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LETTERS TO THE EDITORS

Comments on the H-ZSM-5 Catalyzed Formation of Ethylene from Methanol or Higher Olefins

Dessau (*1*), in a recent study of the conversion of heptene-1 and of methanol to light olefins over H-ZSM-5 zeolite, considered "the mechanism of methanol conversion and ethylene formation." He concluded that ethylene "is formed by secondary re-equilibration of the primary olefinic products, propylene and butene," and that the mechanism for ethylene formation during a "rather limited initiation phase remains speculative and irrelevant to the overall mechanism of methanol conversion to hydrocarbons." It is, therefore, necessary to draw attention to various pieces of evidence, presented in earlier papers from this laboratory (*2, 3*), which indicate the mechanistic complexity of methanol conversion, and which are not consistent with Dessau's conclusions.

First the ^{13}C distribution in ethylene derived from aqueous mixtures of [^{13}C]methanol and unlabeled *n*-propanol (used as a convenient source of propylene) has been compared with various models (*2*). The best fit of the data was to a model in which the ethylene was obtained in part directly from two methanol molecules (contrary to Dessau's conclusion) and in part indirectly from species derived from both unlabeled *n*-propanol (i.e., propylene) and labeled methanol (consistent with Dessau's mechanism).

Second, exchange of isotopic hydrogen from water into dimethyl ether (*2*) has been observed and shown to be concurrent with the formation of deuterated ethylene and other deuterated olefins from methanol; no exchange occurs if no olefin is formed. An oxonium ylide mechanism (*4*) for ethylene formation explains this result.

Third, aromatic hydrocarbons play a cocatalytic role in methanol conversion to ethylene (Ref. (*3*) and references therein), and when ^{13}C-labeled benzene is utilized, significant incorporation of the ^{13}C label into ethylene occurs (*3, 5*).

Dessau's paper shows that ethylene is formed by olefin equilibration at low feed concentration (ca. 1 Torr), moderate space velocity (10^3 hr^{-1}), and high temperature, and in so doing draws attention once more (see also Ref. (*6*)) to formation of C_2 hydrocarbons by high-temperature cracking over ZSM-5 zeolite, despite conventional wisdom that cracking produces mainly C_{3+} hydrocarbons.

However, ethylene can be formed relatively selectively under quite different, milder conditions—for example, when "water diluent is co-fed with methanol and/or dimethyl ether . . . [and] . . . the hydrocarbon effluent contains about 25 to 40 wt% ethene" (*7*, see also Ref. (*2*)). At these relatively low temperatures and in the presence of water diluent, ethylene is neither readily formed from propylene nor highly reactive (*8*). It is obviously not a secondary product produced from higher olefins by olefin equilibration, but a primary product, which undergoes further reaction with greater difficulty than does propylene.

Since most of the methanol can be converted to hydrocarbon and water under these conditions, it is hard to regard what happens as "a rather limited initiation phase." It is also hard to dismiss the relevant mechanisms as speculative without proper consideration of the evidence (*2, 3*).

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