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# Conversion of Methanol to Ethylene over ZSM-5 Zeolite: A Reexamination of the Oxonium–Ylide Hypothesis, Using $^{13}$Carbon- and Deuterium-Labeled Feeds[1]

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$^{13}$Carbon- and deuterium-labeled feeds have been used to examine the conversion of aqueous methanol to hydrocarbons over ZSM-5 zeolite in the presence of various ($C_3$ and $C_4$) alcohols. Particular attention has been paid to the carbon-labeled ethylene product and deuterium-labeled dimethyl ether. The isotopic composition of the ethylene requires that only part of the ethylene is formed *directly* from methanol or dimethyl ether. The rest of the ethylene is formed *indirectly* and incorporates the carbon of the other alcohol as well as the carbon of the methanol. The best explanation for the *directly* formed ethylene, and for hydrogen-isotope exchange in dimethyl ether, still appears to be the oxonium–ylide mechanism.

## INTRODUCTION

ZSM-5 zeolite is an excellent catalyst for the conversion of methanol to hydrocarbons and water (*1*, *2*), but the mechanism of conversion is still not understood. It is generally accepted that conversion involves

(i) rapid, reversible formation of dimethyl ether,[2]

$$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O, \quad (1)$$

(ii) conversion of the components of equilibrium (1) to olefins, and

(iii) hydrogen transfer and cyclization reactions whereby the olefins give (iso) alkanes and alkylbenzenes.

A particularly notable feature of the conversion is its autocatalytic character (*4–6*). There seems to be no doubt that the olefinic products of conversion are active in the autocatalysis (*4–6*), and their role can be understood in terms of the homologation/cracking mechanism for methanol conversion (*5*, *7*, *8*).

This paper is concerned with the conversion of aqueous methanol in the presence of added higher alcohols, which provide a convenient source of small amounts of the corresponding olefins. Particular attention is paid to the formation of ethylene (and $C_3$ hydrocarbons) and to the autocatalytic nature of conversion.

Evidence is presented on

(i) the acceleration by added alcohols of (a) conversion and (b) incorporation of deuterium (of $D_2O$) into residual dimethyl ether,

(ii) the isotopic label of products from $^{13}$C-methanol in the presence of added alcohols, and

(iii) possible exchange of isotopic hydrogen between deuterated dimethyl ether and (unlabeled) added alcohol.

Mechanistic conclusions are drawn and the validity and role of the oxonium–ylide mechanism (*9*, *10*)[3] are reassessed. The

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[1] Dedicated to William von Eggers Doering on his 65th birthday.

[2] This would cause carbon label to be scrambled between doubly labeled and unlabeled dimethyl ether, so that such a mixture would necessarily give hydrocarbon products of scrambled label (as found by Perot *et al.* (*3*)).

[3] Professor G. A. Olah has drawn my attention to his own postulate of an oxonium–ylide mechanism (*11*).

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work complements and extends that recently reported by Dessau and La Pierre (*12*).

In the following paper incorporation of the carbon of benzene and alkylbenzenes into ethylene is examined, and the role of aromatics in methanol conversion is defined.

## EXPERIMENTAL

(*a*) *ZSM-5 zeolite.* ZSM-5 zeolite was prepared from commercial sodium silicate solution (56 g), water (194 g), sodium hydroxide (1.0 g), sulphuric acid (4.9 g), and tetra-*n*-propylammonium bromide (7.0 g), and was crystallized for 2 days at 175°C. The aluminate impurity in the silicate served as the aluminum source. The zeolite was filtered, washed with water, calcined at 500°C in air, refluxed gently with 0.3 molar hydrochloric acid overnight, then refiltered and washed. The final product contained 0.71% aluminium and 0.02% sodium, was completely crystalline ZSM-5 zeolite by X-ray powder pattern, and consisted of clustered noneuhedral crystals of 1- 5-$\mu$ size. This material will be referred to as ZSM-5/1.

Other experiments utilized a second ZSM-5 sample, previously described (*10*) and now referred to as ZSM-5/2. This contained 1.28 wt% aluminium and 0.04 wt% sodium, and consisted mainly of euhedral crystals of 2- 8-$\mu$ size.

(*b*) *Apparatus.* The microreactor and analytical system were as previously described (*10*). The zeolite sample (0.15 or 0.20 g) of mesh size 60–100 or 80–100 was packed between quartz-wool plugs in a 6-mm-o.d. quartz reactor tube. In use the catalyst bed was continuously purged by a stream of vector gas (nitrogen or argon), and the temperature was measured at the exit end of the bed. Aqueous alcohol (or other) liquid feed was delivered from a motorized glass syringe via a long syringe needle inserted directly into the vector-gas purged reactor tube. At the conclusion of the experiment, the zeolite was normally regenerated *in situ* in a stream of oxygen at 500°C overnight and then reused.

Products were analyzed using an on-line Varian 3700 gas chromatograph as previously described (*10*). Mass spectra were measured on materials separated by the gas chromatograph, using an on-line UTI quadrupole mass spectrometer, again as previously described (*10*). Observed mass spectra were compared with those observed for nonlabeled materials. Isotopic analyses of dimethyl ether, ethylene, and propylene were based on the spectra in the parent ion region (i.e., $m/e$ = 28,27,26 for $C_2H_4$ and $m/e$ = 32–26 for deuterated ethylene; $m/e$ = 46,45 for dimethyl ether and $m/e$ = 52–45 for deuterated dimethyl ether; etc.). Random selection of deuterium/hydrogen in fragmentation of the parent ions was, of course, assumed in the analyses.

## RESULTS

(*a*) *Products of aqueous methanol conversion.* Fresh samples of ZSM-5/1 and ZSM-5/2 were each fed with water/methanol (2.75/1 w/w) at various temperatures close to the minimum required for complete conversion: 320–330°C for ZSM-5/1,[4] and about 300°C for ZSM-5/2. ZSM-5/1 differs from ZSM-5/2 in mode of preparation, morphology, and aluminium content; the higher aluminium content of ZSM-5/2 may be responsible for its higher activity.

Table 1 summarizes the products obtained over fresh ZSM-5/1 and ZSM-5/2. The ethylene yield is a maximum (ca. 25C%) at or just below the temperature of complete conversion and falls steadily to ca. 10C% over a 30° temperature rise. Methane and ethane are formed in negligible amounts. The $C_3$ hydrocarbons, formed in ca. 20C% yield over the temperature

[4] ZSM-5/1 which had been used with aqueous methanol at ca. 320°C for some 30 days (with overnight regeneration at 500°C in oxygen) was significantly less active than fresh ZSM-5/1. The aged sample required 347°C for complete conversion and then gave products similar to those obtained over fresh ZSM-5/1 at 330°C.

TABLE 1

Yields of Products from Aqueous Methanol over ZSM-5 Zeolite[a]

| | | ZSM-5/1[b] | | | ZSM-5/2[b] | |
|---|---|---|---|---|---|---|
| Temperature (°C) | 311 | 320 | 330 | 341 | 300 | 330 |
| Conversion (C%) | ca. 10 | >95 | 100 | 100 | 100 | 100 |
| $C_2H_4$ | ca. 5 | 30 | 22 | 15 | 18 | 11 |
| $C_3H_6 + C_3H_8$[c] | ca. 5 | 22 | 17 | 19 | 13 | 17 |
| $C_4$ Hydrocarbons[d] | — | 18 | 22 | 27 | 22 | 26 |
| $C_5$–$C_7$ hydrocarbons[e] | — | 15 | 17 | 18 | 27 | 17 |
| Toluene | — | 1 | 2 | 3 | 2 | 4 |
| $C_8$ aromatics[f] | — | 12 | 15 | 15 | 10 | 16 |
| Ethyltoluene | — | 1 | 2 | 2 | 3 | 4 |
| 1,2,4-Trimethylbenzene[g] | — | 1 | 1 | 1 | 2 | 3 |

[a] Water–methanol (2.75/1 w/w) was fed to the catalyst (0.20 g) at a rate of 0.88 g/hr in nitrogen vector gas (270 ml/hr). All yields (or conversions) refer to the percentage of the carbon content of the methanol converted to particular hydrocarbons (or hydrocarbons generally).

[b] Fresh zeolite samples were used. ZSM-5/1, 0.71% Al; ZSM-5/2, 1.28% Al.

[c] Mainly propylene below 100% conversion. The propane/propylene ratio increases over the temperature range, to ⅓ for ZSM-5/1 and to ca. ⅔ for ZSM-5/2.

[d] Mainly isobutane and various butenes.

[e] Excluding aromatic hydrocarbons.

[f] Xylene isomers and a little ethylbenzene.

[g] Yields may be unreliable (due to lower volatility).

range studied, consist mainly of propylene at or below the temperature of complete conversion, but the propane content rises sharply with temperature. The $C_4$ hydrocarbons and $C_{5-7}$ nonaromatic hydrocarbons are complex mixtures. $C_8$ aromatics comprise 10–15C% of the product; *p*-xylene is the major component (>50% of $C_8$ aromatics) at low temperatures, although *m*- and *o*-xylene are also present in substantial amounts. Toluene is found in small amounts, but the amount increases with temperature (1 to 4C%). The ethyltoluene, formed in 1–4C% amounts, is a mixture of *m* and *p* isomers.

(*b*) *Dependence of conversion on time.* Freshly regenerated ZSM-5/2 catalyst (0.15 g) was fed with aqueous methanol (2.75/1 w/w; 1.06 g/hr) in a stream of nitrogen vector gas (150 ml/hr) at various temperatures (280–302°C) at and below that required for complete "steady-state" conversion.[5] Figure 1 shows how the percentage of residual oxygenates and total yield of $C_{2-3}$ hydrocarbons (ethylene, propylene, and propane) change with time (up to 2½ hr) at the various temperatures. The figure indicates that product yields increase slowly with on-stream time. This effect is more marked at lower temperature, but is obvious even at 302°C, where complete steady-state conversion is ultimately attained. The effect is attributed to the accumulation of reaction products which have autocatalytic character. There is independent evidence (*13*) that the increase in conversion with time is not due to temperature runaway.

The variation with temperature of the C% distribution (measured after 1.5 hr on-stream) is shown in Fig. 2. This confirms the sharp increase in conversion (i.e., fall in residual dimethyl ether/methanol) with temperature which is evident in Table 1 (cf. Ref. (*10*)), and which has been discussed earlier by Chen and Reagan (*4*) (cf. Ref. (*13*)).

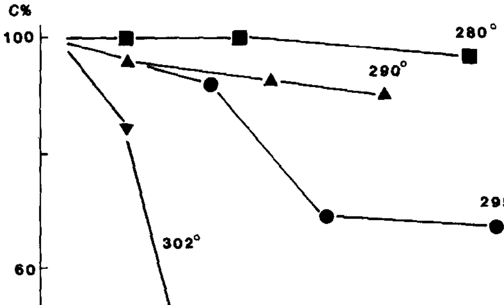

FIG. 1. Conversion and product yields (C%) as a function of time over ZSM-5/2 catalyst at various temperatures. ■ 280°C, ▲ 290°C, ● 295°C, ▼ 302°C; — unconverted MeOH + $Me_2O$, -- $C_2 + C_3$ hydrocarbons.

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[5] The catalyst was regenerated before repeating the experiment at a new temperature.

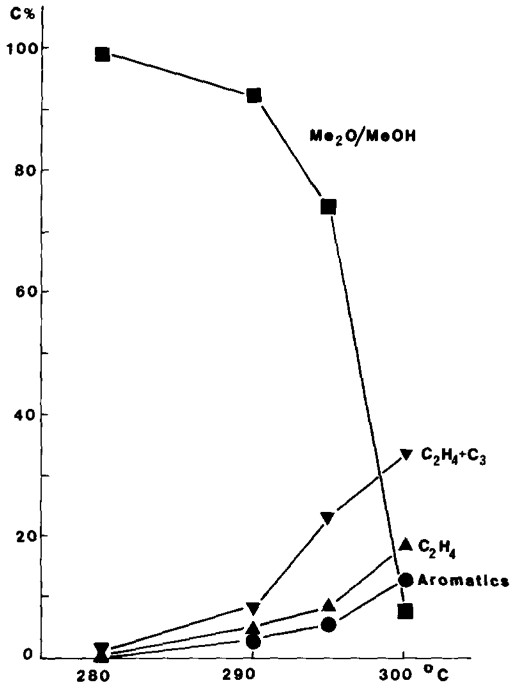

FIG. 2. Yields (C%) of hydrocarbon products and residual oxygenates as a function of temperature over ZSM-5/2 catalyst (after 1½ hr on-stream).

(*c*) *Effect of added alcohols*[6] *upon conversion of aqueous methanol.* The effect of added alcohols on conversion was demonstrated by a study of the conversion of aqueous methanol at 280°C in the presence of 6.5(±0.5)C% of other alcohols (ethanol, *n*- and isopropanol, and *t*-butanol).[6] The results are summarized in Fig. 3. For comparison it should be noted that

(i) aqueous methanol alone at 280°C gave a conversion to $C_2$ + $C_3$ hydrocarbons which did not exceed 1% within 1 hr of on-stream time (see Fig. 1), and

(ii) simple dehydration of the alcohol to olefin (*14, 15*) should give 6.5C% propylene from the *n*- and isopropanol, 6.5C% isobutylene from the *t*-butanol, and 6.5C% ethylene from the ethanol, respectively.

Figure 3 shows the variation of the yields of ethylene and $C_3$ hydrocarbons (dominantly propylene) with time. It can be seen that added ethanol has no effect other than generation of the expected amount of ethylene. *t*-Butanol accelerates conversion of the methanol, leading to >5% yields of ethylene and $C_3$ hydrocarbons within ½ hr. *n*-Propanol and isopropanol also accelerate conversion of the methanol, but the effect is less rapid; within 1 hr the ethylene yield is >5% and the propylene yield is >10%.

(*d*) *Conversion of methanol/$D_2O$ in the presence of* n-*propanol.* ZSM-5/2 catalyst was fed first with $D_2O$/methanol, then with $D_2O$/methanol containing a small amount of *n*-propanol. Conversions, yields of ethylene and propylene, and the isotopic composition of dimethyl ether, ethylene, and propylene were measured at various temperatures for each of the two feeds. Details of the experiments and results are summarized in Table 2. It can be seen that a very small amount of *n*-propanol (6.6C% w.r.t. methanol) not only increases the level of conversion of methanol to hydrocarbons but also accelerates deuteration of the residual dimethyl ether.

(*e*) *Reactivity of ethylene and propylene under conditions of aqueous methanol conversion.*[7] ZSM-5/2 catalyst (0.2 g) was preconditioned with aqueous methanol at 311°C[8] and was then fed with liquid $D_2O$ (1.1 ml/hr), either ethylene or propylene gas (150 ml/hr), and nitrogen vector gas (150 ml/hr). Conversion of ethylene to higher hydrocarbons at 311°C was 40% initially, and 30% after 2 hr. One-third of the converted material was a propylene/propane mixture. The propylene produced was dominantly $d_5$–$d_6$ labeled. The mass spectrum of the unconverted ethylene indicated an isotopic composition: $d_0$ 30%, $d_1$ 40%, $d_2$ 20%, $d_3$ 10%; i.e., the average D/H ratio is 0.4 (as compared with a 5–6 : 1 ratio of [D of $D_2O$]/[H of $C_2H_4$] in the feed).

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[6] These are added as convenient sources of small amounts of the corresponding olefins.

[7] The results obtained are consistent with an earlier study.

[8] The 311°C temperature is adequate for complete conversion of methanol.

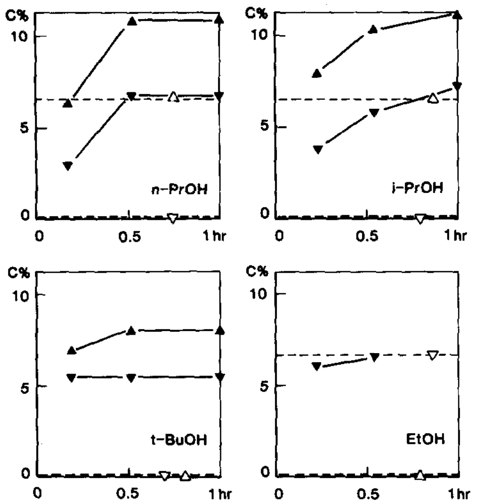

FIG. 3. Yields of ethylene and $C_3$ hydrocarbons from aqueous methanol containing 6.5C% of added alcohol over ZSM-5/2 catalyst at 280°C. Added alcohol: (a) *n*-propanol, (b) *iso*propanol, (c) *t*-butanol, and (d) ethanol. $C_3$ hydrocarbon: ▲ observed, △ expected. $C_2H_4$: ▼ observed, ▽ expected.

Propylene was much more reactive than ethylene, and both deuteration and conversion to higher hydrocarbons were observed at temperatures in the range 218–278°C. At 218°C, conversion was only ca. 10%, and the extent of deuteration was low; propylene was mainly labeled with 0–2 deuterium atoms and had an average D/H ratio of 0.1. At 238°C, conversion was ca. 50% and the residual propylene was $d_3$–$d_6$ labeled, with an average D/H ratio of 2. At 259 and 278°C, deuteration was similar but conversion was ca. 80%. The [D of $D_2O$]/[H of $C_3H_6$] ratio was 3 for the feed.

(*f*) *Conversion of aqueous* $^{13}$*C-methanol in the presence of* n-*propanol or* t-*butanol.* These experiments examine the extent to which the ethylene produced from aqueous $^{13}$C-methanol (of 90% isotopic label) incorporates the unlabeled carbon of an added higher alcohol. The higher alcohol is simply a convenient way of supplying the corresponding olefin—propylene from *n*-propanol, and isobutylene from *t*-butanol (*14*, *15*). Two series of experiments were carried out.

In the first series of experiments using ZSM-5/1 catalyst (see Table 3), the yield and isotopic composition of the ethylene product were estimated. Two feeds, differing mainly in their content of *n*-propanol, were examined at a temperature near the minimum for complete methanol conver-

TABLE 2

Conversion of Deuterium Oxide Containing Feeds over ZSM-5/2 Catalyst[a]

| Feed | (g) | Temperature (°C) | Conversion (C%)[b] | Yields (C%) | Average D/H ratio in Dimethyl ether | Ethylene | Propylene |
|---|---|---|---|---|---|---|---|
| $D_2O$<br>Methanol | 4<br>1.4 | 296 | ca. 12 | $C_2H_4$ 6<br>$C_3H_6$ 6 | 0.3 | 1.5 | 3.5 |
| | | 291 | <1 | | 0 | — | — |
| $D_2O$<br>Methanol<br>*n*-Propanol | 4<br>1.36<br>0.06 | 291 | ca. 45[c] | $C_2H_4$ 5½<br>$C_3H_6$ 7<br>$C_3H_8$ 2 | 0.7 | 1.6 | 2.4 |
| | | 280 | ca. 20[c] | $C_2H_4$ 2<br>$C_3H_6$ 6½<br>$C_3H_8$ 2 | 0.4 | 1.3 | 2.1 |

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[a] Regenerated ZSM-5/2 (0.15 g) was fed with the $D_2O$/methanol liquid (1.1 ml/hr) in nitrogen vector gas (150 ml/hr) at various temperatures (cf. Mole and Whiteside (*10*)). The catalyst was regenerated *in situ* and then fed with the $D_2O$/methanol/*n*-propanol feed under similar conditions.

[b] Conversion (C%) with respect to total feed (including *n*-propanol).

[c] The *n*-propanol might be expected to lead to a 6.6% conversion of feed to propylene and derived products.

TABLE 3

Conversion of Aqueous [$^{13}$C]-Methanol/*n*-Propanol Feed over ZSM-5/1 Catalyst

| Feed[a] | 1 | 2[b] | 2[b] |
|---|---|---|---|
| $^{13}CH_3OH$[c] mmole | 3.80 | 1.55 | 1.55 |
| *n*-$C_3H_7OH$ mmole | 0.67 | 1.52 | 1.52 |
| $H_2O$ mmole | 21 | 8.5 | 8.5 |
| $^{13}C/^{12}C$ | 1.43 | 0.30 | 0.30 |
| Temperature (°C) | 302 | 292 | 382 |
| Ethylene | | | |
| Yield[d] | 9% | 4% | 4% |
| Composition (%)[e] | | | |
| $^{13}C_2H_4$ | 53 | 29 | 15 |
| $^{12}C^{13}CH_4$ | 31 | 45 | 37 |
| $^{12}C_2H_4$ | 16 | 26 | 48 |
| Av $^{13}C/^{12}C$ | 2.2 | 1.1 | 0.5 |

[a] 0.30 ml/hr of the mixed liquid feed was delivered to 0.20 g of ZSM-5/1 in 240 ml/hr nitrogen vector gas. The ZSM-5/1 had previously been regenerated and then preconditioned with aqueous methanol at 302°C.

[b] Prepared by adding extra *n*-propanol to a portion of feed 1.

[c] Isotopic purity, 90% (Merck Sharp and Dohme of Canada).

[d] Yield (C%) based on total carbon of the feed (methanol plus propanol).

[e] ± ca. 5%.

sion, and the feed with the higher content of propanol was also examined at a substantially higher temperature (382°C).

In the second series of experiments, using ZSM-5/2 catalyst, three feeds were used, two containing $^{13}$C-methanol and propanol in differing ratios, and one containing $^{13}$C-methanol and *t*-butanol. The isotopic compositions of both ethylene and propylene were examined, and in the case of the *t*-butanol-containing feed, the isobutylene could also be examined. Details are given in Table 4.

In every case ethylene is extensively $^{13}$C labeled, and so is derived largely from the methanol. However, it is less extensively labeled than we would expect if it were derived exclusively from methanol.

(*g*) *Conversion of deuterated methanol in the presence of isopropanol or* t*-butanol.* These experiments examine the extent to which exchange of hydrogen atoms takes place between deuterated methanol/dimethyl ether on the one hand and unlabeled isopropanol or *t*-butanol on the other. The isopropanol or *t*-butanol undergoes dehydration and further reactions under the conditions chosen and so serves as a source of carbocations and olefins (isopropyl cation and propylene from isopropanol, and *t*-butyl cation and isobutylene from *t*-butanol) and further reaction products.

The mixture of methanol-$d_4$ (5–8 mmole) with isopropanol or *t*-butanol (1 mmole) without water diluent was passed over ZSM-5/2 catalyst at temperatures (240–

TABLE 4

Conversion of Aqueous [$^{13}$C]-Methanol Admixed with *n*-Propanol or *t*-Butanol over ZSM-5/2 Catalyst[a]

| Feed | 3 | 4 | 5 |
|---|---|---|---|
| $^{13}CH_3OH$ (mmole) | 4.92 | 2.71 | 3.92 |
| Other alcohol | *n*-Propanol | *n*-Propanol | *t*-Butanol |
| (mmole) | 1.67 | 2.50 | 1.50 |
| $H_2O$ (mmole) | 29.2 | 23.1 | 18.8 |
| $^{13}C/^{12}C$ | 0.81 | 0.31 | 0.55 |
| Dimethyl ether | | | |
| Composition (%)[b] | | | |
| $^{13}C_2$ | 75 | 80 | 73 |
| $^{13}C_1$ | 25 | 20 | 27 |
| $^{13}C_0$ | 0 | 0 | 0 |
| Ethylene | | | |
| Composition (%)[c] | | | |
| $^{13}C_2$ | 37 | 22 | 29 |
| $^{13}C_1$ | 38 | 36 | 40 |
| $^{13}C_0$ | 25 | 42 | 31 |
| Av $^{13}C/^{12}C$ ratio | 1.3 | 0.7 | 1.0 |
| Propylene | | | |
| Composition (%)[d] | | | |
| $^{13}C_3$ | 6 | 0 | 0 |
| $^{13}C_2$ | 20 | 6 | 25 |
| $^{13}C_1$ | 15 | 6 | 23 |
| $^{13}C_0$ | 60 | 87 | 51 |
| Av $^{13}C/^{12}C$ ratio | 0.3 | 0.06 | 0.3 |
| Isobutylene | | | |
| Av $^{13}C/^{12}C$ ratio | | | 0.04[e] |

[a] 0.15 g of ZSM-5/2 catalyst was regenerated before each experiment, preconditioned with aqueous methanol, and then treated with 0.6 ml/hr of feed at 309°C in nitrogen vector gas (150 ml/hr). Two gc/ms analyses were conducted over a ½-hr period.

[b] ± ca. 5%. The deviation from the expected composition ($^{13}C_2H_4$ 81%, $^{13}C^{12}C_2H_4$ 18%, $^{12}C_2H_4$ 1%) is probably not significant.

[c] ± ca. 5%.

[d] These data are much less reliable than that for dimethyl ether and ethylene, first, because of the poor separation of propylene from propane on the Porapak Q column and second, because of the complex mass spectrum of propylene in the parent ion region (*m/e* 42 to 37).

[e] i.e., largely unlabeled.

TABLE 5

Conversion of $CD_3OD$ Admixed with Isopropanol or *t*-Butanol over ZSM-5/2 Catalyst[a]

| Feed | Temperature (°C) | Ratio $\frac{d_5\text{-dimethyl ether}}{d_6\text{-dimethyl ether}}$ |
|---|---|---|
| $CD_3OD$ | 266 | $0.1$[b] |
| $CD_3OD$<br>iso-PrOH[c] | 270 | $0.3^5$ |
| | 240 | $0.2^5$ |
| $CD_3OD$<br>*t*-BuOH[d] | 280 | 0.2 |
| | 242 | $0.1^5$ |

[a] Liquid (0.25 ml/hr) was fed to regenerated ZSM-5/2 catalyst (0.20 g) in argon vector gas (300 ml/hr).

[b] Expected for 99% isotopic purity of the $CD_3OD$, 0.06.

[c] 842 mg (23 mmole) $CD_3OD$ plus 273 mg (4.5 mmole) iso-PrOH. OD/total H ratio ~ 0.6. Total D/H ratio ~ 2.5. The propylene product was deuterated, up to a $d_5$ level at 270°C.

[d] 812 mg (22 mmole) $CD_3OD$ plus 212 mg (2.9 mmole) *t*-BuOH. OD/total H ratio ~ 0.8. Total D/H ratio ~ 3. The isobutylene was deuterated up to a $d_6$ level.

280°C)[9] below that of complete methanol conversion. Details are given in Table 5.

The mass spectrum of the dimethyl ether, in the parent ion region, consisted essentially of a pattern of peaks at $m/e = 52$, 51, 50, and 49 (peaks of $m/e = < 49$ were much weaker), which corresponds to hexadeutero-dimethyl ether and pentadeutero-dimethyl ether parent ions and fragments from loss of one deuterium atom. The intensity of the $m/e = 51$ peak relative to that of the $m/e = 52$ peak is a measure of the amount of $CD_3OCHD_2$ relative to $CD_3OCD_3$.

The results, shown in Table 5, all indicate loss of deuterium from the deuterated dimethyl ether. The loss observed in the absence of added alcohol may be within experimental error, but losses represented by $d_5/d_6$ ratios $\geq 0.15$ are regarded as significant. The $d_5/d_6$ ratio of 0.25 observed in the presence of isopropanol at 240°C corresponds to a 20% chance of loss of one deuterium of the hexadeutero-dimethyl ether molecule and a residual H/D ratio of 0.03.

## DISCUSSION

### *A. General*

*Products.* Many organic feedstocks undergo conversion over ZSM-5 zeolite at moderate temperature (300–400°C) to products which are typically those expected from an acid-catalyzed "cracking" reaction, and which do not include large amounts of ethylene (*2, 7, 16, 17*). By contrast methanol conversion over ZSM-5 zeolite gives ethylene in substantial (ca. 20%) yields, but over only a very limited range of mild reaction conditions. Aqueous methanol (water/methanol 2.75/1 w/w) gives a substantial ethylene yield (10–30%) over a much wider temperature range (ca. 30°C) than does pure methanol. However, a mixture of products is still formed. It appears that aqueous methanol cannot be converted exclusively to a single product over ZSM-5 catalyst even under conditions of mild or partial conversion. Ethylene and $C_3$ hydrocarbons (propylene plus propane) are formed in comparable (C%) amounts, and any high degree of conversion also involves the formation of aromatics.

*The effect of added alcohols.* The observed dependence of aqueous methanol conversion upon temperature and time is consistent with the now well-established (*4, 6*) autocatalytic character of methanol conversion.

The finding (cf. Refs. (*6, 20*)) that added *n*- or isopropanol or *t*-butanol accelerates conversion of aqueous methanol is also consistent with the autocatalytic character. The added alcohols are known to dehydrate to the corresponding olefins (*14, 15*) (propylene or isobutylene), and so the most important active species are thought to be olefins.[10] It is important to recognize that the

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[9] Dehydration of the methanol-$d_4$ to dimethyl ether is slow below 240°C.

[10] See, however, Section C, below.

added alcohols accelerate conversion generally, not conversion to ethylene specifically. Specificity for ethylene production appears to be lowered, rather than raised, by the presence of the added alcohols.

The finding that ethanol does not increase conversion is consistent with recent work of Langner (*20*), but is at variance with the finding of Ono and Mori (*6*) that ethylene cocatalyzes methanol conversion. However, Ono and Mori used a recycle reactor, and their result could be attributed to the recycle of oligomerization products of ethylene.[11] The present paper shows that ethylene undergoes some conversion under conditions of methanol conversion.

When *n*- or isopropanol is added to a methanol conversion reaction, it does not serve simply as a source of propylene. Propylene undergoes extensive reaction under conditions of methanol conversion. Thus the propanols necessarily give propylene and many products derived from propylene, including other olefins, aromatic hydrocarbons, and isoalkanes.[12] For this reason it is hard to specify the particular species responsible for the observed acceleration of conversion. However, homologation of olefins by methanol, as discussed later, does provide a rational explanation of the results.

TABLE 6

Experimental and Calculated $^{13}$C-Distribution in Ethylene

| | Experiment | | | | | |
|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI |
| Feed | | | | | | |
| Number | 1 | 2 | 2 | 3 | 4 | 5 |
| Temperature (°C) | 302 | 292 | 382 | 309 | 309 | 309 |
| Overall % $^{13}$C | 59 | 23 | 23 | 45 | 24 | 36 |
| Observed isotopic distribution[a] | | | | | | |
| % $^{13}C_2H_4$ | 53 | 29 | 15 | 37 | 22 | 29 |
| % $^{13}C^{12}CH_4$ | 31 | 45 | 37 | 38 | 36 | 40 |
| % $^{12}C_2H_4$ | 16 | 26 | 48 | 25 | 42 | 31 |
| Factor $f$[b] | 1.1 | 2.6 | 2.0 | 1.6 | 1.4 | 1.8 |
| Calculated origin[c] | | | | | | |
| % Direct | 58 | 15 | 10 | 33 | 19 | 17 |
| % Indirect | 42 | 85 | 90 | 67 | 81 | 83 |
| % $^{13}$C in indirect "pool" | 40 | 45 | 27 | 39[d] | 28[e] | 37[f] |

[a] Data of Tables 3 and 4.

[b] $f = (\% \, ^{13}C^{12}CH_4)^2/(\% \, ^{13}C_2H_4)\,(\% \, ^{12}C_2H_4)$.

[c] Calculated assuming ethylene is formed simultaneously by the direct and indirect routes.

[d] The isotopic composition of the propylene can be interpreted as 50% unlabeled and 50% derived on a random basis from this "pool." Predicted: $^{13}C_3H_6$ 3, $^{13}C_2{}^{12}CH_6$ 14, $^{13}C^{12}C_2H_6$ 22, and $^{12}C_3H_6$ 61%. Found 6, 20, 15, and 60%, respectively.

[e] The isotopic composition of the propylene can be interpreted as 80% unlabeled and 20% derived on a random basis from this "pool." Predicted: $^{13}C_3H_6$ 0.4, $^{13}C_2{}^{12}CH_6$ 3, $^{13}C^{12}C_2H_6$ 9, and $^{12}C_3H_6$ 87%. Found 0, 6, 6, and 87%, respectively.

[f] The isotopic composition of the propylene can be interpreted as 35% unlabeled and 65% derived on a random basis from this "pool." Predicted: $^{13}C_3H_6$ 3, $^{13}C_2{}^{12}CH_6$ 17, $^{13}C^{12}C_2H_6$ 29, and $^{12}C_3H_6$ 51%. Found 0, 25, 23, and 51%, respectively.

### *B. Origin of Ethylene from $^{13}$C-Labeled Methanol and Unlabeled Alcohols*

If the ethylene were produced entirely from the labeled methanol of 90% isotopic abundance, then it should be 81% doubly labeled, 18% singly labelled, and 1% unlabeled. The data of Tables 3 and 4 show clearly that ethylene is by no means as heavily labeled as this, and so must incorporate the carbon of the unlabeled alcohol. However, the $^{13}C/^{12}C$ ratio in the ethylene product is in every case much higher than the $^{13}C/^{12}C$ ratio in the feed confirming that the ethylene is preferentially derived from the methanol. The ethylene is more extensively $^{13}$C-labeled than as described by Dessau and La Pierre (Table 3 of Ref. (*12*)). However, Dessau and La Pierre used relatively large amounts of olefins (and did not specify closely the conversion temperature).

For ease of consideration the isotopic ethylene data from Tables 3 and 4 is summarized in Table 6. One possible explanation of the data is that all the ethylene is produced by one path and that it incorporates on a random basis all or a part of the carbon of the methanol and part of the carbon of the other alcohol. If this were so, the ratio $(\%^{12}C^{13}CH_4)^2/(\%^{13}C_2H_4)(\%^{12}C_2H_4)$ should be 4. This ratio (factor $f$) is given in

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[11] See, for example, Refs. (*18*) and (*19*).

[12] See, for example, Refs. (*18*) and (*19*).

Table 6 for each experiment and is not equal to 4.

Another possible explanation of the observed isotopic distribution is that the ethylene is derived from one carbon atom of methanol and one carbon atom derived in part from methanol and in part from the other alcohol. In this case the percentage of $^{12}C_2H_4$ should not exceed 10%, but it does.

It is therefore necessary to assume that the ethylene is produced by two routes rather than one: first, *directly* from two molecules of methanol; and second, *indirectly,* with the ethylene carbon being drawn, on a random basis, from a carbon "pool" derived in part from methanol and in part from the unlabeled other alcohol. This model gives an excellent and plausible fit to the observed isotopic distribution as is shown in the lower half of Table 6. Details of the analysis are given in the Appendix.

### *C. Direct Ethylene Formation*

It is now clear that most ethylene is formed "directly" from two molecules of methanol if large amounts of olefins of three or more carbon atoms are not present. Stoichiometrically, the simplest direct reaction is (2a) or (2b):

$$2\,CH_3OH \rightarrow C_2H_4 + 2H_2O \qquad (2a)$$

or

$$CH_3OCH_3 \rightarrow C_2H_4 + H_2O. \qquad (2b)$$

Ethylene formation by reaction (2b) has been proposed, with the rate determining step being formation (4) of an oxonium–ylide (*10*).

$$CH_3OCH_3 + R^+ \rightleftharpoons CH_3\text{–}\overset{+}{O}(R)\text{–}CH_3 \qquad (3)$$

$$CH_3\text{–}\overset{+}{O}(R)\text{–}CH_3 + B \rightarrow BH^+ + CH_3\text{–}\overset{+}{O}(R)\text{–}\overset{-}{C}H_2 \qquad (4)$$

(R = H or alkyl).

Oxonium–ylide formation (4) is preceded by more rapid O-protonation (3; R = H) or O-alkylation (3; R = alkyl) of the dimethyl ether. The essential piece of evidence for the oxonium–ylide intermediate is incorporation of the deuterium of $D_2O$ into the dimethyl ether under conditions of methanol conversion (but not otherwise). The oxonium–ylide should be subject to facile C deuteration (5), and to competing facile rearrangement (6):

$$CH_3\text{–}\overset{+}{O}(R)\text{–}\overset{-}{C}H_2 + D^+ \rightarrow CH_3\text{–}\overset{+}{O}(R)\text{–}CH_2D \qquad (5)$$

$$CH_3\text{–}\overset{+}{O}(R)\text{–}\overset{-}{C}H_2 \rightarrow CH_3\text{–}CH_2\text{–}OR \qquad (6a)$$

$$CH_3\text{–}\overset{+}{O}(R)\text{–}CH_2^- \rightarrow CH_3\text{–}O\text{–}CH_2R. \qquad (6b)$$

Rearrangement (6a; R = H or alkyl) followed by dehydration gives ethylene. Rearrangement (6b; R = alkyl) and dehydration gives an olefin of three or more carbon atoms. We have already noted that conversion of methanol over ZSM-5 zeolite never gives exclusively ethylene. If the sequence of reactions (3)–(6) were much more facile for R = alkyl than for R = H, then the failure to form ethylene exclusively even under conditions of mild and partial conversion is explained. So too is the present finding that added $C_3$ and $C_4$ alcohols accelerate the deuteration of residual dimethyl ether as well as the conversion of aqueous methanol.[13]

According to the oxonium–ylide mechanism, the carbon of ethylene product should be derived solely from the carbon of methanol, and should not incorporate the carbon of any added olefin (or alcohol). Thus, we identify the oxonium–ylide mechanism as the route whereby methanol/dimethyl ether gives ethylene directly.

### *D. Indirect Ethylene Formation*

The second, indirect route to ethylene incorporates the carbon of added *n*-propanol or *t*-butanol. A reasonable hypothesis (*5, 7, 8*) is that methanol extends the carbon chain of olefin product (or propylene from

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[13] Thus added alcohols appear to accelerate conversion in two ways: first (and probably most significantly), by giving olefins which undergo homologation; and second, by producing trialkyl oxonium ions, then oxonium ylides.

*n*-propanol, or isobutylene from *t*-butanol) to give a larger molecule which eventually eliminates ethylene.

It has previously been argued (*5, 7, 8*) that an olefin must be subject to electrophilic methylation (7) by methanol:

$$C_nH_{2n} + CH_3\overset{+}{O}H_2 \rightarrow C_{n+1}H_{2n+3}^+ + H_2O \quad (7a)$$

$$C_{n+1}H_{2n+3}^+ \rightarrow C_{n+1}H_{2n+2} + H^+. \quad (7b)$$

Repeated reaction (8) gives an extended olefin, which can undergo Brønsted acid-catalyzed cracking (9) to two olefin molecules:

$$C_nH_{2n} + m\ CH_3OH \xrightarrow{H^+} C_{n+m}H_{2n+2m} \quad (8)$$

$$C_{n+m}H_{2n+2m} \xrightarrow{H^+} C_nH_{2n} + C_mH_{2m}. \quad (9)$$

This proposal explains how methanol conversion is autocatalytic and how the products typically resemble products of acid-catalyzed cracking. For such a mechanism, selective production of ethylene is not to be expected. However, selectivity for the ethylene production only appears to be high (20–30%) if most of the ethylene is formed directly rather than indirectly. It is not known whether the indirectly formed ethylene is produced by a homologation/cracking mechanism, as outlined above. However, the products of methanol conversion include some ethyl–aromatics (see Table 1), and in the following paper it is shown that deethylation of ethyl–aromatics can occur under conditions of methanol conversion. Thus the indirectly formed ethylene may be produced mainly by the formation and deethylation of ethyl–aromatic compounds, rather than by the homologation/cracking mechanism. In this sense ethylene formation may be quite different from formation of higher hydrocarbons.

### *E. Competition between Direct and Indirect Conversion*

In examining the competition between direct and indirect ethylene formation, comparison of Experiments (I), (II), (IV), and (V) of Table 6, all of which used *n*-propanol at temperatures (292–309°C) near the minimum for complete methanol conversion, shows that as the methanol/(methanol + propanol) ratio falls so the fraction of ethylene produced indirectly increases, with corresponding decrease in the fraction produced directly. In the limit where there is no propylene or other olefin of >3 carbon atoms, all the ethylene should be produced directly. However, olefins of ≥3 carbon atom are produced by methanol conversion, and so exclusive direct formation of ethylene can only occur at low conversion of methanol to hydrocarbons. It is probable that most of the ethylene produced in the previous methanol/$D_2O$ work (*10*) was produced directly, so that the previous conclusions (*10*) about the oxonium–ylide mechanism are not invalidated.

Direct ethylene formation is thus seen as initiating methanol conversion in the limit of low conversion. In the other limit, when conversion is complete, when the temperature is not minimal, and when light hydrocarbon gases (which include olefins) are recycled, almost all the ethylene will be produced indirectly and with low selectivity. These are the conditions for Mobil's methanol-to-gasoline manufacture.

Dessau and La Pierre's study (*12*) of conversion of $^{13}C$-labeled methanol in the presence of unlabeled propylene and hexene-1 was clearly carried out under relatively severe conversion conditions and gave poorly labeled ethylene, presumably with low selectivity.

### *F. Possible Hydride Transfer Reactions*

Hydride transfer reactions are significant in the overall mechanism of methanol conversion, and must be implicated in the formation of alkanes and aromatics from the olefin products. Aromatization probably involves rate-limiting transfer of hydride anion from olefin or other unsaturated hydrocarbon to carbocations.[14]

[14] Cyclization is unlikely to be the rate-determining step, since it is only a special case of oligomerization, which is facile.

Hydride transfer from methanol or dimethyl ether would afford an oxymethyl cation ($ROCH_2^+$, $R$ = H or methyl). Such a species does not provide a simple direct route to ethylene. However, it might offer a mechanism for indirect conversion of methanol to olefins, via the Prins reaction. This mechanism has been discussed in detail by Langner (*20*).

If such a mechanism did largely account for methanol conversion, then it might also account for the concurrence of conversion and isotopic hydrogen exchange, previously observed in methanol/$D_2O$ experiments (*10*) and taken as proof of the oxonium–ylide hypothesis. The $D_2O$ should in this case be regarded not as a supply of $D^+$ to oxonium–ylide but as a source of deuterated olefins (reaction 10)); the deuterated olefins would in turn supply $D^-$ to oxymethyl cations. When this possibility was tested, but using *deuterated* methanol and *nonlabeled* isopropanol or *t*-butanol (as a source of undeuterated olefin and $H^-$) some incorporation of hydrogen into the hexadeutero-dimethyl ether was observed, but not rapid and extensive exchange. Thus, oxymethyl cation formation by reaction (11) is not facile, and indirect conversion by a Prins mechanism is not probable.

$$C_nH_{2n} + 2nD^+ \rightleftharpoons C_nD_{2n} + 2nH^+ \qquad (10)$$

$$R'OCD_3 + R^+ \rightarrow R'OCD_2^+ + RD \qquad (11)$$

(R′ = $CD_3$, etc.; R = isopropyl, *t*-butyl, etc.)

## APPENDIX: ANALYSIS OF THE $^{13}$C-ISOTOPIC DISTRIBUTION OBSERVED FOR ETHYLENE

The analysis assumes that ethylene is derived concurrently: (a) directly from two molecules of 90% $^{13}$C-methanol (in the absence of isotope effect, 81% of the ethylene should be doubly labeled, 18% singly labeled, and 1% unlabeled), and (b) indirectly from a "pool" incorporating some or all of the carbon of the methanol and some or all of the carbon of the other alcohol.

Random selection of the carbon of the "pool" is assumed, and the natural 1% abundance of $^{13}$C is ignored. Thus if the fraction of the carbon of the "pool" having a $^{13}$C label is $x$, then the chance of a double label is $x^2$, of a single label is $2x(1 - x)$, and of no label is $(1 - x)^2$.

TABLE 7

Analysis of Isotopic Composition of Ethylene

| | I | II | IIII | IV | V | VI |
|---|---|---|---|---|---|---|
| $x$ | 0.40 | 0.45 | 0.27 | 0.39 | 0.28 | 0.37 |
| $y$ | 0.42 | 0.85 | 0.90 | 0.67 | 0.81 | 0.83 |
| $F^d$ observed | 0.53 | 0.29 | 0.15 | 0.37 | 0.22 | 0.29 |
| $F^d$ calcd. direct contribn. | 0.47 | 0.12 | 0.08 | 0.27 | 0.15 | 0.19 |
| $F^d$ calcd. indirect contribn. | 0.06 | 0.18 | 0.07 | 0.10 | 0.07 | 0.10 |
| $F^s$ observed | 0.31 | 0.45 | 0.37 | 0.38 | 0.36 | 0.40 |
| $F^s$ calcd. direct contribn. | 0.10 | 0.03 | 0.02 | 0.06 | 0.03 | 0.04 |
| $F^s$ calcd. indirect contribn. | 0.20 | 0.42 | 0.36 | 0.32 | 0.33 | 0.36 |
| $F^u$ observed | 0.16 | 0.26 | 0.48 | 0.25 | 0.42 | 0.31 |
| $F^u$ calcd. direct contribn. | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $F^u$ calcd. indirect contribn. | 0.15 | 0.26 | 0.48 | 0.25 | 0.42 | 0.31 |

Let $y$ be the fraction of the ethylene formed indirectly and $(1 - y)$ be the fraction formed directly. Then the total fractions doubly labeled ($F^d$), singly labeled ($F^s$), and unlabeled ($F^u$) are given by Eqs. (12)–(14), respectively.

$$\begin{array}{lll} \underline{\text{Indirect}} & \underline{\text{Direct}} & \\ F^d = yx^2 & + \ 0.81\,(1 - y) & (12) \\ F^s = 2yx(1 - x) & + \ 0.18\,(1 - y) & (13) \\ F^u = y(1 - x)^2 & + \ 0.01\,(1 - y). & (14) \end{array}$$

Thus

$$y = (0.81 - F^d)/(0.81 - x^2) \qquad (15)$$

and

$$F^s - 0.18 = y(2x - 2x^2 - 0.18). \qquad (16)$$

Eliminating $y$, and putting $(F^s - 0.18)/(0.81 - F^d) = Z$, gives

$$(2 - Z)x^2 - 2x + (0.81Z + 0.18) = 0. \qquad (17)$$

Solution of quadratic equation (17) gives $x$; thus a unique sensible solution for $x$ and $y$ is obtained. The values obtained for Experiments (I)–(VI) of Table 6, and the fractional contributions of the direct and indirect ethylene routes to $F^d$, $F^s$, and $F^u$, are shown in Table 7.

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