

## An Oft-Studied Reaction That May Never Have Been: Direct Catalytic Conversion of Methanol or Dimethyl Ether to Hydrocarbons on the Solid Acids HZSM-5 or HSAPO-34

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Since its discovery in 1977,<sup>1</sup> the conversion of methanol to olefins (MTO) and other hydrocarbons on microporous solid acids, especially the aluminosilicate HZSM-5 and more recently the silico-aluminophosphate HSAPO-34, has been one of the most often studied problems in catalysis. A recent review<sup>2</sup> identified more than 20 distinct mechanistic proposals for the reaction by which methanol or dimethyl ether (DME) somehow form the “first” C–C bond.<sup>3</sup> Some of these mechanisms can be grouped into classes based on whether the key intermediates are oxonium ylides, carbenes, carbocations, free radicals, or surface-bound alkoxy species. All of these direct routes for the conversion of methanol/DME to hydrocarbons involve the participation of two to four carbon atoms and the formation of either ethylene, propene, a butene (in a few proposals), or an oxygenate that immediately decomposes to ethylene or propene under reaction conditions. This long-standing, profound lack of consensus on the nature of the reaction hints at a problem.

A handful of papers considered indirect routes from methanol/DME to olefins. In 1983 Mole and co-workers reported that deliberately introduced toluene acted as a “cocatalyst” for methanol conversion on HZSM-5.<sup>4</sup> They proposed a mechanism by which methyl substituents on benzene rings underwent side-chain alkylation followed by olefin elimination. Kolboe later observed that the activity of either HZSM-5 or HSAPO-34 for methanol conversion was dependent upon the catalysts’ exposure to ethylene or ethanol and that hydrocarbon products from methanol incorporated some carbon label from ethanol.<sup>5</sup> Kolboe et al. proposed that a “hydrocarbon pool” of unspecified structure formed in the catalysts and that this undergoes methylation and olefin elimination. Recently we applied *in situ* NMR, isotope tracing, and theoretical chemistry to methanol conversion chemistry and identified specific hydrocarbon pool species, cyclic carbenium ions and methylbenzenes.<sup>6</sup> We proposed a vestigial role for the direct route as an “induction reaction” that inefficiently transforms an organic-free catalyst into a working catalyst.

We realized that if the rate of the direct reaction was very low it might in fact be zero. Here we report very careful experimental work using highly purified reagents and catalysts that shows that methanol/DME is not reactive on either of the two most important catalysts in the absence of a primordial hydrocarbon pool. The oft-studied direct reaction, which has even prompted a number of theoretical investigations, is an artifact of impurities in the methanol, incomplete combustion of organics on the catalyst, trace impurities in the carrier gas, or other sources of contamination.

We found that even reagent methanol samples contain more than enough organic impurities to create a hydrocarbon pool on microporous solid acids. For example, Mallinckrodt AR (ACS, low

acetone) methanol contained 36 ppm ethanol (GC, FID detector). Some reagent samples also contained acetone or other precursors to cyclic hydrocarbon species. We purified Spectrum Unisolv methanol (99.99%) through a series of distillations including fractional distillation on a four-foot column operated at an 8:1 recycle split. The purified methanol sample used here (fractionally distilled methanol) was 1 ppm ethanol and ca. 11 ppm total organic impurities.

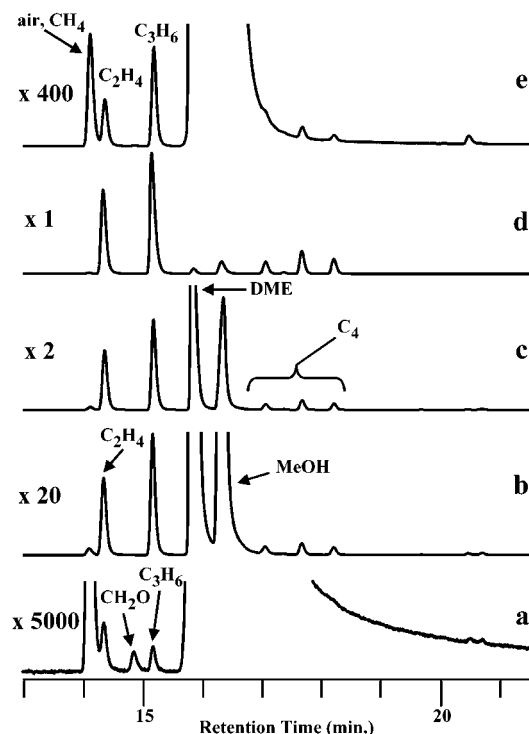
Given that tens of liters of He gas pass over a catalyst bed prior to a typical MTO catalytic study, even ultrahigh-purity carrier gas (99.999%) is a potential source of contamination. We installed a two-stage hydrocarbon trap before our reactor: first an Alltech model 7008 commercial trap rated at <3 ppb nonmethane hydrocarbon outflow and then a home-built cryotrap (77 K) packed with activated zeolite HY pellets.

A third and quite serious source of hydrocarbon contamination proved to be the calcined solid acid itself. Using acid digestion we found very low but detectable amounts of phenanthrene, naphthalene, and other aromatics after conventional calcination procedures in which HSAPO-34 was heated in static air at 600 °C for several hours. We added a second, rigorous calcination in the reactor with flowing 100% air (also at 600 °C) prior to switching to purified He for catalyst testing. We used X-ray powder diffraction to verify that the second calcination did not reduce crystallinity.

HSAPO-34<sup>7</sup> forms ethylene and propene with high selectivity. Aromatic hydrocarbons, even benzene, cannot escape the cages of this catalyst once formed from impurities in methanol or by secondary reactions of olefinic products. Thus, a catalyst bed of HSAPO-34 retains all hydrocarbon pool species formed during its lifetime (although they may age into less active polycyclic rings). Figure 1a shows that the first pulse of fractionally distilled methanol onto rigorously calcined HSAPO-34 resulted in only 26 ppm yield of hydrocarbons in the product stream.<sup>8</sup> Hydrocarbon yields greatly increased for both the second (Figure 1b) and third (Figure 1c) methanol pulses, and conversion approached quantitative once this catalyst bed contained a significant hydrocarbon pool (Figure 1d). In Figure 1e we highlight the role of hydrocarbon pool species formed and retained on the catalyst during a conventional calcination procedure. The first pulse of fractionally distilled methanol onto this catalyst bed achieved 590 ppm yield, a factor of 20 greater than that for an identical experiment on a rigorously calcined catalyst.

Olefins are very reactive on zeolite HZSM-5<sup>9</sup> and readily form cyclic cations, aromatics, and alkanes. Most methylbenzenes readily exit HZSM-5, but large aromatic products and cyclopentenyl carbenium ions can persist in the catalyst and serve as reaction centers. Figure 2 reports GC (FID detector) analyses of product streams (C<sub>2</sub> to C<sub>5</sub> shown) sampled 2.4 s after injections of methanol onto HZSM-5 catalyst beds. Figure 2, a and b, depicts analyses from consecutive 12.5  $\mu$ L injections of fractionally distilled

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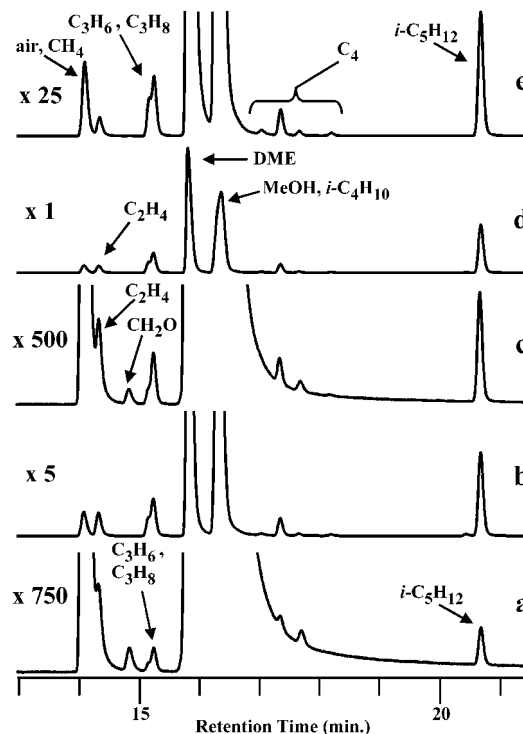
**Figure 1.** GC (FID detector) analyses of the product streams sampled 2.4 s after pulsing 12.5  $\mu\text{L}$  methanol onto 300 mg beds of HSAPO-34 with purified He flowing at 10  $\text{cm}^3\text{s}^{-1}$ . (a–d) are from a single bed of rigorously calcined HSAPO-34 following a series of pulses of fractionally distilled methanol delivered in 30 min intervals. (a) Following the first pulse, the total yield of volatile hydrocarbons was ca. 0.0026% (26 ppm). (b) Following a second, identical methanol pulse the yield of volatile hydrocarbon products greatly increased to 1.5%. (c) Following a third, identical methanol pulse the hydrocarbon yield further increased to 10% as a result of the growing hydrocarbon pool. (d) This catalyst bed was reacted with an additional 200  $\mu\text{L}$  of methanol to create a larger hydrocarbon pool. Thirty minutes later 12.5  $\mu\text{L}$  of methanol was pulsed, and the product stream showed nearly complete conversion. (e) Following the first pulse of fractionally distilled methanol onto a fresh HSAPO-34 bed prepared using the standard calcination procedure but not the more rigorous second calcination. The volatile hydrocarbon yield, 590 ppm, was substantially higher without rigorous calcination, cf. (a). Small amounts of methane and CO are formed on the reactor wall.

methanol onto a catalyst bed prepared by rigorous calcination. Conversion to light hydrocarbons was only ca. 0.02% following the first methanol pulse, but much greater after the second pulse. The same results were obtained using a commercial HZSM-5 with 30% alumina binder.

When Mallinckrodt AR methanol (36 ppm ethanol) was substituted for fractionally distilled methanol, the hydrocarbon yields were considerably higher after both the first and second pulses (Figure 2, c and d). This underscores the role of feed impurities in the creation of a hydrocarbon pool. Figure 2e demonstrates that incomplete combustion of organics during calcination can also contribute an initial hydrocarbon pool on HZSM-5.

We conclude that if there is a direct route from methanol/DME to hydrocarbons at 375  $^{\circ}\text{C}$  on any of the catalysts we studied, it operates at a rate so low as to be eclipsed by even trace impurities in the methanol feed, the catalyst, or the carrier gas. The indirect route (hydrocarbon pool) is the only established mechanism for this chemistry. Impurities may also play important roles in other reactions catalyzed by solid acids as was proposed many years ago for alkane cracking by Weisz<sup>10</sup> and others.<sup>11</sup>

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**Figure 2.** GC (FID detector) analyses of the product streams sampled 2.4 s after pulsing 12.5  $\mu\text{L}$  methanol onto 300-mg catalyst beds of HZSM-5 with purified He flowing at 10  $\text{cm}^3\text{s}^{-1}$ . With the exception of (e), all catalyst beds were prepared using a second, rigorous calcination. (a) Following a first pulse of fractionally distilled methanol. The total yield of volatile hydrocarbons was ca. 240 ppm. (b) Following a second, identical pulse yield greatly increased to 7.9%. (c) Following a first pulse of Mallinckrodt AR methanol (36 ppm ethanol). The total yield of volatile hydrocarbons was 650 ppm. (d) Following a second, identical pulse of Mallinckrodt AR methanol the yield increased to 34%. (e) Following injection of fractionally distilled methanol onto a catalyst bed prepared using only standard calcination. The yield of volatile hydrocarbons was 1.4%, cf. Figure 1a.

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- A Hewlett-Packard model 6890 gas chromatograph with flame-ionization detector was used to analyze gases sampled from the reactor product streams using a Valco valve. The column was 150 m dh150 (Supelco) operated isothermally at 323 K. The identities of all products were verified using mass spectrometry.
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