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Response to Comments on the H-ZSM-5 Catalyzed Formation of Ethylene from Methanol

Before responding to the specific points raised by Mole (*1*), I find it necessary to restate our views regarding the source of ethylene produced from methanol, based on evidence presented both in our recent paper (*2*) and in an earlier publication (*3*).

The bulk of the ethylene produced from methanol (though not all) is derived by secondary reequilibration of higher olefins. It is only during a relatively short initiation phase, before sufficient olefins exist for the autocatalytic conversion (*4*), that ethylene is formed directly. This direct formation may involve oxonium ions (*5*) or carbenes (*6*) or a variety of other possibilities. This mode of ethylene formation, however, is responsible for producing only a very small fraction of the total ethylene normally observed. As soon as sufficient olefins exist, methylation of these olefins accounts for the bulk of the methanol conversion. Virtually all olefins, including ethylene, produced during this dominant autocatalytic phase, derive from repeated methylation, oligomerization, and cracking of higher olefins.

Incontrovertible evidence supporting this view includes the observations that the methanol reaction is autocatalytic and catalyzed by added olefins (*4*), carbon atoms which can be incorporated in the ethylene produced (*3*), and the failure to observe measurable amounts of ethylene from methanol even at partial conversions (*2*) under low partial pressure conditions (conditions shown to limit olefin reequilibration).

The ^{13}C-labeling experiments (*3*) we conducted established that, in the presence of added olefins and under a variety of conditions, the major portion of the ethylene produced was not formed directly, but was formed indirectly via addition of methanol to the olefins followed by cracking. We also showed that the fraction of doubly-labeled ethylene, presumably formed by direct coupling of methanol, was exaggerated by diffusion disguise caused by incomplete mixing of the olefins produced from methanol with the added olefin pool. Similarly, we found fully-labeled aromatics formed from [^{13}C]methanol even in the presence of excess toluene. Would one propose direct interaction of ten methanol molecules to produce durene? A similar desorption disguise in the production of aromatics from methanol at low temperatures was reported by Haag *et al.* (*8*).

The extent of this diffusion disguise was, furthermore, shown to be a function of catalyst crystal size and activity (*3*), as expected. High aluminum content and large crystal ZSM-5 catalysts, such as those used by Mole (*9*), would tend to exaggerate the apparent contribution of the direct pathway for ethylene formation.

The exchange of isotopic hydrogen into dimethyl ether, observed by Mole and others (*9, 10*), is not inconsistent with the propagation mechanism we have proposed. The exchange reaction is quite likely related to the initiation phase of the methanol conversion, possibly via the methyl carbenium ion–carbenoid (called ylide when associated with dimethyl ether) equilibrium suggested by Lee and Wu (*7*):

$$\begin{array}{ccc} CH_{3+} & \rightleftharpoons & :CH_2 + H^+ \\ \downarrow & & \downarrow \\ \text{propagation} & & \text{initiation} \end{array}$$

These workers also observed (*10, 11*) that as the methanol conversion increased from 20 to 60%, the deuterium exchange increased only slightly. This supports our contention that the exchange reaction, as well as the intermediates associated with it,

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occurs largely during the initiation phase of the reaction and is independent of the main autocatalytic propagation reaction responsible for most of the hydrocarbons formed from methanol.

The third point raised by Mole is most surprising. It is difficult to believe that aromatics play a major role in ethylene formation in the absence of added aromatics. Note that ethylene and higher olefins have been obtained under conditions where aromatics were not observed at all (*12*). The kinetic scheme delineated by Chang (*13*) depicts olefin formation long before, and independent of, aromatics formation. Significantly, in radioactive tracer studies (*14*), Hwu and Hightower failed to observe any radioactivity in the nonaromatic products formed from methanol in the presence of labeled benzene. Furthermore, one might expect methylation of olefins, especially isobutylene, to be substantially more rapid than aromatic methylation, thus leading to the propagation mechanism we have advocated. Acceleration of methanol conversion by aromatics may be predominantly a thermal effect caused by the exothermicity of the relatively facile aromatic methylation reaction, since even changes of only a few degrees have been shown to dramatically increase methanol conversion (*15*).

In Mole's letter, he refers to "conventional wisdom that cracking produces mainly C_{3+} hydrocarbons." We agree that under kinetic control, and at higher hydrocarbon partial pressure under thermodynamic control, mainly C_{3+} olefins are formed from heptene. We were able to observe significant ethylene formation from heptene only by operating at low pressures, and then only at contact times sufficiently long to allow primary olefin reequilibration. "Conventional wisdom" has been based on results obtained at higher pressures, where equilibrium values for ethylene are indeed low.

High equilibrium values for ethylene can be obtained from methanol at high temperatures and high dilution (*12*). At 425°C and 25 psia, a 5 : 1 molar mixture of water and methanol will produce at equilibrium 22 wt% ethylene at 25% conversion (to an 80% olefin-selective product). These conditions fall within the broad range disclosed in the reference (*16*) quoted by Mole.

The overall effect of water dilution is quite complicated. Ethylene selectivity is affected by diffusional effects (*17*) as we mentioned in our paper. These effects can be further influenced by water, which could magnify the differences in diffusion rates between ethylene, propylene, and higher olefins in acidic zeolites.

In summary, the methanol conversion mechanism we have advocated readily accounts for the absence of measurable ethylene, both at partial and total conversion, under the low pressure conditions we reported. No other published mechanism will do so.

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