The Conversion of Methanol and Other O-Compounds to Hydrocarbons over Zeolite Catalysts

II. Pressure Effects

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The effect of pressure on the conversion of methanol to hydrocarbons over ZSM-5 class zeolites is reported. Varying reactant partial pressure affects mainly the relative rates of the dehydration and aromatization steps in the reaction sequence.

INTRODUCTION

In the conversion of methanol to hydrocarbons over ZSM-5 class zeolites (1, 2) the composition of the hydrocarbon product can be markedly influenced by changes in reactant partial pressure. In a process study on the synthesis of gasoline from methanol, Chang et al. (3) found that elevated pressures tended to enhance secondary alkylation reactions as reflected by increases in the aromatic chain-to-ring ratio. This resulted in increased selectivity to tri- and tetramethyl benzenes in particular.

The aim of the present work was to examine the effect of pressure on the reaction path for methanol conversion.

EXPERIMENTAL METHODS

Materials. Methanol was Baker Analytical Reagent grade. Ethanol was U.S.P. 190 proof, obtained from Publicker Industries Co.

Catalysts. The catalysts were ZSM-5 class zeolites, as described in a number of patents (3).

Catalytic experiments. The experimental apparatus and analytical procedures have been described elsewhere (2). Experiments at subatmospheric feed partial pressure were carried out by dilution of the feed with N_2. The reaction temperature for all experiments was held at $370 \pm 1°C$. Methanol was reacted at 0.04, 1, and 50 atmospheres (1 atm = 101.3 kPa) partial pressure over a wide range of space velocities. Ethanol was reacted at 50 atm and LHSV = 1.2 hr^{-1}.

RESULTS AND DISCUSSION

The reaction path for methanol conversion over ZSM-5 class zeolites at 1 atm (101.3 kPa) was previously reported (2) and is reproduced in part in Fig. 1. The reaction sequence is seen to comprise three main steps: (a) the dehydration of methanol to dimethyl ether (DME), (b) the dehydration of DME to olefins, and (c) the transformation of olefins to aromatics and paraffins. The initial dehydration step is rapid and reversible with close approach to equilibrium (5). The shaded area in Fig. 1 indicates the overlap of the oxygen-
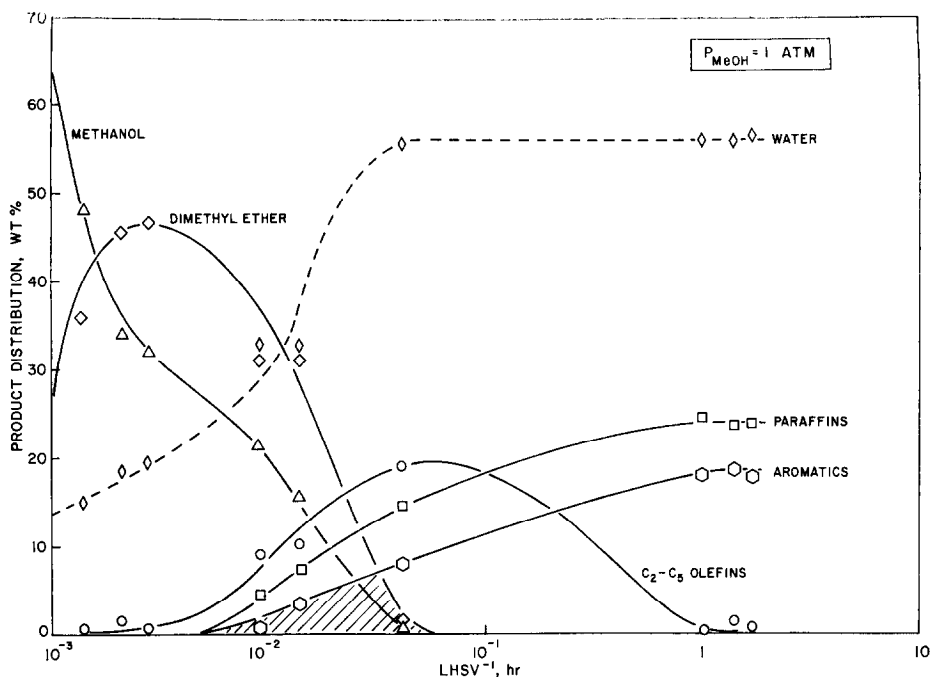
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FIG. 1. Reaction path for methanol conversion to hydrocarbons: 1 atm, 370 ± 1°C.

ates dehydration and aromatic formation reactions, thereby representing a region of maximum alkylation potential. A significant portion of the polymethylbenzenes is believed to originate by this mechanism.

Reduction of the reactant partial pressure to 0.04 atm results in an altered reaction path as shown in Fig. 2. The main reaction products up to oxygenates extinction are now seen to be light olefins. Only minor amounts of aromatics are formed while paraffins comprise less than 10% of the total effluent. The effect of lowered pressure is therefore to decouple the dehydration and aromatization steps of the reaction sequence.

This affords an opportunity to examine some details of the early course of reaction in the absence of complications from competing and consecutive reactions. The detailed olefin distribution is shown in Fig. 3 as a function of residence time at 0.04 atm. Ethylene, which is presumably formed early in the reaction, increases with time albeit slowly and remains at relatively low levels. Propylene and the butenes, on the other hand, rapidly become the predominant olefinic species after an initial induction period. This is in line with the autocatalysis in methanol disappearance observed by Chen and Reagan (6) and provides additional support for the reaction mechanism of Chang and Silvestri (2). According to the latter view, propylene may be formed from ethylene by methylene cycloaddition across the double bond, followed by rapid isomerization of the labile cyclopropane intermediate. Butenes may be formed similarly from propylene. The formation of pentenes and higher olefins, however, can proceed via alternate mechanisms such as oligomerization.

Upon raising the reactant partial pressure to 50 atm, the overlap region of the dehydration and aromatization reactions is greatly expanded, as illustrated in Fig. 4. This provides a rationale for the increase in polymethylbenzenes with pressure. This increase is observed noticeably in durene (1,2,4,5-tetramethyl benzene) yields (4).
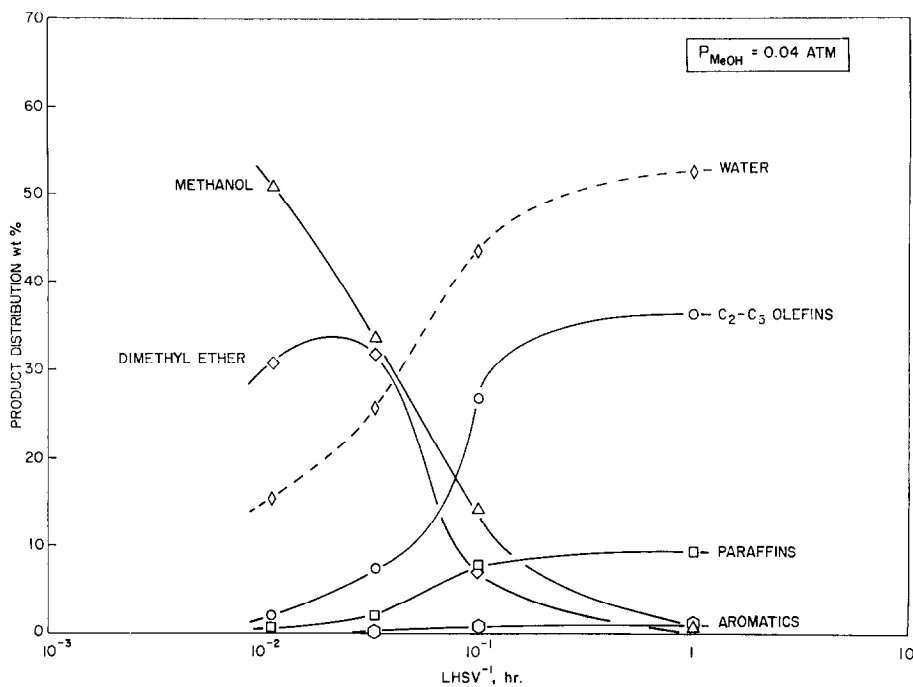
FIG. 2. Reaction path for methanol conversion to hydrocarbons: 0.04 atm, 370±1°C.
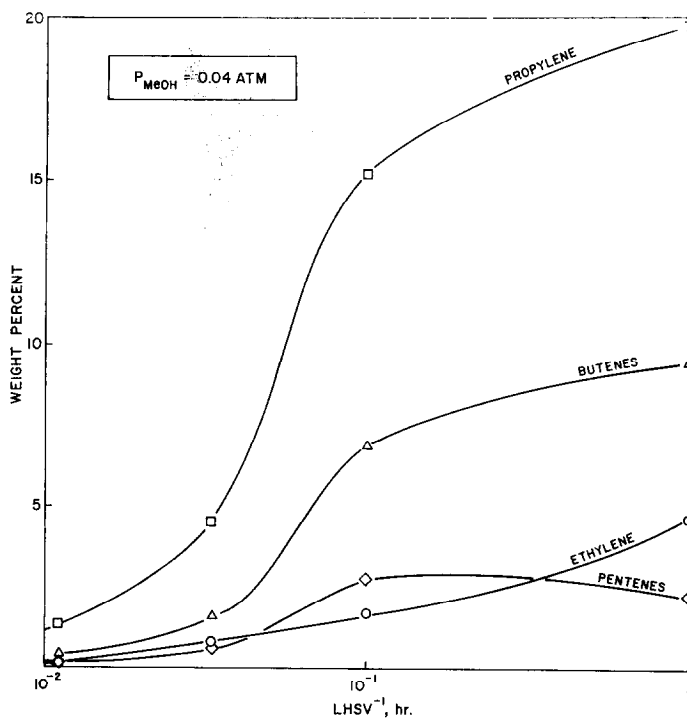

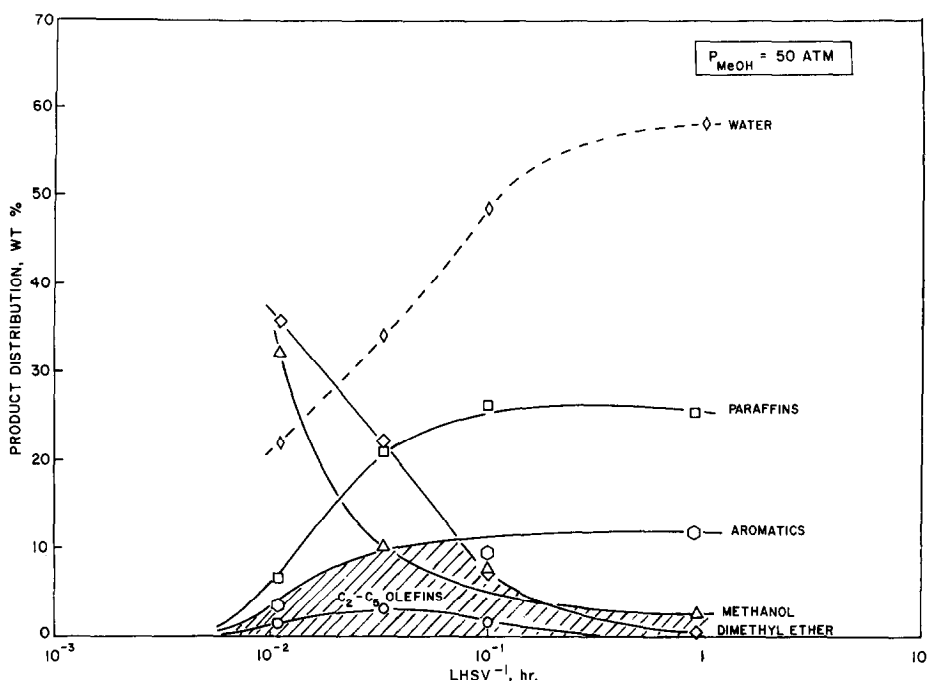FIG. 3. Light olefin selectivity as a function of space time: 0.04 atm, 370 ± 1°C.

FIG. 4. Reaction path for methanol conversion to hydrocarbons: 50 atm, 370 ± 1°C.

As reported previously (2) durene is formed preferentially over the thermodynamically favored 1,2,3,5-isomer as a consequence of the shape-selective nature of the zeolite catalyst. The mechanism of durene formation by methylation was confirmed by a high pressure experiment where ethanol was substituted for methanol. Results of this experiment, conducted at 50 atm, are shown in Table 1, where it is seen that the durene content of the aromatic fraction was <1% while a similar experiment using methanol gave 58.8%. Finally, the experiment with ethanol gave 4.1% ethylbenzenes in the aromatics while methanol gave 0.6%, which is also in accord with the assumed mechanism.

TABLE 1

The Conversion of Methanol and Ethanol to Hydrocarbons over ZSM-5 Class Zeolites[a]

	Methanol	Ethanol
Percentage conversion	99+	99
Hydrocarbon distribution (wt%)		
C_1	1.2	0.1
C_2	0.8	1.8
C_3	6.0	7.6
C_4	12.4	17.3
C_5^+ nonaromatic	44.8	40.2
Aromatics	34.8	33.0
Wt% durene in aromatics	58.8	0.9
Wt% ethylbenzenes[b] in aromatics	0.6	4.1

[a] $T = 370 \pm 1°C$; $P = 50$ atm; LHSV = 1.2 hr^{-1}.
[b] Et benzene, Me Et benzenes, di Me Et benzenes, and di Et benzenes.

CONCLUSION

In summary, the effect of varying pressure is to change the relative rates of the dehydration and aromatization steps in the reaction sequence. Decreasing pressure tends to decouple the two reactions. Increasing pressure enhances the overlap of the two reactions, leading to enhanced selectivity to polymethylbenzenes.

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