Methanol-to-Olefin Process

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Experimental Evidence from H/D Exchange Studies for the Failure of Direct C–C Coupling Mechanisms in the Methanol-to-Olefin Process Catalyzed by HSAPO-34**

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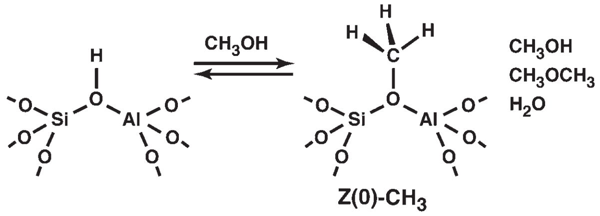
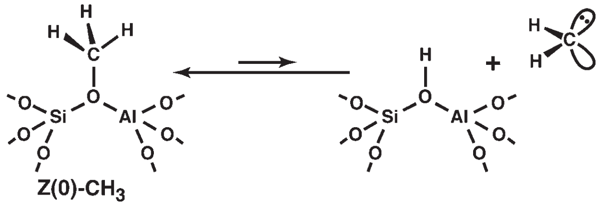
The conversion of methanol to ethylene and propene on microporous solid acid catalysts[1,2] such as the silicoaluminophosphate HSAPO-34 at temperatures of 573 K and above remains a stimulus to mechanistic progress in heterogeneous catalysis. The general features of this reaction on a working catalyst (i.e., following a kinetic induction period) are widely accepted as a hydrocarbon pool mechanism on the basis of experimental[3–6] and theoretical work.[7,8] Prior to recognition of the hydrocarbon pool mechanism, speculation centered on any of a dozen or more "direct" mechanisms in which, typically, an activated single carbon fragment reacted with methanol or dimethyl ether (DME) to form ethylene, methyl ethyl ether, or some other species with a "first" carbon–carbon bond.[1] Note that there are still important additional contributions that theory can make, such as a thorough comparison of detailed hydrocarbon pool reaction steps to putative direct reaction steps. Previously,[9] we used highly purified reagents to call into question whether "direct" mechanisms occur at all, even at very low rates during the kinetic induction period. In this view, the original hydrocarbon pool forms from impurities rather than a "direct" route, and a mature hydrocarbon pool then develops from side reactions of propene or other products.

Very recently, a pair of theoretical papers[10,11] examined essentially all direct pathways from methanol to species with a first C–C bond. Those studies concluded that no combination of direct steps exist that is capable of linking methanol with ethylene, even at a temperature of 720 K. Some of the direct routes examined involved the intermediacy of framework-bound methoxy groups, Z(O)-CH_3, which indisputably form from a fraction of acid sites in the equilibration of methanol, dimethyl ether, and water on the catalyst (Scheme 1).[6,12] The ease with which Z(O)-CH_3 can be observed by spectroscopy has probably contributed to the attraction of framework methoxy groups as key intermediates in proposals of direct reactions of methanol on HSAPO-34[13] or methyl halides on basic catalysts.[14]



Scheme 1. Equilibration of methanol over framework acid sites in the MTO catalyst, HSAPO-34.

In their theoretical study,[11] Waroquier and co-workers reject equilibration of Z(O)-CH_3 with carbene (Scheme 2) as



Scheme 2. Putative dissociation of Z(O)-CH_3 to carbene. Carbene could also insert into an O–D bond[15] to form Z(O)-CH_2D, and H/D exchange would be evident.

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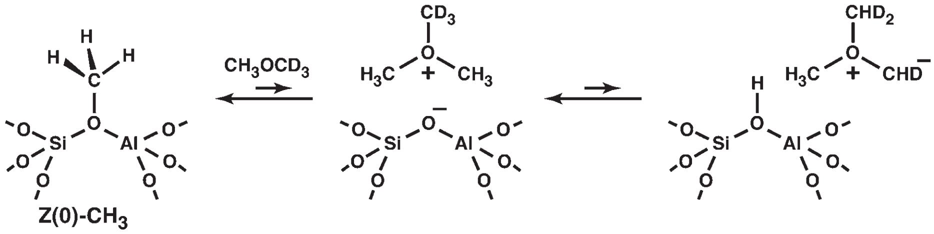
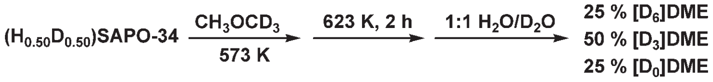
a possible direct route owing to a theoretical barrier of 242.1 kJ mol^{-1} and a theoretical rate constant of 5.3×10^{-7} at 720 K (reaction J1 in reference [11]). A second possibility involving the conversion of Z(O)-CH_3 and dimethyl ether to trimethyloxonium ylide (Scheme 3, reaction X1 and analogous reaction X2 in reference [11]) was also shown not to exist.



Scheme 3. Putative formation of trimethyloxonium ylide from Z(O)-CH_3 and [D_3]DME. Exchange of H/D labels would be facile if the ylide formed at all.

As all possible routes from Z(O)-CH_3 to species with a C–C bond must involve C–H bond activation, we devised a simple and conclusive test of Scheme 2 and, by extension, many other direct reaction mechanisms, based on the measurement of H/D exchange between Z(O)-CH_3 and Z(O)-CD_3 groups that coexist on the catalyst. Note that observation of exchange would not prove any of these mechanisms, but the opposite would be decisive.

The essence of our simple experiment is shown in Scheme 4. By pulsing a particular isotopomer of [D_3]DME (CH_3OCD_3) onto the preferred methanol-to-olefin (MTO) catalyst, HSAPO-34, at 573 K we were able to convert about 30 % of the acid sites in a catalyst bed to methoxy groups, equally Z(O)-CH_3 and Z(O)-CD_3. For the experiment depicted in Scheme 4 we raised the reactor temperature to 623 K and gave the intimate mixture of Z(O)-CH_3 and Z(O)-CD_3 two hours to exchange labels, prior to sweeping the methyl groups out of the catalyst as mixed isotopomers of [D_n]DME using a pulse of HOD (i.e., 50 % D_2O). To ensure an equal balance of hydrogen and deuterium, the catalyst bed was also first treated with 50 % D_2O prior to activation and formation of methoxy groups. As with our previous work,[9] the use of highly purified reagents strongly suppressed the formation of hydrocarbons in these experiments.



$$(H_{0.50}D_{0.50})\text{SAPO-34} \xrightarrow[573\ K]{CH_3OCD_3} \xrightarrow{623\ K,\ 2\ h} \xrightarrow{1{:}1\ H_2O/D_2O} \begin{matrix} 25\ \%\ [D_6]\text{DME} \\ 50\ \%\ [D_3]\text{DME} \\ 25\ \%\ [D_0]\text{DME} \end{matrix}$$

Scheme 4. Formation of framework-bound methoxy groups and their removal without H/D exchange.

The mixture of [D_n]DME isotopomers released from the catalyst was quantified using online GC-MS. Figure 1 reports three hypothetical, simulated ion mass distributions for such an experiment, corresponding to interesting exchange conditions. Figure 1 a shows the case of no exchange. As suggested in Scheme 4, a distribution of 25 % [D_0]DME, 50 % [D_3]DME, and 25 % [D_6]DME arises from the chance pairing of equal amounts of Z(O)-CH_3 and Z(O)-CD_3, and the absence of C–H activation is reflected in the absence of [D_1], [D_2], [D_4], and [D_5] isotopomers. Figure 1 b is the opposite case, with complete, random H/D exchange resulting in a statistical distribution of all isotopomers and a very characteristic mass pattern. Figure 1 c shows the case of blending 90 % no exchange and 10 % complete exchange, allowing for the possibility of exchange at a hypothetical "minority site". This case demonstrates the accuracy of our fits—HSAPO-34 is a highly uniform material and there is no evidence of any site diversity. The experimental mass pattern observed for the experiment in Scheme 4 as well as the fit to the data are shown in

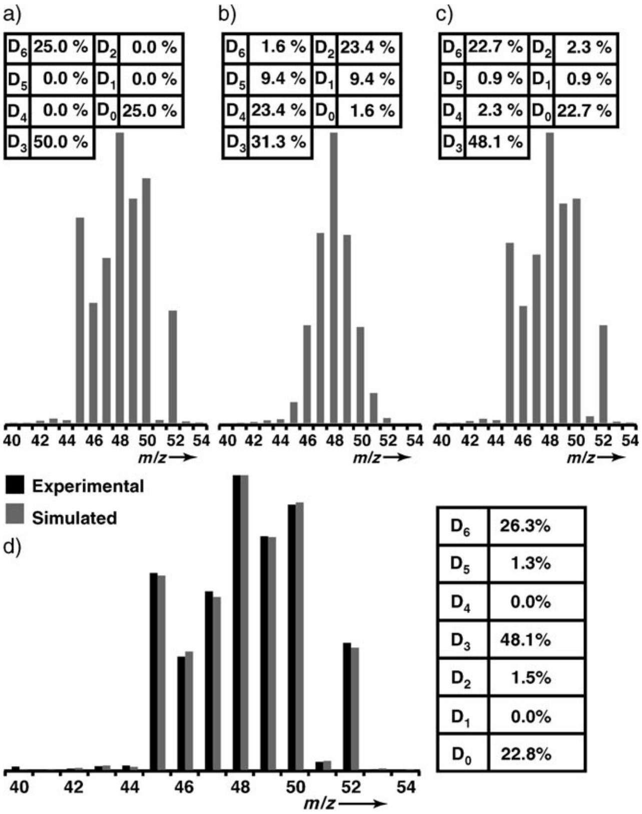


Figure 1. Ion mass distributions for specific mixtures of partially deuterated dimethyl ether, modeling the experiment suggested in Scheme 4. a) Simulated distribution for a mixture of 25 % [D_0]DME, 50% [D_3]DME, and 25 % [D_6]DME (i.e., the case of no H/D exchange beyond recombination of intact methyl and [D_3]methyl groups to dimethyl ether). b) Simulated distribution for complete randomization of hydrogen and deuterium by C–H bond activation. c) Simulated distribution assuming that only 10% of methoxy groups undergo complete exchange. d) Experimental distribution (and best-fit simulation) for dimethyl ether liberated after 120 minutes at 623 K from a catalyst bed deuterated to 50% and then treated with 0.50 equivalents of CH_3OCD_3 to form equal concentrations of [D_0]methoxy and [D_3]methoxy species. It is estimated that our detection limit for methoxy H/D exchange corresponds to 1 % of the acid sites in the catalyst bed. The fit in Figure 1 d is in excellent agreement with experimental data and shows no evidence of H/D exchange whatsoever.

Figure 1 d. The experimental data in Figure 1 d are in outstanding agreement with the prediction for no H/D exchange in Figure 1 a. Indeed, measurements performed at various times and temperatures (see Table 1) show that the low entries for [D$_5$]DME and [D$_2$]DME in Figure 1 d are fitting errors caused by minor variations in the experimental spectra and constraints in the model to preclude negative concentrations. The upper limit on the rate constant for the process in Scheme 2 (J1 in reference [11]) at 623 K is estimated to be 2×10^{-6}, but it could also be much lower.

Table 1: H/D exchange as a function of time in framework-bound methoxy groups on H$_{0.50}$D$_{0.50}$SAPO-34.

[D$_n$]DME	Distribution [%] at various times and temperatures					
	6 min, 573 K	15 min, 573 K	30 min, 573 K	60 min, 573 K	120 min, 573 K	120 min, 623 K
[D$_6$]	26.5	26.8	26.9	26.9	26.9	26.3
[D$_5$]	1.4	1.3	1.3	0.8	0.6	1.3
[D$_4$]	0.3	0.0	0.0	0.0	0.3	0.0
[D$_3$]	48.0	48.4	48.2	48.7	49.1	48.1
[D$_2$]	1.5	1.0	1.4	0.7	1.0	1.5
[D$_1$]	0.0	0.0	0.0	0.0	0.0	0.0
[D$_0$]	22.4	22.5	22.2	22.9	22.2	22.8

We also used GC-MS to determine that neither the methanol or dimethyl ether that exit the reactor in the seconds following the CH$_3$OCD$_3$ pulse showed unexpected isotope exchange. Hence, methoxy groups are not deprotonated by methanol, dimethyl ether, or water at 573 K. Indeed, these observations show that C–H bonds are not broken or made in any reaction step that is reversibly coupled to methoxy formation (see Scheme 3, or either X1 or X2 in reference [11]).

We conclude that the only valid mechanisms for the methanol-to-olefin conversion are hydrocarbon pool mechanisms that describe primary synthesis of olefins on organic reaction centers, such as methylbenzenes, coupled with well-known secondary reactions of olefins. This is true not only for a working catalyst but also for initiation reactions during the kinetic induction period. All conceivable direct mechanisms based on or in equilibrium with the formation of Z(O)-CH$_3$ are invalidated by the failure of framework-bound methoxy groups to undergo H/D exchange at high temperatures. In agreement with recent theoretical studies, our experimental studies preclude both the carbene route (Scheme 2) and the methoxonium ylide route (Scheme 3). The conclusion of both theory and experiment is that the direct mechanisms fail, and chance introduction of a primordial hydrocarbon pool is the only mechanism for MTO initiation in agreement with these findings. The present work in combination with references [10] and [11] disproves the central claims of reference [13] that were recently reiterated in reference [16].

Experimental Section

HSAPO-34 was synthesized using standard procedures,[17] followed by calcination at 873 K. [D$_3$]DME (specifically CH$_3$OCD$_3$) was obtained from Cambridge isotopes (lot number R-444, PSO 4C-117), as was D$_2$O (99.9 % deuterium content).

See Supporting Information for a schematic and detailed description of our reactor. We used 300-mg catalyst beds of HSAPO-34 catalyst, rigorously calcined (873 K, 100 standard cubic centimeters per minute (sccm) flowing air) for 1 h just prior to use. The carrier gas was then switched to flowing He (600 sccm), and the temperature was lowered to 648 K. Then, three pulses (3.3 equiv, 20 μL) of 50 % D$_2$O in H$_2$O were applied at five-minute intervals to bring the catalyst bed to 50 % deuteration. The catalyst bed was held at 648 K with He gas flow for 30 minutes to ensure complete removal of water. At 573 K we loaded the catalyst with an equimolar mixture of [H$_3$]- and [D$_3$]methoxy groups by pulsing two aliquots (0.25 equiv per aliquot) of CH$_3$OCD$_3$ onto the catalyst bed. The reactor temperature was then immediately raised to 623 K and gas flow was maintained for 2 hours (the temperature was lowered back to 573 K just prior to the end of this period), or the temperature was maintained at 573 K for a variable time between 6 minutes and 2 hours, before hydrolyzing the chemisorbed methoxy species with a single pulse (5 equiv) of 50 % D$_2$O in H$_2$O to liberate dimethyl ether for isotopic analysis by GC-MS. (Note: DME was chosen for this analysis to avoid the complication of the readily exchangeable hydroxy proton of methanol; i.e. CH$_3$OD versus CH$_2$DOH.)

An Agilent gas chromatograph equipped with dual 50-m Supelco DH columns and both mass spectrometric and flame-ionization detectors (FID) was used to analyze the reactor effluent gases. The temperarture of the oven was held at 308 K (isothermal). The mass spectrometer was used to obtain isotope distributions as needed, while the FID provided quantified peak integrations (using published response factors) as well as significantly lower detection limits.

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