

Elucidation of the Mechanism of Conversion of Methanol and Ethanol to Hydrocarbons on a New Type of Synthetic Zeolite

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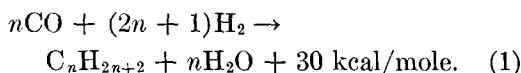
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¹³C nuclear magnetic resonance and vapor-phase chromatography have been used to investigate the conversions of methanol and ethanol to hydrocarbons on a synthetic zeolite of the type H-ZSM-5 as described by Mobil. Methanol is first dehydrated to dimethyl ether and ethylene. Then the reaction proceeds by two competitive paths: first, successive dehydration-methanolation steps to give branched aliphatics, and, second, polycondensation reactions leading to linear aliphatic and aromatic compounds. The basic mechanism is essentially the same for ethanol, with the major difference being that ethylene can also be formed by direct dehydration of ethanol. At variance to earlier proposals, a mechanism involving carbenium ions is proposed which accounts well for the high yield in branched hydrocarbons and the observation of methyl ethyl ether which is detected in the methanol conversion products.

I. INTRODUCTION

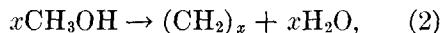
The present energy situation has renewed the interest in catalytic synthesis processes of the Fischer-Tropsch type, i.e., following the equation



This process, however, presents three major drawbacks, namely, the great variety of hydrocarbons that are formed although poor in aromatics, the presence of oxygenated compounds, and a low research octane

number (RON) for the fraction that could be used as gasoline.

Most recently, Chang and Silvestri (1) have described in this *Journal* part of a new and simple process for the conversion of methanol and other oxygen-containing compounds to hydrocarbons as first proposed by Mobil (2) for the conversion of methanol, i.e.,



and as reported in a number of patents [see Ref. (23) of Ref. (1) and Refs. (3-5)] The Mobil process is characterized by a high yield of isoparaffins and aromatics and the hydrocarbon mixture then presents a

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high RON (typically near 95). The catalyst is essentially the acidic form of a new type of synthetic zeolite called ZSM-5 (3) of which the major characteristics are (i) a Si:Al ratio of about 40; (ii) a crystal density smaller than $1.6 \text{ kg}\cdot\text{dm}^{-3}$ (characterizing the number, dimension, and stability of the pores); and (iii) a constraint index in the range 1 to 12 (5), measuring in a relative manner the cracking rates of *n*-hexane and 3-methyl pentane. A high constraint index corresponds to a higher cracking rate for the "linear" *n*-hexane as compared to the "branched" 3-methyl pentane. It characterizes the porous system of the material which is then highly shape selective. Such materials are stable at high temperature, even in the presence of steam, which enables the elimination of carbonaceous residues eventually formed during their operation as catalysts.

The central question still to be resolved is the mechanism by which methanol (and eventually other oxygen-containing compounds) undergo water elimination to form hydrocarbons. The mechanism postulated by Chang and Silvestri (1) and their discussion of previous proposals certainly provide some insight into the process. However, they do not explain important experimental facts such as the high ratio of iso- to normal paraffins and the presence of methyl ethyl ether observed in the conversion of methanol.

In order to ascertain the possible role played by the presence or the absence of β -hydrogens in the feed compound, the present paper reports data obtained for the conversion of methanol (no β -hydrogens) and ethanol (β -hydrogens) under similar conditions on a new type of zeolite which is identical to the H-ZSM-5 catalyst from Mobil.

Gas chromatography data (which compare and give information on the product distributions, not excluding possible side reactions on the separation columns) are compared with ^{13}C NMR data obtained

in situ during the reaction, at less than one monolayer coverage and excluding several secondary effects.

No detailed review of previous related work is included in this paper, as it is meant to be a direct follow-up to the report of Chang and Silvestri (1).

II. EXPERIMENTAL METHODS

Materials. High-purity grade (99 + %) methanol and ethanol were used for the kinetic studies. ^{13}C -Enriched methanol and ethanol (90–95%) from British Oxygen Corporation (B.O.C.) were used for the NMR studies after proper dilution to achieve an effective enrichment of 30% in ^{13}C .

Catalyst. The catalyst consists of the acidic form of the ZSM-5 synthetic zeolite the preparation of which has been previously described (3). A solution of Na-aluminate is added to a solution of silica and tetrapropylammonium hydroxide in water. A precipitate forms which is crystallized by autoclave heating at 150°C for 5 to 7 days. The ZSM-5 zeolite is identified by its diffraction pattern (3) and the following analytical molar ratio $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2 = 0.33:1.00:26.3$. The acidic form of this material, i.e., H-ZSM-5, is obtained by exchanging the Na cations with HCl at 80°C and drying at 600°C . The analytical molar ratio for this compound is $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2 = 0.022:1.00:43.6$.

The H-ZSM-5 zeolite is used pure for the static ^{13}C NMR studies. For the kinetic studies, however, it is embedded in $\text{SiO}_2(1:1)$ using as a silica source Ketjensol 40 AS. The pH of the suspension is adjusted to 5 using ammonia and HNO_3 . A gel forms upon heating which is dried overnight at 110°C . The resulting powder is meshed and only the particles with sizes in the range 0.125–0.3 mm are retained for the kinetic studies as catalyst.

The constraint index (5) of this catalyst has been determined using a 1:1 mixture

TABLE 1
 Zeolite-Catalyzed Hydrocarbon Formation from Methanol^a

Product Flow rate (ml·hr ⁻¹)	250°C			300°C				350°C				400°C			
	0.31 ^b	0.62	1.24	0.15	0.31	0.62	1.24	0.15	0.31	0.62	1.24	0.15	0.31	0.32	1.24
Methanol	14.3	14.8	14.5	—	—	9.5	17.6	—	—	—	—	—	—	—	—
Dimethyl ether	83.3	76.9	74.4	—	—	— ^c	49.3 ^c	—	—	—	—	—	—	—	—
Aliphatics															
C ₂	2.2	3.6	4.0	3.2	4.7	18.7	10.3	3.0	2.4	3.2	3.4	6.1	4.9	4.0	3.8
C ₃	—	3.6	5.9	22.0	18.5	14.9	11.4	27.7	23.6	20.4	16.4	33.5	30.0	26.4	20.8
C ₄	—	—	—	33.2	24.6	27.7 ^d	— ^d	26.3	25.5	26.7	24.3	21.8	23.9	25.2	25.2
C ₅	—	—	0.6	14.4	14.7	8.1	3.4	7.3	9.0	12.8	13.8	4.5	5.6	7.8	9.7
C ₆	0.2	1.1	0.6	7.0	7.7	6.3	2.6	1.9	3.3	6.8	8.3	0.6	1.1	2.4	4.0
C ₇	—	—	—	1.6	4.1	3.5	1.9	0.5	0.7	1.2	1.7	—	—	0.5	0.8
C ₈	—	—	—	0.7	1.9	1.4	0.8	0.1	0.2	0.4	0.8	—	—	0.1	0.1
Cyclics															
C ₅	—	—	—	0.1	0.1	—	—	0.2	0.2	0.4	0.4	0.2	0.2	0.3	0.5
Methyl-C ₅	—	—	—	0.9	1.0	0.4	0.9 ^e	0.3	0.6	1.0	1.1	0.1	0.2	0.5	1.3
C ₇	—	—	—	—	0.8	0.3	0.2	—	0.2	0.4	0.6	—	—	0.2	0.2
Aromatics															
Benzene	—	—	—	—	—	—	—	0.7	0.9	1.4	1.9	1.4	2.1	2.0	1.7
Toluene	—	—	—	2.4	2.6	1.2	—	7.6	8.0	6.4	5.5	7.4	9.1	10.0	9.3
Ethylbenzene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
+ <i>m</i> -, <i>p</i> -xylenes	—	—	—	7.1	9.4	4.1	1.6	13.0	13.3	11.4	11.8	14.0	13.4	13.3	13.1
<i>o</i> -xylene	—	—	—	1.9	1.3	0.3	—	3.0	2.7	2.0	1.7	3.6	3.0	3.0	3.0
<i>m</i> , <i>p</i> -Ethyl toluenes	—	—	—	1.0	4.6	1.0	—	3.2	2.8	2.9	5.0	2.8	1.9	1.0	3.8
1,2,4-Trimethylbenzene	—	—	—	4.5	4.0	2.6	—	4.2	5.8	2.6	3.3	4.0	4.6	3.3	2.7
Other C ₉	—	—	—	—	—	—	—	1.0	0.8	—	—	—	—	—	—

^a Catalyst: 1.0 g; He: 3.9 ml·min⁻¹. The product distribution is exclusive of water. It is calculated by multiplying the number of moles of a given hydrocarbon by the number of C atoms in its molecular formula. The total intensity is normalized to 100%.

^b Flow rate in milliliters per hour.

^c There is some ether near the C₄ hydrocarbons peak.

^d There is some C₄ hydrocarbon(s) near the ether peak.

^e Mostly methylcyclopentene.

of *n*-hexane and 3-methylpentane (0.31 ml·hr⁻¹) diluted by He (3.0 ml·min⁻¹) and 1 g of powder. This index compares relatively the cracking rates of *n*-hexane and 3-methylpentane; it is equal to 6.14 after 20 min of operation at 300°C and to 5.23 after 135 min.

Kinetic studies: Apparatus and procedure. A fixed-bed continuous-flow microreactor was used, which had been made from a 33-cm-long, 1.13-cm-diameter, Pyrex tube and which contained 1 g of catalyst. Methanol and ethanol are charged as liquids at the preheated input of the reactor using a Sage Model 355 injection pump; their vapors were then diluted with He the flow of which was kept constant and equal to 3.9 ml·min⁻¹. Injection rates for the liquids were in both cases 0.155, 0.310, 0.620, and 1.24 ml·hr⁻¹, the reactor

temperatures being 250, 300, 350, and 400°C. Analysis of the reaction products is carried out by gas chromatography following sampling after 45 min for the given operating conditions. Two separation columns are used in sequence: a precolumn consisting of 25% diglycerol on Chromosorb P (95–130°C) and a second one of Porapak P (165°C). Helium, used as the vector gas, was purified using the BASF R3-11 catalyst followed by a molecular sieve (Union Carbide, 4A).

¹³C NMR studies: *Apparatus and procedure.* A Bruker WP-60 NMR spectrometer working in the external lock mode and using a broad band decoupling at the proton frequency (in order to eliminate the ¹³C–¹H couplings and simplify the spectra) was used. All spectra were recorded at 40°C, the chemical shifts being determined using

TABLE 2
 Zeolite-Catalyzed Hydrocarbon Formation from Ethanol^a

Product	250°C				300°C				350°C				400°C			
	0.15 ^b	0.31	0.62	1.24	0.15	0.31	0.62	1.24	0.15	0.31	0.62	1.24	0.15	0.31	0.62	1.24
Ethanol	0.3	—	0.2	0.44	—	—	—	—	—	—	—	—	—	—	—	—
Diethyl ether	—	1.4	0.7	0.02	—	—	—	—	—	—	—	—	—	—	—	—
Aliphatics																
C ₂	19.9	89.0	95.8	98.8	2.6	2.5	15.0	46.0	2.6	2.2	2.3	2.2	4.7	4.0	3.5	3.3
C ₃	4.8	— ^c	— ^c	— ^c	14.0	14.5	13.3	9.2	21.8	19.8	17.6	15.7	33.5	30.6	25.5	20.6
C ₄	25.2	4.3	1.6	0.59	37.6	28.2	24.0	18.2	32.0	32.5	31.4	30.9	24.3	26.5	28.1	28.8
C ₅	20.8	1.4	0.7	0.06	18.5	14.7	16.1	13.4	8.4	10.6	11.8	12.5	4.7	5.4	7.1	9.3
C ₆	14.7	2.1	0.7	0.04	5.0	5.5	9.4	7.9	1.6	2.7	3.6	5.2	0.6	0.7	1.2	2.4
C ₇	7.8	1.1	0.2	0.03	1.9	3.0	5.4	1.7	0.5	0.4	0.9	1.8	—	—	—	0.2
C ₈	5.8	0.5	0.1	—	—	0.8	1.8	0.6	—	0.1	0.2	0.4	—	—	—	—
Cyclics																
C ₅	—	—	—	—	0.2	0.1	0.1	0.1	0.3	0.2	0.3	0.3	0.2	0.3	0.4	0.5
Methyl-C ₅	—	—	—	—	1.0	1.0	—	—	0.5	0.7	1.2	1.9	0.4	0.4	0.6	1.4
C ₇	0.6	0.2	—	—	0.2	0.5	1.1	0.3	0.2	0.2	0.3	0.6	—	—	—	0.2
Aromatics																
Benzene	—	—	—	—	—	—	—	—	2.9	2.6	2.0	1.6	5.0	4.6	3.8	3.0
Toluene	0.1	—	—	—	3.5	5.0	1.9	0.2	12.5	11.7	10.0	7.8	14.4	14.1	13.6	11.2
Ethylbenzene	—	—	—	—	1.3	2.2	1.1	0.2	2.6	2.5	2.7	2.5	1.5	1.5	1.7	1.8
<i>p</i> -Xylene	—	—	—	—	3.9	6.5	3.3	0.5	7.1	7.2	7.8	7.3	7.3	7.6	8.3	11.7
<i>o</i> -Xylene	—	—	—	—	1.1	0.8	0.6	0.1	2.0	1.7	1.8	1.2	1.9	2.2	2.4	1.8
<i>m</i> -, <i>p</i> -, Ethyl toluenes	—	—	—	—	5.9	12.1	6.6	1.6	5.0	4.5	5.7	7.3	1.5	2.1	3.0	3.2
1,2,4-Trimethylbenzene	—	—	—	—	2.5	1.6	0.3	—	—	0.4	0.4	0.8	—	—	0.8	0.6
Other C ₉	—	—	—	—	0.8	1.0	—	—	—	—	—	—	—	—	—	—

^a Catalyst: 1 g; He: 3.9 ml·min⁻¹. The product distribution is exclusive of water. It is calculated by multiplying the number of moles of a given hydrocarbon by the number of C atoms in its molecular formula. The total intensity is normalized to 100%.

^b Flow rate in milliliters per hour.

^c Not evaluated because of overlap with the C₂ aliphatics peak.

benzene as an external reference. NMR spectra are obtained directly for the adsorbed species. Typically, after activation of the H-ZSM-5 at 400°C in a vacuum of 10⁻⁶ Torr, 0.08 ml of alcohol is adsorbed on 1 g of powder in the NMR sample cell. The latter is then progressively heated (stepwise from 150 to 350°C) and spectra are recorded (solid + adsorbate: reactants, intermediates, and products) after each thermal treatment. Using ¹³C-enriched reagents and operating the spectrometer in the Fourier transform mode, the typical accumulation times for significant spectra were in the range from 5 to 60 min.

III. RESULTS

Product Analyses Using Gas Chromatography

Table 1 gives details of the methanol conversion products as observed under various

space velocity (LHSV) and temperature conditions, and Table 2 presents the corresponding data for the conversion of ethanol. Data for methanol and ethanol are compared in Table 3 for similar operating conditions (1 g of catalyst, 1.24 ml·hr⁻¹ of liquid alcohol, 3.9 ml·min⁻¹ of He).

For methanol, the reaction clearly proceeds by successive steps. At a temperature below 300°C, methanol is converted mostly to dimethyl ether. At temperatures above 350°C, conversion of methanol reaches 100% with a ratio of paraffins to aromatics in the range 1.5 to 2.3, depending on space velocity and temperature. Increasing the temperature from 300 to 400°C leads to a decrease in the C₅⁺ nonaromatics and olefins as shown in Fig. 1A.

The effect of LHSV is less important and opposite to that of temperature. In Table

TABLE 3
Comparative Effects of Temperature on Methanol and Ethanol Conversion to Hydrocarbons^a

Product	Distribution ^b							
	250°C		300°C		350°C		400°C	
	Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol
Methanol	14.5	—	17.6	—	—	—	—	—
Ethanol	—	0.44	—	—	—	—	—	—
Dimethyl ether	74.4	—	49.3 ^c	—	—	—	—	—
Diethyl ether	—	0.02	—	—	—	—	—	—
C ₂ Aliphatics	4.0	98.82	10.3	46.0	3.4	2.2	3.8	3.3
C ₃ + C ₄ Aliphatics	5.9	0.59	11.4 ^c	27.4	40.7	46.6	46.0	49.4
C ₅ –C ₈ Linear aliphatics ^d	1.2	0.13	8.7	23.6	24.6	19.9	14.6	11.9
C ₅ –C ₇ Cyclic aliphatics	—	—	1.1	0.4	2.1	2.8	2.0	2.1
C ₆ –C ₁₀ Aromatics	—	—	1.6	2.6	29.2	28.5	33.6	33.3

^a Catalyst: 1 g; liquid alcohol: 1.24 ml·hr⁻¹; He: 3.9 ml·min⁻¹.

^b Product distribution calculated by multiplying the number of moles by the number of C atoms in the molecular formula; total value normalized to 100%.

^c Approximate values due to overlap of the dimethyl ether and C₄ peaks.

^d Includes branched noncyclic aliphatics.

4, our data for the conversion of methanol are compared to those of Chang and Silvestri (1), showing the good agreement obtained when the reaction is conducted under closely identical conditions.

From the data in Table 2, it is seen that, when ethanol is converted below 300°C, the major product is ethylene. In the

temperature range 300–350°C, aliphatics are formed with a higher proportion of C₄ compounds than for methanol (for which mostly C₃ compounds were observed). Above 350°C, aromatics appear, the proportion of ethylbenzene and ethyltoluene increasing with temperature (compare with *o*-xylene and trimethylbenzene in the case of methanol).

The differences, at low conversion temperature, and the analogies, at high conversion temperature, in the product distributions observed from methanol and ethanol (see Table 3) suggest a common reaction pathway possibly involving ethylene as an intermediate, as a proportion of the latter remains small in the conversion of methanol and sharply decreases at 350°C in the conversion of ethanol.

Static in Situ Data from ¹³C NMR

For both methanol and ethanol ¹³C NMR data were obtained directly from the hydrocarbons adsorbed on the catalyst. Therefore, the NMR data give: (i) a realistic and faithful picture of the process that occurs on the catalyst surface, excluding side reactions which could have happened during the chromatographic detection; (ii)

TABLE 4
Zeolite-Catalyzed Hydrocarbon Formation
from Methanol

	Chang and Silvestri (1) ^a	This work ^a
Reaction conditions		
Temperature (°C)	371	350
LHSV (hr ⁻¹)	1	2.48
Conversion (%)	100	100
Hydrocarbon distribution (%)		
Methane	0.9	—
Ethane + ethylene	1.1	3.4
Propane + propylene	16.4	16.4
Butanes + butenes	24.7	24.3
Pentanes + pentenes	9.3	14.2
C ₆ ⁺ Aliphatics	4.2	12.5
Benzene	1.8	1.9
Toluene	11.2	5.5
C ₃ Aromatics	18.9	13.5
C ₆ Aromatics	7.9	5.0
C ₁₀ Aromatics	3.4	3.3
C ₁₁ ⁺ Aromatics	0.2	—

^a The product distribution is calculated by multiplying the number of moles of a given hydrocarbon by the number of C atoms in the molecule. The total value is normalized to 100%. Data of Ref. (1) have been recalculated accordingly.

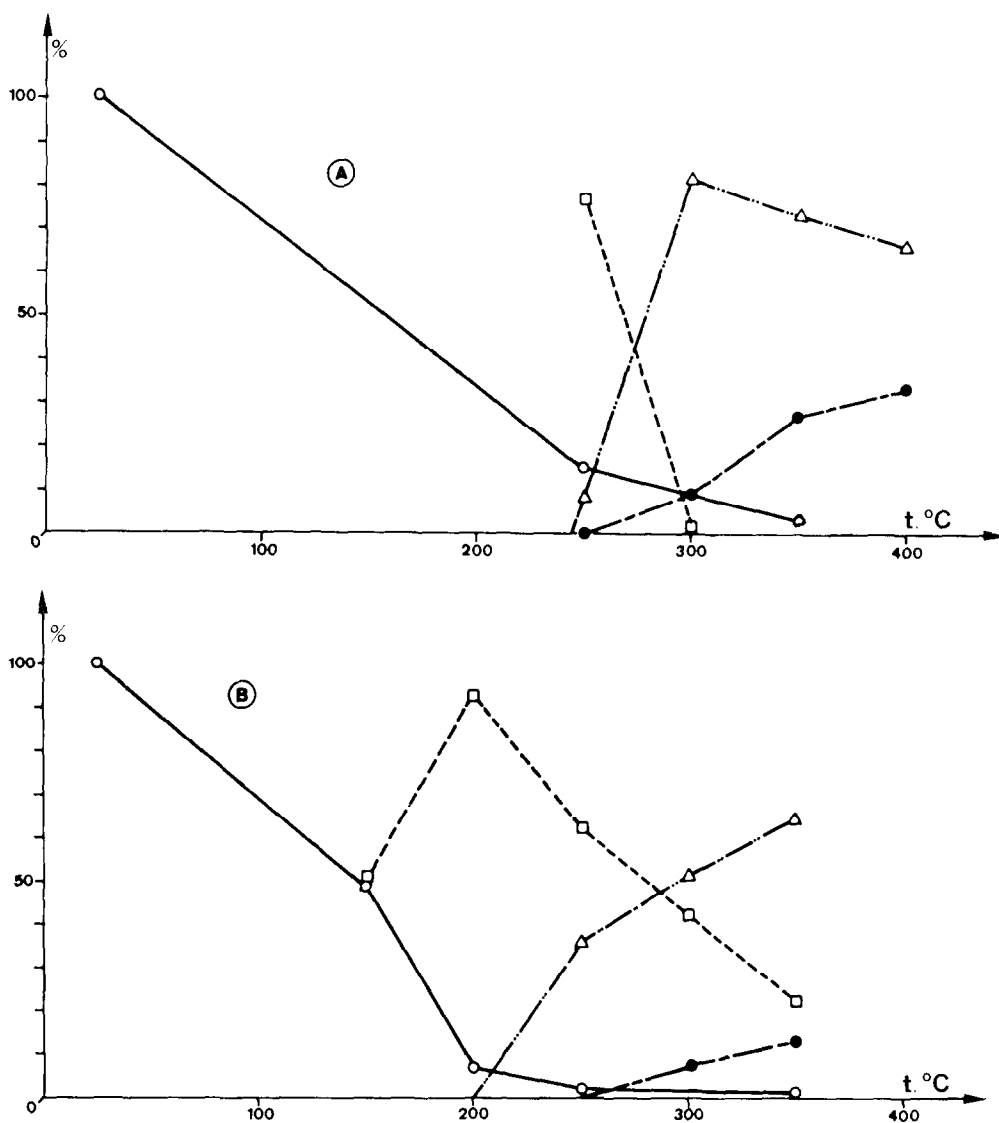


FIG. 1. Zeolite-catalyzed methanol conversion. Yield structure vs temperature, exclusive of water. (A) Gas chromatography results (0.62 ml of methanol·hr⁻¹, 1 atm) (B) ¹³C NMR results (static conditions, 0.08 ml of methanol/g of catalyst). (○) Methanol; (□) dimethyl ether (and other higher ethers, when observed); (△) aliphatics; (●) aromatics.

a quantitative analysis of the reaction intermediates and products which are directly present on the surface (neglecting nuclear relaxation effects on the intensities of the NMR peaks, a reasonable assumption for adsorbed species with rather short ¹³C relaxation times and which will be confirmed by the good agreement between

the NMR and gas chromatography data); note, however, that NMR will identify the functional groups and not the molecules themselves therefore giving all its importance to the comparison between NMR and chromatography data, (iii) information which should preferably be compared with gas chromatography data observed at low

LHSV (or slightly higher temperature) as they are obtained under static conditions.

The presentation, interpretation, and discussion of the NMR data require knowledge of the characteristic chemical shifts. The values of interest to the present work are given in Table 5 as obtained in solution for different types of ^{13}C nuclei. Deviations from these values can be ex-

pected in the adsorbed state although they should be small if there is no considerable charge transfer between the adsorbed species and the adsorption site(s).

Typical spectra for the conversion of methanol are shown in Fig. 2, corresponding to various treatment temperatures and durations. Detailed results are presented in Tables 6 and 7 which show the effect of

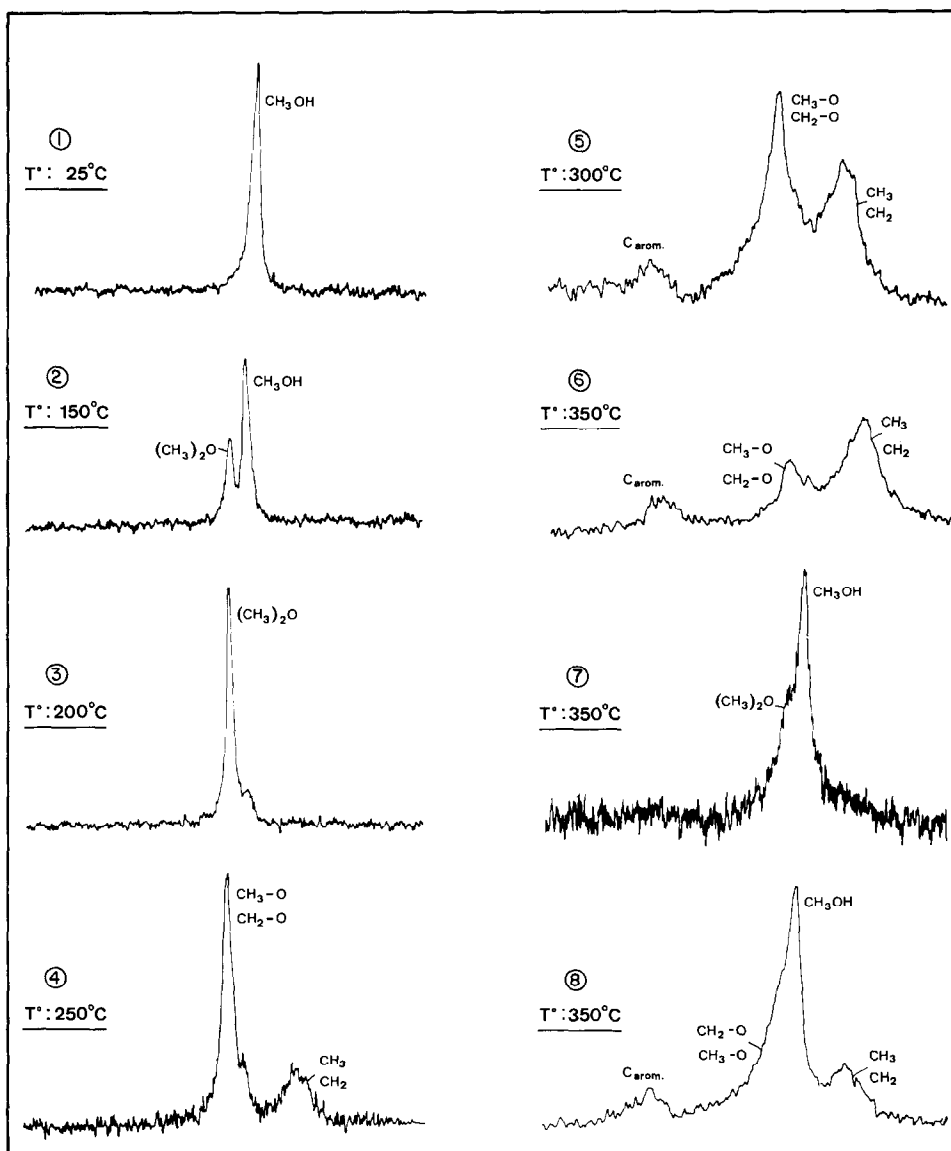


FIG. 2. Typical ^{13}C NMR spectra as observed during the static conversion of methanol. Temperatures are as indicated (see Table 6 for details of treatments and product identification).

TABLE 5
 ^{13}C NMR Chemical Shifts of Different Types
 of Carbon Nuclei

Compound and ^{13}C nucleus (as indicated)	δ (ppm from TMS) ^a
CH_3OH	49.5
$\text{CH}_2\text{-CH}_2\text{OH}$	17.6
$\text{CH}_2\text{-CH}_2\text{OH}$	57.0
$\text{CH}_2\text{-O-CH}_3$	59.4
$\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	17.1
$\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	67.4
$-\text{O-CH}_3 + -\text{O-CH}_2-$	60.7
$\text{CH}_2=\text{CH}_2$	122.1
$-\text{CH}_2- + -\text{CH}_3$ (aliphatics)	14.3
$-\text{CH}_2- + -\text{CH}_3$ (linked to aromatic cycles)	17.3
C from olefins and aromatics	≈ 130
$\text{CH}_2=\text{CH-O-CH}_2\text{-CH}_3$	152.9
$\text{CH}_2=\text{CH-O-CH}_2\text{-CH}_3$	84.6

^a See Ref. (8).

temperature and of reaction time, respectively. Figure 1B plots the distribution of products as a function of temperature as obtained from the intensities of the NMR peaks. It clearly parallels the gas chromatography results.

It is immediately seen that the reaction is very selective below 250°C: Methanol

is almost exclusively converted to dimethyl ether. The spectrum observed at 250°C shows no characteristic NMR resonance for ethylene. However, the peak near 60 ppm is strongly broadened, indicating the progressive formation of a variety of aliphatic ethers (see Table 5 for chemical shifts). When the temperature reaches 300°C, the "ether" characteristic resonance near 60 ppm decreases in intensity while $-\text{CH}_2-$ and $-\text{CH}_3$ resonances appear [indicating the formation of aliphatic compounds or (linked) chains] in the range from 10 to 20 ppm. The latter are shifting to lower field (i.e., increasing δ values) with increasing temperature indicating that a higher proportion of these chains are branched on aromatic nuclei. Interesting information also arises from the comparison of the "aliphatic" to "aromatic" carbon ratio (as obtained from NMR, which means that aliphatic chains branched on aromatics are counted as aliphatics). The final conversion of the initial methanol, as adsorbed at low temperature, leads to an "aliphatic/aro-

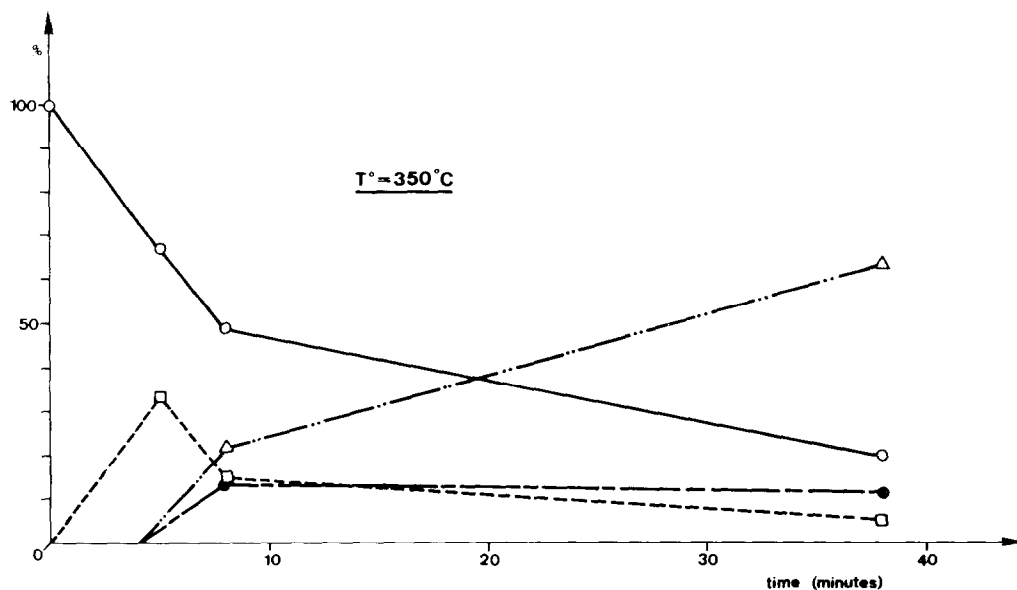


FIG. 3. Zeolite-catalyzed methanol conversion. Yield structure vs time of static conversion at 350°C (exclusive of water, from ^{13}C NMR data). (\circ) Methanol; (\square) ^{13}C nuclei from $\text{CH}_3\text{-O}$ and $-\text{CH}_2\text{-O}$ groups; (\triangle) ^{13}C nuclei from aliphatics and aliphatic chains branched on olefins and aromatics; (\bullet) ^{13}C nuclei from aromatics (and olefins).

TABLE 6
¹³C NMR Data for the Conversion of Methanol on H-ZSM-5 Synthetic Zeolite

Pretreatment ^a		Chemical shift (ppm from TMS)	Linewidth ^b (Hz)	Type of resonance ^c	Intensity ^d (%)	Remarks
Tempera- ture (°C)	Time (min)					
25	60	49.5	70	A	100	—
150	30	49.5	65	A	64.5	—
		56.2	65	B	35.5	
150	100	49.4	—	A	33.2	—
		58.7	50	B	66.8	
150	100	49.6	—	A	7.0	—
200	30	59.1	50	B	93.0	
150	100	49.7	—	A	2.0	—
200	30	58.8	110	B'	62.0	
250	30	19.6	250	C	36.0	
150	100	59.9	220	B'	42.0	Traces of methanol present
200	30	14.8 + 22.1	230	C'	51.0	
250	30	135.3	—	D	7.0	
300	30					
150	100	49.9	—	A	1.0	—
200	30	60.2	190	B'	22.0	
250	30	16.6	340	C'	64.0	
300	30	132.2	250	D	13.0	
350	6					

^a Consecutive treatments of the same sample.

^{b,c,d} All spectra recorded using 200 (25°C spectrum) to 5000 (350°C spectrum) scans accumulated before the Fourier transformation. The maximum instrumental line broadening is 15 Hz.

^b Linewidths measured at half-height.

^c As identified by comparison with reference data as quoted in Table 5. (A) Methanol, (B) dimethyl ether, (B') CH₂-O and CH₂-O from aliphatic ethers, (C) aliphatic methyl and methylene groups, (C') methyl and methylene groups from aliphatics, and/or linked to olefins and aromatics, (D) olefinic and aromatic carbons.

^d Relative intensities: total ¹³C NMR spectrum intensity normalized to 100%. These values are only indicative of the evolution of the spectra with temperature.

matic" ratio of about 5 (see spectrum 6 of Fig. 2). Adsorption of a fresh monolayer of methanol and *direct* conversion at 350°C lead to a ratio of about 2 (see Table 7 and spectrum 8 of Fig. 2) in good agreement with the chromatography data. Hence, the methanol-aliphatics-aromatics conversion should not be considered as sequential but much more as a competition between the

conversion of methanol to aliphatics and aromatics. That will obviously be one of the major points in our discussion of the present results. Note also that a small characteristic methanol peak is always present near 49 ppm (from TMS). Finally, the product yield structure as a function of time at 350°C (see Table 7 and Fig. 3) clearly shows that the methanol conversion

TABLE 7
Product Distribution from Static Methanol Conversion at 350°C: ¹³C NMR Results

Reaction time (min)	Chemical shift (ppm from TMS)	Linewidth ^a (Hz)	Identification ^b	Intensity ^c
0	49.8	170	A	100
5	50.6	140	A	66.5
	59.5	—	B'	33.5
8	50.7	190	A	49.0
	58.5	—	B'	15.0
	20.2	350	C'	22.0
	134.6	310	D	14.0
38	50.3	—	A	20.0
	60	—	B'	5.6
	17.6 + 23.0	—	C'	63.0
	136.8	—	D	11.4

^a Linewidths measured at half-height.

^b By reference to the data from Table 5. See Table 6 for group and compound identifications.

^c Total spectral intensity normalized to 100%.

occurs in two major steps, i.e., the conversion to ethers and the formation of higher hydrocarbons (aliphatics and aromatics).

NMR results for the conversion of ethanol are presented in Figs. 4 and 5 and Table 8. The spectra are more complex as a result of the presence of two ¹³C resonances in the starting material and because of the ¹³C-¹³C spin-spin couplings (broader lines). The initial CH₃ resonance also obscures to some extent the expected transformations that should be observed in the aliphatic region of the spectrum. The data will therefore be presented in some more detail; characteristic chemical shifts are indicated in parentheses in the following (see also Table 8). The typical spectrum of adsorbed ethanol (16.7 and 56.1) is observed at 25°C. Heating at 150°C leads to a broadening of the CH₃ resonance (from 150 to 400 Hz) and to a broadening and shift of the CH₂-O resonance: This corresponds to the formation of diethyl ether of which the characteristic shifts are 17.1 and 67.4 ppm. The diethyl ether spectrum overlaps that of ethanol (see

spectrum 2 of Fig. 5). Further heating at 150°C leads to a resonance near 90 ppm and a very weak and broad peak at about 150 ppm, possibly characteristic of vinyl ethyl ether. Some olefins should also be present as indicated by the resonance at 111 ppm. The first abrupt transformation occurs between 150 and 250°C, as seen from spectra 3 and 4 in Fig. 5. Typical resonances from the alcohol and the ether are progressively disappearing while an olefinic peak becomes clearly distinguishable (relative intensity up to 32%) and shifts toward lower fields (120 ppm): It corresponds to ethylene formation.

The second main process occurs above 250°C (spectra 5 to 8 in Fig. 5). The olefinic peak broadens and progressively disappears (traces of it are still observable at 350°C) while CH₂- and CH₃- resonances are observed as a broad line between 10 and 40 ppm. The maximum of the latter is located between 14 and 23 ppm indicating that these groups are mostly in aliphatic chains. No distinct aromatic peak is observed (expected at 130 ppm) although a

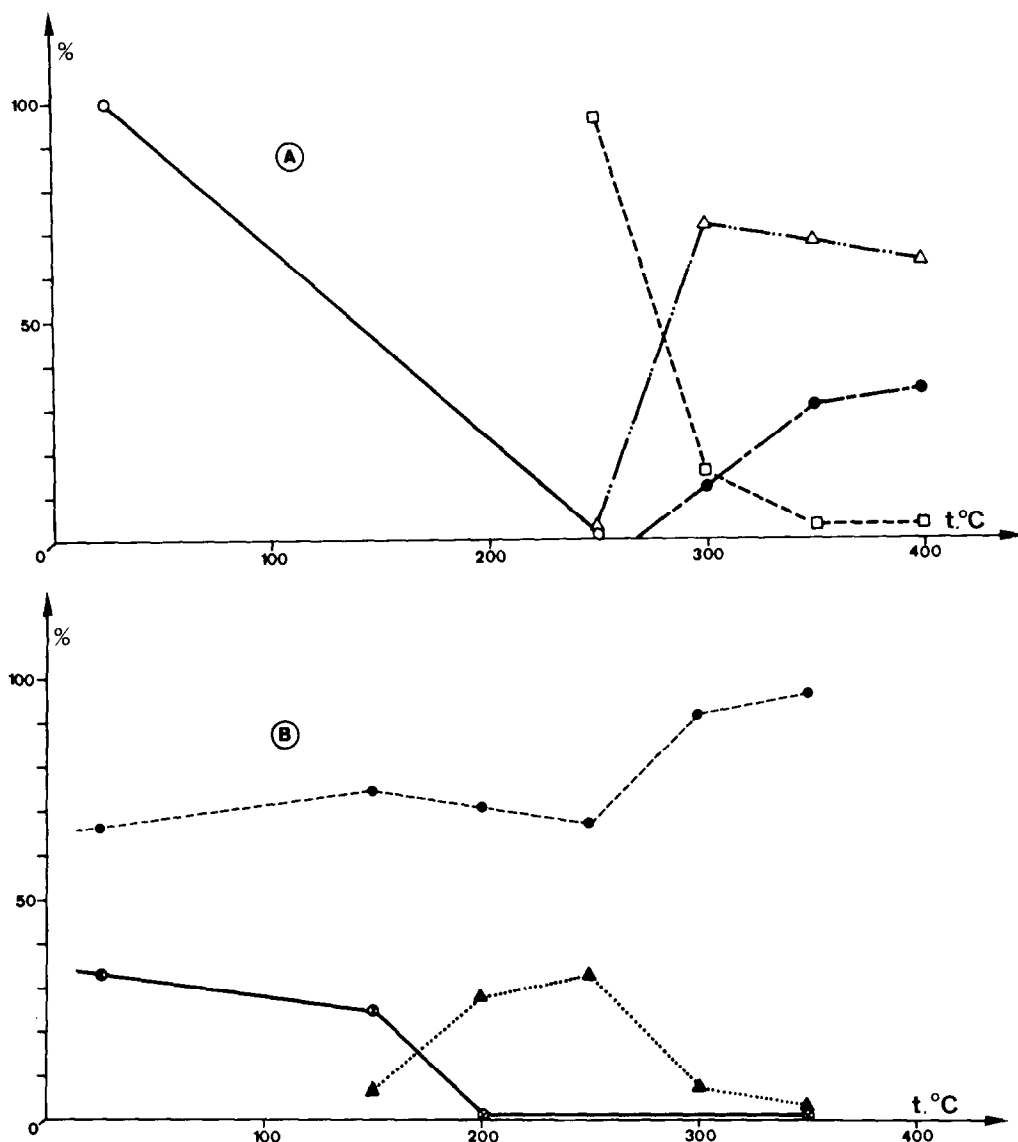


FIG. 4. Zeolite-catalyzed ethanol conversion. Yield structure vs temperature, exclusive of water. (A) Gas chromatography results (0.62 ml of ethanol·hr⁻¹, 1 atm); (B) ¹³C NMR results (static conditions, 0.08 ml of ethanol/g of catalyst). A: (○) Ethanol and diethyl ether; (□) C₂ aliphatics (mostly ethylene); (Δ) higher aliphatics; (●) aromatics. B: (●) ¹³C nuclei from aliphatics (including CH₃-CH₂OH); (⊗) ¹³C nuclei from CH₃-O and -CH₂-O groups; (▲) ¹³C nuclei from olefins.

very broad line could very well be present in this part of the spectrum. Hence, it is again observed that heating at progressively higher temperatures leads preferentially to aliphatics, in agreement with the results obtained for the conversion of

methanol under static conditions. Figure 4 compares the product yield structure from the conversion of ethanol as it is obtained from gas chromatography and ¹³C NMR analyses. Although the agreement is not as surprisingly good as in the case of

TABLE 8
¹³C NMR Data for the Conversion of Ethanol on H-ZSM-5 Zeolite

Thermal treatment ^a		Chemical shift (ppm from TMS)	Linewidth ^b (Hz)	Identification ^c	Intensity ^d (%)
Temperature (°C)	Time (min)				
25	—	16.7	150	A	66.6
		56.1	235	B	33.4
150	20	(14.8) + 18.5	216	A'	63.7
		66.0	413	B'	36.3
150	50	15.5	385	A'	75.0
		67.7	329	B'	25.0
150	110	12.9 + 14.8	319	A'	73.8
		75.4	—	B'	14.5
		92.8	—	C	7.3
		111.6	—	D	4.4
		150.0	Broad	—	—
150	110	12.9	347	A'	81.1
200	10	71.4	Broad	B'	—
		90.0	Broad	C	—
		110.7	169	D	18.9
150	110	10.6 — 33.5	460	A'	71.6
		77.8	—	B'	—
200	40	119.5	146	D	28.4
150	110	20.3 — 39.9	560	A'	67.7
		68.2	—	B'	—
250	15	112.9 — 116.4	403	D	32.3
150	110	20.7	459	A'	92.6
		54.4	—	B'	—
250	75	118.9	—	D	7.4
300	40				

methanol, the main features exist and are reinforced. Ethylene also appears to be a very reactive intermediate and ethers disappear as aliphatics (and aromatics at a higher temperature) are formed.

IV. DISCUSSION

A recent paper by us (7) presents some of the ideas which will be developed in the discussion of the foregoing results. Our aim is to propose an explanation for some

observations which are not fully discussed and accounted for in the paper by Chang and Silvestri (1), i.e., the eventual detection of small amounts of methyl ethyl ether in the reaction products, the high ratio of iso- to normal paraffins, and also the increasing amount of olefins in the reaction products at low conversion (increasing LHSV). We also have to account for new experimental facts brought forward by the present study, namely: (i) the similarity in the reaction product distribution as obtained from the

TABLE 8—*Continued*

Thermal treatment ^a		Chemical shift (ppm from TMS)	Linewidth ^b (Hz)	Identification ^c	Intensity ^d (%)
Temperature (°C)	Time (min)				
150	110	23.1	414	A'	93.6
200	40	61.6	—	B'	—
250	75	119.5	—	D	6.4
300	40				
350	20				
150	110	14.5 + 20.5	369	A'	97.3
200	40	58.9	—	B'	1.3
250	75	133.2	—	D	1.4
300	40				
350	80				
150	110	14.1 + 21.0	336	A'	100
200	40	59.8	—	B'	—
250	75	133.2	Broad	D	Not estimated
300	40				
350	140				

^a Successive treatments on the same sample.

^b Linewidths measured at half-height.

^c With reference to the characteristic chemical shifts listed in Table 5. (A) $\text{CH}_3\text{-CH}_2\text{OH}$, (B) $\text{CH}_3\text{-CH}_2\text{OH}$, (A') aliphatic methyl and methylene groups, (B') $\text{-CH}_2\text{-O-}$ groups, (C) most probably vinyl ethyl ether, (D) olefinic (and aromatic) carbons.

^d Intensities are only quoted in order to give an idea of the spectral changes. The total intensity of the ^{13}C NMR spectrum is normalized to 100%.

high-temperature (350–400°C) conversion of methanol and ethanol; (ii) the role played by the ethers in the alcohol(s) to hydrocarbons conversion; (iii) the high reactivity of ethylene (observed in the methanol conversion at high LHSV (1) and in the ethanol conversion) which seems to be an intermediate; and (iv) the distinct formation of aliphatics and aromatics depending on the conversion conditions (static, as in NMR, or dynamic) which seems to indicate that the conversion pathway is not simply the result of sequential reactions. It will be seen that the main problem which is left is the mechanism by which ethers are converted to the corresponding olefins by intramolecular dehydration. The major part of the discussion will deal with methanol, and reference

to the ethanol conversion will be made when needed.

The various mechanisms which have been proposed up to the present have been reviewed and discussed in the paper by Chang and Silvestri (1) and, hence, we do not feel that there is a need for a further discussion of the existing literature on the subject.

The protonated H-ZSM-5 zeolite is certainly acidic. On the other hand, zeolites with their cages and channels appear as solid crystalline structures in which high electrostatic fields and gradients are prevailing and therefore they act as strong polarizing agents. Both characteristics will favor and stabilize the formation of carbenium ions. Adding to these the gas chromatography results and the original

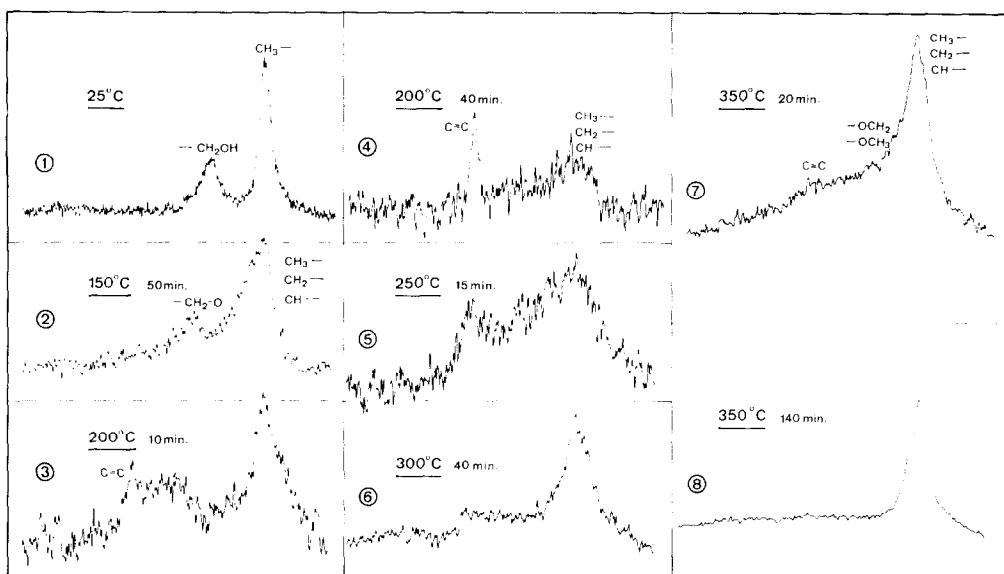
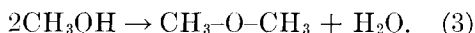


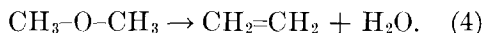
FIG. 5. Typical ^{13}C NMR spectra as observed during the static conversion of ethanol. Temperatures are as indicated (see Table 8 for details of treatments and product identification).

^{13}C NMR data (which give additional information on the adsorbed species which are present *in situ*), a realistic mechanism can be proposed for the conversion of methanol to hydrocarbons.

At low temperature (150–200°C), dehydration of the alcohol occurs and the latter results essentially in dimethyl ether, possibly by a mechanism which has been previously proposed (6, 9, 10):



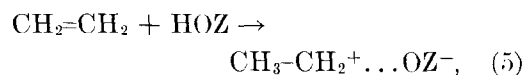
At higher temperature (200–300°C), dimethyl ether may dehydrate to yield ethylene:



This process can be either intermolecular or intramolecular. We would favor the latter possibility on simple grounds: It could eventually be confirmed by studying the dehydration of $^{13}\text{CH}_3\text{-O-}^{12}\text{CH}_3$ using isotope sensitive techniques such as mass spectrometry or ^{13}C NMR.

Ethylene, however, is not observed by

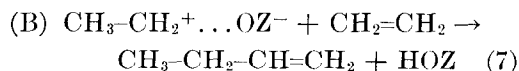
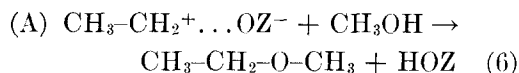
^{13}C NMR and is only present in very small amounts in the effluents analyzed by chromatography for high LHSV (1). One concludes that it is very reactive and that carbenium ions are readily formed by reaction with the Brønsted acid sites of the zeolite:



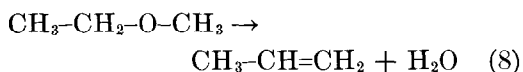
where Z stands for the zeolitic framework.

The carbenium ion can react in two major ways: one is to form *higher ethers* (process A) by reaction with methanol, the second, to yield *linear olefins* by addition on another ethylene (or olefin) molecule according to process B.

Process A seems more probable because of the difference in basicity between the alcohol and the olefin.



Reaction 6 accounts for the formation of ethyl methyl ether which was sometimes observed (1). The latter, in turn, could also be dehydrated by a mechanism similar to that of reaction (4),

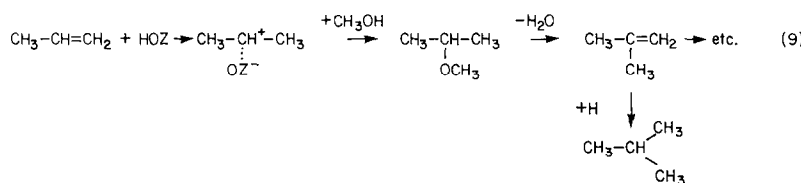


leading to propylene.

According to the former sequence of reactions, the conversion products from methanol at high LHSV (low conversion)

should be mainly propylene, butene, and ethylene, which is essentially the case as seen from the data collected in Table 4 of Chang and Silvestri's paper.

Propylene can be hydrogenated to propane [by hydrogen transfer from other and higher olefins (11)], but it can also react by processes A and B as did ethylene. Secondary carbenium ions being more stable than primary one, process A will mostly form branched molecules (isoparaffins).



This accounts for the large amount of branched compounds as compared to normal paraffins (and thereby the high RON) shown by our data and those previously reported [Table 1 of Ref. (1)], as well as for the progressive broadening of the ¹³C NMR resonance attributed to oxygen-containing compounds (CH₃-O and -CH₂-O groups). The polymerization process (B; addition of the carbenium ion to an olefin) will essentially yield linear olefins which can cyclize and lead to aromatics by hydrogen transfer reactions to other olefins, the latter then being converted to saturated aliphatics (11). This may be the reason why aliphatics and aromatics are formed simultaneously, as observed by ¹³C NMR and gas chromatography, at temperatures in the range 300–400°C. The need for fresh methanol in the formation of aromatics, as observed from the NMR data, lower olefins being formed in the early stages of the methanol conversion, suggests that hydrogen may be preferentially transferred to lower olefins.

We propose therefore that the methanol conversion on the H-ZSM-5 zeolite propa-

gates by successive dehydration–methanolation steps, competing with polymerization–cyclization–aromatization processes. The existence of the dehydration–methanolation mechanism is inferred from the constant observation of a small amount of CH₃OH (by ¹³C NMR *in situ*) on the catalyst. This is not surprising as, at such high temperature in the presence of steam (from the dehydration of methanol), hydrolysis of the ethers can occur. That is in agreement with the closeness of the distribution of hydrocarbons observed when using dimethyl ether as feed (1).

Both NMR and chromatography data for the conversion of ethanol can be interpreted on the basis of the same mechanism. The main difference, however, is the fact that ethylene is one of the major products from ethanol as formed via ether formation and subsequent dehydration or by direct dehydration of ethanol (12). Our proposal that ethylene is an important intermediate in the conversion of methanol to hydrocarbons accounts well for the similarity in the product yields from ethanol and methanol, as observed at high temperature

(see Table 3). This feature adds to the shape-selective character of the zeolite as mentioned by Chang and Silvestri (1).

V. CONCLUSIONS

The combination of ^{13}C NMR and gas chromatography data has enabled us to propose an original mechanism for the conversion of methanol and ethanol to higher hydrocarbons on a new type of shape-selective zeolite. This mechanism can be adapted to account for the conversion of other oxygen-containing compounds.

The proposed carbenium ion formation, by protonation of olefins, and the reaction of the former with either alcohol molecules or olefins seem more probable than the mechanism by carbenes of Chang and Silvestri (1). Indeed, carbenium ions are very strongly stabilized on an acidic and highly polarizing surface such as that of zeolites. The relative stability of tertiary, secondary, and primary carbenium ions accounts very easily for the high yield in branched hydrocarbons, which is not the case for carbenes. It also explains the presence of methyl ethyl ether [detected in the products (1)] and the formation of higher ethers as observed *in situ* by ^{13}C NMR. Finally, our mechanism also explains in a simple manner the analogies in the product yields from ethanol and methanol and their dependence on space velocity.

One question which still remains is the mechanism by which ethers would be dehydrated to the mono-olefin containing the same number of C atoms, possibly by an intramolecular process, although a bimolecular reaction of the type described by Chang and Silvestri (1) between methanol and a methyl ether would also be acceptable.

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