

## Evidence of Autocatalysis in Methanol to Hydrocarbon Reactions over Zeolite Catalysts

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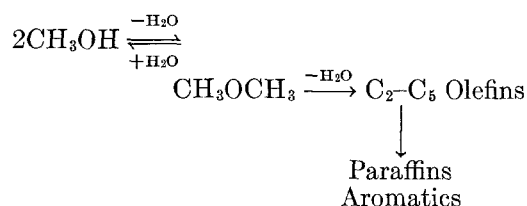
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An analysis of the kinetic data for the conversion of methanol to hydrocarbons and the composition of light olefinic products suggests that autocatalytic reactions between methanol/dimethylether and olefins are important steps in the conversion process. Based on rate data obtained in an isothermal reaction system, the rate of higher olefin formation via an autocatalytic route is 50 times faster than the rate of initial formation of ethylene from methanol/dimethylether. This kinetic interpretation is supported by the observation that propylene instead of ethylene is the major hydrocarbon product at below 15% conversion (on a CH<sub>2</sub> basis). A linear relationship exists between the intrinsic acid activity of the zeolite catalyst and the activity for methanol to hydrocarbon conversion.

### INTRODUCTION

The conversion of methanol and other O-compounds to C<sub>2</sub>-C<sub>10</sub> hydrocarbons with a new class of shape selective zeolites was reported recently by Chang and Silvestri (1). Based on product distribution analyses, the reaction path for methanol conversion to hydrocarbons appears to be reasonably well represented by the following scheme:



The initial dehydration reaction is sufficiently fast, that an equilibrium among methanol, dimethylether, and water is established. Thus, the conversion of oxygenates to hydrocarbons is the rate-limiting

step of this process. One objective of the present study was to focus on the kinetics of the initial stages of the hydrocarbon formation reaction. Several qualitative observations of this system are pertinent to such a study.

The methanol conversion data in Ref. (1) were recalculated on the basis that conversion is defined as the yield of hydrocarbons as a percentage of the hydrocarbon (-CH<sub>2</sub>) portion of the oxygenate feed. These conversion results as a function of residence time are presented in Fig. 1. The rate of conversion of methanol or dimethylether to hydrocarbons is very slow at low conversion levels, i.e., at short residence times. However, the rate accelerates rapidly as the concentration of hydrocarbons increases. This accelerated rate of reaction is reflected in nonisothermal fixed bed reactors by a sigmoidal temperature profile (2) characterized by a narrow hot

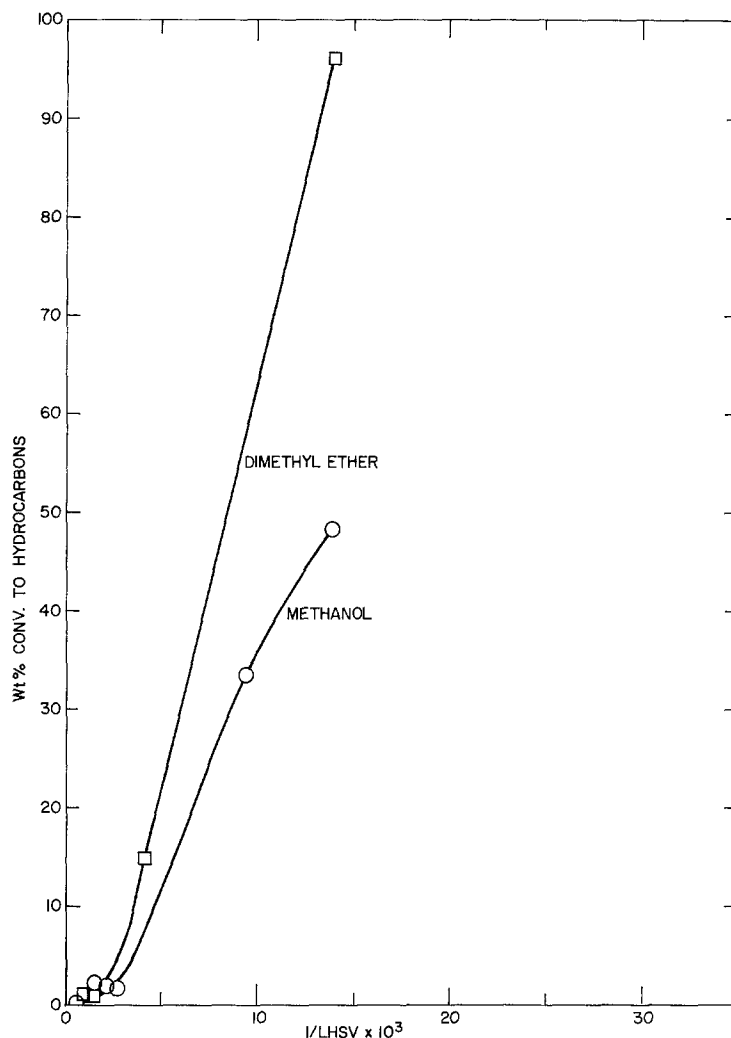


FIG. 1. Dimethylether or methanol conversion vs 1/LHSV. Data from Ref. (1).

zone which moves slowly down the catalyst bed as reaction time progresses.

These observations may be explained by thermal effects since the methanol dehydration and hydrocarbon formation are highly exothermic reactions. The maximum heat of reaction is calculated to be 400 cal/g, corresponding to a maximum adiabatic temperature rise of over 600°C. A second objective of this study was to decouple possible thermal effects from the observed reaction kinetics of the initial hydrocarbon formation from methanol.

A third aspect of this work involves a quantitative comparison between the catalyst acidity required for the conversion of methanol to hydrocarbons and for other acid-catalyzed reactions, such as hydrocarbon cracking. This information may provide a better understanding of the mechanistic aspects of these conversion processes.

#### EXPERIMENTAL

*Equipment.* The experimental runs were carried out with a tubular reactor im-

mersed in a fluidized bath (Techne Fluidized Bath Model SBL-2). The reactor was made of either stainless steel or copper tubing, 18 in. long, wound in a circular shape, fitted with a thermowell. Comparison runs were made with  $\frac{1}{8}$ - and  $\frac{3}{16}$ -in.-o.d. tubing to detect possible nonisothermal effects on conversion.

Methanol was delivered by an ISCO positive displacement pump. The reactor effluent passed through two collection traps, one in an ice bath, followed by one immersed in liquid nitrogen. The non-condensables were collected in a gas holder. Material balance runs ranged from 20 min to 1.5 hr. A two phase product was collected in the first trap. It was separated into an aqueous phase, and a hydrocarbon phase, which were weighed and analyzed separately. Products collected in the liquid nitrogen trap were allowed to expand into an evacuated gas holder of known volume connected to a mercury manometer. The volume of the gas collected was then calculated from the pressure change.

Reaction products were analyzed in a Hewlett Packard Model 5750 gas chromatograph. A 12 ft Poropak Q column was used for the analysis of gaseous products

and the aqueous phase products. A 10 ft 5% diethylphthalate, 5% bentone 34 on Chemosorb W column was used for the analysis of the hydrocarbon liquid products.

*Catalysts.* The zeolites used in the present study are members of the ZSM-5 class of zeolites, similar to that used by Chang and Silvestri (1). Catalysts of different activities were obtained by steam treatments. To assure efficient heat dissipation, the catalysts were diluted to 1.4 to 10% zeolite with inert materials of different thermal conductivities, including  $\gamma$ -alumina, aluminum, and copper metal powders. The mixtures were pelleted and sized to 40/60 mesh or 60/80 mesh.

The intrinsic acid activity of the catalyst was measured by the alpha test. Details of the alpha test have been described elsewhere (3).

## RESULTS AND DISCUSSIONS

### 1. Assurance of Isothermal Reaction Conditions

Four series of runs were made with the following combination of reactors and

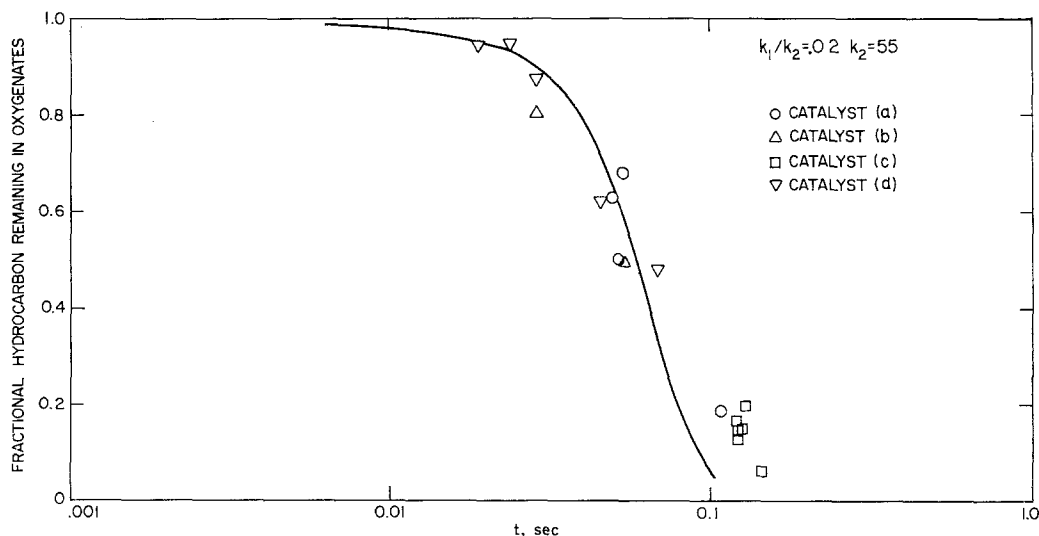


FIG. 2. Methanol conversion at 370°C.

catalysts:

(a) Reactor:  $\frac{1}{8}$ -in.-o.d. copper; catalyst: 10% zeolite diluted with  $\gamma$ -alumina.

(b) Reactor:  $\frac{1}{8}$ -in.-o.d. copper; catalyst: 1.4% zeolite diluted with 50/50 copper powder and  $\gamma$ -alumina.

(c) Reactor:  $\frac{3}{16}$ -in.-o.d. copper; catalyst: 3% zeolite diluted with 50/50 copper powder and  $\gamma$ -alumina.

(d) Reactor:  $\frac{3}{16}$ -in.-o.d. stainless steel; catalyst: 10% zeolite diluted with  $\gamma$ -alumina.

The conversion of pure methanol was studied at 370°C and 30 to 150 weight hourly space velocity (based on weight of active zeolite component). The results are shown in Fig. 2 with fractional hydrocarbon remaining in oxygenates plotted against residence time.

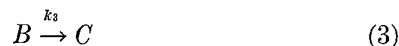
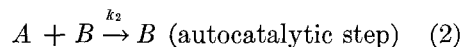
The reactor system was designed to approach as close to isothermal reaction conditions as possible. Any nonisothermal effects due to the use of too large a reactor or too much catalyst would result in an apparent increase of conversion. The deviation from isothermicity would be expected to increase with conversion as the amount of heat of reaction to be dissipated increases.

However, the experimental results show no significant difference in reaction rate among the four combination of reactors and catalysts. They confirm the earlier observation (1) that the rate of methanol conversion is very slow at low conversion and accelerates as the concentration of hydrocarbon increases. We conclude that the observed rate acceleration at high conversion is not the result of temperature runaway or a heat transfer problem and that we have achieved an isothermal reaction condition with the reactor system.

## 2. An Autocatalytic Kinetic Model

If we assume that the rate of disappearance of oxygenates is accelerated by

the reaction of oxygenates with olefins:



where  $A$  = oxygenates,  $B$  = olefins,  $C$  = aromatics + paraffins, then

$$-\frac{dA}{dt} = k_1A + k_2AB. \quad (4)$$

At low conversions, the reaction of olefins to aromatics and paraffins [Eq. (3)] may be ignored. The rate constant,  $k_2$ , can be obtained by integrating Eq. (4):

$$k_2 = \frac{1}{(1+R)t} \ln \frac{(R+B)A_0}{RA} \quad (5)$$

where  $R = k_1/k_2$ .

A reasonable fit of the kinetic model to the rate data in Fig. 2 was obtained with  $k_2 = 55$  and  $k_1 = 0.02k_2$ . The fit is excellent up to about 50% conversion of the oxygenates. At higher conversion levels, the observed rate is lower than that predicted by the model. This is to be expected since at higher conversion levels, the reaction of olefins to aromatics and saturates lowers the concentration of  $B$  in Eq. (5) and Eq. (3) can no longer be ignored.

The ratio of  $k_1/k_2$  equal to 0.02 indicates that the autocatalytic rate constant,  $k_2$ , is much larger than the first order rate constant,  $k_1$ .

A discussion of the detailed mechanism of the various reaction steps taking place on the catalytic surface is beyond the scope of the present study. However, the values of these rate constants suggest that the initial rate of formation of ethylene from oxygenates is much slower than the rate of reaction of oxygenates with the product olefins.

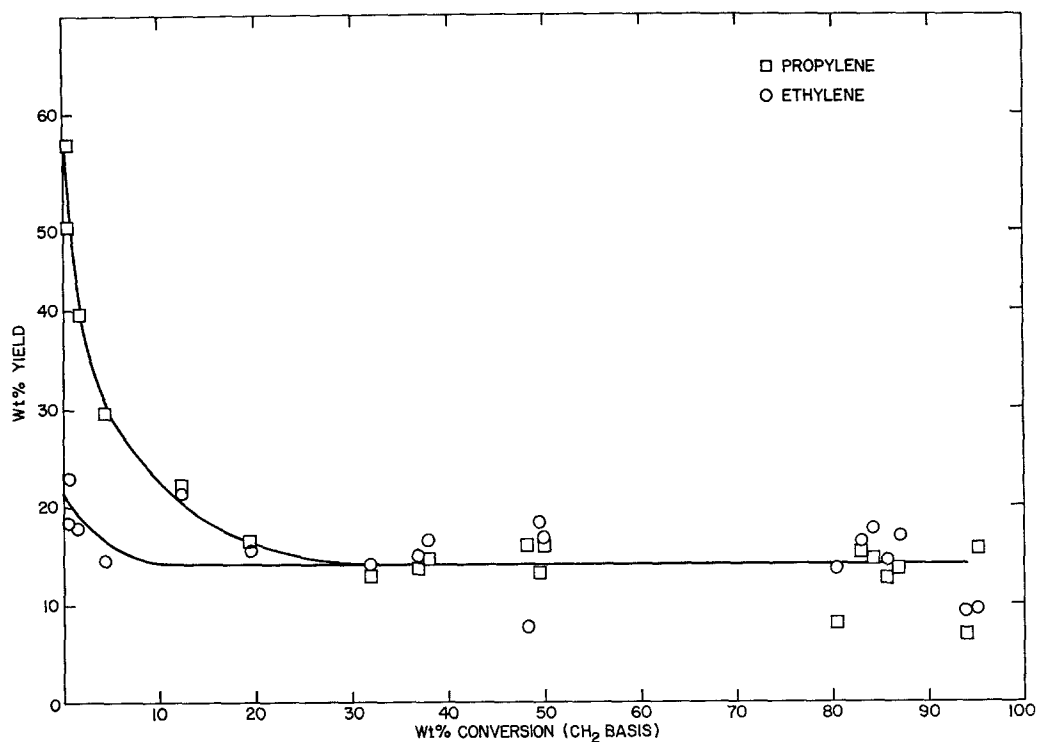


FIG. 3. Distribution of light olefins.

3. Distribution of Light Olefinic Products

One of the consequences of assuming an autocatalytic mechanism for the hydro-

carbon forming reactions is that the expected observable hydrocarbon product should be propylene or higher olefins rather

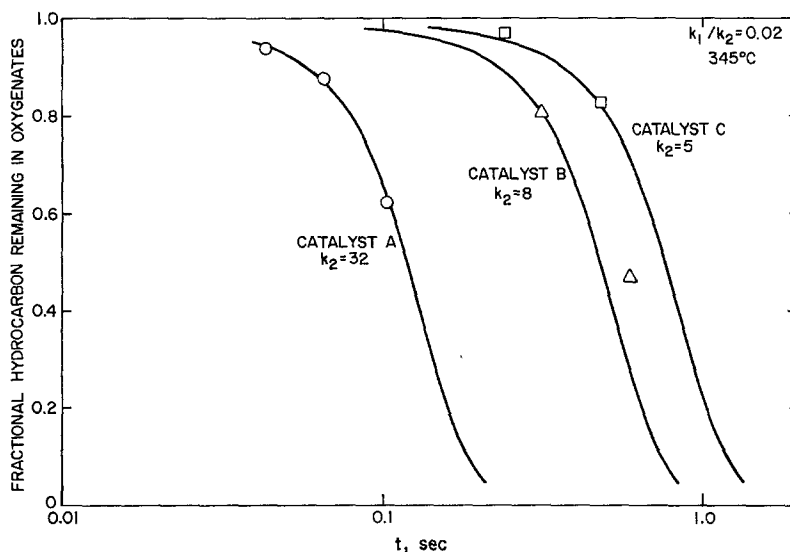


FIG. 4. Rate of methanol conversion to hydrocarbons.

than ethylene. Examination of the distribution of hydrocarbons shows that at below 15% conversion, propylene is indeed the largest single product. These results are consistent with other published data on methanol to hydrocarbon reactions (1, 4). Propylene yield approaches 60% of total hydrocarbon products at below 1% conversion. However, as shown in Fig. 3, the yield of propylene drops quickly with increasing conversion to a ratio of propylene to ethylene of about one beyond 20% conversion, while the yield of  $C_4 +$  products increases to about 70% of the hydrocarbon

product, with ethylene and propylene each at about 14%. In addition to the autocatalytic alkylation reaction, the transmutation of olefins and the hydrogen transfer reaction leading to the formation of aromatics and paraffins also take place as the reaction severity is increased. A complete kinetic modeling of the conversion process is beyond the scope of the present study.

The reaction mechanism in methanol/dimethylether conversion to olefins has been recently discussed by Chang and Silvestri (1). The postulate was that the

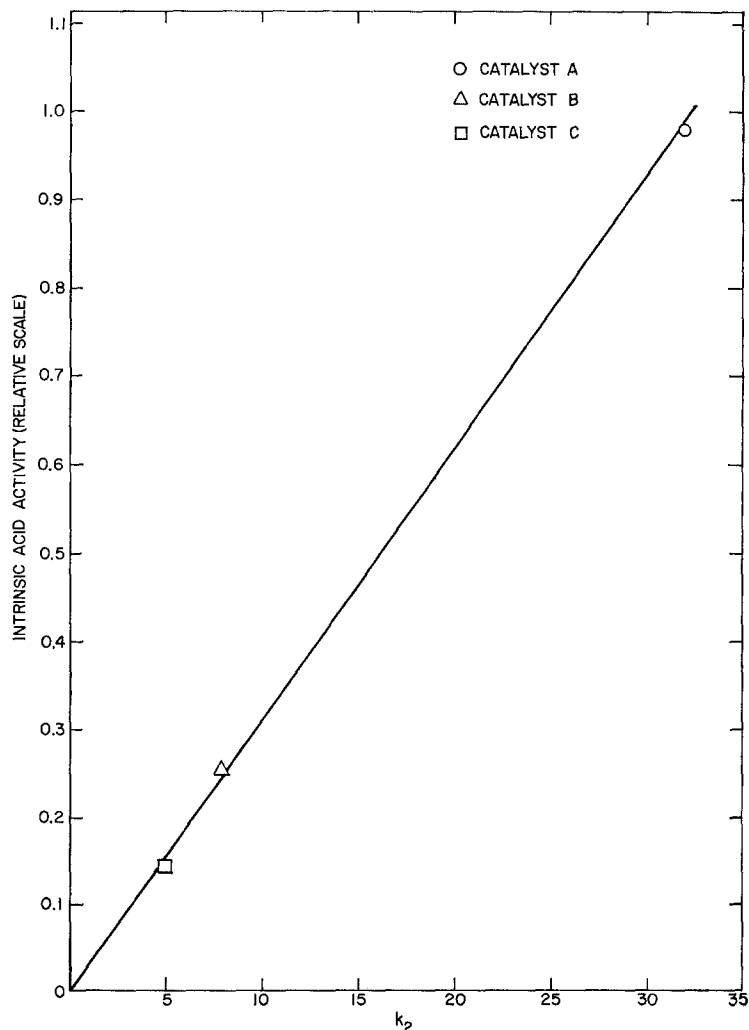


FIG. 5. Methanol rate constant,  $k$  vs intrinsic acid activity.

formation of ethylene is preceded by the formation of an ethyl ether or alcohol which is formed either via a bimolecular reaction between the oxygenates (methanol of dimethylether) or via methylene insertion in methanol or dimethylether. The present study can contribute little to resolving the detailed mechanism of the olefin initiation reaction. However, it does suggest an additional reaction, i.e., the autocatalysis of an olefin with an oxygenate via alkylation is an important and dominant reaction in the initial phase of the methanol to hydrocarbon conversion process.

Derouane *et al.* (4) proposed that ethylene formed is very reactive and that carbenium ions are readily formed by reaction with the Brønsted acid sites of the zeolite. We believe that it is more likely that the alkylation reaction proceeds first with the interaction of methanol with the acid zeolite, forming a reactive intermediate, such as a methyl carbenium ion which attacks an olefin.

#### 4. Comparison of Methanol Rate Constants and $\alpha$ Values

Three catalysts of different intrinsic acid activity were tested for their methanol conversion activity. The methanol conversion data obtained at 345°C are presented in Fig. 4. The rate constants  $k_1$  and  $k_2$  were obtained by fitting the data with the autocatalytic kinetic model. This was done by assuming a constant value for  $k_1/k_2$  of 0.02 and varying the value of  $k_2$  to obtain a best fit of the data. Again, a reasonable

fit was obtained for all three catalyst samples at below 40% conversion.

In Fig. 5, the methanol conversion rate constants,  $k_2$ , are compared with the relative intrinsic acid activities. The linear relationship between  $\alpha$  and  $k_2$  at constant  $k_1/k_2$  suggests that quantitatively similar catalytic sites (probably Brønsted acid sites) are responsible for all the reactions under consideration. The changes of intrinsic acid activity among the catalysts have a similar effect upon hexane cracking and upon methanol conversion. Thus, it is apparent that only the number of active sites is changed and catalytic selectivity remains unchanged.

It is also likely that similar mechanistic pathways (involving carbenium ion intermediates) are operative in both types of reactions.

#### ACKNOWLEDGMENTS

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