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Conversion of Methanol to Ethylene over ZSM-5 Zeolite in the Presence of Deuterated Water

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When methanol, mixed with two volumes of deuterated water, is converted to ethylene and other hydrocarbons over ZSM-5 zeolite at 300°C, deuteration of the residual dimethyl ether accompanies ethylene formation. The ethylene is also extensively deuterated. The data are interpreted in terms of an oxonium ylide mechanism (Stevens-type rearrangement) for ethylene formation.

INTRODUCTION

Considerable interest is attached to the conversion of methanol to hydrocarbons plus water over ZSM-5 zeolite catalyst (*1*, *2*). There seems to be no doubt that the catalyst is active by virtue of its Brönsted acidity (*3*), and that the product selectivity is determined by the size and arrangement of the molecular channels of the zeolite (*4*). The conversion is thought to involve the reaction sequence:

$$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad \textit{fast at } 300°C, \qquad (1)$$

$$CH_3OH \text{ or } CH_3OCH_3 \rightarrow \text{olefins} + \text{water}, \qquad (2)$$

$$\text{olefins} \rightarrow \text{aromatics and alkanes}. \qquad (3)$$

Little is known of the reactions (*2*) whereby carbon–carbon bonds form from methanol or dimethyl ether. It has been shown that the toluene produced from benzene and a CD_3OD/H_2O feed at 207°C contains the fully deuterated CD_3 group (*3*). Because of this and because olefins are much more subject to electrophilic attack than benzene, one of us has suggested that reactions of type (2) consist largely of the electrophilic methylation of olefins of three or more carbon atoms (*3*). The net result is homologation (4).

$$C_nH_{2n} + CH_3OH \rightarrow C_{n+1}H_{2n+2} + H_2O. \qquad (4)$$

Repeated homologation followed by carbonium ion cracking leads to two molecules of olefin for renewed homologation (4). This mechanism for carbon–carbon bond formation explains, at least in part, the known autocatalytic nature of methanol conversion (*5*).

Derouane *et al.* (*6*) have held the conflicting view that carbon–carbon bond formation involves conversion of methanol or dimethyl ether to ethylene. The relatively low reactivity of ethylene under conditions of methanol conversion (*3*, *7*) makes it unlikely that most methanol is converted to higher hydrocarbons via ethylene. However, conversion of methanol to ethylene is an important practical objective, and its mechanism may throw light on methanol conversion more generally.

The mechanism of ethylene formation is unknown, but van den Berg *et al.* (*8*) have recently suggested, without experimental proof, that rearrangement of an O-ylide to an ethoxy group could be the reaction whereby the carbon–carbon bond of ethylene is formed. We are now able to provide experimental support for this suggestion.

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EXPERIMENTAL

(*a*) *ZSM-5 Zeolite*

The zeolite was crystallized from a seeded mixture of *n*-propanol (1 part by wt), sodium silicate solution (9.2% Na_2O, 28.6% SiO_2; 9 parts by wt), and an aqueous solution (16 parts by wt) of $Al_2(SO_4)_3 \cdot 18H_2O$ (1.9 wt%) and sulfuric acid (4.5 wt%) in a stirred autoclave at 175°C for 24 hr.

The zeolite was washed well with water, calcined at 500°C, and treated with 0.3 *M* hydrochloric acid overnight at 95–100°C to convert it to the proton form. It then had the characteristic X-ray powder pattern of completely crystalline ZSM-5 zeolite and contained 1.28% Al and 0.04% Na.

(*b*) *Conversion of Methanol/Deuterium Oxide*

Acid-washed zeolite was pelleted, crushed, and sieved to 80/100 mesh size. A sample (0.15 g) was packed into a 6-mm o.d. quartz microreactor tube in a wire-wound furnace. The catalyst was dried at 450°C in nitrogen, then fed continuously with a liquid D_2O/methanol feed (2:1 v/v; 1.1 ml hr^{-1}) from a motorized 5-ml syringe via a long 20-gauge needle (directly into the furnace zone). Nitrogen diluent gas (2½ ml min^{-1}) was also fed to the reactor. The pressure was 1 bar and the temperature was varied in the range 291–300°C (±1°C).

The reactor effluent was diluted with further nitrogen (<30 ml min^{-1}). Part of the product water was condensed, then the effluent was continuously carried by heated lines to gas-sample valves of a Varian 3700 gas chromatograph, fitted with independent ⅛-in. o.d. stainless-steel columns packed with Porapak Q (2-m) (for C_{1-3} and dimethyl ether analysis) and OV 101/Chromasorb (3-m) (for other analysis), and having flame ionization and thermal conductivity detectors.

Mass spectra were measured using a UTI quadruple mass spectrometer, on line to the effluent of the Porapak Q column/thermal conductivity detector combination. Mass spectra (unit m/e resolution) were recorded by fast uv recorder for the ethylene and dimethyl ether effluent peaks. Isotopic compositions were assigned for dimethyl ether by comparison of the observed peak intensities at m/e = 45 to 52 with those observed for unlabelled dimethyl ether at 45, 46. For ethylene the observed intensities at m/e = 26 to 32 were compared with those of unlabelled ethylene at 26 to 28. Random selection of H/D in the fragmentation of partially labeled dimethyl ether and ethylene was, of course, assumed.

The derived isotopic compositions of dimethyl ether and ethylene and the corresponding conversions of methanol, and hydrocarbon and ethylene yields are given in Table 1. Yields and conversions given in Table 1 and elsewhere in this paper are expressed as C%, that is as the percentage of the carbon content of the methanol feed converted to a particular product or to hydrocarbons generally.

RESULTS AND DISCUSSION

(*a*) *Catalytic Activity*

There is little doubt that most reactions which occur over ZSM-5 catalyst are Brönsted-acid-catalyzed (*3*). The question which we seek to address is how such catalysis might apply to the conversion of methanol to ethylene.

The ZSM-5 zeolite used, with 1.28% Al, has a low concentration of Brönsted acid sites—roughly three for every hundred $SiO_2(AlO_2)$ units in the zeolite skeleton. It may be misleading to refer a "site" of Brönsted acidity, particularly in the conversion of aqueous methanol, because the zeolite acts as host to a large amount of water, as well as methanol, dimethyl ether, and hydrocarbon products. The protons are unlikely to be localized (at particular oxygen atoms), but are probably mobile between lattice oxygens and the various guest molecules. Many of the guest molecules (methanol, dimethyl ether, and water) and the lat-

TABLE 1

Conversion of Methanol/D_2O over ZSM-5 Catalyst[a]

Temperature (°C)	Conversion of methanol/dimethyl ether to hydrocarbons (%C)	Ethylene yield (%C)	Ethylene label	Dimethyl ether label
291	<1%	0%		Average D/H ~ 0 entirely D_0
296	12%	6%	Average D/H ~ 1.4 D_4 D_3 D_2 D_1 D_0 15 30 30 20 5%	Average D/H ~ 0.3 D_4 D_3 D_2 D_1 D_0 10 20 5 25 40%
300	90%	25%	Average D/H ~ 1.6	Average D/H ~ 0.7 D_5 D_4 D_3 D_2 D_1 D_0 5 25 25 15 25 5%

[a] Results were obtained after a minimum 30 min on stream at the stated temperature. The sharp increase in conversion with temperature is highly reproducible but the temperature for any specified conversion may not be so reproducible from one catalyst sample to another (see text).

tice oxygens can be regarded as basic in that they should readily be protonated. Furthermore, unsaturated and aromatic hydrocarbons can undergo protonation. It is possible for these various bases to accept protons not only from oxygen (i.e., from zeolitic Brönsted acid), but also from organic molecules, for example, from positively charged organic molecules such as might be implicated in methanol conversion.

The role of the channel structure of ZSM-5 in determining its selectivity and freedom from "coking" has already been widely discussed elsewhere (*1*, *2*, *4*, *9*). The low concentration of Brönsted acid sites may also be of importance in determining selectivity and freedom from "coking" (see for example Bremer *et. al.* (*10*)). Many reports on methanol conversion deal with zeolites of high silica content, and much of the discussion, above and later, may be pertinent to high-silica zeolites besides ZSM-5.

(*b*) *Products*

Hydrocarbons of three or more carbon atoms are the typical products of the conversion of methanol over the proton form of ZSM-5 catalyst (*2*). Ethylene is formed in typically small amounts, and is obtained in substantial yields (of 5–10%) only over a particularly narrow temperature range (ca. 10°C) at the temperature (ca. 300°C) required for complete conversion. The narrowness of this temperature range is somehow related to the strongly autocatalytic nature of the reaction, which is a poorly understood phenomenon (*5*).

When aqueous methanol (2 : 1 v/v $D_2O : CH_3OH$ in the present work; i.e., 9 : 2 mole ratio) is used as the feed instead of methanol, a higher ethylene yield (15–25%) is obtainable over a wider temperature range (ca. 30°C) at and above the temperature (ca. 300°C) required for complete conversion. Reasonably reproducible studies of ethylene formation thus become possible.

Although this paper is restricted to the relatively simple question of how ethylene is formed, the ethylene is one hydrocarbon product of a complex mixture, so it is necessary to describe briefly the products normally obtained from a ca. 2 : 1 v/v water/methanol feed over ZSM5 catalyst.

At the temperature (ca. 300°C) of 90–100% conversion to hydrocarbons, the ethylene yield is highest (ca. 25%). Further increase in temperature lowers the ethylene yield (to ca. 15% for a 30° increase). C_3 and C_4 hydrocarbons are each formed in 15–

20% yield. The C_4 product is a complex mixture of butenes and butanes. The C_3 product consists almost entirely of propylene at 90–100% conversion but the propane/propylene ratio increases, to ca. 40/60 over a 30° rise. Nonaromatic higher hydrocarbons (C_{5-7}) also comprise 15–20% of the product, but the most remarkable higher product is a mixture of xylenes (10–15% yield, increasing with temperature). A few percent of toluene and C_9 aromatics are formed, but very little benzene, ethane, or methane. This product distribution should be compared with that commonly reported for a neat methanol feed under conditions of complete conversion (*2*).

The temperature range of interest in the present work is that just below the temperature of complete conversion. Table 1 shows an increase in conversion from <1% to ca. 90% as the conversion temperature is increased from 291 to 300°C. We have observed the ca. 300°C temperature required for complete conversion to vary by as much as 20°C from one zeolite preparation to another and to vary to some extent with catalyst history. The remarkable and reproducible feature is that a very small temperature rise (here 9°C) causes an increase in the percentage conversion from a low value (1) to a high value (90).

This feature is undoubtedly related, as in the case of neat methanol feed, to the autocatalytic character of reaction. We have previously pointed out that the homologation/cracking mechanism can account for the autocatalysis of conversion of methanol to olefins of three or more carbon atoms. The explanation does not extend to ethylene formation.

Olefins and aromatic hydrocarbons are basic and can be protonated. Van der Waals bonding of these hydrocarbons to dimethyl ether is to be expected in the zeolite channels, and might facilitate proton transfer within a proton/hydrocarbon/dimethyl ether assembly. Such facilitation of proton transfer might contribute to the observed autocatalysis. In this context, it is worth noting that *p*-xylene vapor, added to the stream of nitrogen carrier gas in our experiments, lowers the temperature required for methanol conversion by 10° or more (*11*).

(*c*) *Deuteration Results and Their Mechanistic Significance*

The second significant feature shown in Table 1 is as follows. At 291°C, where conversion and ethylene yield are below 1%, the dimethyl ether (the dominant product from methanol at low conversion) is unlabelled by the deuterium of the D_2O. At 300°C, by contrast, where the ethylene yield is near maximum, the dimethyl ether is extensively deuterated. The correlation between ethylene formation (and overall conversion) and deuteration of the dimethyl ether suggests strongly that the deuteration and ethylene formation share a common rate-determining step. This step should lead to two facile competing steps: one the formation of a C–D bond in dimethyl ether, and the other the formation of a carbon–carbon bond.

O-Deuteration (and protonation) of dimethyl ether can be presumed (for example, on the basis of rapid attainment of equilibrium (1)) to be fast and reversible.

$$CH_3\text{-}O\text{-}CH_3 + D^+ \rightleftharpoons CH_3\text{-}O^+(D)\text{-}CH_3 \quad \textit{fast.} \qquad (5)$$

Deprotonation of a carbon atom by base (B) would then give an oxonium ylide.

$$CH_3\text{-}O^+(D)\text{-}CH_3 + B \rightleftharpoons CH_3\text{-}O^+(D)\text{-}CH_2^- + BH^+, \quad \textit{slow} \qquad (6)$$

We cannot specify the base (B) unambiguously, but refer to our discussion above of the existence of various bases in the zeolite under the conditions of aqueous methanol conversion. Reaction (6) involves breaking of a strong C–H bond by a weak base, and so must be slow. The resulting oxonium ylide could be expected to be reactive, and so should abstract D^+ from a deuterated acid rapidly. Reaction (7) depicts the abstraction of D from D_3O^+; it is the reverse of (6) for the case B = D_2O.

$$CH_3\text{-}O^+(D)\text{-}CH_2^- + D_3O^+ \rightarrow CH_3\text{-}O^+(D)\text{-}CH_2D + D_2O \quad \textit{fast.} \quad (7)$$

A Stevens-type rearrangement (8) of the oxonium ylide would also be expected to be fast, and the ethanol so produced should dehydrate to ethylene.

$$CH_3\text{-}O^+(D)\text{-}CH_2^- \rightarrow CH_3\text{-}CH_2\text{-}OD. \quad \textit{fast} \quad (8)$$

A mechanism of the type expressed in reactions (5)–(8) may, therefore, account in essence for our observation that deuteration of dimethyl ether coincides with ethylene formation. It is very similar to that already postulated by van den Berg *et al.* (*8*) and should also be compared with the carbene mechanism of Chang and Silvestri (*2*).

A dimethyl ether molecule may undergo the deuteration sequence (5)–(7) several times and so be several-fold deuterated (up to six times). The events may be well separated (if diffusion of the dimethyl ether occurs between successive deuterations), in which case we refer to single deuteration. Alternatively the slow step (6) may occur so readily at particular locations that there is little opportunity for diffusion between successive deuterations, in which case we refer to multiple deuteration. The fact that the concentration of D_3-labeled dimethyl ether in the 296° experiment of Table 1 is markedly higher than that of D_2-labeled dimethyl ether has to be taken as indicative of multiple deuteration.

Multiple deuteration is not surprising in view of the diffusion limitations within zeolite channels. It is worth noting that the aluminium content of ZSM-5 zeolite can vary widely (the SiO_2/Al_2O_3 ratio can range from about 20 : 1 to near infinity). Thus there may be substantial variations in Brönsted acidity from one unit cell to another within a ZSM-5 crystal (cf. von Ballmoos and Meier (*12*).

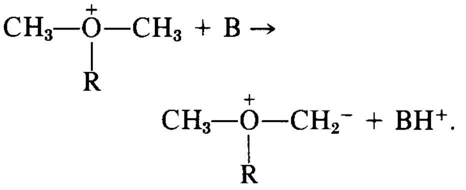
The observed pattern of deuteration of the dimethyl ether suggests a superposed pattern of single deuteration and triple deuteration. The triple deuteration indicates superficially that only one of the two methyl groups of a dimethyl ether molecule undergoes deuteration. However, the same result would be produced if a dimethyl ether molecule underwent complete deuteration, since equilibrium (1) is rapidly established and would result in the scrambling of methyl groups between dimethyl ether molecules (thus a mixture of fully deuterated and undeuterated dimethyl ether would give triply deuterated dimethyl ether). Multiple deuteration up to the D_6 level is very much more plausible than multiple deuteration up to the D_3 level.

Rearrangement (8), leading to ethylene, might compete with the C-deuteration step (7) either in the case of stepwise deuteration or in the case of multiple deuteration. In the former case we might expect the level of ethylene deuteration to broadly parallel that of dimethyl ether deuteration, which it does not.

If rearrangement (8) occurred to a significant extent only in the circumstances of multiple deuteration, then highly deuterated ethylene might be expected, and is indeed found. We do not suggest that the Stevens-type rearrangement is restricted to the circumstances of multiple exchange. It may simply be that, under the effective conditions within the zeolite channels, C-deuteration (7) is more rapid than rearrangement (8), even though both are fast reactions. Then rearrangement (8), leading to ethylene, competes poorly with deuteration (7) in single exchange and at low levels of multiple exchange. However, at higher levels of multiple deuteration, the chance of further deuteration is limited by the following considerations. The mole ratio of D_2O to methanol is $4\frac{1}{2}$: 1 in our experiments, and each mole of methanol necessarily gives a mole of H_2O at complete conversion, so that at complete conversion the water has a D/H ratio of 4.5 : 1 (less if allowance is made for the extensive deuteration–deprotonation of hydrocarbons of more than two carbon atoms—see Anderson *et al.* (*3*). However, at the higher levels of multiple deuteration, the rate of rearrangement (8) is in no way diminished. Hence rearrangement competes more effectively with further net deuteration for the more highly deuterated dimethyl ether molecules, and so the level of ethylene deuteration may be high compared with that of the dimethyl ether, as observed.

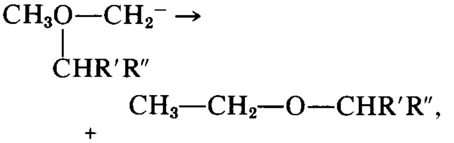
The oxonium ylide mechanism discussed above accounts for the coincidence of ethylene formation and deuteration of dimethyl ether, and for the deuteration data presented. It accounts for the autocatalysis only in so far as the olefinic and aromatic products are able to assist the proton transfer steps. It is of interest to speculate on variants of the mechanism which might provide alternative explanations of the autocatalysis.

The oxonium ylide does not necessarily have to be derived from protonated dimethyl ether. It might be derived from alkylated dimethyl ether:

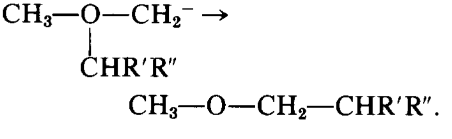


$$CH_3-\underset{\underset{R}{|}}{\overset{+}{O}}-CH_3 + B \rightarrow CH_3-\underset{\underset{R}{|}}{\overset{+}{O}}-CH_2^- + BH^+. \tag{9}$$

When R is a methyl group from methanol or dimethyl ether, the rearrangement still necessarily leads to ethylene. However, when R is an alkyl group derived from protonation of an olefin, there are two alternative Stevens-type rearrangements. One (10) leads to ethylene, and the other (11) to a new higher olefin.



$$CH_3\underset{\underset{CHR'R''}{|}}{\overset{+}{O}}-CH_2^- \rightarrow CH_3-CH_2-O-CHR'R'', \tag{10}$$



$$CH_3-\underset{\underset{CHR'R''}{|}}{\overset{+}{O}}-CH_2^- \rightarrow CH_3-O-CH_2-CHR'R''. \tag{11}$$

This mechanism would not only provide an explanation of the autocatalysis, but would also explain why ethylene is always accompanied by mixed higher olefins. It should be remembered that olefins higher than ethylene readily undergo both protonation and conversion to other olefins higher than ethylene (by oligomerization/cracking) on ZSM5 catalyst (*3*).

It is obviously not possible to define the nature of the oxonium ylides closely. Nor is it possible to assess the extent to which oxonium ylides account for methanol conversion broadly. What is clear is that some kind of oxonium ylide mechanism is consistent with the deuteration of dimethyl ether reported above. The carbonium ion mechanism of Kagi (*13*) (cf. Olah (*14*)) does not appear to accommodate the deuteration results.

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