materials consumed assuming that no ethylene (Run N) or propylene (Run Q) were produced from methanol. Conversion recorded for olefin is a minimum value.^f Starting material.

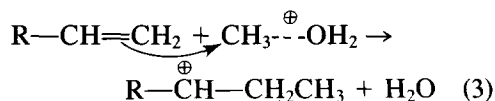
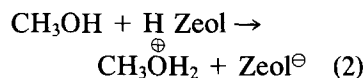
the reaction of methanol or ethylene (with water) alone. Alkylation of ethylene with methanol is a fast and major reaction path to produce propylene.

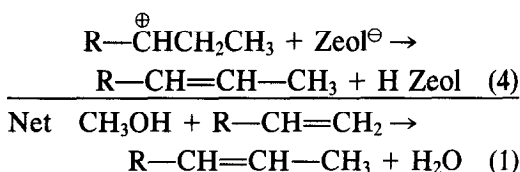
In Run Q, aqueous methanol and propylene were used with HZSM-5, SiO₂/Al₂O₃, 1600/1, at 312°C. Methanol conversion to hydrocarbons was 11% and net propylene conversion was 40%. The major products were butenes (42%) and pentenes (24%). Under similar conditions, propylene with water (Run R), was relatively unreactive (6.5% conversion). Furthermore, of the amount converted, the C₆ propylene dimer was the major product observed (48.2%). Again, this set of experiments demonstrated that the rate of reaction of methanol with propylene was much faster than the reaction of each individual compound alone.

In Run S, 1-butene was more reactive than propylene (Run R). Under even milder

reaction conditions, 66% of 1-butene was converted to other olefins. Similarly, compare Run R with P, propylene was more reactive than ethylene. This is a general phenomenon for olefins as reported earlier (5).

At early and intermediate stages of reaction, methanol, water, and low-molecular-weight olefins are all present in the catalyst bed. An acid-catalyzed reaction mechanism with carbenium ion intermediates has been proposed for substitution of the methyl group at the unsaturated carbon of the olefinic double bond (5, 15, 17):





This is directly analogous to established electrophilic substitution reactions on the aromatic ring with Friedel-Crafts catalysts (18-20). Perhaps the zeolite catalyst is unique because of its high hydrophobicity (21) and high reaction temperature.

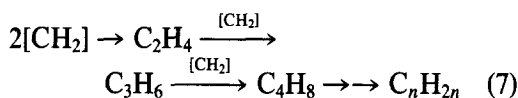
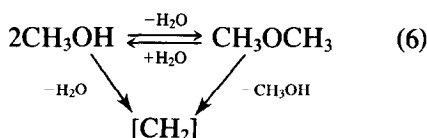
C. Flory Equation Applied to Methanol Conversion

The Flory equation provides a macroscopic method to predict the molecular weight distribution of polymerization processes with a specified extent of polymerization in a dynamic equilibrium state (11):

$$\ln M_x = \chi \cdot \ln P + \ln \frac{1 - P}{P} \quad (5)$$

In this equation, M_x is the mole fraction of a polymer with χ monomers and P is the extent of polymerization or the probability for a monomer to react. This equation is derived from a statistical treatment of the reaction system, based on the assumption that all the functional groups involved in the polymerization process have the same reactivity. It has been applied successfully by Flory to model molecular weight distributions of linear condensation polymers (11) and to hydrocarbons produced from the Fischer-Tropsch reaction first by Anderson and co-workers (22, 23) and subsequently others (24).

Condensation of methanol to produce hydrocarbons over ZSM-5 type zeolites can be visualized as a polymerization process. Methanol (the monomer) eliminates water and the residue condenses stepwise to produce higher hydrocarbons (polymer):



In this scheme, the reactive intermediate produced from methanol by the zeolite catalyst is indicated by $[\text{CH}_2]$ (Eq. (6)). It is convenient to use this notation for stoichiometric "bookkeeping" purposes to indicate the end result (Eq. (7)). We do not wish to infer that free carbene is the reactive intermediate. We prefer the protonated carbene (carbenium ion) and an acid-catalyzed electrophilic alkylation reaction proposed previously (Eqs. (1)-(4)).

If the rate of ethylene formation is the same as propylene and all of the higher olefins (up to C_9 hydrocarbons), a plot of the logarithm of the mole fraction of hydrocarbons with the same carbon number (including olefins and the small amount of paraffins), starting from C_2 , versus the number of $[\text{CH}_2]$ units condensed (Flory plot) should produce a straight line of slope $\ln P$ and intercept $\ln(1 - P)/P$. The Flory plot (Fig. 2) of a representative experiment, Run G, shows a significant departure from linearity for the ethylene point. Similar results were observed for all the runs with ZSM-5 with the highest silica/alumina ratio (Runs A to C, H, L, and M).

However, if propylene is chosen as the first olefin produced by the stepwise growth process, a Flory plot starting from the C_3 - C_9 olefin fraction of Run G (Fig. 3) produced a good straight line. This set of data, analyzed by the least-square, simple regression method (25), according to the Flory equation, gives an excellent correlation coefficient of 0.99. A similar fit was observed when the other runs with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1600/1 (Runs A and H to M) are plotted in a similar manner (Fig. 4). The P values, the probability of alkylation reaction, can be calculated from the slope of intercepts of these lines.

A summary of the probability values (P) and correlation coefficients (R) for all the

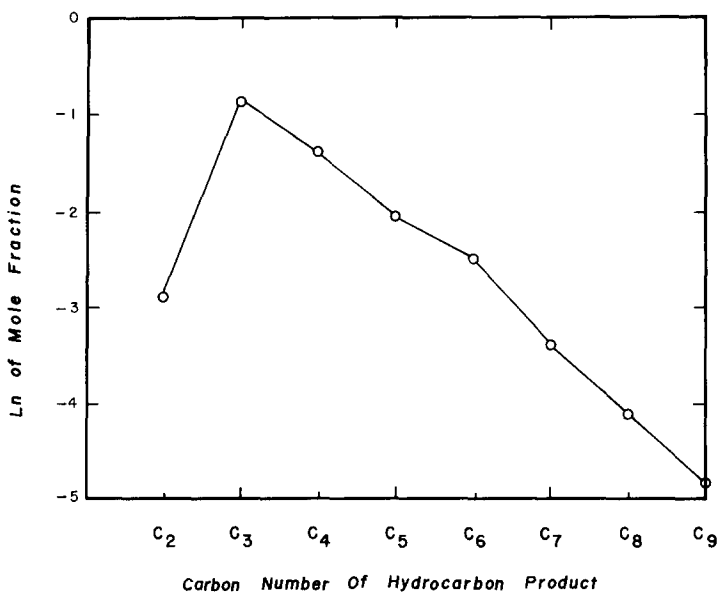


FIG. 2. Flory plot of mole fraction of hydrocarbon produced from methanol over ZSM-5, SiO₂/Al₂O₃, 1600/1. Run G, start with C₂H₄.

runs of Tables 1 and 2 is shown in Table 4. For ZSM-5 SiO₂/Al₂O₃, 1600/1 (Runs A and G to M), the molar hydrocarbon product distribution starting from propylene was modeled with the Flory chain-growth equation and high correlation coefficients, *R*, of 0.90–0.99 (1.0 is perfect correlation) were

observed. When catalysts with higher activities were used, Runs D–F of Table 3, successive reactions, which consumed olefins to produce aromatics and paraffins, dominated with an expected decrease in the Flory correlation.

Significantly, the olefin product distribu-

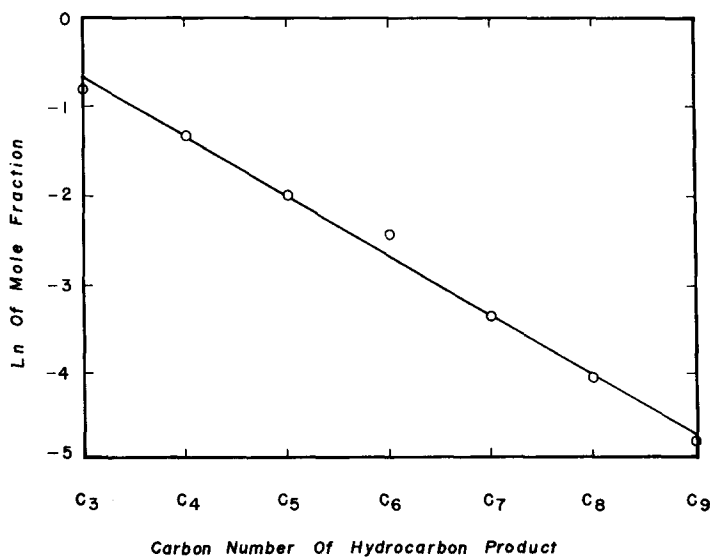


FIG. 3. Flory plot of mole fraction of hydrocarbon produced from methanol over ZSM-5, SiO₂/Al₂O₃, 1600/1. Run G, start with C₃H₆.

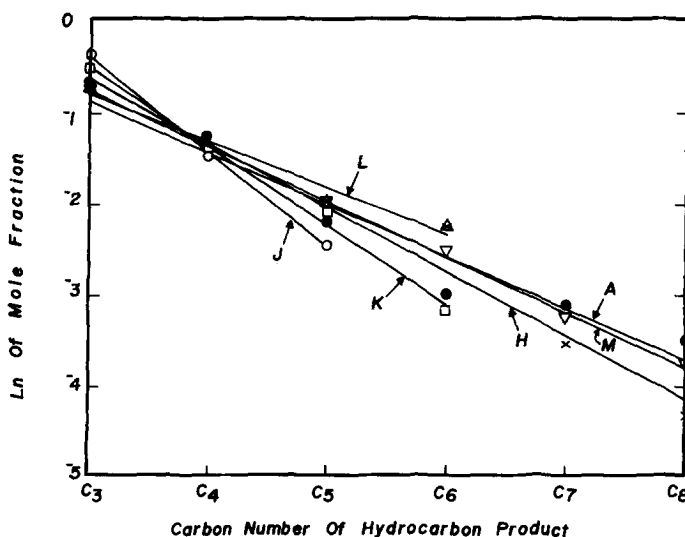


FIG. 4. Flory plot of runs H, and J to K, starting with propylene. ●, Run A; ×, Run H; ○, Run J; □, Run K; △, Run L; ▽, Run M.

tion starting with methanol and ethylene or propylene, Run N and Q, also gave excellent correlation coefficients to the Flory equation.

D. Comparison of Olefin Mixtures Isolated From Methanol Converted Over ZSM-5 Catalyst with the Corresponding Calculated Thermodynamic Mixtures

The high degree of correlation with the Flory equation observed for the products obtained from methanol with a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ZSM-5 catalyst, over a wide range of conversions, but especially at medium to low conversion, is consistent with a stepwise addition reaction of methanol with propylene and higher olefins present, to give the next higher molecular weight analog (Eq. (1)). However, ZSM-5 is known to catalyze olefin dimerization and cracking reactions which would also occur after formation of the initial olefins (10, 26). Indeed, ethylene and propylene dimerization at very low conversion, in the absence of methanol, was shown to be the favored reaction, Run P and R (Table 3). Furthermore, the higher olefins react faster than the lower molecular weight olefins, $C_4 > C_3$

$> C_2$, to scrambled products, Runs S, R, and P (Table 3).

In order to gain some insight to the importance of this olefin scrambling reaction, calculation of the thermodynamic equilibrium mixture of olefins for comparison with our experimental results was desired. A convenient computer program for this purpose, for all 29 isomers of the C_2 - C_6 olefins, had been prepared by Krambeck (27), modified by Kuo (28), and was kindly made available for our use. The thermodynamic equilibrium concentration of C_2 to C_6 olefins as a function of temperature and hydrocarbon partial pressure can be conveniently calculated. Although C_7 and higher olefins were not included in this calculation, their equilibrium concentrations were very low at the conditions under consideration. This should not affect our final conclusion (see below).

As we have indicated in Section C and Table 4, the hydrocarbons with three or more carbons produced from methanol over ZSM-5 followed the Flory chain-growth kinetics. Thus, for comparison purposes, the calculated thermodynamic equilibrium composition of olefins, under conditions of temperature and pressure

TABLE 4

Flory Correlation of C₃ and Higher Hydrocarbon Product Distributions over HZSM-5 with Various Silica to Alumina Ratios^a

Run	SiO ₂ /Al ₂ O ₃	MeOH Conv.	P ^b	R ^c
A	1600	100	0.58	0.90
B	500	100	0.60	0.90
C	280	100	0.60	0.89
D	140	100	— ^d	0.61
E	70	100	— ^d	0.54
F	35	100	— ^d	0.21
G	1600	100	0.54	0.99
H	1600	100	0.50	0.98
I	1600	0.03	— ^e	— ^e
J	1600	0.5	0.35	0.99
K	1600	0.2	0.42	0.99
L	1600	17.0	0.58	0.95
M	1600	31.2	0.54	0.99
N	1600	19.0	0.49	0.98
Q	1600	11.3	0.39 ^f	0.97 ^f

^a Reaction conditions and products of Runs A to H were shown in Table 1, Runs I to M in Table 2, Runs N and Q in Table 3. Calculations based on concentrations of C₃–C₇ olefin products.

^b The probability of alkylation, P, as defined in the Flory equation (Eq. (2)) can be calculated from either slope or intercept of the plot. The average number from the two calculations is shown.

^c R, the square of the simple correlation coefficients, measured the strength of the data, fitted to Flory equation (Eq. (2)).

^d The P value of this run is meaningless and not calculated because of the very poor correlation.

^e The correlation of this run cannot be calculated since propylene was the only higher olefin in the product.

^f In Run Q, propylene was alkylated with methanol to produce C₄H₈ and higher olefins. Therefore, the correlation starting from C₄ was calculated.

comparable to the experimental conditions used with methanol, were also subjected to the Flory treatment to calculate correlation coefficients (R) and alkylation probabilities (P). Results are summarized in Table 5. A sample plot of the experimental results, Run M, and the calculated equilibrium composition is shown in Fig. 5. Comparisons with the experimental results showed differences. First, the alkylation probabilities, P, for the calculated equilibrium distribution were consistently lower than for ex-

perimental runs. Second, the correlation coefficients for the thermodynamic results were also consistently lower than experimental results with low to medium methanol conversions (Runs G, J, K, L, M, and N). We interpret this as indicating that a contribution by reaction paths involving thermodynamic equilibration is small for production of the olefin mixture observed at low conversion.

If the P-values represent the true probability of a stepwise reaction of the Flory type reaction, higher values were observed starting with methanol and/or methanol ether plus olefins than for reactions which lead to the thermodynamic equilibrium mixture, under all conditions used in Table 5. In a similar manner, the Flory correlation coefficients for experimental runs, in every case, were also higher than the calculated thermodynamic values.

SUMMARY AND CONCLUSIONS

1. Olefins are the major products iso-

TABLE 5

Comparison of Alkylation Probabilities (P), and Correlation Coefficients (R), for Hydrocarbon Distribution from Thermodynamic Equilibrium Calculations and Experimental Runs over HZSM-5, SiO₂/Al₂O₃, 1600/1^a

Run	Conditions		P		R	
	Temp., °C	Pressure psi ^b	Thermo. calc.	Exp. obs.	Thermo. calc.	Exp. obs.
A	450	3	0.41	0.58	0.88	0.90
G	450	5	0.47	0.54	0.84	0.99
H	450	2	0.36	0.50	0.90	0.98
J	327	0.002	0.07	— ^c	0.95	— ^c
K	332	0.02	0.21	0.35	0.93	0.99
L	356	0.1	0.29	0.42	0.90	0.99
M	380	0.3	0.33	0.58	0.89	0.95
N	389	0.6	0.38	0.54	0.86	0.99
N	332	2	— ^d	0.49	0.21	0.98
Q	312	0.4	— ^d	0.39	0.51	0.97

^a Reaction conditions and products of Runs A, G and H were shown in Table 1, Runs I to M in Table 2, Runs N and Q in Table 3. Calculations based on concentrations of C₃–C₇ olefin products.

^b The hydrocarbon partial pressure was estimated based on the amount of hydrocarbon produced from methanol in each run.

^c The correlation of this run was not calculated since propylene was the only higher hydrocarbon produced.

^d The P values of this thermodynamic equilibrium hydrocarbon distribution were meaningless because the data of the very low corresponding R values had an extremely poor correlation to equation.

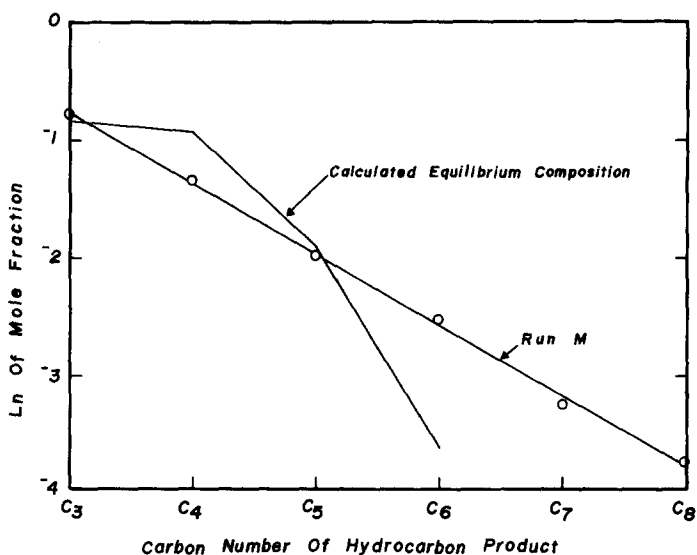


FIG. 5. Comparison of Flory plot of experimental results from run M vs calculated equilibrium composition under comparable conditions.

lated from methanol over a high $\text{SiO}_2/\text{Al}_2\text{O}_3$, 1600/1, HZSM-5 catalyst. Correlations with the Flory equation were excellent ($R = .95-.99$) at low-medium conversions (.2–31%) and good ($R = .90$) at high conversion (100%).

2. Ethylene was the major initial hydrocarbon (excluding methane) from methanol.

(a) Ethylene was the major product produced from methanol (68% excluding methane) at very low conversion.

(b) Alkylation of ethylene with methanol is the most favorable reaction of ethylene.

(c) Propylene and to a diminishing amount higher hydrocarbons are produced by an alkylation reaction with methanol.

3. Formation of C_3 to C_9 hydrocarbons from methanol at low conversion (<31%) are consistent with the Flory type chain-growth mechanism with excellent correlation coefficients. Ethylene production does not fit the Flory equation and is produced by a different mechanism than propylene and other hydrocarbons.

4. Under conditions of low/medium methanol conversion:

(a) Reaction of ethylene or propylene

with methanol is much faster than reactions (dimerization, cracking) of the olefins alone, with water as a diluent.

(b) The major products of the fast reaction were the next higher olefin (first) followed by the olefin with two more carbon atoms.

(c) Reaction of methanol with olefins is the major reaction for consumption of methanol or methyl ether.

(d) With 1-butene (water present), rapid scrambling occurred to produce propylene and higher olefins.

5. At least two major reaction types occur to product higher olefins isolated from methanol.

(a) Alkylation of olefins with methanol.

(b) Olefin scrambling—dimerization, cracking, and skeletal and double bond isomerization—the thermodynamic equilibrium reaction.

6. The Flory correlation coefficients, R , are generally higher for experimental runs than with the corresponding calculated thermodynamic equilibrium olefin mixtures (Table 5). At low and even intermediate conversions, we believe this is evidence for dominance of the alkylation reaction for

production of propylene and higher olefins from methanol. At 100% methanol conversion, however, Run A (Table 5), the R values are similar. It is, therefore, impossible to segregate contributions from alkylation or equilibration reactions to the olefin mixture finally isolated.

7. The mechanism for production of the initial hydrocarbon or hydrocarbons from methanol remains an elusive mystery. We believe that ethylene is an initial hydrocarbon product, that alkylation of olefins with methanol to produce the next higher analog is dominant at low and moderate conversions and that equilibration reactions at medium to high conversions determine the final olefin composition.

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