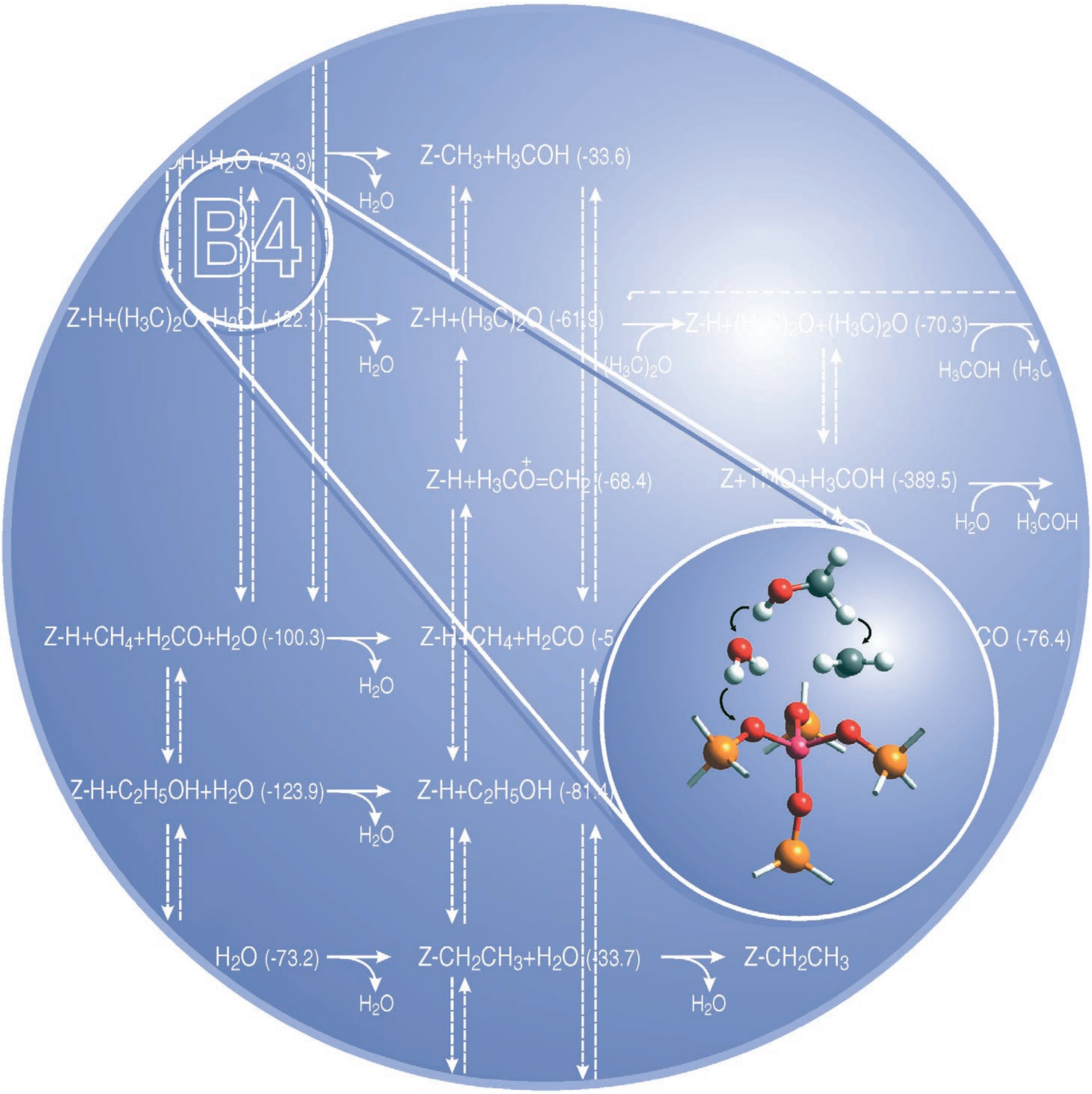
DOI: 10.1002/anie.200503824



An unprecedented number of possible direct reaction steps from methanol to ethylene are tied together in a single integrated scheme. Calculations show that every imaginable combination of direct reactions fails completely in the formation of the initial carbon–carbon bond. For more details, see the Communication by M. Waroquier and co-workers on the following pages.

DOI: 10.1002/anie.200503824

Understanding the Failure of Direct C–C Coupling in the Zeolite-Catalyzed Methanol-to-Olefin Process[**]

David Lesthaeghe, Veronique Van Speybroeck,
Guy B. Marin, and Michel Waroquier[*]

The mechanism of the methanol-to-olefin (MTO) process on zeolite H-ZSM-5 has been the source of significant debate by both industrial and academic researchers. Much still remains uncertain, and the literature is replete with diverse and often conflicting propositions. A crucial step is the formation of the first carbon–carbon bond, for which more than 20 distinct mechanistic proposals exist.[1] Early research focused mainly on mechanisms based on the direct formation of small olefins from only methanol and methanol derivatives. Advanced theoretical calculations on these "direct mechanisms" are fragmented throughout the literature, and straightforward comparison is cumbersome owing to the large array of methods employed. Only a handful of papers suggest and compare multiple direct routes,[2,3] but these are limited to low levels of theory calculations on extremely small 1T/3T zeolite clusters.

Recent developments suggest, however, that direct mechanisms might not be responsible for the observed boost in hydrocarbon synthesis.[4] A plausible alternative is given by the "hydrocarbon pool" model,[4,5] in which impurities in the mixture undergo repeated methylation and subsequent olefin elimination. This latter proposal is consistently gaining experimental and theoretical support, which advocates methylbenzenes and methylcyclopentenyl cations as key species.[6,7] Because of an observed kinetic induction period preceding the hydrocarbon formation, the hydrocarbon pool model implies that reactions occurring during this induction period need not necessarily be similar to those on a working catalyst. It is still unresolved, though, which—if any—induction reactions give rise to the hydrocarbon pool.

As the literature currently stands, two important questions regarding direct mechanisms remain unanswered: 1) From a theoretical viewpoint it is still unclear why the numerous proposed direct mechanisms should fail in consistent production of ethylene. 2) From a more practical perspective, it is still unknown what role certain directly formed intermediates might play both during the induction period and during hydrocarbon synthesis. Although experimental methods are often incapable of evaluating individual reaction steps, DFT-based calculations can provide these answers.

An extensive scheme is proposed, tying together a large variety of possible direct reactions, which include several previously overlooked, parallel pathways. On the basis of calculated adsorption energies, reaction barriers (at 0 K), and rate coefficients (at 720 K), it is possible to deduce whether ethylene can be produced from only methanol, and which stable intermediates might be formed directly to finally enhance our understanding of the first carbon–carbon bond formation.

Our aim was to integrate a whole range of reactions in an orderly and concise manner, as shown in Scheme 1. The adsorbed species form the main building blocks, with the total adsorption energy (in $\mathrm{kJ\,mol^{-1}}$) shown in brackets. Horizontal movement between these species corresponds to adsorption or desorption of a required molecule. Vertical arrows represent an elementary reaction step for which both forward and reverse intrinsic energy barrier heights at 0 K (in $\mathrm{kJ\,mol^{-1}}$) as well as rate coefficients at 720 K (in $\mathrm{s^{-1}}$) are included. For simple referencing purposes, each reaction step is identified by a specific code. The starting point (top left corner) is a single methanol molecule adsorbed near the acid site Z-H, leading finally to the creation of ethylene (bottom row). For clarity, we omit connections for which both the forward and reverse reactions are highly activated ($\Delta E_0 > 200\ \mathrm{kJ\,mol^{-1}}$) and which are therefore unlikely to proceed in either direction.

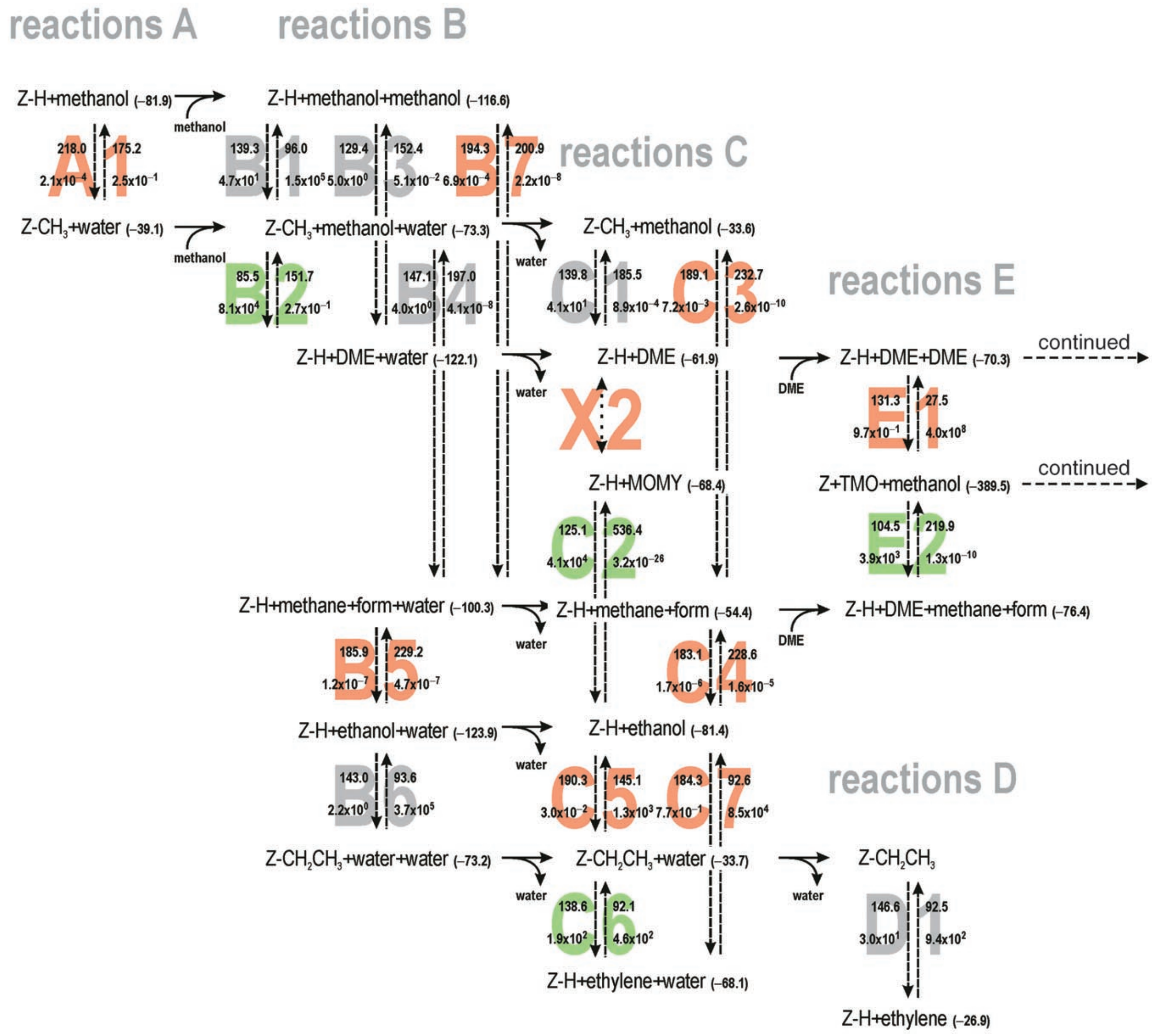
The conversion of methanol is known to start with rapid dehydration to dimethyl ether (DME). This proceeds either via an intermediate methoxide species Z-CH_3 (reactions coded A1/B1/B2/C1),[8] or through co-reaction of a methanol dimer (B3). The two-step pathway B1/B2 is facilitated by methanol/water successively lowering the reaction barriers as "assisting molecules", allowing more-favorable transition-state geometries. This first preequilibrium phase in the methanol-to-olefin process is theoretically well documented, ranging from small clusters[9–11] to fully periodic DFT calculations,[12–14] which all lead to similar conclusions.

From this initial mixture, the direct formation of the trimethyl oxonium ion (TMO) has been proposed through nucleophilic attack by adsorbed DME on a framework-bound methoxide species (G1).[15] Alternatively, TMO can also be formed through co-reaction of two DME molecules (E1) or DME and methanol (F1). Owing to the extremely low reverse reaction barriers, one would at first glance expect TMO to be an exceptionally short-lived intermediate. However, positively charged TMO forms an ion pair with the negative aluminum defect, and therefore cannot be adequately described in the small cluster approach. Our previous ONIOM calculations, however, have shown that TMO is additionally stabilized by the zeolite framework,[16] a similar result to that obtained through periodic calculations in chabazite,[17] and that TMO remains an important product formed directly from the equilibrium mixture.

---

[*] Ir. D. Lesthaeghe, Dr. Ir. V. Van Speybroeck, Prof. Dr. M. Waroquier
Center for Molecular Modeling
Ghent University
Proeftuinstraat 86, 9000 Gent (Belgium)
Fax: (+32) 9-264-6697
E-mail: michel.waroquier@ugent.be
Prof. Dr. Ir. G. B. Marin
Laboratorium voor Petrochemische Techniek
Ghent University
Krijgslaan 281-S5, 9000 Gent (Belgium)

[**] This work was supported by the Fund for Scientific Research–Flanders (FWO) and the Research Board of Ghent University.



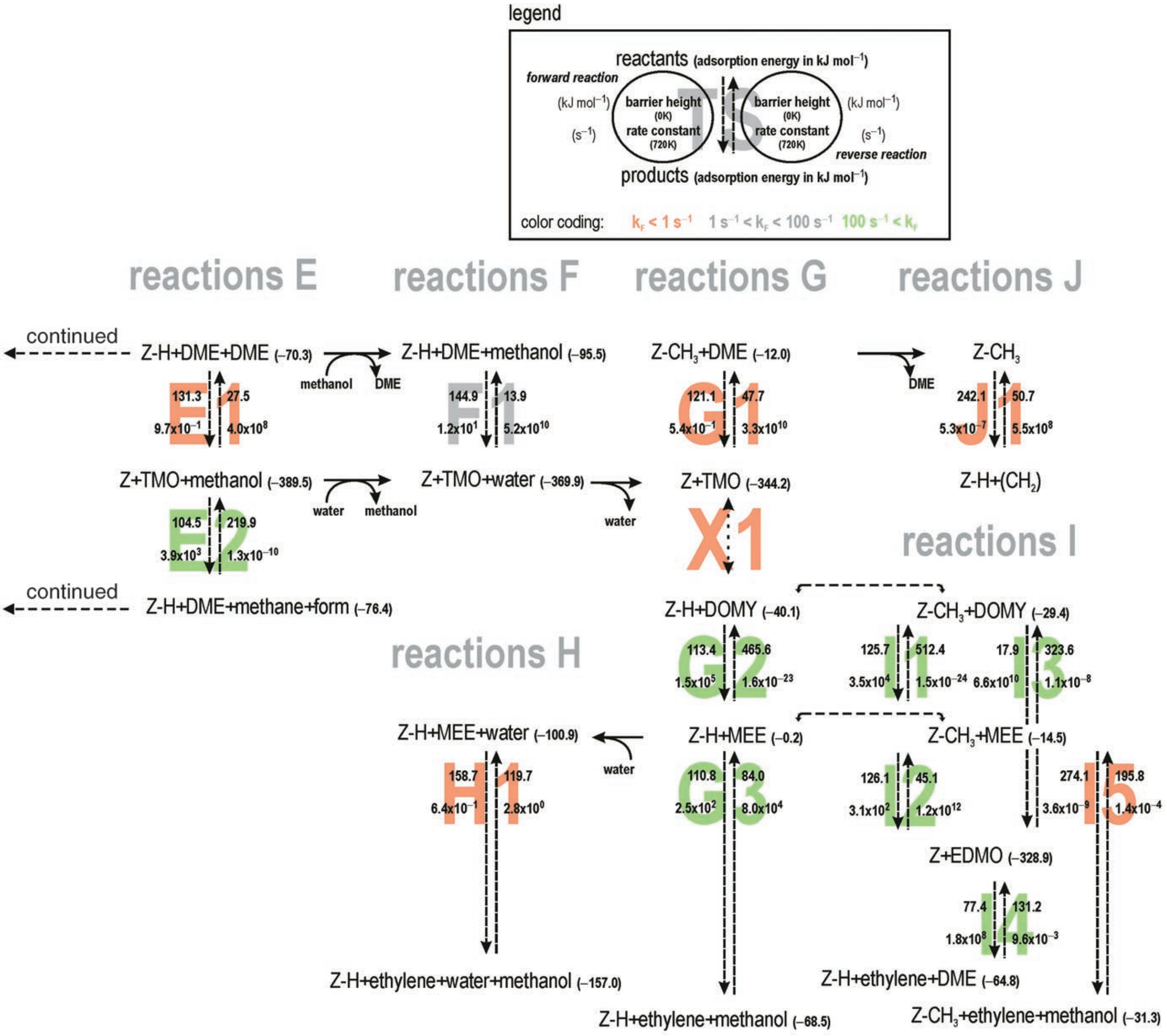
Scheme 1. Direct routes in the methanol-to-olefin process. Horizontal arrows correspond to an adsorption/desorption step, vertical arrows denote a reaction step. Intrinsic energy barriers at 0 K are shown in kJ mol^{-1}, rate coefficients at 720 K are expressed in s^{-1}.

Once TMO is successfully formed, it might be deprotonated by an adjacent basic site (reaction step X1) to form dimethyl oxonium methylide (DOMY).[15] The next step is an intramolecular Stevens rearrangement (G2/I1) to methyl ethyl ether (MEE) or an intermolecular methylation (I2/I3) to form the ethyl dimethyl oxonium ion (EDMO). EDMO readily undergoes β elimination to form ethylene and dimethyl ether (I4). From MEE, several alternative pathways lead directly to ethylene (H1/G3/I5). However, our previous work has shown that there is no possible route from TMO to DOMY (X1).[16] Moreover, the zeolite framework does not offer any supplementary stabilization, which results in DOMY being a highly energetic species.

Alternatively, methyl oxonium methylide (MOMY) has been proposed as a possible intermediate.[18] Adsorbed dimethyl ether could form a dimethyl oxonium ion (DMO), after which it would be deprotonated to MOMY (X2). A Stevens-type rearrangement would lead to ethanol (C2), thus forming the required carbon–carbon bond. Yet again, we have found this step to be non-existent and MOMY to be highly unstable.[16] An altogether different ylide, incorporated into the framework, can be formed by deprotonation of a framework-bound methyl group (J1).[19] This step was found to be highly activated as well.

Generally speaking, the oxygen bridge seems to be insufficiently basic to form the desired ylides. We also state that alternative pathways based on oxonium ylides are highly improbable owing to the high instability of these species. The instability of the ylides consequently rules out the role of MEE as a crucial intermediate as well as the pathway through EDMO.

There are several routes to methane and formaldehyde (form), starting from two methanol molecules (B7),[3] from a surface methoxy species and methanol (B4/C3), or from TMO



Scheme 1. (Continued).

jointly adsorbed with methanol (E2). Once formed, however, only extremely high reaction barriers (B5/C4) allow the formation of ethanol. From ethanol, ethylene could be immediately formed (C7), but the fastest routes would be through the formation of a framework-bound ethoxide species (B6/C5) and subsequent ethylene production (C6/D1).

As mentioned earlier, conversions showing both forward and reverse barriers larger than 200 kJ mol^{-1} are not shown in Scheme 1, and a closer investigation of the omitted reaction steps is necessary. In Figure 1 (blue arrows) we show a model representing the steps that were too highly activated to be incorporated, as they all follow a similar concerted reaction mechanism: hydrogen abstraction from a methanol/DME methyl group by a zeolite basic oxygen bridge (alternatively assisted by a water "vehicle molecule") combined with the formation of a carbon–carbon bond with a methanol/DME/

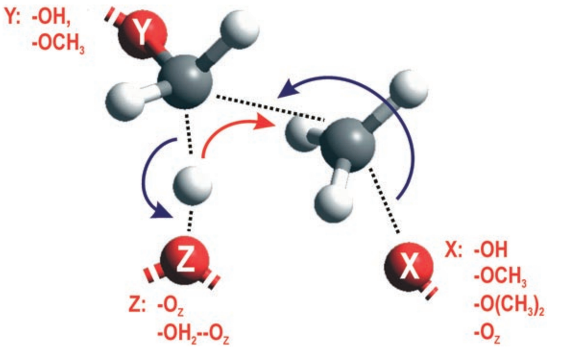


Figure 1. Highly activated reactions corresponding to concerted C–C bond formation and C–H bond breaking by zeolite basic oxygen O_Z (blue arrows). Protonation of the methyl group to form methane (red arrow) is observed instead.

TMO/framework-bound methyl group. The unprotonated oxygen bridge apparently lacks the strong basic character needed to break the highly covalent C–H bond. An equally strong C–H bond is preferably formed, which is why the system evolves to a nearby transition state, thus leading to methane instead (red arrow in Figure 1). This is similar to observations in molecular-dynamics simulations.[20,21] These concerted reactions form the main bottleneck of the direct mechanism proposal, whereas currently suggested hydrocarbon pool reactions avoid similar concerted steps through the formation of an intermediate carbenium ion.

In conclusion, a large set of direct mechanisms (>80 stationary points) in the MTO process was studied theoretically, providing both rate coefficients at 720 K and reaction barriers at 0 K. Direct comparisons allowed the qualitative evaluation of which steps are likely to proceed. The crucial reaction steps were identified, into which further research is currently underway.

We failed to find a successive pathway from methanol leading all the way to ethylene (or to any intermediate containing a C–C bond), which is in accordance with methanol/DME not being noticeably reactive on H-ZSM-5 in the absence of organic impurities that provide a primordial hydrocarbon pool.[22] From our results, two bottlenecks can be clearly identified: on the one hand the instability of the ylide intermediates and on the other hand the high energy barriers for the often proposed concerted C–C bond-formation reactions, both of which are a direct result of the weak basic character of the zeolite oxygen bridge. It is also possible to define clearly which intermediate species are likely to be directly formed and may consequently interact with the hydrocarbon pool. These intermediates are not limited solely to the mixture of methanol with well-known condensation products DME and water but also TMO, which might act as a viable source of methyl groups, together with methane and formaldehyde.

Summarizing our conclusions, we have tied the numerously proposed reaction mechanisms together to find that not a single combination of direct reaction steps can link methanol to ethylene. This theoretical conclusion provides strong additional support for alternative proposals,[4–7] which bypass the highly activated concerted steps.

Methods Section

Geometry optimizations were performed on pentatetrahedral (5T) clusters with the Gaussian 03 package[23] at the B3LYP/6-31g(d) level of theory.[24–26] The cluster selection was motivated by the large amount of species taken into account (more than 80 distinctly different stationary points). Moreover, our recent study using ONIOM calculations on extended 30T and 46T clusters showed that the energy profile is only significantly altered in the case of adsorbed ion pairs.[16] Initial interpretation on the 5T level allowed us to evaluate which reactions require further detailed investigation. The cluster was left unconstrained to verify the true nature of stationary points, and zero-point energy (ZPE) corrections were included. Starting from transition-state geometries, the quasi-IRC approach allowed the product geometries to be acquired.[27] Rate coefficients were obtained by using transition-state theory (TST) by calculating the partition functions at 720 K. As elementary reaction steps were considered separately from adsorption/desorption requirements, only intrinsic energy barriers are shown (in kJ mol^{-1}): $\Delta E_0 = E_0$(transition state)$-E_0$(adsorbed reactants). Additionally, each elementary reaction was modeled assuming prior adsorption of necessary reagents, resulting in intrinsic rate coefficients (in s^{-1}).

Received: October 28, 2005
Revised: November 29, 2005

Keywords: ab initio calculations · C–C coupling · heterogeneous catalysis · methanol-to-olefin process · zeolites

---

[1] M. Stöcker, *Microporous Mesoporous Mater.* **1999**, *29*, 3–48.
[2] S. R. Blaszkowski, R. A. van Santen, *J. Am. Chem. Soc.* **1997**, *119*, 5020–5027.
[3] N. Tajima, T. Tsuneda, F. Toyama, K. Hirao, *J. Am. Chem. Soc.* **1998**, *120*, 8222–8229.
[4] W. Song, D. M. Marcus, H. Fu, J. O. Ehresmann, J. F. Haw, *J. Am. Chem. Soc.* **2002**, *124*, 3844–3845.
[5] I. M. Dahl, S. Kolboe, *J. Catal.* **1994**, *149*, 458–464.
[6] J. F. Haw, J. B. Nicholas, W. Song, F. Deng, Z. Wang, T. Xu, C. S. Heneghan, *J. Am. Chem. Soc.* **2000**, *122*, 4763–4775.
[7] B. Arstad, J. B. Nicholas, J. F. Haw, *J. Am. Chem. Soc.* **2004**, *126*, 2991–3001.
[8] W. Wang, A. Buchholz, M. Seiler, M. Hunger, *J. Am. Chem. Soc.* **2003**, *125*, 15260–15267.
[9] C. M. Zicovich-Wilson, P. Viruela, A. Corma, *J. Phys. Chem.* **1995**, *99*, 13224–13231.
[10] P. E. Sinclair, C. R. A. Catlow, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 333–345.
[11] S. R. Blaszkowski, R. A. van Santen, *J. Phys. Chem. B* **1997**, *101*, 2292–2305.
[12] E. Sandre, M. C. Payne, J. D. Gale, *Chem. Commun.* **1998**, 2445–2446.
[13] M. Hytha, I. Stich, J. D. Gale, K. Terakura, M. C. Payne, *Chem. Eur. J.* **2001**, *7*, 2521–2527.
[14] M. C. Payne, M. Hytha, I. Stich, J. D. Gale, K. Terakura, *Microporous Mesoporous Mater.* **2001**, *48*, 375–381.
[15] G. A. Olah, H. Doggweiler, J. D. Felberg, S. Frohlich, M. J. Grdina, R. Karpeles, T. Keumi, S. I. Inaba, W. M. Ip, K. Lammertsma, G. Salem, D. C. Tabor, *J. Am. Chem. Soc.* **1984**, *106*, 2143–2149.
[16] D. Lesthaeghe, V. Van Speybroeck, G. B. Marin, M. Waroquier, *Chem. Phys. Lett.* **2006**, *417*, 309–315.
[17] R. Shah, J. D. Gale, M. C. Payne, *J. Phys. Chem. B* **1997**, *101*, 4787–4797.
[18] O. Dewaele, V. L. Geers, G. F. Froment, G. B. Marin, *Chem. Eng. Sci.* **1999**, *54*, 4385–4395.
[19] P. E. Sinclair, C. R. A. Catlow, *J. Phys. Chem. B* **1997**, *101*, 295–298.
[20] C. Lo, C. A. Giurumescu, R. Radhakrishnan, B. L. Trout, *Mol. Phys.* **2004**, *102*, 281–288.
[21] C. S. Lo, R. Radhakrishnan, B. L. Trout, *Catal. Today* **2005**, *105*, 93–105.
[22] J. F. Haw, D. M. Marcus in *Handbook of Zeolite Science and Technology* (Eds.: S. M. Auerbach, K. A. Carrado, P. K. Dutta), Marcel Dekker, New York, **2003**, pp. 833–866.
[23] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J.

Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2003**.

[24] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652.

[25] S. A. Zygmunt, R. M. Mueller, L. A. Curtiss, L. E. Iton, *J. Mol. Struct.* **1998**, *430*, 9 – 16.

[26] D. Lesthaeghe, V. Van Speybroeck, M. Waroquier, *J. Am. Chem. Soc.* **2004**, *126*, 9162 – 9163.

[27] S. Svelle, B. Arstad, S. Kolboe, O. Swang, *J. Phys. Chem. B* **2003**, *107*, 9281 – 9289.