

THEORETICAL STUDY ON ELEMENTARY REACTIONS IN THE METHANOL-TO-OLEFIN PROCESS

David Lesthaeghe¹, Bart De Sterck¹, Veronique Van Speybroeck¹, Guy B. Marin², Michel Waroquier¹

¹*Center for Molecular Modeling, Ghent University, Proeftuinstraat 86 B-9000 Gent, Belgium*

²*Laboratorium voor Petrochemische Techniek, Ghent University, Krijgslaan 281-S5 B-9000 Gent, Belgium*

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 of oil-based chemicals calls for the development of new technologies based on alternative natural sources. Among these processes, the methanol-to-hydrocarbons (MTH) technology¹ is one of the most promising and currently even ready for commercial use. Methanol is made from synthesis gas (CO+H₂), which can be formed either by steam reforming of natural gas or by gasification of coal or biomass. Methanol can then be converted to a pre-equilibrium mixture of methanol, dimethyl ether and water, which can be processed catalytically to olefins (methanol-to-olefins, MTO) or gasoline (methanol-to-gasoline, MTG).

Quite remarkably, for more than 30 years the actual mechanism of the MTO process in acidic zeolites has been the source of considerable debate, fueled by the countless diverse 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.¹ Early speculation mainly centered on mechanisms based on the 'direct' formation of small olefins from only methanol, dimethylether and single-carbon derivatives.²⁻³ More recent developments suggest, however, that these direct mechanisms might not be responsible for the observed boost in hydrocarbon synthesis after all.⁴ A plausible alternative is given by the 'hydrocarbon pool' model,⁵ in which impurities in the mixture undergo repeated methylation and subsequent olefin elimination.⁶⁻⁷

Our goal is to unequivocally determine the underlying mechanism of the MTO process from a theoretical viewpoint, as experimental methods are often impractical for evaluating individual reaction steps. Before looking into alternative hydrocarbon pool proposals, we need to explain why the numerous direct carbon-carbon coupling mechanisms proposed fail in consistent production of ethylene. Furthermore, we need to identify the directly formed species which might interact with the hydrocarbon pool species. In this extended abstract we summarize our approach for this primary investigation and give more detail on some crucial points.

Computational details

Density functional theory (DFT) calculations were performed within the Gaussian03 software package.⁸ Initial calculations were performed on small pentatetrahedral (5T) clusters, which are frequently used to provide reliable qualitative results.⁹ For certain key

pre-equilibrium mixture, a direct formation of TMO has been proposed through nucleophilic attack by adsorbed DME on a framework-bound methoxide species (R1).¹⁵ Alternatively, TMO can also be formed through co-reaction of two DME molecules (R2) or DME and methanol (R3). Energies (in kJ/mol) for all stationary points are shown in Table 1. Both parallel routes with a barrier below 100 kJ/mol form further theoretical evidence for the successful formation of TMO.

Table 1. Energies of stationary points (in kJ/mol) for the formation of TMO in a 46T H-ZSM5 model at the B3LYP:HF/6-31+g(d,p) level

Trimethyl oxonium ion (TMO) formation	
Z-CH ₃ + DME	0.0
Transition State (R1)	96.6
Z + TMO ⁺	27.7
Z-H + DME + DME	0.0
Transition State (R2)	132.3
Z + TMO ⁺ + CH ₃ OH	22.0
Z-H + DME + CH ₃ OH	0.0
Transition State (R3)	94.0
Z + TMO ⁺ + H ₂ O	31.6

The main difficulties arise once TMO is effectively formed and oxonium ylides are the next suggested intermediates (red rectangles in Figure 1). For instance, TMO could be deprotonated by an adjacent basic site to form dimethyl oxonium methylide (DOMY), shown in Figure 2.¹⁵ The next step (forming the essential carbon-carbon bond) is an intramolecular Stevens' rearrangement to methylethyl ether, or an intermolecular methylation, forming the ethyldimethyl oxonium ion. However, our previous work using 46T clusters has shown that there exist no transition states corresponding to a possible route from TMO to DOMY.¹² 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 methylide (MOMY) is also a possible candidate. Adsorbed dimethyl ether could form a dimethyl oxonium ion, after which it would be deprotonated to MOMY. A Stevens-type rearrangement would lead to ethanol, forming the required carbon-carbon bond. Yet again, this step is non-existent and MOMY is highly unstable.¹² Generally speaking, the oxygen bridge is insufficiently basic to form the desired ylides, which are the first main bottleneck. Based on these theoretical results, a recent experimental H/D exchange study has since confirmed our findings.¹⁶

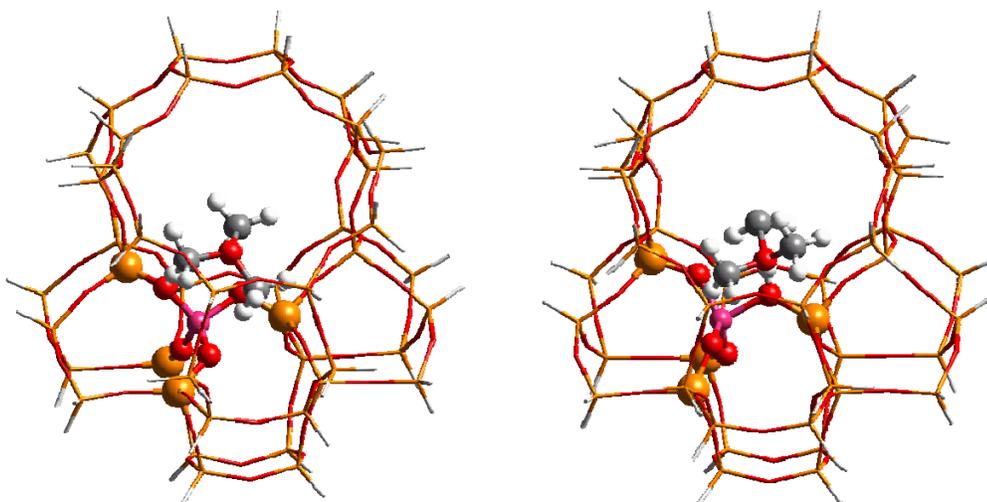


Figure 2. Trimethyl oxonium ion (TMO) and dimethyl oxonium methylene (DOMY) formed in H-ZSM-5 cage.

Alternative direct routes, bypassing the ylide formation, encounter similar complications. Figure 3 (blue arrows) illustrates a model representing the reaction steps that are generally too highly activated to proceed, as they all follow a similar concerted reaction mechanism: a hydrogen abstraction from a methanol/DME methyl group by a zeolite basic oxygen bridge (possibly assisted by a water molecule) combined with the formation of a carbon-carbon bond from a methanol/DME/TMO/framework-bound methyl-group. These reaction steps exhibit barriers larger than 200 kJ/mol and were consequently excluded in order not to overcrowd Figure 1.

The unprotonated oxygen bridge lacks the strong basic character needed to activate the highly covalent carbon-hydrogen bond. The system evolves to a nearby transition state leading to methane instead (red arrow in Figure 3). However, from methane and formaldehyde, all reaction barriers leading to a C2 species are too highly activated to proceed (blue rectangle in Figure 1). Combined with the concerted reactions in Figure 3, this forms the second main bottleneck of the direct mechanism proposal. The key to success of currently suggested hydrocarbon pool reactions might be their avoidance of similar concerted steps through the formation of an intermediate carbenium ion.⁶⁻⁷

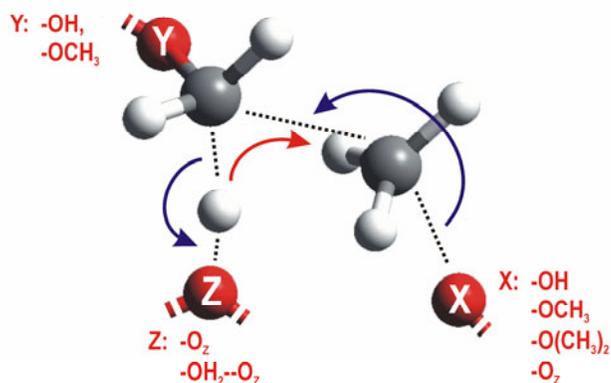


Figure 3. Highly activated reactions corresponding to concerted carbon-carbon bond formation and carbon-hydrogen bond activation by zeolite basic oxygen OZ (blue arrows). Protonation of the methyl group forming methane (red arrow) is observed instead.

Conclusions

In a first stage towards theoretical identification and clarification of the true mechanism of the methanol-to-olefin process, we have studied a large set of direct mechanisms (over 80 stationary points). The crucial reaction steps have been identified, and more advanced calculations using an embedding technique have been performed when necessary.

Our results imply that no complete direct pathway from methanol leading all the way to ethylene (or to any intermediate containing a carbon-carbon bond) exists. This is in perfect accordance with the experimental observation of methanol/DME not being noticeably reactive on H-ZSM-5 in the absence of organic impurities that provide a primordial hydrocarbon pool.^{4,16} From our results, two critical points can be clearly recognized: on the one hand the instability of the ylide intermediates and on the other hand the high energy barriers for the often-proposed concerted carbon-carbon bond formation reactions. Both bottlenecks are a direct result of the weak basic character of the zeolite oxygen bridge.

Additionally, we have identified several directly formed species. Among these, the trimethyl oxonium ion deserves special interest as it is found to be strongly stabilized by the zeolite framework. Furthermore, TMO might play an important role as a methylating agent towards certain hydrocarbon pool species.

Hopefully, this theoretical conclusion ends some of the existing controversy by providing strong additional support for alternative proposals that bypass the highly activated reactions. An obvious next step is the extension of this comprehensive theoretical approach to elementary reaction steps in the hydrocarbon pool hypothesis, which we are currently actively pursuing.

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References

1. Stocker M. *Microporous Mesoporous Mater.* **1999**, 29, 3-48.
2. Blaszkowski, S.R.; van Santen, R.A. *J. Am. Chem. Soc.* **1997**, 119, 5020-5027.
3. Tajima, N.; Tsuneda, T.; Toyama, F.; Hirao, K. *J. Am. Chem. Soc.* **1998**, 120, 8222-8229.
4. Song, W.; Marcus, D. M.; Fu, H.; Ehresmann, J. O.; Haw, J. F.; *J. Am. Chem. Soc.* **2002**, 124, 3844-3845.
5. Dahl, I. M.; Kolboe, S. *J. Catal.* **1994**, 149, 458-464.
6. Haw, J. F.; Nicholas, J. B.; Song, W.; Deng, F.; Wang, Z.; Xu, T.; Heneghan, C. S. *J. Am. Chem. Soc.* **2000**, 122, 4763-4775.
7. Arstad, B.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **2004**, 126, 2991-3001.
8. Gaussian 03, Revision B.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; *Gaussian, Inc.*, Wallingford CT, **2003**.
9. Lesthaeghe, D.; Van Speybroeck, V.; Waroquier, M. *J. Am. Chem. Soc.* **2004**, 126, 9162.
10. Solans-Monfort, X.; Sodupe, M.; Branchadell, V.; Sauer, J.; Orlando, R.; Ugliengo, P. *J. Phys. Chem. B* **2005**, 109, 3539-3545.
11. Fermann, J.T.; Moniz, T.; Kiowski, O.; McIntire, T.J.; Auerbach, S.M.; Vreven, T.; Frisch, M.J. *J. Chem. Theor. Comp.* **2005**, 1, 1232-1239.
12. Lesthaeghe, D.; Van Speybroeck, V.; Marin, G. B.; Waroquier, M. *Chem. Phys. Lett.* **2005**, 417, 310-316.
13. Lesthaeghe, D.; Van Speybroeck, V.; Marin, G. B.; Waroquier, M. *Angew. Chem.* 2006, 118, 1746-1751; *Angew. Chem. Int. Ed.* **2006**, 45, 1714-1719.
14. Wang, W.; Buchholz, A.; Seiler, M.; Hunger, M. *J. Am. Chem. Soc.* **2003**, 125, 15260-15267.
15. Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inaba, S. I.; Ip, W. M.; Lammertsma, K.; Salem, G.; Tabor, D. C. *J. Am. Chem. Soc.* **1984**, 106, 2143-2149.
16. Marcus, D. M.; McLachlan, K.A.; Wildman, M. A.; Ehresmann, J.O.; Kletnieks, P.; Haw, J. F. *Angew. Chem.* **2006**, 118, 3205-3208; *Angew. Chem. Int. Ed.* **2006**, 45, 3133-3136.