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Production of Chemicals from Methanol

I. Low Molecular Weight Olefins

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Methanol has been converted to water and hydrocarbons, with up to 70% selectivity to C_2–C_4 olefins, at 100% conversion, over ZSM-5 class zeolite catalysts modified with phosphorus compounds. Ethylene is proposed as the initial hydrocarbon produced. Evidence for the alkylation of olefins with methanol or methyl ether over these catalysts to produce higher molecular weight olefins is presented.

I. INTRODUCTION

The announcement of a new low-pressure process for the production of methanol from synthesis (syn) gas ($CO + 2H_2$), by Imperial Chemical Industries in the late 1960s, clearly indicated potential for a significant decrease in production costs in large industrial plants (*1*). Construction of single-train 1300-ton/day reactors (*2*) and designs for 5-million-pound/day plants have subsequently been reported (*3*).

Since enormous quantities of hydrocarbon gas were and are being flared in oil fields remote from markets, it was appealing to consider converting it to syngas and then methanol. The latter is a liquid which may be transported to markets in conventional tankers making possible the utilization of this valuable resource. The more recent large increases in the cost of oil and the potential uncertainty of supply have further stimulated interest in the production of syngas from abundant sources of coal in the United States for subsequent conversion to hydrocarbons or methanol as an alternative primary source of liquid fuels.

A variety of zeolites had been synthesized at Mobil Laboratories which were effective catalysts for hydrocarbon transformations. The rare earth-exchanged faujasites, for example, are at present universally used in refinery cracking processes to increase the yield of gasoline (*4, 5*). Following this, new generations of crystalline aluminosilicate zeolites were synthesized with unique structures and high stability and activity. The timely availability of these materials and associated technology prompted us to begin a search for new chemical reactions, starting with methanol, using these zeolite catalysts.

II. EXPERIMENTAL METHODS

Materials. Methanol, methyl ether, ethylene, propylene, and the individual butylenes were high-purity reagents (99 + %) and were used without further purification.

Catalysts. The ZSM-5 class of catalysts was prepared according to directions reported in a number of patents (*6–9*) including techniques for modification with phosphorus compounds (*10*).

Apparatus and procedure. One to five grams of catalyst was placed in a fixed-bed, continuous-flow, electrically heated, cylindrical, quartz reactor, 1.1 × 15 cm, contain-

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ing a centered quartz thermowell. Temperatures were measured at three positions in the catalyst bed. Methanol was delivered by a metering pump to a vaporizer and where appropriate, mixed with gases with rates determined by mass flowmeters. The reaction temperature was recorded as the highest reading in the bed.

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. The equipment was automated to permit continuous, unattended operation. Generally, reaction products were collected for 1- to 2-hr periods after equilibration; however, much longer periods were frequently used.

III. RESULTS AND DISCUSSION

General

The first experiments concerned with the reaction of methanol over this new ZSM-5 class of crystalline aluminosilicates immediately revealed that methyl ether and water were formed initially and at high rates (*8*). By operating at relatively low temperatures (250°C) the ether could be produced as the major product in excellent yield. At higher temperatures the ether reacted further with the elimination of more water and the production of a mixture of hydrocarbons. A detailed discussion of products produced from methanol and related oxygen-containing compounds, over this catalyst, has been reported by Chang and Silvestri (*11*). Additional information regarding the use of this technology for conversion of methanol to gasoline has been described by Meisel *et al.* (*12*).

In this laboratory we have been concerned primarily with the transformation of methanol into chemical products. The mixture of hydrocarbons produced at various temperatures, amounting to a theoretical 44 wt% of the methanol converted (56% water), is shown in Table 1. The aromatic and C_2–C_4 olefins are the most valuable products. An objective of this work was to improve the yield of light olefins, especially ethylene, at the expense of paraffins and higher molecular weight aliphatics. This would increase the value of the hydrocarbon product. The ratio of C_2–C_4 olefins/paraffins initially observed was only approximately 0.6 in the range 400–500°C.

TABLE 1

Conversion of Methanol to Hydrocarbons over ZSM-5 Class Zeolite

Reaction conditions[a]			
Temperature (°C)	400	450	500
Conversion (wt%)[b]	100	100	100
Hydrocarbon	Weight percentage		
Methane	0.7	2.6	4.1
Ethane	0.2	0.9	1.2
Propane	6.9	11.4	14.9
Butanes	20.1	19.8	19.3
Total C_2–C_4 paraffins	27.2	32.1	35.4
Ethylene	3.4	6.4	6.8
Propylene	3.9	6.4	7.3
Butylenes	9.6	7.4	6.4
Total C_2–C_4 olefins	16.9	20.2	20.5
C_5–C_{10} aliphatics	39.9	23.0	15.5
Aromatics[c]	15.3	22.1	24.5
Total	100.0	100.0	100.0
C_2–C_4 olefin/paraffin ratio	0.62	0.63	0.58

[a] Atmospheric pressure; weight hourly space velocity = 1.

[b] To hydrocarbons and water.

[c] Primarily benzene, toluene and xylenes.

Modification of Zeolites with Phosphorus

During the course of our work to change and control the selectivity pattern of the reaction products from methanol, the zeolite crystals were treated with a variety of phosphorus compounds. An interaction occurred with trimethyl phosphite which, after calcination in air, resulted in a permanent attachment of phosphorus in the catalyst. We propose bonding to the zeolite framework through oxygen (Fig. 1) involving a displacement of methanol at an acid site (*10*). Measurement of zeolitic acidity by Kerr's ammonia desorption technique (*13*) has indicated that the number of acid sites was increased significantly and that they were weaker in strength compared with those in the unmodified zeolite.

Although the precise structure of the phosphorus-modified zeolite is speculative at present, an extensive change in catalytic effect was evident. An equilibrium is rapidly established between methanol, methyl ether, and water over these catalysts. Methanol (56% water) and methyl ether (35% water) were used independently as starting materials and found to give substantially the same products under similar conditions of reaction. Results starting with methyl ether are shown in Table 2.

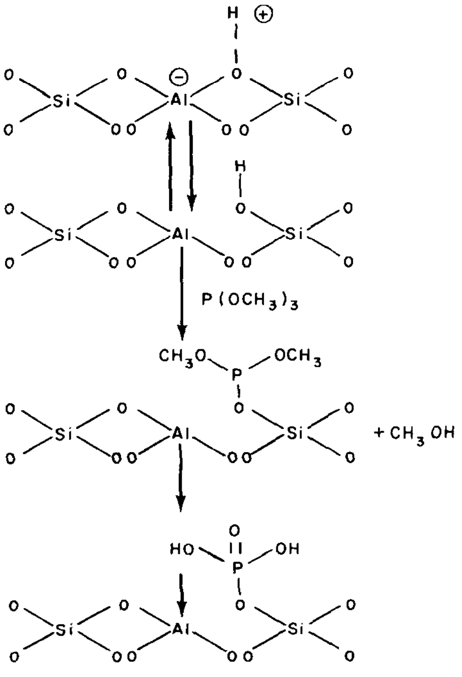


FIG. 1. Phosphorus-modified zeolites.

The phosphorus-modified catalyst was somewhat less active than the original untreated catalyst as shown by the lower conversion at 400°C. A dramatic increase in the relative yields of C_2–C_4 olefins was observed at all temperatures and was especially pronounced in the range 400–600°C.

Production of paraffinic, aromatic, and higher molecular weight aliphatic compounds was reduced proportionally. The selectivity to C_2–C_4 olefins was 60–75 wt% at 80–100% conversion of methanol/methyl ether. By modification of the zeolite catalyst with phosphorus, it was possible to produce C_2–C_4 olefins as the major products of reaction starting from methanol.

Low molecular weight olefins also were prepared in high yield with the original, unmodified zeolite catalyst by significantly reducing the contact time (*11*). Initial products are thereby removed before they can react further. This observation is consistent with the sequential reaction schemes proposed.

At 700°C methane, carbon monoxide, and hydrogen were the major products observed, indicative of hydrogen transfer and some reversal back to synthesis gas.

Reaction Mechanism

Chemical reactions with zeolite catalysts generally are assumed to occur primarily within the internal pore structure. This is a unique medium for organic reactions by comparison with homogeneous solutions, or the surface of irregular amorphous catalysts. With zeolites, reacting molecules must diffuse into the pores and interact at catalytic sites, and the products must diffuse out. Within certain zeolite cages, geometric limitations are imposed on the positions of reacting molecules. Molecular

TABLE 2

Conversion of Methyl Ether to Hydrocarbons over Phosphorus-Modified Zeolites[a]

Reaction conditions[b]						
Temperature (°C)	300	350	400	500	600	700
Conversion (wt%)[c]	1.8	22.2	80.9	100	100	100
Hydrocarbon	Weight percentage					
Methane, CO, H_2	0	0.4	0.9	2.7	3.9	76.6
Ethane	11.4	1.4	0.2	0.4	0.6	1.0
Propane	8.2	1.8	0.2	0.7	1.3	0.2
Butanes	6.9	3.9	1.0	1.6	1.2	0
Total C_2–C_4 paraffins	26.5	7.1	1.4	2.7	3.1	1.2
Ethylene	11.2	8.0	2.5	2.8	16.2	5.2
Propylene	32.8	30.9	29.4	34.6	38.7	7.3
Butylenes	12.5	16.2	36.4	21.6	19.7	3.6
Total C_2–C_4 olefins	56.5	55.1	68.3	59.0	74.6	16.1
C_5–C_{10} aliphatics	12.0	30.4	24.1	33.2	13.1	2.5
Aromatics	5.0	7.0	4.3	2.4	5.3	3.6
Total	100.0	100.0	100.0	100.0	100.0	100.0
C_2–C_4 olefin/paraffin ratio	2.1	7.8	48.8	21.9	24.1	13.4

[a] $P = 3.48$ wt%.

[b] Atmospheric pressure; weight hourly space velocity = 2.3.

[c] To hydrocarbons and water.

weights can be limited and isomeric products may be favored that differ widely from the usual product spectrum obtained in a homogeneous solution. This concept is especially interesting and the potential was recognized, demonstrated, and termed "shape selectivity" by Weisz and coworkers many years ago (*14*). The information in a landmark summary of organic reactions catalyzed by zeolites by Venuto and Landis over a decade ago (*15*) is now being expanded as a result of the appearance of new generations of synthetic high silica/alumina ratio zeolite catalysts of the type pioneered at Mobil Research and Development Corporation Laboratories, and a growing recognition of their catalytic potential for organic reactions is evident by recent activity.

Chang and Silvestri have described in considerable detail the effect of temperature, space velocity, and other factors on the conversion of methanol to products and have discussed various reaction pathways (11).

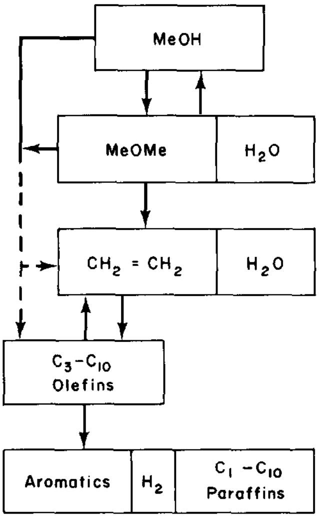


FIG. 2. Reaction pathways of methanol over ZSM-5 class crystalline aluminosilicate.

TABLE 3

Products at Low Conversion over Phosphorus-Modified Zeolites[a]

	M	N	O	P	Q	R
Reaction conditions[b]						
Temperature (°C)	300	350	350	350	300	350
Feed A	MeOH	MeOH	N_2	MeOH	MeOH	MeOH
B	N_2	N_2	C_2H_4	C_2H_4	C_3H_6	C_3H_6
WHSV[c] A	2.1	2.1	2.1	2.5	3.1	2.9
B	2.1	2.1	2.1	2.1	3.2	3.2
Conversion (wt%)						
MeOH, Total[d]	90.5	83.7	—	82.3	41.1	79.3
MeOH, To HC[e]	3.5	3.6	—	—	—	—
B	—	—	25	3.8	10.2	40.1
	Selectivity to hydrocarbon products (wt%)					
C_2–C_4 paraffins	0	0	3.3	2.9	8.8	6.0
Ethylene	100	92.2	SM[f]	SM	2.6	5.2
Propylene	0	7.8	22.6	55.8	SM	SM
Butylenes	0	0	34.3	23.7	38.3	35.3
C_5[g]	0	0	20.7	17.6	31.9	20.9
C_6–C_7[g]	0	0	15.6	0	4.6	14.5
BTX[h]	0	0	0	0	1.8	5.3
$C_8{}^{+}$[g]	0	0	3.5	0	12.0	12.8
Total	100	100	100	100	100	100

[a] $P = 2.82$ wt%.

[b] Atmospheric pressure.

[c] wt feed/wt catalyst/hr.

[d] Methanol conversion to ether, hydrocarbons, and water.

[e] Portion of methanol converted to hydrocarbons; balance is methyl ether and water.

[f] Starting material.

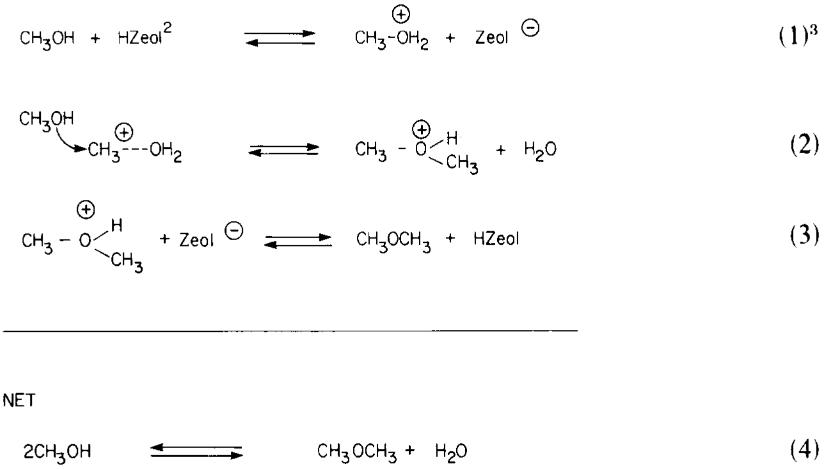
[g] Analysis not made to distinguish between olefins and paraffins.

[h] Benzene, toluene, xylenes, and ethylbenzene.

More recently Derouane and co-workers (*16*) have provided evidence for an alkyl ether mechanism.

We would like to supplement these proposals by focusing attention on some of the individual reactions which occur and indicate an overall sequential mechanism to account for products formed under various conditions. A schematic diagram is shown in Fig. 2. The dashed line indicates that methanol or methyl ether may react with ethylene or higher molecular weight olefins rather than being transformed directly to the C_3–C_{10} olefins. The phosphorus-modified zeolites have proved useful in examining products at low conversion and we have tentatively assumed that the mechanism has not been changed by this treatment.

(*1*) *Alkylation of methanol with methanol.* The initial, facile production of methyl ether and water from methanol may be viewed as an acid-catalyzed alkylation of methanol with methanol. By a suitable choice of catalyst and mild reaction conditions it can be the principal reaction. In Table 3, column M, about 90% of the methanol was converted to ether and water with only a small hydrocarbon yield. A further reduction in temperature to 250°C gave methyl ether and water as the exclusive products at high conversion (80%). A mechanism proposed for this reaction is shown in Eqs. (1)–(4).



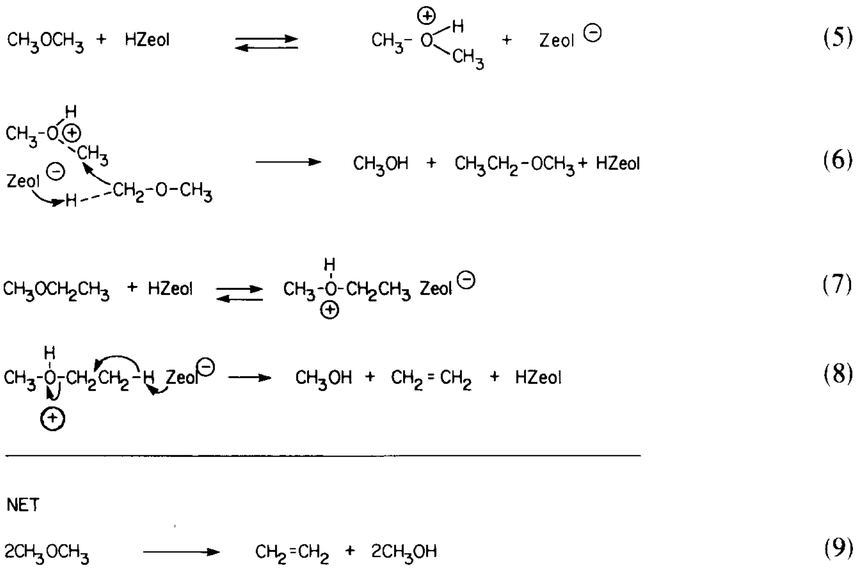
$$CH_3OH + HZeol^2 \rightleftharpoons CH_3\text{-}\overset{\oplus}{O}H_2 + Zeol^{\ominus} \quad (1)^3$$

$$CH_3\overset{\oplus}{O}\begin{smallmatrix}H\\CH_3\end{smallmatrix} + Zeol^{\ominus} \rightleftharpoons CH_3OCH_3 + HZeol \quad (3)$$

NET

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad (4)$$

(2) *Conversion of methanol to ethylene.* Under very mild conditions of reaction, methanol or/and its ether was converted to ethylene exclusively at low conversions (Table 3 column M) over the phosphorus-modified catalyst. This appears to be *the* initial hydrocarbon product. A possible sequence of steps is shown in Eqs. (5)–(9), with methyl ethyl ether as the intermediate which we have detected in product mixtures. This compound has also been identified previously in the reaction products in trace amounts (*11*).



$$CH_3OCH_3 + HZeol \rightleftharpoons CH_3\text{-}\overset{\oplus}{O}\begin{smallmatrix}H\\CH_3\end{smallmatrix} + Zeol^{\ominus} \quad (5)$$

$$CH_3OCH_2CH_3 + HZeol \rightleftharpoons CH_3\text{-}\overset{H}{\underset{\oplus}{O}}\text{-}CH_2CH_3\ Zeol^{\ominus} \quad (7)$$

NET

$$2CH_3OCH_3 \longrightarrow CH_2{=}CH_2 + 2CH_3OH \quad (9)$$

The key step proposed is the generation of a negative center on the methyl group of methyl ether (or methanol), aided by an anionic site on the catalyst, followed by attack on an incipient methyl carbonium ion

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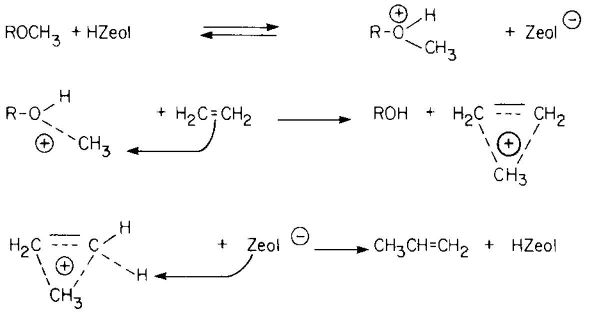
[2] Denotes an acidic site in the zeolite catalyst.

[3] In this and all of the equations which follow, the positively charged carbonium ions are not "free" as shown but probably are closely associated with or bonded to the anionic site on the wall of the zeolite catalyst.

of a protonated methyl ether (or methanol) (Eq. (6)). The subsequent conversion of methyl ethyl ether (Eqs. (7) and (8)) may be inferred by the close structural relationship to ethyl ether and ethanol which are known to produce ethylene with great facility (*16*). The details shown in Eq. (6) are speculative. However, it serves to focus attention on the possible events leading to the formation of the first carbon–carbon bond from methanol or its ether and to indicate our preference for using the ionic transfer of hydrogen consistent with the strong acid character of the catalyst.

Derouane and co-workers also favor an ether mechanism without indicating any detail for the initial carbon–carbon bond formation (*16*). They have proposed that higher ethers are also produced in a similar manner and account for propylene and higher olefin production. We favor a combination of alkylation of lower olefins with methanol or methyl ether and olefin oligomerization/cracking as discussed in the following sections.

(*3*) *Alkylation of olefins with methanol.* As the reactions above proceed significant concentrations of methyl ether, methanol, and ethylene would be present in the catalyst bed. In order to simulate this possible condition equimolar amounts of methanol and ethylene were passed over the catalyst under mild conditions to discover reaction products at low conversion (Table 3, column P). It is evident that methanol was converted primarily to its ether (82%), as expected, and that a low yield of hydrocarbons was produced (3.8%). Propylene was the major hydrocarbon produced along with significant amounts of C_4 and C_5 olefins. We propose that these products arise by the alkylation of ethylene with methanol or its ether to give propylene initially. The latter is subsequently alkylated to give butylenes, etc. by the same mechanism, Eqs. (10)–(13).



(10)

(11)

(12)

NET

$$R\text{-}OCH_3 + H_2C{=}CH_2 \longrightarrow CH_3CH{=}CH_2 + ROH \qquad (13)$$

$R = H$ or CH_3

The largest product group produced when methanol and propylene were passed over the catalyst was C_4 olefins (Table 3, columns Q and R). Propylene is considerably more reactive than ethylene as indicated by higher conversion to hydrocarbon products under similar conditions of reaction (Table 3, columns P and R).

In another experiment where a mixture of propylene and methyl ether was passed over a phosphorus-treated zeolite (Table 4), butylenes were produced exclusively at low

TABLE 4

Alkylation of Propylene with Methyl Ether[a] over P-ZSM-5 Class Crystalline Aluminosilicate

$$\underset{A}{C_3H_6} + \underset{B}{CH_3O\,CH_3} \rightarrow \underset{C}{C_4H_8} + \underset{D}{C_5H_{10}}$$

Conversion (%)		Temperature (°C)	WHSV	Selectivity (%)	
A	B			C	D
<1	<1	250	2	100	0
3	1	300	2	85	13
21	40	350	2	45	18
42	100	400	2	33	21

[a] Equimolar amounts of methyl ether and propylene fed to reactor; atmospheric pressure; P = 3.7 wt%.

conversion. As the temperature was increased, significant methylation of the butylene product to produce C_5 olefins was observed.

(*4*) *Olefin oligomerization/cracking.* An equimolar mixture of ethylene and nitrogen was passed over the catalyst to determine products of reaction which might occur independent of interactions with methyl ether or methanol (Table 3, column O). Acid-catalyzed oligomerization/cracking reactions are proposed to account for the products observed as shown in part in Eqs. (14)–(18). This is consistent with a considerable body of earlier work concerned with the reaction of olefins over a variety of faujasite-type zeolites (*15, 17*). Of particular interest was the passage of ethylene over REX at 213°C (*18*). The gases evolved after 60 min of operation contained about 40% ethylene, 23% propane, and 38% butane. Low concentrations of isopentane appeared about 10 min later. The catalyst was severely deactivated by a complex mixture of highly alkylated aromatics trapped within the pore structure which were isolated and identified by dissolving away the zeolite after the reaction. A series of reactions were proposed initially involving an acid-catalyzed oligomerization of ethylene followed by cycloparaffin formation and subsequent hydrogen transfer to form aromatics and paraffins.

$$CH_2{=}CH_2 + HZeol \rightleftharpoons \overset{\oplus}{CH_3CH_2}\,Zeol^{\ominus} \qquad (14)$$

$$\overset{\oplus}{CH_3CH_2} + CH_2{=}CH_2 \rightleftharpoons CH_3CH_2CH_2\overset{\oplus}{CH_2} \longrightarrow CH_3CH_2\overset{\oplus}{CH}CH_3 \qquad (15)^4$$

$$C_4H_9^{\oplus} + C_2H_4 \rightleftharpoons C_6H_{13}^{\oplus} \rightleftharpoons \text{etc.} \qquad (16)$$

$$C_6H_{13}^{\oplus} + Zeol^{\ominus} \rightleftharpoons 2CH_3CH{=}CH_2 + HZeol \qquad (17)^5$$

NET

$$3CH_2{=}CH_2 \longrightarrow 2CH_3CH{=}CH_2 \qquad (18)$$

When ethylene was passed over the phosphorus-modified ZSM-5 class zeolite (Table 3, column O), the ethylene dimer

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[4] See footnote 3.

[5] Many other combinations occur to give the C_3–C_{10} mixtures observed, not just propylene as shown in this model reaction.

was the largest single product fraction with a 34.3 wt% selectivity to butylenes and 2.5 wt% to butanes. The product selectivity to propylene and propane was 22.6 and 0.6 wt%, respectively. The latter compounds with odd numbers of carbon atoms arise from a cracking reaction of the type proposed in Eq. (17). The presence of phosphorus inhibited the reactions leading to aromatics and paraffins which were primary products with the more active REY catalyst.

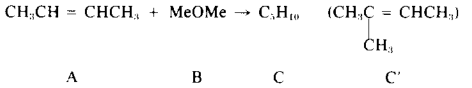
A comparison of the products in Table 3, columns O and P, suggests that the oligomerization/cracking reaction discussed above is suppressed considerably in the presence of methanol, methyl ether, and water. The alkylation of ethylene with methanol is dominant. This may be due to a stronger affinity of these more polar, oxygen-containing compounds for the catalytic sites. However, possible production of butene by dimerization of ethylene or C_5 olefin by reaction of ethylene and propylene cannot be eliminated at this point.

(5) *Ring formation and hydrogen transfer.* Under more severe conditions of reaction, with unmodified catalyst, substantial quantities of aromatic and paraffinic compounds are produced. A detailed discussion of this reaction and mechanism will be the subject of a future publication.

With the assumption that olefins are alkylated with methanol to give water and another olefin with one additional carbon atom, the potential for preparation of the isoprene skeleton from *n*-butene and methanol, at practical conversions, was studied. The results are summarized in Table 5. A C_5 olefin mixture was produced in significant yield. Furthermore, the olefins with an isoprene skeleton accounted for well over half of the isomers produced in this fraction.

TABLE 5

Alkylation of Butene-2 with Methyl Ether over Phosphorus-Modified ZSM-5 Class Crystalline Aluminosilicate[a]



$$\underset{A}{CH_3CH=CHCH_3} + \underset{B}{MeOMe} \rightarrow \underset{C}{C_5H_{10}} \quad \underset{C'}{(CH_3\underset{CH_3}{\underset{|}{C}}=CHCH_3)}$$

Conversion (%)		Temperature (°C)	WHSV	Selectivity (wt%)	
A	B			C	C′ (% of C)[b]
30.5	22.6	300	4.8	40.6	74.5
52.9	45.1	325	4.8	32.4	67.3
58.0	58.1	350	4.8	37.6	61.9
78.3	88.8	375	4.8	29.3	56.2
79.0	94.9	400	4.8	27.5	60.9

[a] $P = 3.7$ wt%.

[b] The thermodynamic equilibrium concentration for 2-methyl-2-butene in the pentene mixture varies from about 60% at 300°C to 51% at 400°C.

A complex and extensive series of reactions is required for the transformation of methanol to hydrocarbon mixtures containing up to 10 or more carbon atoms per molecule and consisting of mixtures of paraffins, olefins, and aromatics. Five reaction types have been proposed to account for the products observed under various reaction conditions. Evidence has been presented for the production of ethylene as the initial hydrocarbon produced from methanol and for the alkylation of olefins with methanol or its ether to give another olefin with one additional carbon atom. By proper control of reaction conditions and catalyst treatment it has been possible to maximize production of methyl ether, olefins, or aromatics and paraffins. If the potential large-scale conversion of gas and coal to methanol is realized in the future, to supplement the supply of liquid hydrocarbon fuels, zeolite catalysts of the ZSM-5 class could provide an alternate means of preparing the basic olefins and aromatics required by the chemical industry.

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