Methanol Conversion to Olefins over ZSM-5

II. Olefin Distribution

CYNTHIA T-W. CHU AND CLARENCE D. CHANG

Mobil Research and Development Corporation, Central Research Division, P. O. Box 1025,
Princeton, New Jersey 08540

The distribution of olefins from methanol conversion over ZSM-5 zeolite is examined. Thermodynamic equilibrium is approached at low conversion levels. With increasing conversion, olefin distribution is governed by kinetics, due to autocatalysis and competitive sorption of water. Ethylene is the initial olefin.

INTRODUCTION

Light olefins are intermediates in the conversion of methanol to hydrocarbons over ZSM-5 zeolites (*1*). Garwood (*2*) has investigated the equilibration of C_2–C_{10} olefins over ZSM-5 at 271–277°C and subatmospheric partial pressure, and found the distribution to be thermodynamically controlled.

It was of interest to determine whether the distribution of olefins from methanol conversion is similarly constrained. Of particular interest, furthermore, is the olefin distribution at very low conversions, since this bears on the question of the "first" olefin, which has been subject to much debate.

EXPERIMENTAL METHOD

Experimental details are similar to those in Part I of this series with the exception that a pressure transducer (Validyne, Model CD23, 0–1000 Torr) was used to monitor pressure drop across the catalyst bed.

RESULTS AND DISCUSSION

Experiments were carried out at 300 and 500°C, 101.3 kPa (nominal), and 2–892 hr^{-1} weight hourly space velocity (WHSV). Most of the experimental data were obtained at 500°C. Detailed results appear in Table 1.

Normalized C_2–C_5 olefin distributions are plotted in Figs. 1 and 2 against increasing olefin partial pressure up to the point of methanol/dimethyl ether extinction. The curves represent the thermodynamic equilibrium distribution between olefins calculated using an algorithm due to Krambeck (*3*) with thermodynamic data from Stull *et al.* (*4*).

Considering first the calculated distributions, it is seen that partial pressure (equivalent to the level of oxygenates conversion) exerts a profound influence on the equilibria between olefins. The calculations indicate that as the conversion approaches zero, ethylene selectivity approaches 100%. The effect of increasing temperature, over the same range of partial pressure, is to shift the distribution toward the lower olefins.

Experimental olefin distributions, on the other hand, approach thermodynamic equilibrium only at low conversions as seen in the 500°C data, contained in Fig. 2. It is clear that ethylene is approaching 100% at very low conversion (<2%). At 300°C (Fig. 1), even lower conversion (≤1%) would be required to give similar selectivity to ethylene. With the present experimental

TABLE 1

Methanol Conversion to Olefins

Catalyst												
SiO$_2$/Al$_2$O$_3$	1600	1600	500	500	500	500	500	500	500	500	500	500
Temp (°C)	300	300	500	500	500	500	500	500	500	500	500	500
Total P(kPa)	101.40	101.40	208.40^a	178.60	137.20	134.50	134.50	133.00	133.00	132.00	111.70	110.40
Olefins P(kPa)	0.014	0.14	0.020	0.036	0.15	0.44	1.2	3.74	11.79	14.97	20.48	21.38
WHSV	6.40	2.00	892.00	572.00	285.00	250.00	205.00	160.00	130.00	89.80	25.90	18.00
Product distribution (mole %)												
H$_2$O	15.8952	29.3408	27.0271	30.2822	36.1338	35.5963	44.2398	45.3717	48.7081	66.4226	72.4125	74.6813
DME	11.8436	26.1515	30.6268	28.6113	35.6294	36.1448	33.0483	26.6381	20.8219	10.3191	2.0087	0.7818
MeOH	72.1748	44.2741	42.1123	39.8503	24.7175	23.3081	19.8939	22.4170	15.7293	9.0705	2.2817	0.7798
CO	0.0014	0.0003	0.0000	0.0562	0.2783	0.3788	0.0919	0.1727	0.4620	0.0374	0.0899	0.0874
CO$_2$	0.0067	0.0007	0.0000	0.0072	0.0779	0.1985	0.0361	0.0132	0.1176	0.0119	0.0229	0.0222
H$_2$	0.0495	0.0000	0.0003	0.7868	2.0257	2.8075	0.8201	1.5601	2.4434	0.9169	1.8883	1.7124
CH$_4$	0.0017	0.0030	0.2132	0.3779	1.0055	1.0592	0.5675	0.6973	1.7231	0.5453	0.7486	0.7691
C$_2$	0.0000	0.0001	0.0009	0.0037	0.0112	0.0107	0.0090	0.0130	0.0291	0.0153	0.0382	0.0414
C$_2$O	0.0036	0.0226	0.0179	0.0203	0.0766	0.1499	0.2594	0.4911	2.1544	1.3611	2.7639	3.0357
C$_3$	0.0012	0.0122	0.0000	0.0002	0.0008	0.0013	0.0061	0.0088	0.0397	0.0596	0.1326	0.1810
C$_3$O	0.0038	0.0544	0.0013	0.0025	0.0238	0.0930	0.5605	1.3714	4.1255	5.8084	9.7710	10.4441
i-C$_4$	0.0021	0.0194	0.0000	0.0002	0.0004	0.0003	0.0116	0.0134	0.0567	0.1063	0.1329	0.1747
n-C$_4$	0.0006	0.0061	0.0000	0.0002	0.0022	0.0081	0.0023	0.0045	0.0115	0.0271	0.0377	0.0499
C$_4$O	0.0043	0.0385	0.0001	0.0012	0.0088	0.0513	0.2774	0.6822	1.9335	2.7000	4.0138	4.3634
i-C$_5$	0.0047	0.0278	0.0000	0.0000	0.0003	0.0002	0.0056	0.0144	0.0257	0.1048	0.1172	0.1307
n-C$_5$	0.0002	0.0039	0.0000	0.0000	0.0016	0.0012	0.0075	0.0171	0.0364	0.0720	0.0752	0.0718
C$_5$O	0.0020	0.0190	0.0000	0.0000	0.0022	0.0435	0.0778	0.3067	0.7972	1.4487	1.8049	1.5363
C$_6$+PON	0.0046	0.0260	0.0000	0.0000	0.0039	0.1473	0.0852	0.2074	0.4244	0.7185	0.9193	0.6265
Aromatics	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.3605	0.2545	0.7407	0.5105

^{a} Diluted with N$_2$ (N$_2$/MeOH = 1, mole ratio).

method, quantitative mass balances were impractical at such minimal conversions, therefore most of the data were obtained at 500°C. With increasing conversion, the distribution is increasingly governed by kinetics. This is particularly evident in the case of propylene. In Fig. 2 it is seen that propylene undergoes a marked increase in a particular region of the reaction path, following an apparent induction period. This behavior is characteristic of C$_3$$^+$ olefins from methanol (5) and is attributed to autocatalysis (6) during early C–C bond formation. The autocatalytic step is believed to involve mainly alkylation by reactive C$_1$ intermediate (6, 7) generated from methanol/
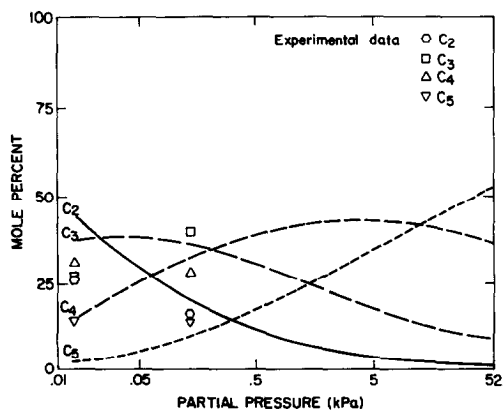

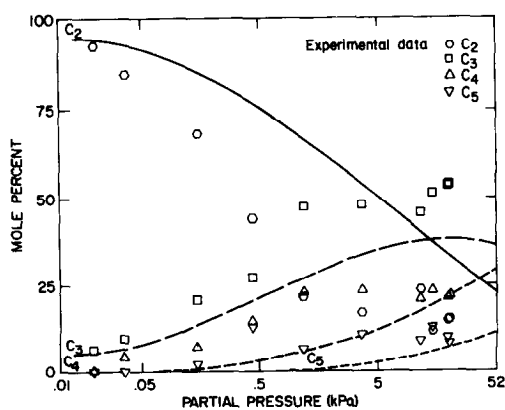FIG. 1. Olefin distribution at 300°C (lines are calculated).

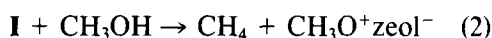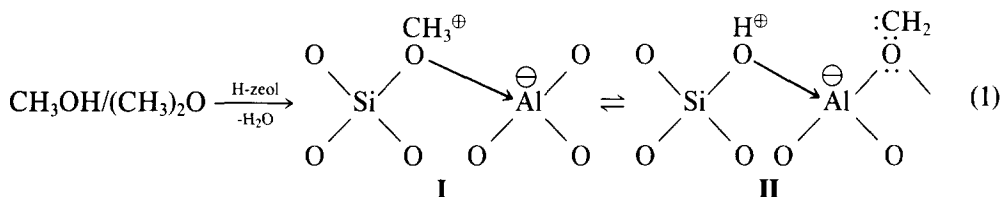FIG. 2. Olefin distribution at 500°C (lines are calculated).

dimethyl ether. Propylene would be formed in this manner from ethylene, butene from propylene, etc. by a chain mechanism (15, 18) in the early stages of the reaction. In this autocatalytic regime, C_3^+ olefin selectivities will be higher than calculated by thermodynamics. Subsequent steps include oligomerization, β-scission, and aromatization with H-transfer to olefin. These reactions may also compete against the equilibration between olefins. It is interesting that in fluid-bed pilot studies of hydrocarbon synthesis, propene is the only olefin still affected by kinetics at 100% oxygenates conversion, while the other olefins are roughly equilibrated (23).

Aside from the kinetic control of olefin distribution due to autocatalysis, competitive sorption of water (8, 9), produced in increasing amounts as the reaction progresses, may be another factor inhibiting subsequent olefin equilibration although the effect will be more pronounced at low tem-
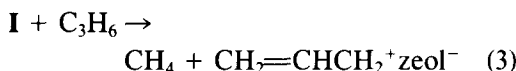
peratures. It has been reported that olefin distributions are modified when methanol is reacted over ZSM-5 in the presence of excess water (10).

The above differs therefore from Garwood's reaction (2), in that the latter proceeds principally by way of olefin oligomerization and β-scission, and in the absence of water. Under these circumstances, evidently, thermodynamic control of the olefin distribution obtains.
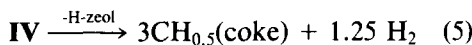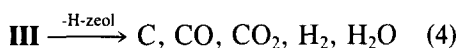
It will be noted (Table 1) that at low conversion levels methane constitutes a significant fraction of the hydrocarbon product, although the absolute amount of methane remains small with increasing conversion. This is indicative of initial coke laydown, competitive with the initiation/propagation of the C–C bond formation reactions. Small amounts of H_2, CO, and CO_2 are also present. The following are some possible reaction pathways to light gases and coke in the early stages of reaction:

$$CH_3OH/(CH_3)_2O \xrightarrow[-H_2O]{\text{H-zeol}} \quad \mathbf{I} \rightleftharpoons \mathbf{II} \tag{1}$$

$$\mathbf{I} + CH_3OH \rightarrow CH_4 + CH_3O^+zeol^- \tag{2}$$
$$\mathbf{III}$$

$$\mathbf{I} + C_3H_6 \rightarrow$$
$$CH_4 + CH_2{=}CHCH_2^+zeol^- \tag{3}$$
$$\mathbf{IV}$$

$$\mathbf{III} \xrightarrow{\text{-H-zeol}} C, CO, CO_2, H_2, H_2O \tag{4}$$

$$\mathbf{IV} \xrightarrow{\text{-H-zeol}} 3CH_{0.5}(coke) + 1.25 H_2 \tag{5}$$

Equations (2) + (4) are similar to the mechanism of Wu et al. (21) for CH_4 formation in decomposition of surface methoxyl groups on zeolites. Methane, CO, and H_2 could also arise via a radical pathway from dimethyl ether pyrolysis (22). Initiation and

propagation of C–C bond formation would be through II (2).

As mentioned previously, the question of whether ethylene is the "first" olefin from methanol has been controversial. Ethylene was originally thought to be the first olefin formed from methanol, based on mechanistic arguments (1, 11). Subsequent investigations on the reactivity of ethylene (12–14), attempts to observe the earliest olefin (15–17), and various tracer experiments (19, 20) yielded conflicting results, which either supported or contradicted the original postulate. In light of the present findings, it is clear that most of the confusion stems from neglect of thermodynamic and

kinetic (autocatalysis) contributions, i.e., nonrecognition of the location on the reaction path where the experimental observation has been made.

The present study provides substantive evidence that ethylene is the initial olefin.

CONCLUSIONS

The distribution of olefins from methanol conversion over ZSM-5 approaches thermodynamic equilibrium at low conversion levels. With increasing conversion the distribution becomes subject to kinetic control on account of autocatalysis. Water may also exert an influence through competitive sorption. It is concluded that ethylene is the initial olefin formed from methanol/dimethyl ether.

ACKNOWLEDGMENTS

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