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# The Rise and Fall of Direct Mechanisms in Methanol-to-Olefin Catalysis: An Overview of Theoretical Contributions

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Over the past 30 years, the methanol-to-olefin (MTO) process on acidic zeolites has been subject to a vast number of studies from both industrial and academic researchers, leading to numerous controversies regarding the most probable reaction mechanism. Improvement of computational facilities during the past decade led to a sudden boost of theoretical contributions that, when considered individually, all seemed to provide reasonable evidence for partial pathways of the commonly proposed direct mechanisms. Not only the reactions suggested by experimental studies were investigated, but in addition novel potential routes were discovered by theoreticians as well. However, when all of the individual reactions scattered throughout the literature were recently combined, theoretically obtained rate coefficients turned out to show the exact opposite, that is, the complete failure of the direct mechanisms to produce ethylene from methanol only. In this paper, we give a detailed overview of the theoretical contributions that initially supported the direct mechanism proposal, but which finally culminated in its demise.

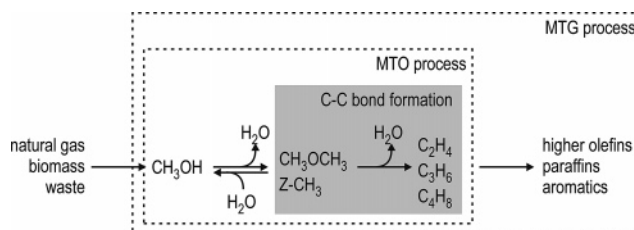
## Introduction

Light olefins, which are vital components for the petrochemical industry, are traditionally obtained through the refinement of crude oil. However, the rapidly increasing demand for oil-based chemicals calls for the development of new technologies based on alternative natural sources. Among these processes, the zeolite-catalyzed methanol-to-hydrocarbons (MTH) technology<sup>1</sup> is one of the most promising as well as being currently ready for commercial use. MTH conversion starts from methanol, which on its turn can be made from synthesis gas ( $\text{CO} + \text{H}_2$ ), formed by steam re-forming of natural gas, or even through conversion of any gasifiable carbonaceous material like biomass or waste. Although, in principle, bio-methanol could be used directly as motor fuel, MTH technology allows upgrading of bio-methanol to other fuels and even to chemicals in general.

Scheme 1 shows the catalytic conversion of methanol to a pre-equilibrium mixture containing dimethyl ether (DME) and water. This mixture can then be processed to olefins (methanol-to-olefins: MTO) or even further to high-octane gasoline (methanol-to-gasoline: MTG). Through this technology, methanol provides an excellent feedstock for the entire petrochemical industry: one could make almost anything out of methanol that can currently be made out of crude oil. In this paper, we will focus entirely on the MTO process, which is also assumed to initiate MTG conversion.

Quite remarkably, for more than 30 years the actual mechanism of the conversion of methanol to olefins in acidic zeolites has been the source of considerable debate, fueled by countless different and often conflicting propositions. The trickiest step to elucidate has always been the formation of the first carbon–carbon bond, for which more than 20 distinct mechanisms have been proposed.<sup>1</sup> Speculation mainly centered on mechanisms based on the “direct” formation of small olefins from only

**Scheme 1. Conversion of Natural Gas, Biomass, or Waste to Fuels and Chemicals through the Methanol-to-Olefin Process (Z = Zeolite)**



methanol, dimethyl ether, and other single-carbon derivatives.<sup>2,3</sup> Even though current beliefs are steadily shifting toward alternative “hydrocarbon pool” proposals,<sup>4</sup> the direct mechanisms have received the most widespread attention, both from experiment and from theory.

While experimental methods are often impractical for evaluating individual reaction steps, theoretical methods are ideally suited for uncovering the underlying mechanism of the MTO process. Theoretical calculations have experienced a huge boost over the past decade, mainly because of the development of rapid yet highly accurate methods such as density functional theory (DFT), improved parallelization algorithms, and increased computing power. Over the years, not only have many experimentally suggested mechanisms been intensively tested by theoretical calculations, but numerous new routes have sprouted from theoretician’s minds as well. In this paper, we aim to give a complete and detailed overview of all of the theoretical contributions that, taken separately, initially supported the direct mechanism concept in MTO chemistry, but when considered in their entirety, also finally led to its downfall. Although still not universally accepted, this failure is in agreement with recent experimental observations.<sup>5</sup>

Until recently, theoretical calculations on the direct mechanisms tended to be fragmentary and severely scattered. Moreover, straightforward comparison was cumbersome due to the wide variety of methods employed. Only a handful of papers suggested and compared multiple direct routes,<sup>2,3</sup> but these were (due to historical reasons) limited to low level of theory

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calculations on extremely small 1T/3T zeolite clusters, and they formed a nowhere near to complete survey. Furthermore, the focus was always solely on theoretical reaction barriers, rather than reaction rate coefficients, which combine both thermodynamic and entropic contributions. While the mere existence of individual direct reactions demonstrated in many theoretical papers was always considered strong evidence for the direct mechanism proposal, there was never a theoretical guarantee that the direct mechanisms came together to form a complete route that actually proceeds under reaction conditions.

To resolve this complex issue, we proposed an extensive reaction scheme (Scheme 2) in a recent communication,<sup>6</sup> tying together a large variety of possible direct reactions and even including several previously overlooked, parallel pathways. On the basis of not only reaction barriers at 0 K but also rate coefficients at 720 K (obtained from classical transition state theory) at the 5T level, we were able to deduce which stable intermediates are formed directly, and where bottlenecks in the direct mechanism proposal lie. In this paper, we will focus on the most deep-rooted direct mechanism proposals, the onium ylide, carbene, and methane-formaldehyde routes.

### Computational Details

Zeolites are bulky materials and contain an enormous number of atoms, which impedes the search for methods that adequately describe these complex systems. New force fields for zeolites are constantly developed, allowing rapid optimization of almost any zeolite framework structure. However, these force fields are useless when describing bond breaking and bond formation. Classical force fields are thus incapable of modeling chemical reactions, and a quantum-mechanically (QM) based treatment of the electronic many-body problem is essential. Because of the enormous computational cost of current QM methods, especially for extended systems like zeolites, this has led to new developments in computational chemistry, which all attempt to provide an excellent description of chemical reactivity at a reasonable computational cost. In this paragraph, we will give a brief overview of three such methods that have been commonly applied in zeolite chemistry and the MTO process in particular.

The cluster technique is the simplest and most widespread method used to model reactions in zeolites. In this approach, the chemically active part is just cut from the zeolite framework. As this involves the breaking of several silicon–oxygen bonds, this cluster would be chemically unstable, were it not for additional hydrogen atoms placed to saturate the dangling bonds. Figure 1a shows both a silicon-free 1T cluster with H-termination on the oxygen atoms and a larger 5T cluster with H termination on the silicon atoms. For zeolites containing ring structures like CHA, a ring-shaped cluster is often used. The main advantage of this method is the limited amount of atoms that are taken into account. This permits the use of highly accurate levels of theory within reasonable time. On the other hand, it is clear that the cluster method does not guarantee a complete description of the system, especially not when zeolite framework effects play a crucial role on reaction kinetics. In a previous paper, we compared small cluster results to more advanced techniques and found that even in the small cluster approach energy barriers are generally well reproduced. Only for a very limited number of reactions where charged intermediates are formed is a larger model required to obtain correct reaction barriers.<sup>7</sup>

Ideally, the zeolite cluster would be extended until all necessary framework effects are taken into account. For these

clusters that are consequently too large to be fully described at a high QM level, a “divide and conquer” strategy provides optimal results: the relatively small acid site and guest-molecules are treated at the necessary high QM level (high-level or HL region), while the larger surrounding framework (which does not actively participate in the reaction) can be described at a computationally much faster low QM level or even a force-field (low-level or LL region). This separation of the system is demonstrated on a 46T cluster (a HL 5 T-cluster and a LL 41 T-cluster) cut from H-ZSM5 in Figure 1b.<sup>7,8</sup> The ONIOM method as currently implemented in the Gaussian software package<sup>9</sup> is an example of a hybrid HL/LL method.

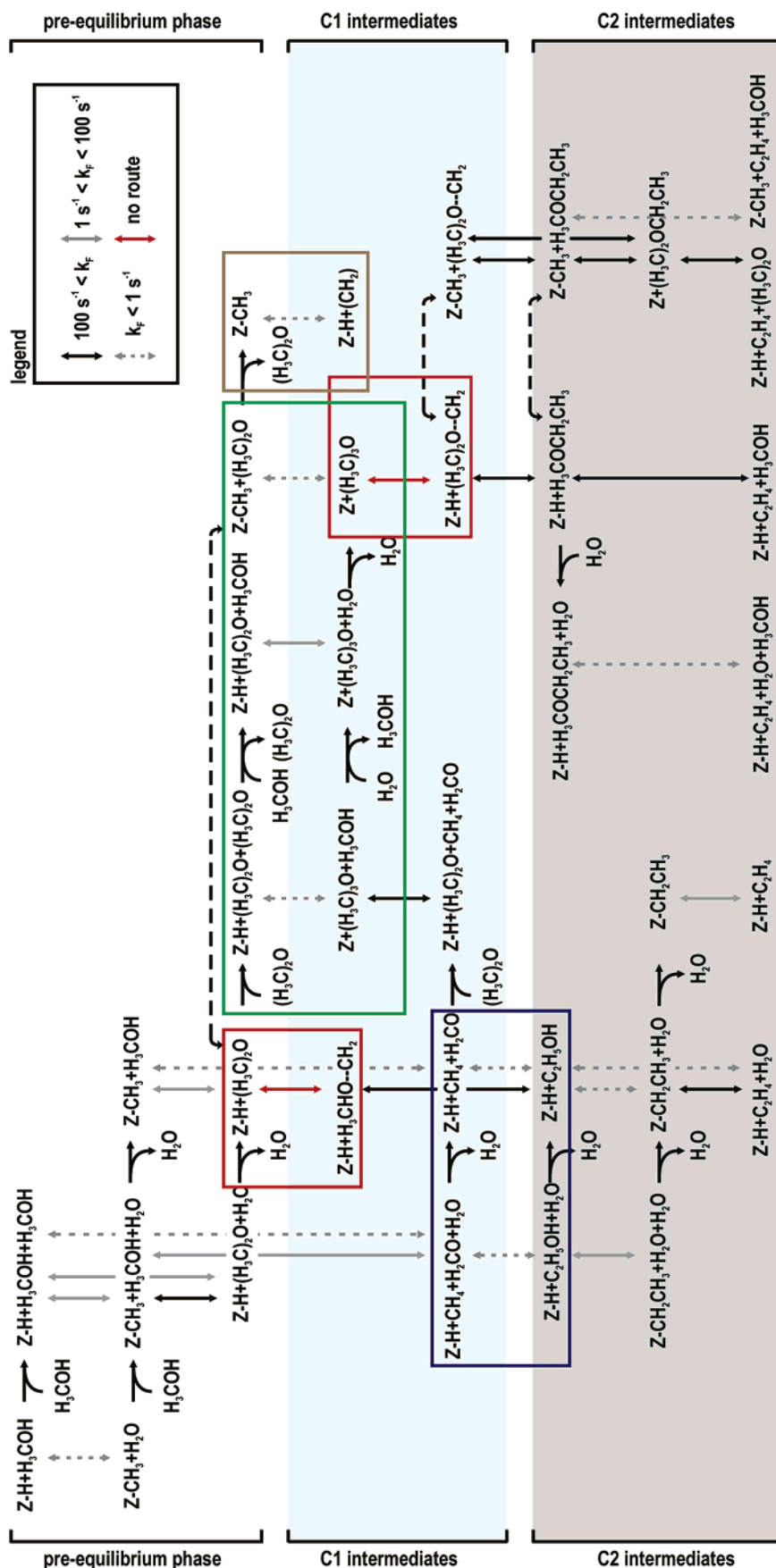
Finally, fully periodic QM software codes would seem to provide the most natural description of a zeolite system. However, the industrially most important zeolites are often built from rather large unit cells: for example, the unit cell of ZSM-5 contains no less than 288 atoms. The corresponding computational cost is too high for practical purposes, which is the main reason why periodic calculations on zeolites are currently still limited to systems with very small unit cells like CHA, as illustrated in Figure 1c, and will not be considered in this paper.

All calculated numerical values reported in this paper were obtained through density functional theory (DFT) calculations with the B3LYP functional within the Gaussian 03 software package.<sup>9</sup> Initial calculations were performed on frequently used pentatetrahedral (5T) clusters (Figure 1a). For certain key reaction steps where charged intermediates are formed, this approach was extended to a 5T high-level B3LYP cluster embedded in a 41T low-level QM cluster at the HF//MNDO level<sup>7,8</sup> using the ONIOM approach to include the bulk electrostatic effects induced by the zeolite framework. This 46T model (illustrated in Figure 1b), which was cut from the MFI crystallographic structure, is considered to be large enough to cover all important framework effects on both the active site and the adsorbate.

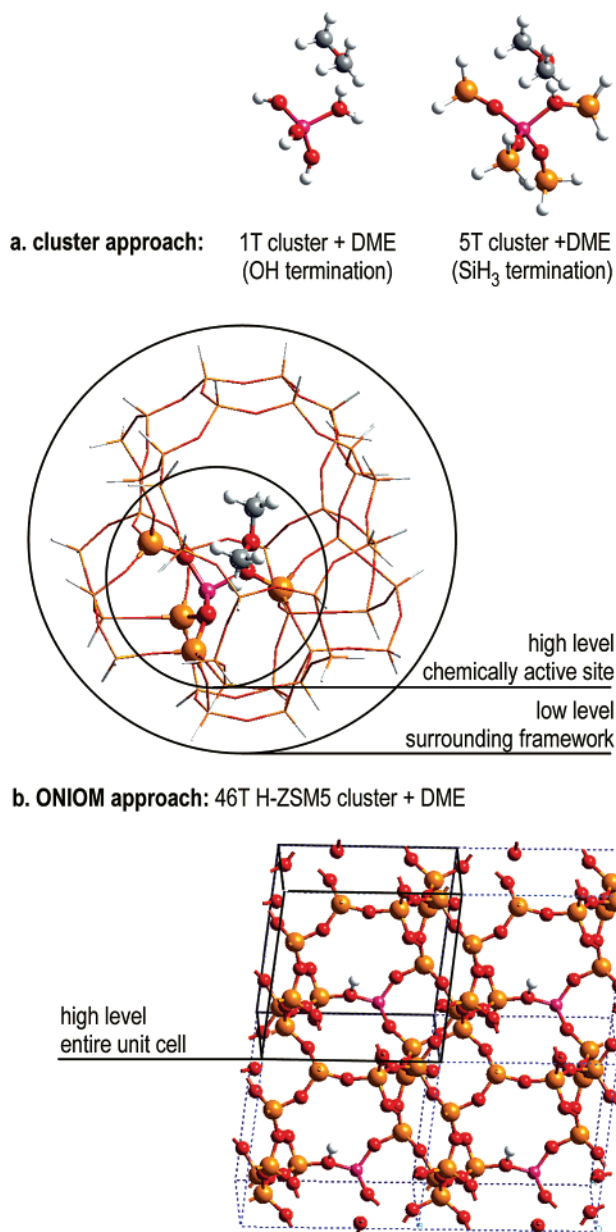
### Results and Discussion

Our results confirm the well-documented first step, which is the development of a pre-equilibrium, as well as several other C1-species. Our work identifies, however, three bottlenecks, which prevent direct carbon–carbon coupling of these C1 species to C2-species.

**Pre-equilibrium Phase.** As shown in Scheme 1, the conversion of methanol is known to start with rapid dehydration to DME. This step proceeds either via an intermediate methoxide species Z-CH<sub>3</sub> and methanol or through co-reaction of a methanol dimer, as presented in the top left corner of Scheme 2. Single molecular dehydration of methanol is prohibited, but a two-step pathway is facilitated by methanol or water successively lowering reaction barriers, not as spectator or solvating molecules, but rather as “assisting molecules”, allowing for more favorable transition-state geometries. This first pre-equilibrium phase in the MTO-process has been extremely well-documented from a theoretical viewpoint, ranging from very small, yet pioneering cluster calculations by Zicovich-Wilson et al.,<sup>10</sup> Sinclair et al.,<sup>11</sup> and Blaszkowski et al.<sup>12</sup> to more recent fully periodic DFT calculations by Payne and co-workers.<sup>13–15</sup> All studies revealed similar mechanisms independent of the method used, and this pre-equilibrium phase is currently very well understood. From our calculated rate coefficients using the 5T approach in Table 1, it is clear that especially the steps with assisting molecules have higher rate coefficients and both dimethyl ether and framework-bound methoxide groups will be formed. This is in perfect accordance with the experimental

Scheme 2. Combined Overview of All Direct Reactions, Starting from Methanol (Top Row) and Leading to the Formation of Ethylene (Bottom Row)<sup>a</sup>

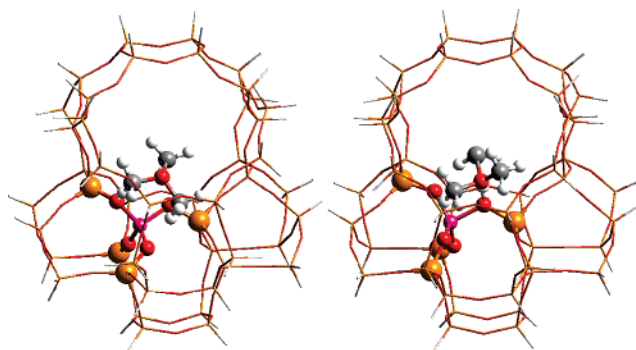
<sup>a</sup> Horizontal movement corresponds to the adsorption or desorption of a reactive molecule, while vertical arrows represent elementary reaction steps. The elementary reactions are divided into four categories based on the values of forward rate coefficients at 720 K (adapted from ref 6).



**Figure 1.** Various methodologies for theoretical calculations on zeolite systems.

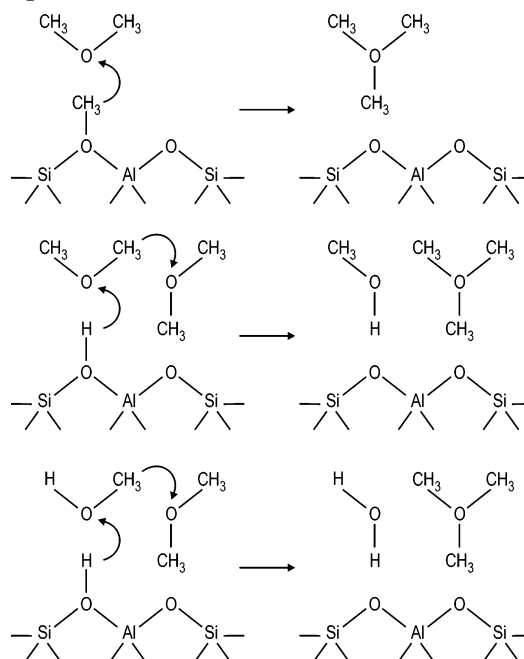
observation of this pre-equilibrium preceding the olefin formation. This pre-equilibrium, however, does not yet provide the crucial and highly sought-after carbon–carbon bond.

**Formation of the Trimethyl Oxonium Ion.** From the initial mixture, a direct formation of the trimethyl oxonium ion (TMO) has been proposed through nucleophilic attack by adsorbed DME on a framework-bound methoxide species or through co-reaction of DME and methanol. These steps were respectively studied on 3T clusters by Tajima et al.<sup>3</sup> and 1T clusters by Blaszkowski et al.<sup>2</sup> Alternatively, TMO could also be formed through co-reaction of two DME molecules. All routes to TMO are situated in the green rectangle in Scheme 2 and are illustrated in more detail in Scheme 3. Because of the extremely low reverse reaction barriers (green rectangles in Table 1) observed in our 5T cluster calculations, one would at first glance expect TMO to be an exceptionally short-living intermediate. However, positively charged TMO forms an ion-pair with the negative aluminum defect and therefore cannot be adequately described



**Figure 2.** Trimethyl oxonium ion (TMO) and dimethyl oxonium methylide (DOMY) formed in H-ZSM-5 cage (46T cluster).

**Scheme 3.** Different Routes to Trimethyl Oxonium Ion (TMO) Formation from the Pre-equilibrium Mixture (Green Rectangle in Scheme 2)



in the small cluster approach. Furthermore, our previous ONIOM calculations on larger 46T clusters demonstrated that TMO is additionally stabilized by the zeolite framework,<sup>7</sup> a result similar to that obtained through periodic calculations by Shah et al. in the chabazite topology.<sup>16</sup> In their periodic calculations, however, Shah et al. did not calculate any reaction barriers for the formation of TMO. To resolve this issue, we performed advanced calculations using the ONIOM technique, providing lower barriers. Adjusted energies (in kJ/mol) for all stationary points are shown in Table 2. Two parallel routes with a barrier below 100 kJ/mol provide theoretical evidence for TMO remaining an important product formed directly from the equilibrium mixture.

**First Bottleneck: Ylide and Carbene Intermediates.** The main difficulties arise, however, once TMO is effectively formed, and oxonium ylides (a carbene group coordinated to methanol or DME) are the next suggested intermediates (red rectangles in Scheme 2). For instance, once TMO is successfully formed, it might be deprotonated by an adjacent basic site to form dimethyl oxonium methylide (DOMY),<sup>7</sup> as shown in Figure 2. The next step (forming the desired carbon–carbon bond) could be an intramolecular Stevens' rearrangement to methylethyl ether (MEE), or an intermolecular methylation, forming the ethyldimethyl oxonium ion (EDMO), as shown in



Table 1. Kinetic Parameters of Both Forward and Reverse Reactions, Calculated in Reference 6 at the B3LYP/6-31g(d) Level on 5T Zeolite Clusters<sup>a</sup>

reactants	products	E <sub>a</sub> (kJ/mol) 670-770K	forward A (1/s) 670-770K	k (1/s) 720K	E <sub>a</sub> (kJ/mol) 670-770K	reverse A (1/s) 670-770K	k (1/s) 720K	other ref.
Z-H+H <sub>3</sub> COH	Z-CH <sub>3</sub> +H <sub>2</sub> O	223.6	3.44E+12	2.1E-04	176.2	1.50E+12	2.5E-01	10-12
Z-H+H <sub>3</sub> COH+H <sub>3</sub> COH	Z-CH <sub>3</sub> +H <sub>3</sub> COH+H <sub>2</sub> O	142.3	9.87E+11	4.7E+01	95.7	1.29E+12	1.5E+05	11-12
Z-CH <sub>3</sub> +H <sub>3</sub> COH+H <sub>2</sub> O	Z-H+(H <sub>3</sub> C) <sub>2</sub> O+H <sub>2</sub> O	84.8	1.14E+11	8.1E+04	155.0	4.64E+10	2.7E-01	12
Z-H+H <sub>3</sub> COH+H <sub>3</sub> COH	Z-H+(H <sub>3</sub> C) <sub>2</sub> O+H <sub>2</sub> O	129.7	1.27E+10	5.0E+00	153.4	6.77E+09	5.1E-02	12-15
Z-CH <sub>3</sub> +H <sub>3</sub> COH+H <sub>2</sub> O	Z-H+CH <sub>3</sub> +H <sub>3</sub> CO+H <sub>2</sub> O	146.8	1.79E+11	4.0E+00	185.1	1.10E+06	4.1E-08	-
Z-H+CH <sub>3</sub> +H <sub>3</sub> CO+H <sub>2</sub> O	Z-H+C <sub>2</sub> H <sub>5</sub> OH+H <sub>2</sub> O	173.7	4.84E+05	1.2E-07	231.5	2.93E+10	4.7E-07	19-20
Z-H+C <sub>2</sub> H <sub>5</sub> OH+H <sub>2</sub> O	Z-CH <sub>3</sub> -CH <sub>3</sub> +H <sub>2</sub> O+H <sub>2</sub> O	147.2	1.05E+11	2.2E+00	93.1	2.08E+12	3.7E+05	2
Z-H+H <sub>3</sub> COH+H <sub>3</sub> COH	Z-H+CH <sub>3</sub> +H <sub>3</sub> CO+H <sub>2</sub> O	196.4	1.24E+11	6.9E-04	188.1	9.86E+05	2.2E-08	19-20
Z-CH <sub>3</sub> +H <sub>3</sub> COH	Z-H+(H <sub>3</sub> C) <sub>2</sub> O	141.0	6.99E+11	4.1E+01	187.6	3.65E+10	8.9E-04	12
Z-H+H <sub>3</sub> CHO-CH <sub>3</sub>	Z-H+C <sub>2</sub> H <sub>5</sub> OH	129.3	9.93E+13	4.1E+04	545.2	1.12E+14	3.2E-26	7
Z-CH <sub>3</sub> +H <sub>3</sub> COH	Z-H+CH <sub>3</sub> +H <sub>3</sub> CO	189.9	4.31E+11	7.2E-03	221.6	3.15E+06	2.6E-10	2-3
Z-H+CH <sub>3</sub> +H <sub>3</sub> CO	Z-H+C <sub>2</sub> H <sub>5</sub> OH	172.6	5.81E+06	1.7E-06	233.4	1.33E+12	1.6E-05	3
Z-H+C <sub>2</sub> H <sub>5</sub> OH	Z-CH <sub>3</sub> -CH <sub>3</sub> +H <sub>2</sub> O	198.0	6.84E+12	3.0E-02	148.5	7.95E+13	1.3E+03	2
Z-CH <sub>3</sub> -CH <sub>3</sub> +H <sub>2</sub> O	Z-H+C <sub>2</sub> H <sub>5</sub> +H <sub>2</sub> O	139.4	2.46E+12	1.9E+02	83.5	5.27E+08	4.6E+02	2
Z-H+C <sub>2</sub> H <sub>5</sub> OH	Z-H+C <sub>2</sub> H <sub>5</sub> +H <sub>2</sub> O	193.2	7.94E+13	7.7E-01	87.8	1.98E+11	8.5E+04	2-3
Z-H+(H <sub>3</sub> C) <sub>2</sub> O	Z-H+H <sub>3</sub> CHO-CH <sub>3</sub>	-	-	0.0E+00	-	-	0.0E+00	7
Z-CH <sub>3</sub> -CH <sub>3</sub>	Z-H+C <sub>2</sub> H <sub>4</sub>	153.0	3.83E+12	3.0E+01	89.4	2.89E+09	9.4E+02	2
Z-H+(H <sub>3</sub> C) <sub>2</sub> O+(H <sub>3</sub> C) <sub>2</sub> O	Z+(H <sub>3</sub> C) <sub>2</sub> O+H <sub>3</sub> COH	135.7	6.81E+09	9.7E-01	28.2	4.42E+10	4.0E+08	-
Z+(H <sub>3</sub> C) <sub>2</sub> O+H <sub>3</sub> COH	Z-H+(H <sub>3</sub> C) <sub>2</sub> O+CH <sub>3</sub> +H <sub>2</sub> CO	105.7	1.83E+11	3.9E+03	208.4	1.66E+05	1.3E-10	-
Z-H+(H <sub>3</sub> C) <sub>2</sub> O+H <sub>3</sub> COH	Z+(H <sub>3</sub> C) <sub>2</sub> O+H <sub>2</sub> O	147.3	5.70E+11	1.2E+01	12.7	4.35E+11	5.2E+10	2
Z-CH <sub>3</sub> +(H <sub>3</sub> C) <sub>2</sub> O	Z+(H <sub>3</sub> C) <sub>2</sub> O	120.5	2.98E+08	5.4E-01	52.9	2.29E+14	3.3E+10	2-3
Z-H+(H <sub>3</sub> C) <sub>2</sub> O-CH <sub>3</sub>	Z-H+H <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	117.9	5.31E+13	1.5E+05	470.5	2.24E+11	1.6E-23	7
Z-H+H <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	Z-H+C <sub>2</sub> H <sub>5</sub> +H <sub>3</sub> COH	113.8	4.53E+10	2.5E+02	80.8	5.77E+10	8.0E+04	-
Z+(H <sub>3</sub> C) <sub>2</sub> O	Z-H+(H <sub>3</sub> C) <sub>2</sub> O-CH <sub>3</sub>	-	-	0.0E+00	-	-	0.0E+00	3,7
Z-H+H <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub> +H <sub>2</sub> O	Z-H+C <sub>2</sub> H <sub>5</sub> +H <sub>2</sub> O+H <sub>3</sub> COH	159.2	2.25E+11	6.4E-01	115.2	6.32E+08	2.8E+00	2
Z-CH <sub>3</sub> +(H <sub>3</sub> C) <sub>2</sub> O-CH <sub>3</sub>	Z-CH <sub>3</sub> +H <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	130.4	1.02E+14	3.5E+04	521.3	1.02E+14	1.5E-24	-
Z-CH <sub>3</sub> +H <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	Z+(H <sub>3</sub> C) <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	127.6	5.62E+11	3.1E+02	49.7	4.67E+15	1.2E-12	-
Z-CH <sub>3</sub> +(H <sub>3</sub> C) <sub>2</sub> O-CH <sub>3</sub>	Z+(H <sub>3</sub> C) <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	18.9	1.56E+12	6.6E+10	331.9	1.30E+16	1.1E-08	7
Z+(H <sub>3</sub> C) <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	Z-H+C <sub>2</sub> H <sub>5</sub> +(H <sub>3</sub> C) <sub>2</sub> O	84.7	2.55E+14	1.8E+08	127.1	1.62E+07	9.6E-03	-
Z-CH <sub>3</sub> +H <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	Z-CH <sub>3</sub> +C <sub>2</sub> H <sub>5</sub> +H <sub>3</sub> COH	281.2	9.17E+11	3.6E-09	193.1	1.46E+10	1.4E-04	-
Z-CH <sub>3</sub>	Z-H+(CH <sub>3</sub> )	244.8	3.08E+11	5.3E-07	51.9	3.16E+12	5.5E+08	17

<sup>a</sup> References to other theoretical papers covering each specific reaction barrier (but not the corresponding rate coefficient) are given in the right-hand column. Colored rectangles highlight the crucial reactions from Scheme 2.

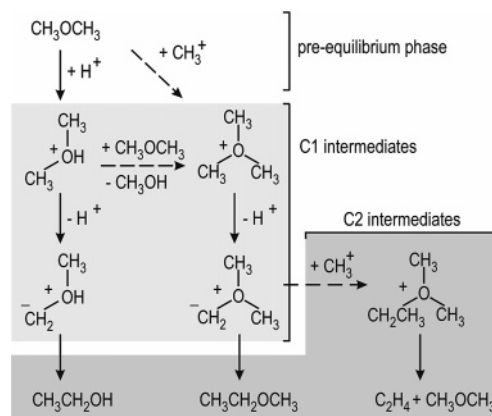
Table 2. Energies of Stationary Points (in kJ/mol) for the Formation of TMO in a 46T H-ZSM5 Model at the B3LYP/6-31+g(d,p):HF/6-31+g(d,p)/B3LYP/6-31+g(d,p):MNDO Level

trimethyl oxonium ion (TMO) formation	
Z-CH <sub>3</sub> + DME	0.0
transition state	96.6
Z <sup>-</sup> + TMO <sup>+</sup>	27.7
Z-H + DME + DME	0.0
transition state	132.3
Z <sup>-</sup> + TMO <sup>+</sup> + CH <sub>3</sub> OH	22.0
Z-H + DME + CH <sub>3</sub> OH	0.0
transition state	94.0
Z <sup>-</sup> + TMO <sup>+</sup> + H <sub>2</sub> O	31.6

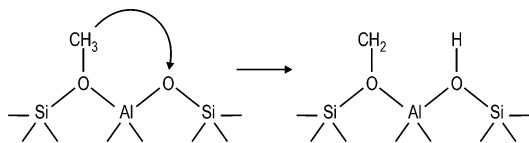
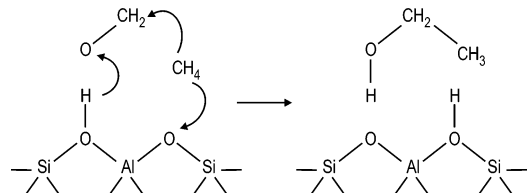
Scheme 4. The ethyldimethyl oxonium ion readily undergoes  $\beta$ -elimination, forming ethylene and dimethylether. From MEE, there exist several alternative pathways leading directly to ethylene. However, our previous work using the ONIOM method on large 46T clusters has shown that there is no possible route from TMO to DOMY.<sup>7</sup> Moreover, even though the zeolite framework offers supplementary stabilization for TMO, this does not hold for the ylide, which results in DOMY being a highly energetic species.

Methyl oxonium methylene (MOMY) is also a possible candidate. Adsorbed dimethyl ether could form a dimethyl

Scheme 4. Possible Routes from DME to Ylides and Subsequent Carbon–Carbon Coupling. (Adapted from Reference 7)



oxonium ion (DMO), after which it would be deprotonated to MOMY. A Stevens-type rearrangement would lead to ethanol, forming the required carbon–carbon bond. Yet again, we have found this step to be nonexistent and MOMY to be highly unstable.<sup>7</sup> Generally speaking, we find the oxygen bridge to be

**Scheme 5. Formation of a Framework-Bound Carbene****Scheme 6. Formation of Ethanol from Methane and Formaldehyde**

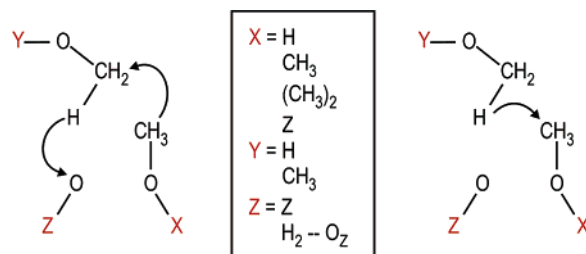
insufficiently basic to form the desired ylides. Alternative pathways based on oxonium ylides are also highly improbable due to the high instability of these species. This consequently rules out the role of MEE as a crucial intermediate as well as the pathway through EDMO.

An altogether different type of carbene, which is incorporated into the framework, can be formed by deprotonation of a framework-bound methyl group, as shown by the brown rectangle in Scheme 2 and schematically depicted in Scheme 5. Sinclair and Catlow investigated this step and found a relatively unstable carbene and an extremely high reaction barrier.<sup>17</sup> Our rate coefficients for the formation of this framework-coordinated carbene are extremely low (brown rectangle in Table 1), corresponding with the high reaction barrier of this step.

The severe instability and the corresponding nonexistence of not only the ylides but also the framework-coordinated carbene form the first main bottleneck for the direct approach in MTO chemistry. Based on these theoretical results, an experimental H/D exchange study has just recently confirmed the nonexistence of these exotic species.<sup>18</sup>

**Second Bottleneck: Methane/Formaldehyde Route.** Alternatively, there are multiple potential routes to methane and formaldehyde, starting from two methanol molecules, from a surface methoxy species and methanol, or from TMO jointly adsorbed with methanol. The methane/formaldehyde route has been widely hailed as a possible MTO route, not only in small cluster calculations by Tajima et al.,<sup>3</sup> but also in molecular dynamics simulations by Lo et al.<sup>19,20</sup> Once formed, however, only extremely slow reactions lead to the formation of ethanol (blue rectangle in Scheme 2, detailed reaction in Scheme 6). From ethanol, ethylene could quite rapidly be formed, the fastest route running along a framework-bound ethoxide species and subsequent ethylene production. Nevertheless, even though methane and formaldehyde will undoubtedly be formed, the conversion of this mixture to ethanol proceeds too slowly to be considered viable. As is clear from the blue rectangles in Table 1, the rate coefficient for this step in particular is not mainly determined by the activation energy  $E_a$ , but more so by the very small pre-exponential factor  $A$ , reflecting the major decrease in entropy which accompanies this reaction. The failure of methane and formaldehyde to easily convert to a C2 species forms the second main bottleneck in the direct mechanism proposal.

**Third Bottleneck: Extremely High Barrier for Concerted C–C Coupling.** So as to not overcrowd Scheme 2, conversions showing both forward and reverse barriers larger than 200 kJ/mol (which would not proceed in either direction) are not shown in Scheme 2. However, a closer investigation of the omitted

**Scheme 7. Prohibited Reactions Corresponding to Concerted Carbon–Carbon Coupling and Carbon–Hydrogen Bond Activation by Zeolite Basic Oxygen  $O_z$  (Left Diagram)<sup>a</sup>**

<sup>a</sup> Protonation of the methyl group forming methane (right diagram) will proceed far more rapidly (adapted from ref 6).

reaction steps reveals crucial information on the failure of these steps. As they all follow a similar concerted reaction mechanism, we show a general model in Scheme 7 (left diagram) representing the steps that had too high-energy barriers to be incorporated: a hydrogen abstraction from a methanol/DME methyl group by a zeolite basic oxygen bridge (possibly assisted by a water vehicle molecule) combined with the formation of a carbon–carbon bond with a methanol/DME/TMO/framework-bound methyl group.<sup>6</sup> Many of these concerted steps were first studied in the pioneering 1T cluster study by Blaszkowski et al.,<sup>2</sup> who even then already observed exceptionally high reaction barriers. The unprotonated oxygen bridge lacks the strong basic character needed to activate the highly covalent carbon–hydrogen bond. An equally strong carbon–hydrogen bond is preferably formed, which is why any perturbation of the transition state leads the system to automatically evolve to a nearby transition state, forming methane instead (right diagram in Scheme 7). This outspoken formation of methane is quite similar to what was observed in the molecular dynamics simulations by Lo et al.<sup>19,20</sup> As previously mentioned, though, the mixture of methane and formaldehyde does not succeed in supplying the first carbon–carbon bond. Thus, these prohibited concerted reactions form the third and final bottleneck of the direct mechanism proposal.

## Conclusions

We have worked toward the theoretical identification and clarification of all direct mechanisms behind the methanol-to-olefin process by not only giving an overview of the many individual reactions suggested in the literature, but by also calculating and recombining every single step in each pathway to allow for an overall picture and for direct comparison between the individual steps. This has allowed for the crucial reaction steps to be identified, and more advanced calculations using an embedding technique have been performed when necessary.

As long as reaction barriers for partial pathways remained scattered over the literature, it seemed that there were multiple possibilities for direct conversion of methanol to ethylene. However, the combination of these results in complete pathways and calculation of rate coefficients as well as just barrier heights shows that no complete direct pathway from methanol leading all of the way to ethylene (or to any C2 intermediate) exists. Three critical points can be clearly recognized: first, the instability of the ylide or carbene intermediates, second, the low conversion rates of methane and formaldehyde to ethanol, and, third, the concerted carbon–carbon coupling reactions, which convert to the formation of methane and formaldehyde instead.

Hopefully, this theoretical conclusion ends some of the existing controversy surrounding the direct mechanisms. Al-

ternatives to the direct mechanism concept, like the "hydrocarbon pool" proposal, should be based on reactions and intermediates that somehow bypass the earlier-mentioned bottlenecks. As this alternative proposal is based on bulky and charged intermediates, topology effects will play a crucial role in reaction kinetics, and the small cluster approach will not be sufficient in its description.<sup>21,22</sup>

As the methanol-to-olefin process is a key step in the switch from fossil fuels to green chemistry,<sup>23</sup> additional insights into the mechanism to control product distribution would be highly desirable, yet only achievable through strong interaction between experimental and theoretical research.

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