

Methanol Conversion to Olefins over ZSM-5

I. Effect of Temperature and Zeolite SiO₂/Al₂O₃

CLARENCE D. CHANG, CYNTHIA T-W. CHU, AND RICHARD F. SOCHA

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

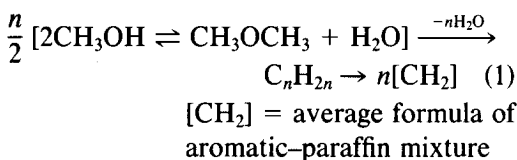
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The conversion of methanol to olefins over ZSM-5 zeolites is described. The interdependence of reaction parameters *T*, *P*, contact time, and catalyst Brønsted acidity in controlling olefin selectivity is characterized and interpreted. It is found that olefin formation can be decoupled from aromatization via a combination of high temperature and low catalyst acidity.

INTRODUCTION

The catalytic conversion of methanol to olefins has received increasing attention in recent years. Aside from its considerable mechanistic interest, the reaction relates to the broader question of converting syngas to light olefins for petrochemical use, or for synthesis of distillate hydrocarbons (1).

Olefins are intermediates in the conversion of methanol to aromatic hydrocarbons over zeolites (2):



The steps in this sequence are generally coupled. The problem at hand is to find conditions under which the final aromatization step can be minimized or suppressed.

Numerous approaches to this problem have been taken. The simplest strategy is to backtrack along the reaction path by decreasing contact time and/or temperature. Here maximum olefin selectivity may be obtainable only at partial conversion, thus necessitating separation and recycle of unreacted feed (3, 4). Essentially complete decoupling of olefination from aromatiza-

tion can be achieved by reducing oxygenate partial pressure (5). At sufficiently low partial pressures, generally below atmospheric, this method affords high olefin yields at complete conversion.

Improvement in olefin selectivity through ZSM-5 modifications using P (20), Mg (21), and silanes (22) has been reported.

Small pore zeolites which cannot sorb aromatics, such as erionite and chabazite, have been found to produce light olefins from methanol (6-10).

As earlier reported (2), olefin selectivity is enhanced at high temperatures. Additional improvement gained through using high SiO₂/Al₂O₃ ZSM-5 catalysts in conjunction with high temperature has been recognized (11).

This paper explores the interaction between catalyst SiO₂/Al₂O₃, temperature, and pressure in methanol conversion to olefins over ZSM-5.

EXPERIMENTAL METHOD

Materials. The catalysts used were ZSM-5 zeolites, synthesized with SiO₂/Al₂O₃ of molar ratio varying from 35 to 1670 according to the method of Argauer and Landolt (12). The zeolite was converted to the H-form via conventional NH₄⁺ exchange followed by calcination at 538°C (13). Some

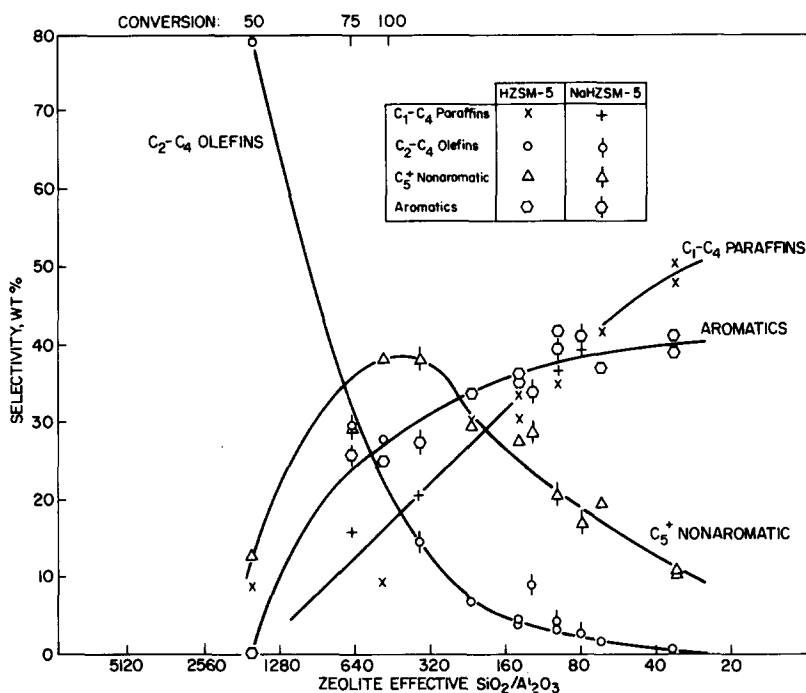


FIG. 1. Methanol conversion over HZSM-5. Hydrocarbon selectivity. $371 \pm 1^\circ\text{C}$, 1 atm (101.3 kPa), 1 LHSV.

samples were partially exchanged to give intermediate levels of effective $\text{SiO}_2/\text{Al}_2\text{O}_3$.

Methanol was reagent grade (Baker).

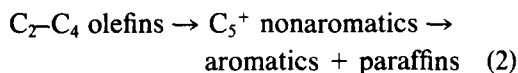
Apparatus and method. Reactions were carried out in fixed-bed 8-mm-i.d. Pyrex, stainless-steel or titanium microreactors. Titanium was used in higher temperature runs to minimize methanol decomposition. The microreactors contained 3 cm^3 catalyst (14/30 mesh). Temperature was measured by means of a thermocouple in an axial thermowell (3 mm o.d.) running the length of the reactor. Pressure was controlled with a back-pressure regulator at the reactor exit and products were analyzed by gas chromatography. Liquids were fed with a positive-displacement pump. Nitrogen diluent was fed through a Brooks mass flow controller.

RESULTS AND DISCUSSION

Influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$

The effect of varying catalyst $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Brønsted acidity) at constant space ve-

locity, T , and P is to delineate the methanol reaction path. This is demonstrated through two series of runs, each carried out at 370°C , 1 LHSV, and 101.3 kPa. In the first, zeolite $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was varied from 35 to 1670. In the second, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ was held constant at 70, while the Na/Al atomic ratio was varied from 0.12 to 0.895 by partial Na exchange. It is assumed that this is equivalent to a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio range of 80 to 667 based on proton concentration. These two sets of data are brought together in Fig. 1, which plots hydrocarbon selectivity on an oxygen-free basis against catalyst effective $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The sequence



is clearly evident, and is identical to the reaction path (Eq. (1)) established by variation of contact time (2).

It is also clear from Fig. 1 that under the

TABLE 1

Methanol Conversion to Olefins Over ZSM-5 (370°C)

Catalyst SiO ₂ /Al ₂ O ₃	1670	70
LHSV, hr ⁻¹	0.5	24
Conversion, %	99.3	95.0
Hydrocarbon distribution		
C ₁ -C ₅ Paraffin	22.8	24.2
C ₂ -C ₃ Olefin	30.0	46.1
C ₆ ⁺ Nonaromatic	25.7	10.1
Aromatics	21.5	19.6

reaction conditions little decoupling of olefination takes place save at partial feed conversion. Moreover when the space velocity was adjusted (LHSV = 0.5 hr⁻¹) to effect complete conversion in the high selectivity region (SiO₂/Al₂O₃ = 1670), significant aromatics were made as shown in Table 1. Included for comparison are data for a SiO₂/Al₂O₃ = 70 catalyst obtained also at 370°C, but at a space velocity (LHSV = 24 hr⁻¹) to yield similar olefin and aromatics selectivity at high conversion. These data further illustrate, albeit qualitatively, the trade-off between contact time and catalyst Brønsted acidity.

Significant decoupling of olefination becomes observable at 450–500°C. The effect

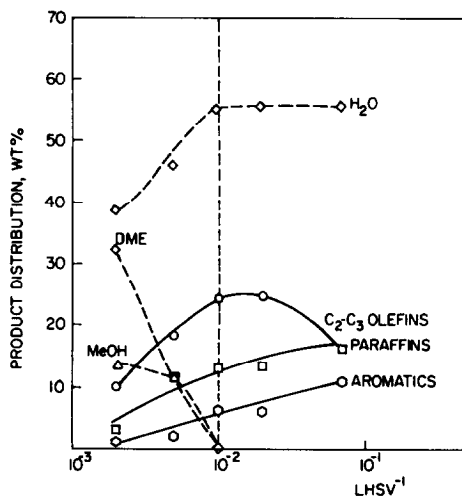


FIG. 2. MeOH conversion over HZSM-5 (SiO₂/Al₂O₃ = 70) 500°C (932°F), atmospheric pressure.

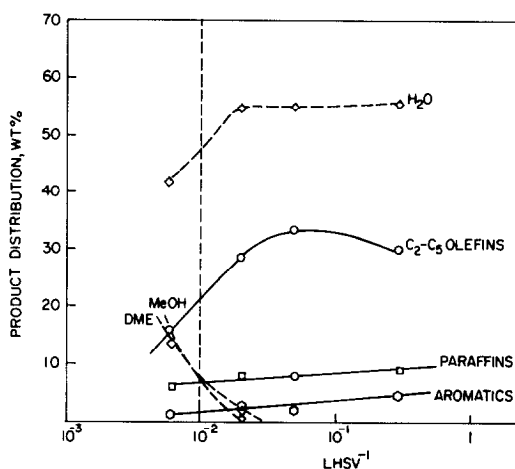


FIG. 3. MeOH conversion over HZSM-5 (SiO₂/Al₂O₃ = 142) 500°C (932°F), atmospheric pressure.

of increasing SiO₂/Al₂O₃ ratio from 70 to 1670 at 500°C on the reaction path is shown in Figs. 2–5, which plot selectivity vs space-time, τ . For convenience, $\tau = 10^{-2}$ hr has been indicated as a common reference in these figures to aid in their comparison. This is the space-time at which oxygenates conversion is essentially complete for SiO₂/Al₂O₃ = 70. Figure 2 shows that olefination and aromatization are coupled at SiO₂/Al₂O₃ = 70, despite the high temperature. Upon increasing SiO₂/Al₂O₃, however, decoupling is quickly established, as seen in Figs. 3–5, though higher contact times are then required for complete conversion.

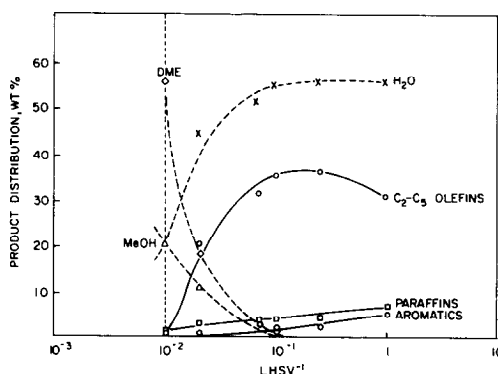


FIG. 4. MeOH conversion over HZSM-5 (SiO₂/Al₂O₃ = 500) 500°C (932°F), atmospheric pressure.

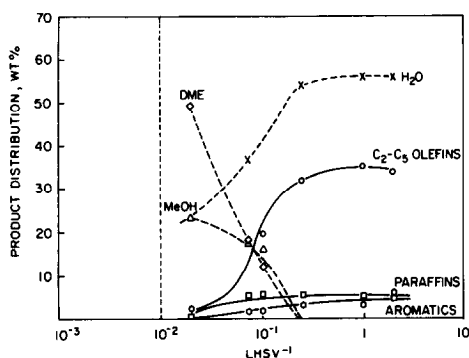


FIG. 5. MeOH conversion over HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 1670$) 500°C (932°F), atmospheric pressure.

The effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ on olefin yield at 500°C is summarized in Fig. 6. Typical product distributions appear in Table 2.

Pressure Effects

As indicated above, olefin selectivity is greatly enhanced by conversion at subatmospheric methanol partial pressures (5). In what follows, the effects of partial pressures of atmospheric and greater will be described.

In one set of experiments, the effective contact time was kept constant by increasing both pressure and space velocity proportionately. Since pure methanol was the feed, methanol partial pressure at the reactor inlet was equal to the total pressure. As seen in Table 3, despite the equivalent contact times of the three runs, the olefin selectivity drops with increasing pressure. These data indicate that simply increasing the space velocity to compensate for a pressure increase does not in itself serve to maintain a constant olefin selectivity.

In another set of experiments the total pressure was kept constant while methanol partial pressure was reduced by cofeeding water. The results of this study are also included in Table 3. This again shows that methanol partial pressure has a very strong effect on olefin selectivity, even above atmospheric pressure.

Kinetic Description

Although a detailed kinetic analysis of the scheme represented by Eq. (1) has not been reported, a number of global schemes

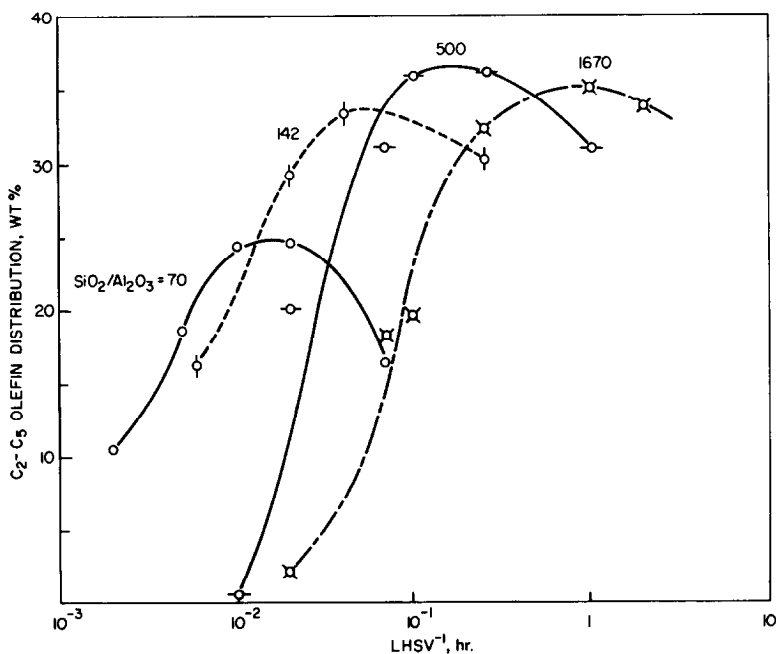


FIG. 6. MeOH conversion over HZSM-5 $\text{SiO}_2/\text{Al}_2\text{O}_3$ effect 500°C (932°F), atmospheric pressure.

TABLE 2

Methanol Conversion to Olefins Over ZSM-5
(500°C, 101.3 kPa)

Catalyst SiO ₂ /Al ₂ O ₃	70	142	500	1670
LHSV, hr ⁻¹	100	50	14.4	10
Total product distribution, wt%				
H ₂ O	55.93	55.96	51.77	54.00
DME	0.20	0.98	3.67	0.59
MeOH	0.29	2.50	2.90	0.95
CO	0.09	0.05	0.10	0.84
CO ₂	0.01	0.01	0.04	0.59
H ₂	0.01	0.02	0.15	0.42
Hydrocarbon	43.47	40.48	43.37	42.53
% Conversion	99.43	96.14	92.00	98.23
Hydrocarbon distribution, wt%				
Methane	0.99	1.26	1.15	3.67
Ethane	0.12	0.13	0.11	0.23
Ethylene	10.48	9.94	7.43	7.75
Propane	3.76	1.92	0.56	0.48
Propylene	22.60	35.14	39.40	37.59
i-Butane	7.82	4.32	0.73	0.60
n-Butane	1.60	0.74	0.21	0.16
Butenes	16.56	17.61	21.58	20.43
i-Pentane	4.80	2.97	0.81	0.62
n-Pentane	0.65	0.52	0.52	0.47
Pentenes	5.91	8.35	12.13	10.25
C ₆ ⁺ Nonaromatic	10.63	9.50	7.59	8.98
Benzene	0.22	0.12	0.17	0.18
Toluene	1.28	0.67	0.70	0.51
Ethylbenzene	0.32	0.18	0.16	0.16
Xylenes	6.87	3.58	3.71	2.80
Ag	4.31	2.55	2.61	3.98
A ₁₀ ⁺	1.09	0.47	0.40	1.48
C ₁ -C ₅	19.74	11.88	4.10	6.24
C ₂ ²⁻ -C ₅ ²⁻	55.55	71.04	80.55	76.03
C ₆ ⁺ PON	10.63	9.50	7.59	8.98
Aromatics	14.08	7.58	7.77	8.72

of varying complexity have been proposed (14). For the present work, a simple kinetic model



A = oxygenates (as CH₂)
B = olefins
C = aromatics + paraffins

has proven satisfactory. This is due partly to the fact that aromatics and paraffins are relatively minor components in the domain

TABLE 3

Effect of Pressure on Olefin Selectivity (482°C)

Total pressure (atm)	1	3	6	3	3
P _{MeOH} (atm)	1	3	6	1	0.4
LHSV (MeOH), hr ⁻¹	2	6	12	2	2
[CH ₂] Conv. (%)	100.0	99.8	96.8	100.0	99.1
C ₂ -C ₅ Olefins in HC (wt%)	58	44	41	65	77
Aromatics in HC (wt%)	13	16	20	12	7

of interest here. In this model methanol and dimethyl ether (together referred to as "oxygenates") are assumed to be at equilibrium (15-17), and can thus be treated as a single kinetic species or "lump." Olefins are lumped together, as are aromatics and paraffins. The disappearance of oxygenates and olefins are assumed to be first-order.

The parameter k_1 was determined from conventional first-order semilog plots of oxygenate disappearance vs τ . Typical data are shown in Figs. 7 and 12 for varying temperature and SiO₂/Al₂O₃ ratio (at 500°C). A small deviation from linearity is apparent at low conversions. This is attributed to autocatalysis (18), which is neglected in the simplified kinetic treatment. The parameter k_2 was then determined from

$$[B] = \frac{k_1}{k_2 - k_1} (e^{-k_1\tau} - e^{-k_2\tau}) \quad (4)$$

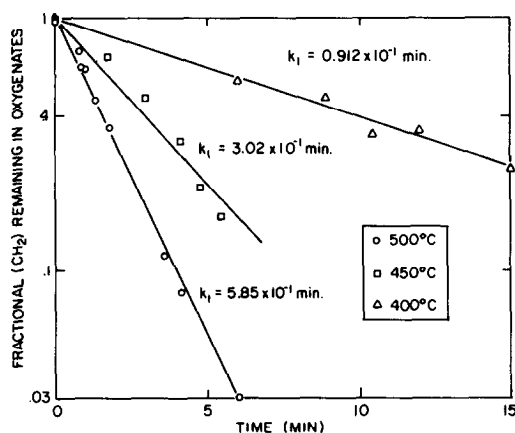


FIGURE 7

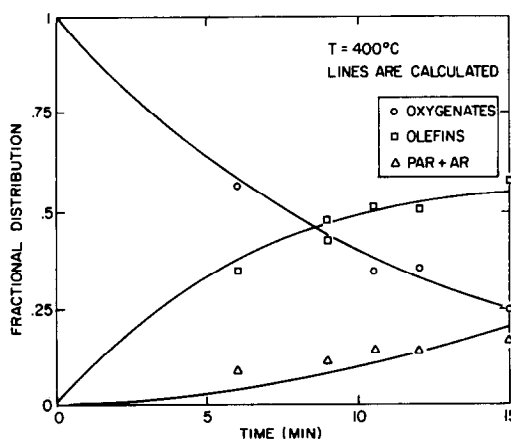


FIGURE 8

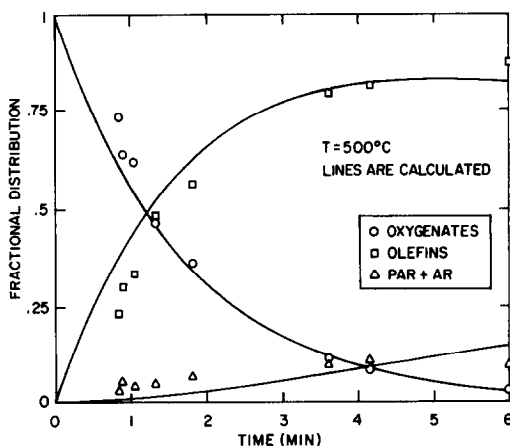


FIGURE 10

using the Newton-Raphson method (19).

Representative data obtained at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 500$ are plotted in Figs. 8, 9, and 10 for 400, 450, and 500°C. Here the curves are generated from the model, and are superimposed on experimental points. Figure 11 is an Arrhenius plot of k_1 and k_2 . As indicated, the apparent activation energy is 19.3 kcal/mole for olefin formation. However, the data show little or no temperature dependency of aromatization. This may be indicative of strong pore diffusion control, although some type of compensation effect cannot be ruled out at present. Nonetheless, this result provides a rationale for tem-

perature effect on selectivity of olefins from methanol.

Figures 13 and 14 are similar to the preceding figures except that temperature was held constant at 500°C for $\text{SiO}_2/\text{Al}_2\text{O}_3 = 400$ and 1670. (For $\text{SiO}_2/\text{Al}_2\text{O}_3 = 500$, see Fig. 10.) Again, the curves displayed are theoretical.

The ratio k_1/k_2 , a measure of olefin selectivity, is plotted against $\text{SiO}_2/\text{Al}_2\text{O}_3$ in Fig. 15 along with supplemental data. It is seen that k_1/k_2 increases with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$, indicating a difference in the degree of dependency on Brønsted acidity between the two reactions.

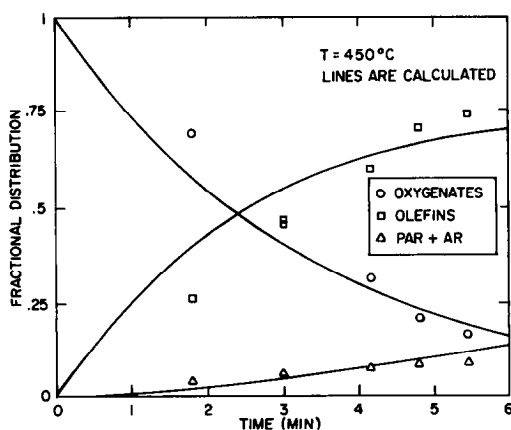


FIGURE 9

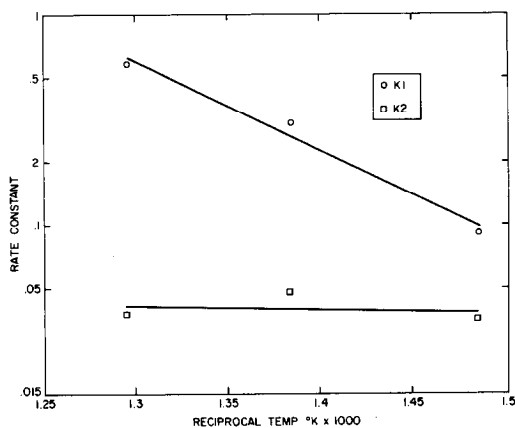


FIGURE 11

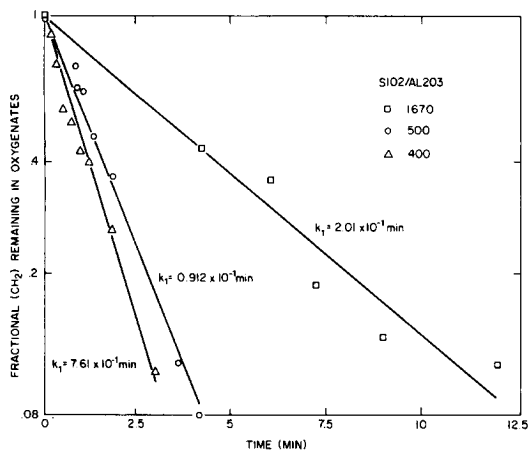


FIGURE 12

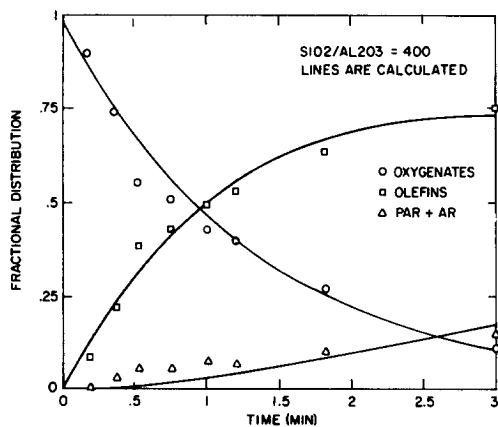


FIGURE 13

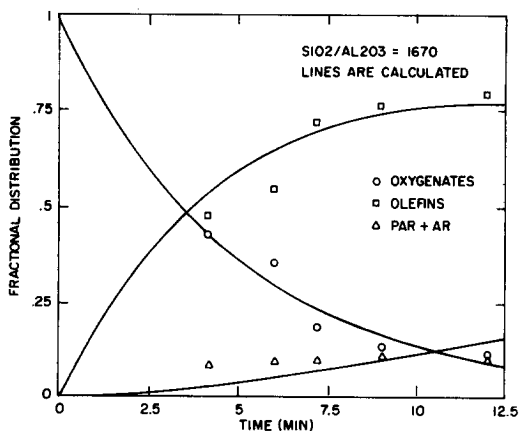


FIGURE 14

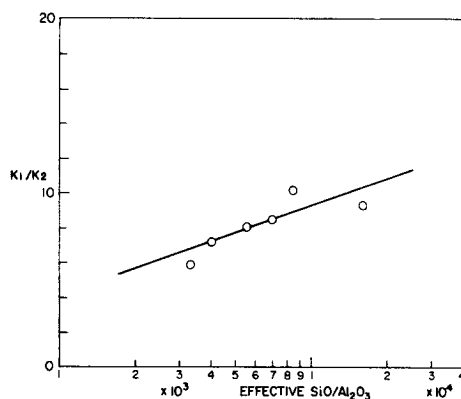


FIGURE 15

The combination of low acidity and high temperature is therefore vital toward maximizing olefin selectivity.

CONCLUSIONS

This study has shown that in the conversion of methanol to hydrocarbons over ZSM-5 zeolites, selectivity to olefins can be enhanced by a cooperative effect of increased temperature and increased catalyst $\text{SiO}_2/\text{Al}_2\text{O}_3$. This selectivity enhancement is due to decoupling of olefin formation from aromatization, brought about by differences in the activation energy and acid-dependency of the two reactions.

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